Global Change Biology (2004) **10,** 618–629, doi: 10.1111/j.1529-8817.2003.00764.x

# Radon fluxes in tropical forest ecosystems of Brazilian Amazonia: night-time $CO_2$ net ecosystem exchange derived from radon and eddy covariance methods

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## Abstract

**Radon-222 (Rn-222) is used as a transport tracer of forest canopy–atmosphere $CO_2$ exchange in an old-growth, tropical rain forest site near km 67 of the Tapajós National Forest, Pará, Brazil. Initial results, from month-long periods at the end of the wet season (June–July) and the end of the dry season (November–December) in 2001, demonstrate the potential of new Rn measurement instruments and methods to quantify mass transport processes between forest canopies and the atmosphere. Gas exchange rates yield mean canopy air residence times ranging from minutes during turbulent daytime hours to greater than 12 h during calm nights. Rn is an effective tracer for net ecosystem exchange of $CO_2$ ($CO_2$ NEE) during calm, night-time hours when eddy covariance-based NEE measurements are less certain because of low atmospheric turbulence. Rn-derived night-time $CO_2$ NEE ($9.00 \pm 0.99\,\mu\mathrm{mol\,m^{-2}\,s^{-1}}$ in the wet season, $6.39 \pm 0.59$ in the dry season) was significantly higher than raw uncorrected, eddy covariance-derived $CO_2$ NEE ($5.96 \pm 0.51$ wet season, $5.57 \pm 0.53$ dry season), but agrees with corrected eddy covariance results ($8.65 \pm 1.07$ wet season, $6.56 \pm 0.73$ dry season) derived by filtering out lower NEE values obtained during calm periods using independent meteorological criteria. The Rn $CO_2$ results suggest that uncorrected eddy covariance values underestimate night-time $CO_2$ loss at this site. If generalizable to other sites, these observations indicate that previous reports of strong net $CO_2$ uptake in Amazonian *terra firme* forest may be overestimated.**

*Keywords:* Amazon *terra firme* forest, canopy gas exchange, $CO_2$ net ecosystem exchange (NEE), eddy covariance, global carbon budget, Radon-222

*Received 23 December 2002; revised version received 2 May 2003 and accepted 7 May 2003*

## Introduction

Net exchange of $CO_2$ and trace gases between primary and human-altered tropical forests and the atmosphere may be an important process in the global carbon cycle and a significant factor in the radiative budget of the earth. Recent eddy covariance measurements of $CO_2$ net ecosystem exchange (NEE) over tropical forests suggest that mature, tropical evergreen forests may be a significant carbon sink (e.g. Grace *et al.*, 1995; Malhi *et al.*, 1998; Andreae *et al.*, 2002) of as much as $6\,\mathrm{Mg\,C\,ha^{-1}}$ annually. The hypothesized role of tropical forests as an important $CO_2$ sink and development of eddy covariance gas flux measurement techniques has provided substantial motivation for long-term tower studies in the large-scale biosphere–atmosphere

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experiment in Amazonia (LBA-ECO). A key question in the use of long-term eddy covariance to determine ecosystem $CO_2$ balance is whether the measurements are biased from day to night (Goulden *et al.*, 1996). Because net carbon uptake reflects the small difference between two larger fluxes, respiratory efflux at night and photosynthetic uptake during the day, a small selective underestimation of flux at night can cause a large overestimation of long-term accumulation. For example, Grace *et al.* (1995) reported an annual uptake of 1 Mg ha$^{-1}$ that reflected the difference between $\sim$10 Mg ha$^{-1}$ uptake during daytime and $\sim$9 Mg ha$^{-1}$ loss at night.

In contrast, Miller *et al.* (2004) estimate that photosynthesis and respiration are approximately equal (16–17 t C ha$^{-1}$ yr$^{-1}$) in the tropical forest near Santarém, Pará, Brazil, where the research reported here was conducted. There is substantial evidence that raw uncorrected eddy flux measurements undersample night-time respiration during calm periods in both temperate (Goulden *et al.*, 1996; Barford *et al.*, 2001), and tropical forests (Araújo *et al.*, 2004; Miller *et al.*, 2004). For this reason, most researchers who use eddy covariance methods to estimate annual carbon balance correct annual sum estimates by filtering out measurements taken during calm night-time periods. This approach remains subject to ongoing research and debate (Lee, 1998; Sakai *et al.*, 2001; Finnigan *et al.*, 2004); estimation of night-time fluxes via independent alternative methods would clearly be a beneficial contribution to addressing this problem.

Here we present initial results from an alternative experimental approach to gas flux measurements utilizing the naturally occurring, radioactive noble gas, radon-222 (Rn-222), as a tracer for continuous measurements of forest canopy–atmosphere gas exchange. Our objective is twofold: to report initial results from new high-accuracy instruments for measuring Rn, and to demonstrate with a simple conceptual framework the potential for these instruments to address mass transport problems in forest canopies. Flux divergence modeling utilizing a denser canopy Rn and $CO_2$ data set from 2003 will be presented elsewhere (C. S. Martens *et al.*, unpublished manuscript). This framework has value in that it can be applied during calm, night-time hours when eddy covariance approaches are most in question because of low-atmospheric turbulence. Continuous measurements of Rn in forest canopy air and biweekly, campaign-style measurements of Rn soil–air flux were made at a tower site, km 67, in the Tapajós National Forest (FLONA Tapajós), Pará, Brazil, in conjunction with independent measurements of eddy covariance $CO_2$ flux in and out of the canopy and canopy $CO_2$ storage. We report results from approximately month-long periods at the end of the wet season (June–July) and the end of the dry season (November–December) in 2001.

### *Rn-222 tracing of canopy–atmosphere gas exchange*

We have developed an independent method for quantifying forest canopy–atmosphere exchange rates for any gas over long time periods (months to years) using continuous measurements of in- and above-canopy Rn activity in combination with determination of the Rn flux from underlying soils. Because most trace gases emitted by the biosphere are either photochemically or biologically reactive, they are potentially unsuitable direct tracers for trace gas transport within, out of, or into vegetated land surfaces. However, Rn-222, a radioactive natural gas, is ideally suited for studies of gas exchange in the tropical forests of Amazônia because: (1) it is emitted almost exclusively from the soil; (2) it is a chemically inert gas, making it suitable for tracing physical exchange between forest soils, canopies and the overlying atmosphere; (3) the only canopy sink for Rn is radioactive decay that can be easily quantified using its known decay constant; (4) its 3.825 day half-life yields nearly conservative behavior in studies of soil/atmosphere and canopy/atmosphere gas exchange; and (5) we have been able to develop the necessary technology to accomplish continuous, multi-altitude Rn activity measurements both within and above the forest canopy at suitable time intervals. Efforts to employ Rn as a tracer of near-surface meteorological processes have been made since the 1960s and 1970s (e.g. Moses *et al.*, 1960; Birot *et al.*, 1970; Larson & Hoppel, 1973; Li, 1974). Turbulent eddy diffusion coefficients used in parameterization of surface exchange rates have frequently been inferred from Rn data (e.g. Liu *et al.*, 1984; Jacob & Prather, 1990). However, direct application of Rn to tracing forest canopy/atmosphere exchange of $CO_2$ and trace gases only began recently with Trumbore *et al.* (1990) who showed that Rn-derived gas exchange rates compared favorably with mixing rates obtained from energy balance by Fan *et al.* (1990) and Fitzjarrald & Moore (1990). Rn-222 was shown to have the potential to provide an independent and reliable measure of gas exchange rates between soils, forest canopy and the overlying atmosphere.

The use of continuous tower-based atmospheric Rn-222 activity measurements was pioneered with measurements using commercially available detectors during NASA's 1988 ABLE 3A mission near Bethel, Alaska (Martens *et al.*, 1992). The development of multidetector arrays provided continuous quantitative gas exchange data during multialtitude measurements every 30 min on an eddy covariance tower as part of the

NASA ABLE 3B mission in the open-canopy, boreal forests of northern Québec, during the summer months of 1990 (Ussler *et al.*, 1994).

The rate of gas exchange can be computed from canopy and soil flux measurements using a simple inventory model (Trumbore *et al.*, 1990):

$$h\frac{\partial C}{\partial t} = S - k\big(\langle C\rangle - C^{\mathrm{t}}\big) + \int (P - L)\,\mathrm{d}z, \qquad (1)$$

where $h$ is the canopy height, $S$ is the soil flux, $k$ is a canopy gas exchange coefficient, $\langle C\rangle$ is the spatial mean trace gas concentration within the canopy, $C^{\mathrm{t}}$ is the concentration of the trace gas in the overlying atmosphere and $P$ and $L$ are production and loss, respectively, of trace gas by the above-ground vegetation. In practice the term on the left is evaluated by comparing concentration profiles at successive time points. Evapotranspiration is not an important source of Rn within the Amazonian forest canopy, and radioactive decay loss of Rn over the time scale of the exchange is insignificant as well (see Trumbore *et al.*, 1990), so the integral term on the right side of (1) is negligible and can be eliminated. The equation can thus be solved for the canopy gas exchange coefficient, $k$:

$$k = S - h\frac{\partial C}{\partial t}\Big/\big(\langle C\rangle - C^{\mathrm{t}}\big). \qquad (2)$$

The gas exchange coefficient, $k$, with units of $\mathrm{m\,s^{-1}}$, is related to total aerodynamic resistance, $R_\tau$:

$$k = \frac{1}{R_\tau} \qquad (3)$$

and the mean residence time ($\tau$) of gases in the canopy prior to exchange with the atmosphere is

$$\tau = R_\tau h. \qquad (4)$$

### *Old-growth forest experimental site near Santarém, Pará, Brazil*

The work presented in this paper was conducted at a forested eddy flux tower site located in undisturbed, old-growth (primary) forest in the FLONA Tapajos, approximately 67 km south of Santarém, Pará, Brazil. The Rn measurements at the km 67 tower were made in collaboration with studies of heat, momentum, $CO_2$, $H_2O$ and other gas transport by other investigators (see Goulden *et al.*, 2004; Miller *et al.*, 2004; Saleska *et al.*, 2004) and with soil gas flux chamber studies (e.g. Keller *et al.*, 2002; Chambers *et al.*, 2004). Together, these studies are designed to provide direct quantification of the changes in canopy inventories (storage) and physical exchange of $CO_2$ and trace gases including $CH_4$ and $N_2O$ between soils, the forest canopy, and the overlying atmosphere in undisturbed primary forest vs. low impact logged areas in the same forest tract.

The km 67 tower site is located in the Tapajós National Forest, Pará, Brazil, accessed by an entrance road at km 67 along the Santarém–Cuiabá Highway (BR-163). As part of the LBA-ECO, an international research initiative led by Brazil, we have installed permanent forest research transects and instrumented an eddy flux tower 1 km east of the access road (S – 2.85500; W – 55.03639; GPS coordinates: UTM zone 21M, 726 889 E, 9 684 049 N). Temperature, humidity and rainfall average 25 °C, 85% and 1920 mm per year, respectively (Parotta *et al.*, 1995). Soils are predominantly nutrient-poor clay oxisols with some sandy utisols (Silver *et al.*, 2000), both of which have low organic content and cation exchange capacity. The canopy has a significant number of large emergent trees (to 55 m height), *Manilkara huberi* (Ducke) Chev., *Hymenaea courbaril* L., *Betholletia excelsa* Humb. & Bonpl., and *Tachigalia* spp. and a closed canopy at ~40 m. With large logs, many epiphytes, uneven age distribution and emergent trees, the forest can be considered primary, or 'old-growth' (Clark, 1996). It shows no signs of recent anthropogenic disturbance.

## Materials and methods

### *Rn canopy to atmosphere and soil flux measurements*

We have developed and constructed two new types of Rn measurement instruments for the work presented here. Patents are being applied for. The first type is a continuous flow-through design that allows for counting over periods as short as 1 min. A modification of this design for battery-powered campaign-style measurements is utilized for soil flux measurements. Continuous Rn-222 activity profiles within and above the forest canopy were measured with detector array systems of eight or more flow-through detectors controlled by custom software on portable computers. The same computers were also used for data storage. The flow-through detectors proved to have a precision of better than $\pm 0.74\,\mathrm{Bq\,m^{-3}}$ [95% confidence limits, based on a bootstrap analysis (Efron & Gong, 1983)] of Rn activity based on binning 15 min of counts. The detector arrays included a nafion tubing water removal system that utilized recirculated pump air to exhaust water vapor removed from ambient air arriving from eight sampling heights on the tower.

### *Continuous-sampling flow-through Rn detector*

The flow-through detector is based on a pulse-ionization Rn counting air chamber. The counting chamber consists of a large sealed aluminum vessel (~20 L active sample volume) with coaxially mounted ion collection electrode. The air sample to be analyzed is introduced into the chamber at flow rates ($\sim 1\,L\,min^{-1}$) consistent with an adequate sample exchange rate. Up to eight counting chambers may be connected in a single detector system.

$\alpha$ Particles released through decay of Rn-222 in the air sample volume and Po-218 and Po-214 in the air sample or adsorbed on the central electrode provide the fundamental basis for Rn assay. Negative and positive ions produced along $\alpha$-particle ionization tracks drift towards chamber walls and a central electrode, respectively, producing pulses in the central electrode. After amplification these pulses are counted. Control of the detector system and compilation and management of accumulated data files is performed by a standard notebook-format MSDOS-compatible PC.

### *Portable* in situ *Rn ground flux monitor*

Our Rn soil flux measurement instruments are modified flow-through detectors capable of $>36$ h of field Rn counting at 1 min intervals. The portable *in situ* Rn ground flux monitors (called fluxometers) are based on the same physics as the flow-through detector. In operation, the fluxometers are transported and placed over permanently installed ground collars distributed about the tower research sites. The accumulation ('grow-in') of Rn-222 soil–air flux during a suitable interval ($\sim 1$ h) is assayed via high-resolution $\alpha$-particle counting using pulse-ionization technology. Battery-powered digital memory internal to the fluxometer acquires Rn data for later upload to portable computers and subsequent reduction to final soil flux measurements. Soil flux measurements have been made throughout the year on a biweekly basis.

All soil Rn flux measurements were made after sealing the base openings of the fluxometers onto 0.30 m diameter PVC flux collars with electrical tape. The collars were driven into the soil in pairs at five sites around the base of the km 67 tower. All collars were left in place several months prior to the measurements reported here. Generally two fluxometers were deployed simultaneously. Between measurements, the fluxometers were lifted off collars and stored on their sides so as to promote mixing through the base opening with ambient air containing lower Rn activity. One minute count data were obtained and stored in fluxometer memory. At the laboratory following fieldwork, the data were downloaded to a portable laptop computer and analyzed for flux determinations. The raw 1 min count data were corrected for nonequilibrium using a deconvolution program then analyzed via linear regression techniques after throwing away the first two counts at the beginning and end of collar attachment.

Soil volumetric water content (VWC) was measured at four to eight locations within a meter of each collar during fluxometer measurements with a portable, two-prong probe (Hydrosense Corp., Campbell Scientific Inc., Logan, UT, USA) that converted resistivity to percent soil water content (SWC) using the default factory calibration. Uncertainty in reported VWC values for the same period is calculated from repetitive measurements over that period at multiple collars.

### *Calibrations*

The detectors for the continuous-sampling flow-through system are calibrated regularly using a Ra-226 RNC Rn source, serial number 106. This source was commercially produced by Pylon Electronic Inc. (Ottawa, Ontario, Canada). The calibration is a two-step procedure. First, a Rn-free gas is introduced to the detector at $1\,L\,min^{-1}$ using a mass flow controller to ensure accurate and precise delivery. This allows us to correct for background noise within each detector. Then the known Rn source is added in series to calculate the sensitivity calibration coefficient. Both steps are run for a minimum of 24 h to obtain adequate counting statistics. In addition, the system is checked monthly with a field calibration. During this 2-day period, all detectors are valved to the same atmospheric gas. This procedure allows us to check for detector stability and make necessary corrections.

The fluxometers are calibrated similarly but in a closed system. The RNC Rn source is placed in a closed loop with the fluxometer and allowed to grow-in for a minimum of 2 h. The slope of accumulated counts over time (flux) is measured and correlated to the known activity to calculate a sensitivity for each Fluxometer. Less precision is achieved with fluxometer measurements (standard deviation $= 6.3\,mBq\,m^{-2}\,s^{-1}$) because of the shorter counting intervals used to calculate fluxes, detector electrical responses to soil moisture releases and background noise associated with detector transport to the field.

### *Eddy covariance-derived $CO_2$ NEE*

Continuous eddy covariance $CO_2$ fluxes were measured at 58 m, and the canopy $CO_2$ profile was determined from concentrations measured at eight levels (62 m down to 0.9 m) every 20 min (Saleska *et al.*, 2004). Eddy fluxes were calculated over an averaging period of one half-hour: the wind field was rotated into the plane of zero mean vertical wind, mean values of concentrations and vertical wind were removed by linear detrending over the half-hour interval, and half-hourly covariances (fluxes) were calculated on the residuals from the trend line. The biotic flux, or NEE is calculated as

$$NEE_{\mathrm{eddy}} = J(\mathrm{CO_2})_{\mathrm{eddy}} + h\frac{\mathrm{d}\langle(\mathrm{CO_2})\rangle}{\mathrm{d}t}, \tag{5}$$

where $J(\mathrm{CO_2})_{\mathrm{eddy}}$ is the eddy flux at the top of the canopy and the second term is the change in within-canopy $CO_2$ storage as determined from concentration profile measurements.

We tested for the presence of day/night biases in eddy covariance measurements by examining night-time NEE as a function of turbulence, as measured by friction velocity, $u_*$, where

$$u_* = (-\langle u'w' \rangle)^{1/2}, \tag{6}$$

where $u'$ and $w'$ are the horizontal and vertical components of turbulent wind velocity, respectively. In the absence of a flux measurement artifact, we expect the night-time NEE – i.e. the biotic (storage-corrected) flux – to be independent of vertical mixing, since the physiology of respiration (e.g. by tree roots or micro-organisms) is not expected to depend on atmospheric turbulence.

There is generally a significant falloff in mean night-time NEE at this site for $u_* < 0.2\,\mathrm{m\,s^{-1}}$, with mean NEE approaching a threshold value of $\sim$8–9 $\mu\mathrm{mol\,m^{-2}\,s^{-1}}$ for $u_* \geq 0.2$ to $0.3\,\mathrm{m\,s^{-1}}$. This is evidence of 'lost flux' during these periods (Goulden *et al.*, 1996; Barford *et al.*, 2001). Analysis based on meteorological criteria independent of the Rn data indicates that retaining night-time NEE measurements made when $u_* \geq 0.22\,\mathrm{m\,s^{-1}}$ gives values representative of total ecosystem respiration (Saleska *et al.*, 2004). We therefore estimated night-time NEE by averaging all night-time measurements when $u_* \geq 0.22\,\mathrm{m\,s^{-1}}$, and call this $NEE^*_{\mathrm{eddy}}$.

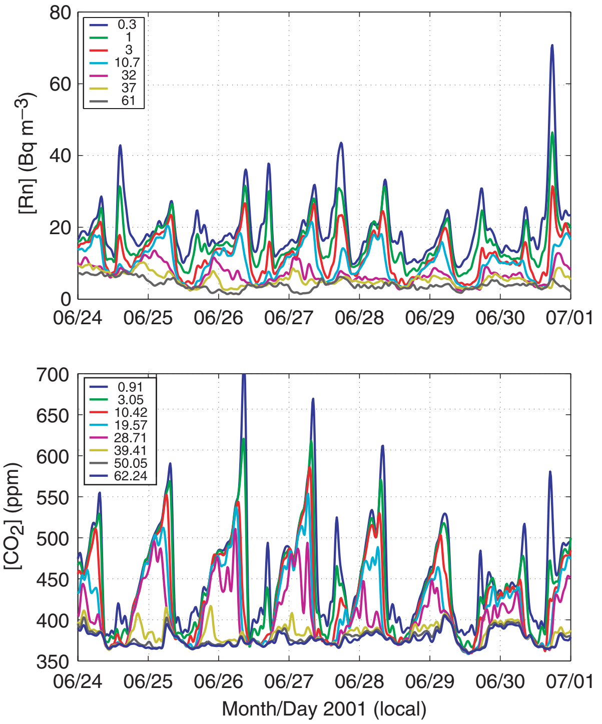

**Fig. 1** Measured radon activity and $CO_2$ concentrations in canopy and above-canopy air at the km 67 eddy covariance tower in the Tapajós National Forest. Each color represents a continuous record at a different specific height on the tower relative to the ground. Mean canopy height is approximately 40 m. Note the pronounced nocturnal buildup and dual daily maxima on most days for both gases.

### *Rn-derived $CO_2$ NEE*

NEE measurements of $CO_2$ were obtained from Rn-222 activity profile and $CO_2$ storage measurements using two central assumptions. The first was that Rn and $CO_2$ behaved similarly during calm night-time hours (21:00–04:00 hours local time), i.e. that variations in their profiles of concentration vs. height were similar (Fig. 1). The second was that scalar and momentum fluxes within the canopy [$J(t,z)$] were assumed to be proportional to mean concentration gradients through an effective eddy diffusivity $K_z$, with the same $K_z$ for both gases. We approximate the mean concentration gradient as the difference between the column-mean concentration within the canopy and that measured at the top of the eddy covariance tower, approximately 20 m above the forest canopy at 61 m height; for example for Rn:

$$\frac{\mathrm{d(Rn)}}{\mathrm{d}z} \approx \frac{\langle(\mathrm{Rn})\rangle - (\mathrm{Rn})^{\mathrm{t}}}{\Delta z} \equiv \frac{\Delta(\mathrm{Rn})}{\Delta z}, \tag{7}$$

where the superscript t denotes the value at the top of the tower. With this approximation and our other assumptions, we can compute the $CO_2$ flux as

$$J(\mathrm{CO_2}) \approx J(\mathrm{Rn})\frac{\Delta(\mathrm{CO_2})}{\Delta(\mathrm{Rn})}, \tag{8}$$

where the Rn flux is given by

$$J(\mathrm{Rn}) = S - h\frac{\mathrm{d}\langle(\mathrm{Rn})\rangle}{\mathrm{d}t}. \tag{9}$$

Finally, combining (5) and (9), we have

$$NEE_{\mathrm{Rn}} = S\frac{\Delta(\mathrm{CO_2})}{\Delta(\mathrm{Rn})}. \tag{10}$$

In order to independently assess raw [$NEE_{\mathrm{eddy}}$ (5)] and corrected [$NEE^*_{\mathrm{eddy}}$] $CO_2$ exchange derived from eddy covariance measurements, we compare them to $CO_2$ exchange [$NEE_{\mathrm{Rn}}$ (10)] derived from Rn canopy air concentrations, Rn soil flux measurements and profile $CO_2$ concentrations.

## Results

### Canopy air Rn activity

Canopy air Rn activity at the km 67 tower site was measured continuously for 1 min intervals at six to eight tower heights during wet and dry periods in 2001. Tower heights generally sampled were at 0.1, 0.3, 1.0, 3.0, 10.7, 32, 37 and 61 m. The data from each height were averaged over 15 min periods in order to obtain count rates allowing for a 95% confidence limit of better than 0.74 Bq $m^{-3}$. Data collected at seven heights for the week of June24–July 1 (Fig. 1) serve to illustrate the daily ranges in canopy and above-canopy Rn activities observed at each tower height. Canopy air $CO_2$ results from Saleska *et al.* (2004) for the same period are also included in Fig. 1.

A useful way to compare the diel variations in Rn and $CO_2$ concentration distributions throughout the canopy is to calculate mean hourly values at all canopy heights and represent these as color changes throughout the period of study. Mean hourly Rn-222 and $CO_2$ concentrations in canopy air for the June–July wet period are illustrated in Fig. 2a and b, respectively.

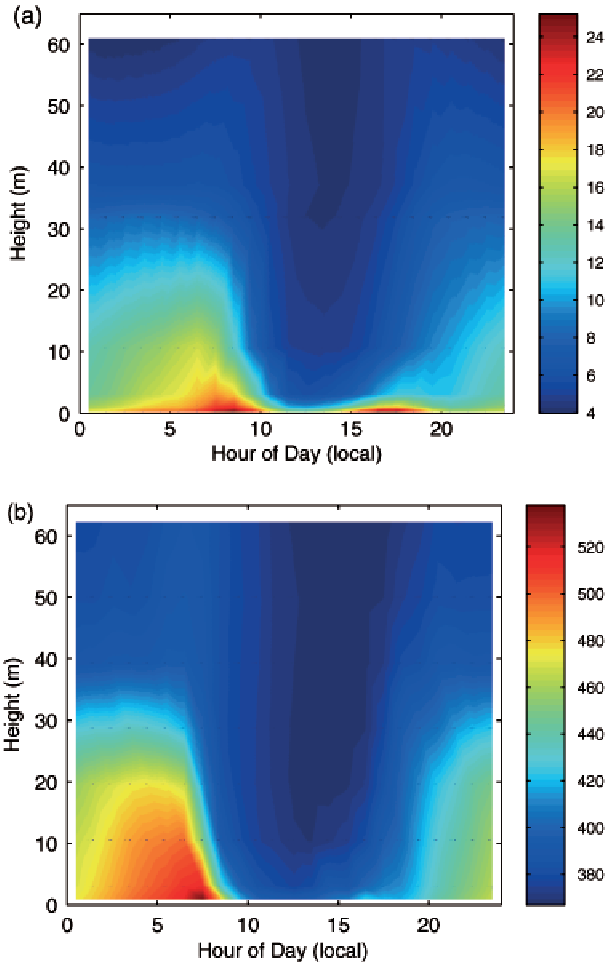

**Fig. 2** Hourly averaged (a) radon activity (Bq $m^{-3}$), and (b) $CO_2$ concentrations (ppm) for the wet period.

### Soil Rn fluxes

Typical soil flux measurements made using our new fluxometers are illustrated in Fig. 3. The average $r^2$ value for 60–120 min fluxometer measurements is 0.72 with a range of 0.55–0.87. Measured fluxes with $r^2$ values below 0.5 were rejected. These low $r^2$ values generally resulted from high background count rates (see Fig. 3) associated with damage to fluxometers from travel on rough logging roads. Problems with maintaining Rn fluxometer electronics under the rough transport and high humidity conditions led to a loss of approximately 40% of the soil flux data.

Results from the two time periods covered in this paper including mean soil VWC ($cm^3$ $H_2O$ $cm^{-3}$ soil) are listed in Table 1.

The higher flux during the October–December period appears largely to be controlled by drier soil conditions as compared with June–July (J. M. S. Moura *et al.*, unpublished data) as previously observed by Schery *et al.* (1994), Ussler *et al.* (1994) and others. Davidson & Trumbore (1995) have demonstrated that soil VWC directly controls the soil diffusivity of Rn in similar

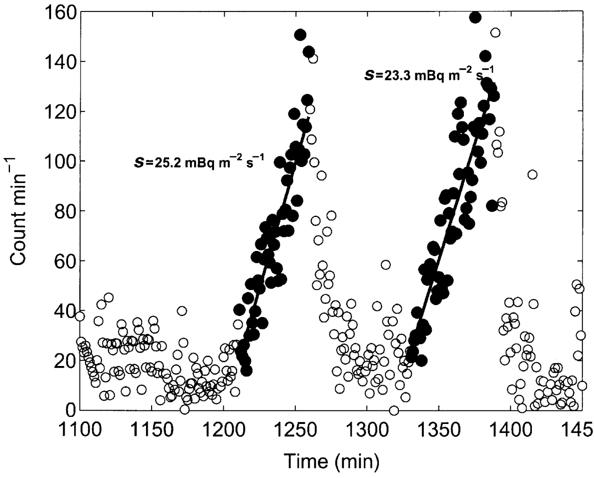

**Fig. 3** Buildup of radon in a soil flux chamber on June 22, 2001. Each data point represents the total number of counts in a 1 min period. The soil flux is determined by robust straight-line fits to the data points shown as filled circles, which begin 10 min after the chamber is placed on the collar and end 2 min before the chamber is removed. The slopes of the fitted lines shown are used along with calibration information to determine the soil flux $S$ in mBq $m^{-2}$ $s^{-1}$.

**Table 1** Radon soil fluxes and percent soil water content measured during wet and dry periods at the km 67 tower site, FLONA Tapajós, Pará, Brazil

| Condition | Months (2001) | Day of year | $S$ (mBq m$^{-2}$ s$^{-1}$) | $n$ | cm$^3$ H$_2$O cm$^{-3}$ soil |
|---|---|---|---|---|---|
| Wet period | June–July | 164–192 | 24.9 ± 3.33 | 17 | 0.36 ± 0.02 |
| Dry period | October–December | 300–360 | 36.5 ± 2.85 | 22 | 0.21 ± 0.02 |

The uncertainties on the $S$ and VWC values are the 95% confidence interval and one sigma uncertainty, respectively. VWC, volumetric water content.

Amazonian soils. SWC systematically drops from an average value of 0.36 ± 0.02 during the wetter period to 0.21 ± 0.02 during October–December during 2001. The uncertainties in soil Rn fluxes are based on summing all the data for each time period and do not take into account possible spatial variability in soil gas flux.

### *Canopy air gas exchange rates and mean residence times*

Eqns (2)–(4) were utilized to calculate whole canopy gas exchange coefficients, $k$, and mean residence times, $\tau$, for the period June 24–July 1, 2001 using the Rn canopy activity data in Fig. 1 and the wet period $S$ value in Table 1. The results are illustrated in Fig. 4a and b, respectively. Values of $k$ ranging from less than 0.003 during stable night-time hours to greater than 0.2 m s$^{-1}$ during more turbulent daytime hours (Fig. 4a) correspond to $\tau$ values ranging from minutes to over twelve hours (Fig. 4b).

Observed night-time values of $k$ and $\tau$ between the hours of 21:00 and 04:00 hours local time are illustrated in Fig. 4c and d, respectively.

### *Similarity in canopy air Rn and CO$_2$ behavior during night-time hours*

Rn activity at 61 m on the km 67 tower just above the forest canopy (Fig. 1) tends to remain near 3.7 Bq m$^{-3}$. This activity is close to the expected ambient air values of around 1.8 Bq m$^{-3}$ or less. However, during the night-time formation of the nocturnal boundary layer and during periods of exceptionally low wind speed a diel variation in Rn activity can be observed at all tower heights (Fig. 2a).

Typical Rn-222 activity and CO$_2$ concentration vs. height profiles averaged over the wet period are illustrated for four time periods between 21:00 and 04:00 hours local time in Fig. 5. The daily-averaged data are normalized to a scale of 0–1.0 by first subtracting the absolute minimum value and then dividing through by the absolute maximum value of these offset averaged values. These data serve to illustrate the similarity in the behavior of Rn and CO$_2$ vertical distributions during night-time hours. Differences in the concentration gradients of the two gases throughout a 24 h period such as a steeper Rn gradient and enhanced CO$_2$ buildup near the ground due to canopy vegetation respiration are discussed below. A simple scatter plot

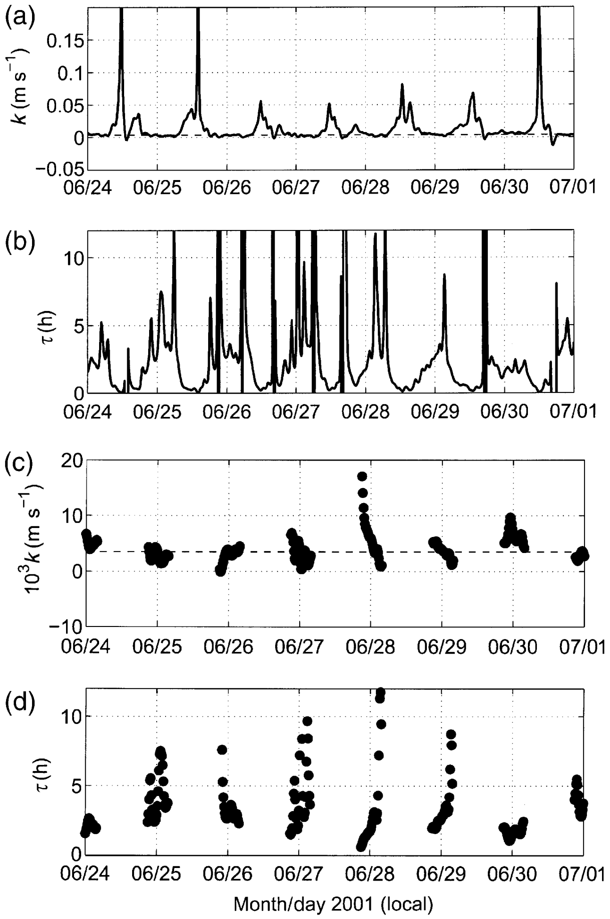

**Fig. 4** (a) Calculated mean canopy gas exchange coefficients ($k$), (b) mean canopy residence times ($\tau$). The dashed line in top panel shows $k$ values determined by Trumbore *et al.* (1990) during evening and night-time hours in an experimental forest near Manaus, Brazil. (c) Calculated mean canopy gas exchange coefficients ($k$) and (d) mean canopy residence times ($\tau$) during night-time only. The dashed line in (c) shows $k$ values determined by Trumbore *et al.* (1990) during evening and night-time hours in an experimental forest near Manaus, Brazil.

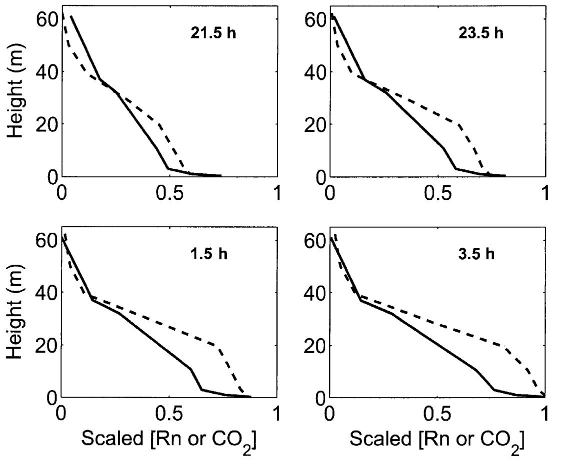

**Fig. 5** Normalized hourly averaged vertical profiles of radon (solid line) and $CO_2$ (dashed line) at the km 67 tower for four times starting at 21:50 hours (21:30 hours local time) during the wet period. Note the night-time buildup of both gases in the lower canopy.

between background-corrected Δ(Rn) (Rn activity minus tower top value) and $\Delta(CO_2)$ for the total wet period data yields an $r^2$ value of 0.8.

### *Rn-derived NEE during night-time hours*

Rn-derived $NEE_{Rn}$ values were calculated for both wet and dry periods using (10) and the respective Rn soil flux ($S$) values listed in Table 1. The median values for the wet season period are plotted in Fig. 6a, and for the dry season in Fig. 6b, together with $NEE_{eddy}$ and $NEE^*_{eddy}$, the uncorrected and corrected eddy covariance-derived net ecosystem $CO_2$ exchange, as taken directly from Saleska *et al.* (2004). The averages were calculated from point etimates (every half-hour) of $\Delta(CO_2)$ and Δ(Rn) and the constant seasonal $S$ values. Median NEE values were used because their distributions are non-Gaussian. The error bars are 95% confidence intervals for the median estimates.

## Discussion

### *Seasonal and spatial variation in soil Rn fluxes*

The observed difference between wet and dry period $S$ values (Table 1) should result, at least in part, from the greater soil permeability associated with lower moisture content during the dry period (Davidson & Trumbore, 1995). We are now observing a similar wet–dry season difference at two other experimental sites where Rn soil flux measurements are being made, one within the FLONA Tapajos and the other at a nearby pasture created from clearing of the *terra firme* Amazonian forest.

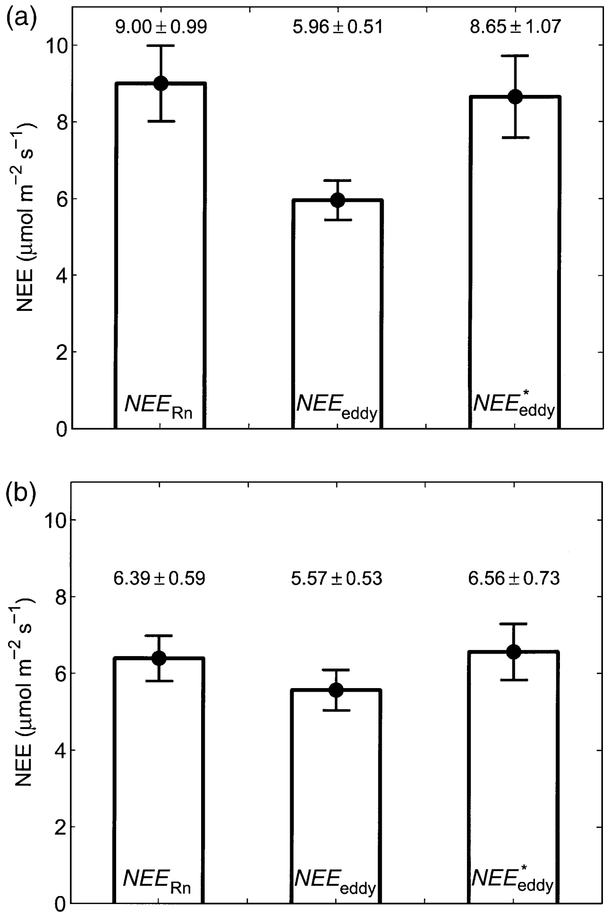

**Fig. 6** Median values of calculated radon-derived, eddy covariance and $u_*$-filtered eddy covariance $CO_2$ NEE for (a) the wet season and (b) the dry season. The error bars are 95% confidence intervals for the estimated medians. Note the agreement between radon-derived and $u_*$-filtered eddy covariance results.

The Rn soil flux values ($S$ in Table 1) are over two times higher than those observed by Trumbore *et al.* (1990) in the Manaus area in the eastern Amazon Basin. However, their measurements were all made during the wet season when higher SWC should produce lower net fluxes. The four fluxometers used to obtain the raw data and calculated $S$ values summarized in Table 1 were calibrated together in the laboratory with a commercial Rn source coupled in series to each detector (see above). A flux precision estimate was obtained with a natural soil by rotating the fluxometers in succession over four different collars implanted in a large aluminum box filled with soil. The latter experiment consistently yielded a precision of 6.3 $mBq\,m^{-2}\,s^{-1}$. The observed differences in $S$ values between our site and those used in previous studies appear to represent regional variations associated with differences in radium activity, soil composition and soil moisture content. Measurements of *S* from soils near Manaus, Brazil, are now being planned in association with tower eddy covariance studies underway there and that work should help to confirm or refute this hypothesized regional variation.

### *Controls on diel variations in canopy Rn activity*

Systematic patterns seen in the profile data (Figs 1 and 2) include (1) the expected rapid increase in Rn activity going from the above-canopy air to the forest floor, (2) expected maximum buildup of Rn activity during night-time hours resulting from decreased wind stress and resulting lower momentum flux into the canopy via turbulent eddy motion and (3) a significant secondary maxima in Rn activity, emphasized near the ground, beginning before sunset and apparently associated with the early evening transition (EET) period (Acevedo & Fitzjarrald, 2001) during which a new stable surface layer develops above the canopy top in association with the rapid decay of turbulent activity. Temperature drops during the EET are extremely rapid relative to the slower cooling occurring during later in the night. An increase in near surface moisture and other scalars with surface fluxes is predicted during the EET.

The secondary Rn buildup associated with the EET dissipates within hours just as night-time stabilization begins and the nocturnal boundary layer develops, helping to create the large overnight increases in inventories of Rn and other surface-derived gases. Maximum observed Rn activity within 3 m of the forest floor during the EET and overnight exceeded 70 Bq m$^{-3}$, an extremely high activity that is approximately 40 times greater than ambient air values in the overlying atmosphere. A similar pattern is observed in the atmospheric $CO_2$ concentrations.

### *Night-time canopy gas exchange rates and residence times*

Our calculated gas exchange rate constants for night-time hours from 21:00 to 04:00 hours local time generally range from 0.001 to 0.01 m s$^{-1}$, with an average of 0.0041 m s$^{-1}$ (Fig. 4c). These results agree with the limited number of values reported by Trumbore *et al.* (1990) even though their soil flux, *S*, was much lower (see above). Their mean *k* value of 0.0035 m s$^{-1}$, based on a short series of evening to night-time canopy Rn profiles, is shown as a dashed line. Our night-time $\tau$ values typically range from 2 to 10 h (Fig. 4d). These long canopy residence times agree with previous eddy covariance studies indicating that much of the Rn and $CO_2$ emitted from soils and vegetation during the night will be retained until turbulent mixing begins during the early morning hours. There is generally little turbulent mixing between the Amazon rain forest and the atmosphere at night due to the formation of the stable nocturnal inversion (Fitzjarrald & Moore, 1995). However, Fitzjarrald & Moore (1990) have demonstrated that decreases in nocturnal radiative cooling associated with cloud formation and turbulent diffusion resulting from increased winds can significantly enhance nocturnal release of $CO_2$. In the absence of such events, gases produced largely in the soil or near the forest floor should experience residence times in excess of the mean canopy $\tau$ values and largely be retained throughout the night-time hours. Thus most of the Rn and $CO_2$ emitted into the lower canopy should be retained there between the hours of 21:00 and 04:00 hours as is seen in the time course profiles of Fig. 5.

### *Rn vs. eddy covariance $CO_2$ NEE*

The greater median Rn-derived NEE, $NEE_{\mathrm{Rn}}$ (relative to uncorrected eddy-derived NEE, $NEE_{\mathrm{eddy}}$) for the wet period (Fig. 6) indicates significant underestimation of night-time $CO_2$ efflux by the raw eddy covariance measurements at this site. Uncertainties prevent making a similar conclusion for the dry period. By contrast, the agreement (Fig. 6) between $NEE_{\mathrm{Rn}}$ and the corrected eddy-derived NEE, $NEE^*_{\mathrm{eddy}}$(which is based on filtering out NEE from low-$u_*$ periods) suggests that the cause of lost flux is due to transport mechanisms other than turbulent flux during calm periods, and lends independent support to the validity of a $u_*$-correction algorithm.

The Rn-derived estimates of night-time errors in raw eddy measurements ($NEE_{\mathrm{Rn}}-NEE_{\mathrm{eddy}}$) are $3.04 \pm 1.11$ and $0.82 \pm 0.79$ μmol m$^{-2}$ s$^{-1}$, in the wet and dry season, respectively. These are increases of 51% and 15%; evidently the magnitude of the night-time measurement problem is highly variable seasonally. If $NEE_{\mathrm{Rn}}$ and $NEE^*_{\mathrm{eddy}}$represent the true night-time flux, then whole-ecosystem respiration is substantially higher in the wet season and lower in the dry season. By contrast, there is no detectable difference between these dry and wet season periods in the uncorrected NEE. If uncorrected NEE were used, not only would the absolute night-time carbon balance be wrong, but the relative differences between wet and dry periods would be missed, and the very strong seasonality evident in corrected $CO_2$ exchange would go undetected, at least during these periods. Soil flux measurements of $CO_2$ with chambers independently suggest that the seasonality of respiration is high (Goulden *et al.*, 2004; Saleska *et al.*, 2004; P. M. Crill, unpublished data, see below), presumably due to the high sensitivity of microbial respiration to availability of surface soil water, and the high seasonality of the latter.

### *Total forest canopy respiration calculated from Rn-derived NEE values*

Rn-derived NEE values should approximate total night-time soil and canopy respiration rates if little exchange with the atmosphere is occurring as indicated by the multiple hour mean canopy residence times ($\tau$, Fig. 4d). The Rn night NEE values for the wet and dry periods (Fig. 6a and b) are $9.00 \pm 0.99$ and $6.39 \pm 0.59\,\mu mol\,m^{-2}\,s^{-1}$, respectively (95% confidence interval). These values compare reasonably with two measures of annual mean total ecosystem respiration rates made by Chambers *et al.* (2004) in a *terra firme* forest near Manaus. They found rates of 7.8 and $8.4\,\mu mol\,m^{-2}\,s^{-1}$ through independent calculations of summed leaf, live wood and soil respiration and through tower eddy covariance measurements at night under sustained high turbulence conditions.

Soil $CO_2$ emissions measured with autochambers at the km 67 site averaged $3.2 \pm 0.4$ and $2.3 \pm 0.4\,\mu mol\,m^{-2}\,s^{-1}$ in the wet and dry seasons, respectively (P. M. Crill *et al.*, unpublished data). If soil fluxes at km 67 are, as in Manaus, about 35% of the total ecosystem respiration flux then we would expect the $CO_2$ flux from all sources to average about 9.1 and $6.5\,\mu mol\,m^{-2}\,s^{-1}$ in the wet and dry seasons, respectively, very similar to the night-time average exchanges measured at the km 67 and the km 83 eddy correlation towers (e.g. Wofsy *et al.*, 2002).

### *Differences in processes controlling Rn and $CO_2$: current limitations of approach*

Differences in Rn activity and $CO_2$ concentration distributions seen during the wet period between the hours of 21:00 and 40:00 hours as well as the rest of the day can be easily assessed through simple eyeball comparisons (Fig. 2). While the general patterns of distribution are the same, there are important differences that could provide useful information. The most obvious differences result from the daytime uptake of $CO_2$ during photosynthesis and night-time $CO_2$ production due to respiration by above-ground vegetation (Wofsy *et al.*, 1988).

The simple analysis framework used here only begins to take advantage of the full strengths of Rn as a conservative tracer. Future work will address the fact that a significant fraction of the night-time $CO_2$ production, perhaps over 20% (Trumbore *et al.*, 1990) occurs in the canopy rather than soils or at the soil surface. While Rn and $CO_2$ concentration profiles largely follow one another during night-time hours (Fig. 5), future analysis will use actual concentration gradients for each gas rather than mean canopy concentrations to calculate fluxes.

## Conclusions

Continuous forest canopy air combined with soil flux measurements of Rn-222 prove that this radioactive noble gas can be used as a powerful tracer of forest canopy–atmosphere gas exchange rates and night-time $CO_2$ NEE. Initial results from an old-growth, tropical rain forest in Pará, Brazil, yield gas exchange rates indicating canopy air residence times ranging from minutes during turbulent daytime hours to hours during calm nights. Rn is a particularly effective tracer for $CO_2$ loss during calm, night-time hours when eddy covariance-based NEE measurements are less certain because of low atmospheric turbulence.

Night-time Rn-derived $CO_2$ NEE during an approximately month-long period at the end of the wet season (June–July) in 2001, is significantly higher than $CO_2$ NEE derived from state-of-the-art, unfiltered, eddy covariance measurements using fast response $CO_2$ detection and sonic anemometers. Differences between Rn- and eddy covariance-determined NEE values at the end of the dry season (November–December) are close to experimental uncertainties. Filtering of the conventional eddy covariance results by correcting data collected below a friction velocity ($u_*$) value of $0.22\,m\,s^{-1}$ yields $CO_2$ NEE values in agreement with Rn-derived values. The magnitude of difference between Rn- and eddy covariance-determined $CO_2$ NEE values during the wet period, and the agreement of Rn results with $u_*$-filtered $CO_2$ NEE suggest that the hypothesis that Amazonian *terra firme* forests are a net $CO_2$ sink should be re-examined.

During night-time hours when gas residence times in the forest canopy are greater than several hours, Rn-derived $CO_2$ NEE approximately equals the total night-time respiration rate of all sources measured in the FLONA Tapajós and in similar forests near Manaus. Total respiration rates and Rn-derived $CO_2$ NEE are significantly higher during the wet period than the dry period.

Application of more sophisticated analyses to the growing Rn data set from the FLONA Tapajós should yield new insights about $CO_2$ and trace gas sources from the soil and by above-ground vegetation, and contribute to the quantification of $CO_2$ NEE in tropical rain forests. Addition of three-dimensional information would provide opportunities to study horizontal as well as vertical transport processes. The method should prove useful in other forest systems.

## Acknowledgements

We thank members of the LBA project team in Santarém for their numerous contributions to the success of the radon studies. In particular, we wish to thank Bethany Reed and Lisa Merry for their leadership at the Santarém LBA-ECO Laboratory. We thank our Brazilian LBA colleagues at INPE, CPTEC and INPA for leadership, friendship and for assistance with student, equipment, travel, visa and other issues vital to the success of our project. We thank the students and faculty of the Universidade Federal de Pará, Santarém for hosting our campus visits and lectures and for politely listening to one of us (C. S. M.) 'speak' Portuguese. We thank the LBA-ECO project office for additional support for radon instrumentation development and William Schlesinger and other Duke University colleagues for supporting field-testing of Brazil-bound equipment at the DOE-supported, FACE project site in Orange County, NC, USA. Student support for J. M. S. de Moura and R. L. Lima was provided by CNPq scholarships. Overall project support was provided by the NASA Earth Science office through the LBA-ECO project. The submitted manuscript benefited significantly from revisions suggested by two anonymous reviewers and Associate Editor Eric Davidson.

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