The CO_2 Budget and Rectification Airborne Study: Strategies for Measuring Rectifiers and Regional Fluxes

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Temporal covariations between atmospheric transport and surface gas fluxes, known as rectifier effects, may lead to significant spatial variations in CO_2 and other gases. Attempts to constrain carbon fluxes using surface background measurements and inverse methods are limited by large uncertainties in these effects. Airborne measurements of the vertical and horizontal distributions of CO_2, CO, O_2, and other tracers have the potential to significantly reduce these uncertainties. In this paper, we discuss observational requirements for quantifying rectifier effects and estimating regional fluxes, and use existing temperate and tropical forest data and model simulations to investigate the most promising measurement strategies. Using relationships between multiple tracers, it should be possible to separate the terrestrial, oceanic, and industrial influences on observed horizontal and vertical CO_2 variations. Summer observations of terrestrial CO_2 signals over land would then provide a direct measure of the diurnal rectifier effect, while comparisons between summer and winter observations would constrain the seasonal rectifier. We have plans for such measurements over North America and the adjacent ocean regions using airborne instrumentation and flask samples, as part of the CO_2 Budget and Rectification Airborne Study. The analyses presented here provide preliminary tests of our measurement approach and reveal evidence of strong diurnal rectifier effects.

1. INTRODUCTION

The sources of atmospheric carbon dioxide (CO_2), including fossil fuel combustion and biomass burning, appear to exceed the sum of atmospheric build up and oceanic uptake by 2 billion tons of carbon per year [e.g. *Schimel et al.*, 1995]. To understand the response of global ecosystems to anthropogenic perturbations and to predict future trends in atmospheric CO_2, it is critical to determine where this excess carbon is being stored and to define the mechanisms for sequestration. Unfortunately, spatial and temporal heterogeneities in ocean and land biospheric CO_2 fluxes make it impractical to derive regional or global values from direct measurement at small scales. Instead, oceanic and terrestrial CO_2 fluxes are currently estimated by inverting measurements of atmospheric CO_2 [*Enting and Mansbridge*, 1989; *Fan et al.*, 1998; *Baker*, 1999; *Dargaville and Simmonds*, 1999; *Taguchi*, 1999], CO_2 and $^{13}CO_2/^{12}CO_2$ [*Enting et al.*, 1993; *Ciais et al.*, 1995], CO_2 and $C^{18}O^{16}O/C^{16}O_2$ [*Peylin et al.*, 1999], or CO_2

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and O_2/N_2 [*Keeling et al.*, 1996] at background stations using numerical transport models.

The background surface stations are located, and sampling times selected, to obtain data representing the largest spatial scales in order to facilitate the determination of global trends. Consequently, most stations are remote from strong source or sink regions and measurement protocols stress sampling of air uncontaminated by regional surface processes. Since the network design deliberately minimizes the influence of surface exchange, the station data are not ideal for determining the loci and magnitudes of regional fluxes, or for understanding gradients associated with atmosphere-surface exchange. It is therefore not surprising that estimates of regional CO_2 sources and sinks derived from inverse model calculations are model-dependent, and especially sensitive to model representations of vertical mixing and horizontal advection. Additional measurements are needed at altitude and over the continents to reduce these uncertainties.

2. RECTIFIER EFFECTS

Denning et al. [1995] showed that temporal covariations between terrestrial CO_2 fluxes and rates of vertical mixing through the planetary boundary layer (PBL) may produce vertical and horizontal CO_2 gradients as large or larger than those resulting from net industrial, terrestrial, or oceanic exchanges. Over the continents during summer, vertical mixing through the PBL is vigorous and the PBL is relatively deep. There is a deficit in CO_2 near the surface associated with the net seasonal flux of CO_2 into the terrestrial biota, but the magnitude of this deficit is mitigated by dilution in the deep PBL [e.g. *Bakwin et al.*, 1998]. In contrast, during winter the PBL is shallow and the increase in CO_2 resulting from the net terrestrial efflux is trapped near the surface. Thus seasonal terrestrial CO_2 exchange, even with zero net annual flux, produces higher annual mean CO_2 concentrations at the surface over land, and model simulations indicate that this elevation of annual-mean concentration propagates over the oceans to remote stations [*Denning et al.*, 1996].

This and other similar processes have been termed "rectifier" effects, by analogy to an electronic circuit that converts an alternating current with a mean of zero volts to a direct current with a finite mean voltage. To begin, we define a rectifier effect as any temporal covariation between a surface flux and atmospheric mixing or transport that produces a time-mean spatial concentration gradient in the atmosphere. This broad definition includes a) the vertical-seasonal terrestrial-CO_2 rectifier just described, b) a similar vertical-diurnal terrestrial-CO_2 rectifier, c) the horizontal-seasonal terrestrial-CO_2 effect described by *Pearman and Hyson* [1980], d) O_2 and isotope-ratio rectifiers corresponding to these terrestrial-CO_2 effects, and e) the horizontal-seasonal and vertical-seasonal marine-O_2 rectifiers described by *Stephens et al.* [1998] and *Stephens* [1999]. Here, we are only concerned with the vertical-seasonal and vertical-diurnal terrestrial-CO_2 rectifier effects, which we will refer to in the remainder of the paper simply as the seasonal and diurnal rectifiers.

The diurnal rectifier, which operates primarily during summer, is depicted in Figure 1. In daytime the photosynthetic uptake is distributed through a thick atmospheric layer associated with the deep PBL. At night the PBL collapses, holding the respired flux near the surface through the night and morning and stranding the low concentrations aloft. Thus over much of the day, and on average, concentrations are higher near the surface over land than at upper levels and over the oceans, even in the presence of net continental CO_2 uptake. Using only surface concentration measurements, it is not possible to distinguish such time-mean signals from those resulting from a net terrestrial CO_2 source.

The model of *Denning et al.* [1996] indicates that the seasonal rectifier accounts for 80% of the total rectification effect, of approximately 2 ppm, predicted at northern marine boundary-layer stations. However, greater uncertainty may be associated with the influence of the diurnal rectifier as it produces even higher predicted concentration anomalies at the surface over the continents, of up to 18 ppm [*Denning et al.*, 1996], and its effect on the marine boundary-layer stations depends critically on the complex coupling between mixing over the continents and over the oceans. If natural rectifiers produce an interhemispheric CO_2 difference on the order of 2 ppm, as several of the models in the TRANSCOM study [*Law et al.*, 1996] predict, an inversion calculation using a model without such rectification would indicate a large, spurious net CO_2 source in the Northern Hemisphere, and vice versa.

Figure 2 shows seven-day averages of CO_2 versus height and longitude at 43°N predicted by the TM2 atmospheric transport model [*Heimann*, 1995], for combinations of realistic oceanic, terrestrial, and fossil fuel sources [*Keeling et al.*, 1989] during winter and summer. The longitudinal patterns in Figure 2 reflect vertical mixing of CO_2 as air moves eastward over North America. The net effect of the terrestrial biosphere is to make North America a source for CO_2 during win-
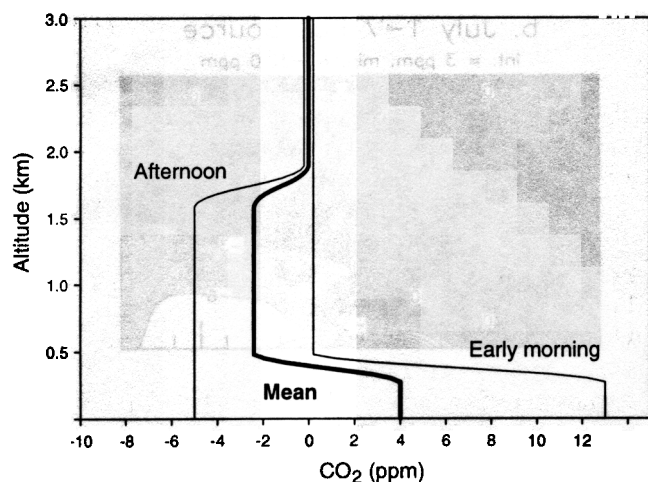
Figure 1. Conceptual continental CO_2 profiles resulting from a diurnally balanced terrestrial source.

ter and a sink during summer. Because TM2 lacks a diurnal rectifier, it predicts a drawdown of CO_2 near the continental surface during summer (Figure 2b). As shown below, existing continental measurements actually show enhanced CO_2 concentrations in this region at this time.

While this discrepancy imparts considerable uncertainty to inverse calculations using such a model, inversions based on current models with more complex boundary-layer parameterizations are not necessarily more accurate. For example, an inverse calculation based on the *Denning et al.* [1996] model, which compared well with diurnal and seasonal continental surface observations, was unable to produce a realistic CO_2 sink distribution [*Denning et al.*, 1999]. High-resolution airborne measurements of CO_2 and other tracers are needed to quantify the effect of rectifiers on surface background stations and to test the representation of vertical mixing in atmospheric transport models. Such measurements would also provide the opportunity to investigate methods of measuring surface CO_2 fluxes on regional and continental scales.

3. MEASUREMENT REQUIREMENTS

In order to quantify vertical and horizontal CO_2 gradients associated with the diurnal and seasonal rectifiers, and to provide data that can be directly compared to coupled terrestrial-atmosphere models, it is necessary to correct for oceanic and industrial influences. As discussed below, a fossil-fuel correction should be possible using correlations between CO_2 and CO [*Bakwin*

et al., 1998], and between CO_2 and O_2, SF_6 and additional industrial tracers. Correlations between CO_2 and O_2 could also help to identify gradients resulting from air-sea gas exchange. Airborne measurements of other species and isotope ratios, such as CH_4, N_2O, O_3, $^{13}CO_2/^{12}CO_2$, and $C^{18}O^{16}O/C^{16}O_2$ would provide additional information on the influences of terrestrial exchange and boundary-layer mixing on observed CO_2 gradients, as well as valuable insights into their own source/sink distributions. Weekly airborne flask measurements of many of these species are currently underway. However, adequately resolving the horizontal and vertical propagation of terrestrial CO_2 signals through the boundary layer, which is ultimately responsible for rectification, requires measurements at significantly higher spatial and temporal resolution.

Intensive measurements at several different times of year would be required on repeated vertical profiles, covering multiple times of day and extending over a wide range of longitude. At a minimum, CO_2 and the predominately industrial tracer CO would need to be measured using continuous instrumentation. Ideally, such high-resolution measurements for CO_2 would produce comparable cross sections to Figures 2a and 2b. Using CO measurements to quantify the fossil fuel component, and to separate it from the terrestrial component of CO_2, would allow direct tests of model simulations of these two components (Figures 2c-f). Summertime measurements of the magnitude of CO_2 enhancement in the PBL would provide direct tests of the diurnal rectification predicted by current and future models. Furthermore, it is the seasonal difference in the efficiency of mixing through the PBL that drives the seasonal rectifier. This mixing controls the rate of vertical propagation, with longitude, of the continental signals shown in Figure 2. Therefore, airborne measurements of the propagation of these signals during summer and winter should provide quantitative tests for model representations of the seasonal rectifier.

In regions remote from oceanic influence, it should be possible to verify the correction for fossil fuel using flask-sample O_2 measurements and differences in the oxidation quotient. Terrestrial photosynthesis and respiration exchange O_2 and CO_2 in the ratio 1.1:1.0 [*Severinghaus*, 1995], whereas non-coal fossil fuel oxidation ratios average approximately 1.4:1.0 [*Keeling*, 1988]. Measurement of $O_2:CO_2$ and $O_2:CO$ ratios would therefore provide strong checks on the separation of terrestrial and industrial signals, and help to identify anomalies or errors. Flask measurements of SF_6 could provide additional tests for the identification of industrial
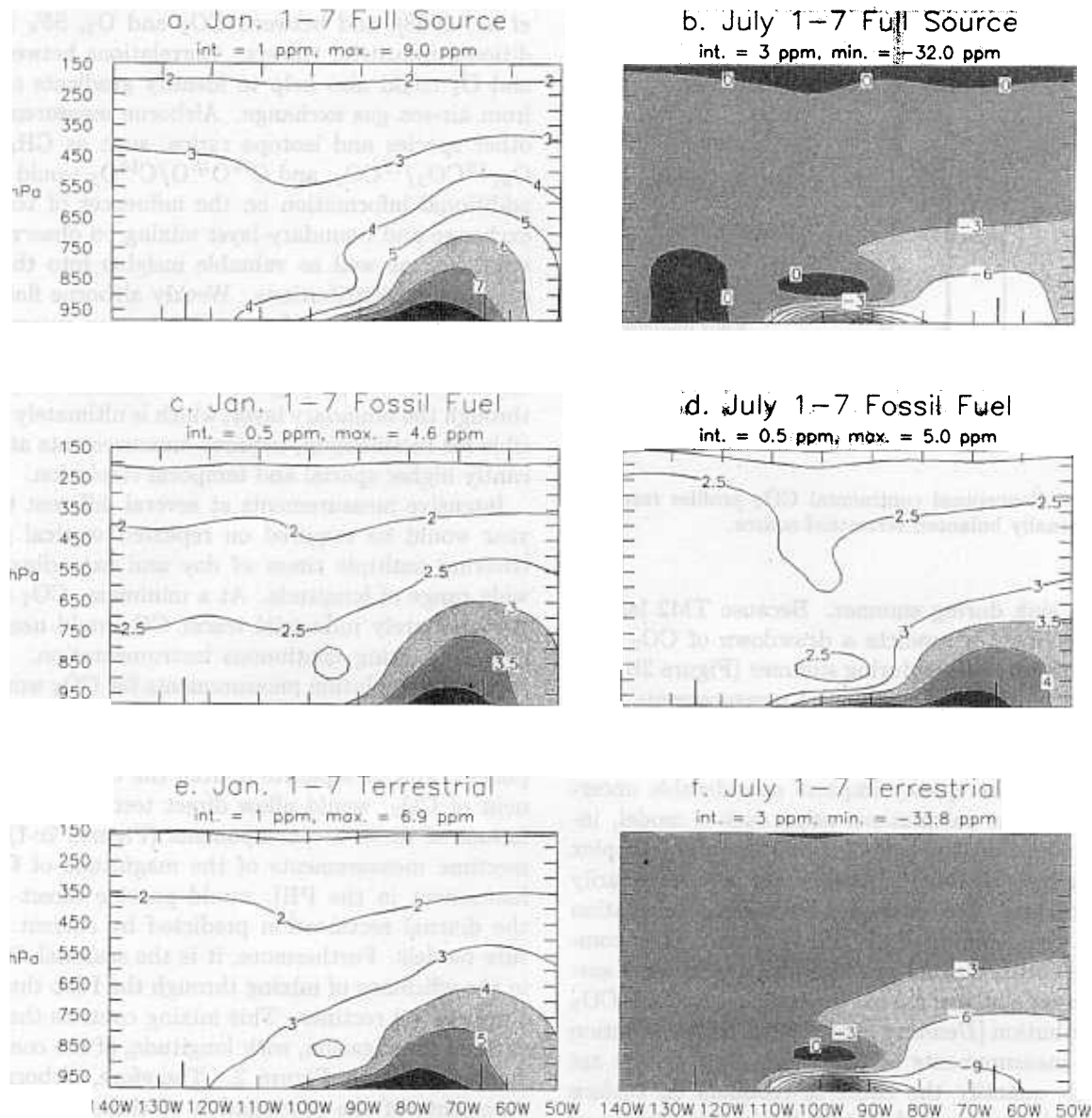
Figure 2. Vertical and longitudinal variations in CO_2 (ppm) as predicted by TM2 for composite, fossil fuel, and terrestrial sources. Plots show 7-day averages in early January and July at 43°N. The large tick marks indicate the edges of North America, and the highest three contour levels in each plot have been sequentially shaded.

signals using continuous CO data. Measurements of $^{14}CO_2/^{12}CO_2$ ratios offer the most robust constraint on industrial CO_2 signals, as fossil fuels have virtually no ^{14}C, however the sample-volume requirements for these measurements are somewhat more demanding than for other tracers.

In an attempt to quantify terrestrial influences on observed CO_2 gradients, flask-sample O_2 measurements could also play an important role in identifying regions affected by air-sea exchange. It is possible to define a derived tracer, atmospheric potential oxygen (APO ≈ O_2 + 1.1 CO_2), that is conserved with respect to terrestrial biotic exchange [*Stephens et al.*, 1998]. After removing fossil fuel influences on observed CO_2 and O_2 gradients using CO correlations, variations in APO should reflect only oceanic exchange. Therefore, air-

borne observations of APO gradients over continents would indicate the potential presence of oceanic CO_2 signals. If estimates of the marine O_2:CO_2 flux ratio were also available from a biological ocean model, then these APO gradients could provide estimates of the direct influence of air-sea exchange on the CO_2 measurements. Airborne measurements of radon would also help to identify marine air that had recently been influenced by terrestrial exchange, and to quantify vertical mixing rates over the continents [*Ramonet et al.*, 1996].

Observations of the propagation of oceanic signals over land and terrestrial signals over the oceans would provide a basis for investigating the coupling between terrestrial and oceanic boundary-layer mixing, helping to determine the impact of the diurnal rectifier on remote marine boundary-layer stations. A basic requirement for such an analysis is that the CO_2 observations be traceable to the calibration scales maintained by the laboratories responsible for measurements from the network of marine boundary-layer stations. Summertime continental/marine concentration differences for various species would constrain the magnitude and extent of the diurnal rectifier, while observed seasonal variations in these differences would provide quantitative information on the influence of the seasonal rectifier on interhemispheric gradients measured at background stations.

Accurately distinguishing terrestrial and industrial CO_2 signals, and relating them to background-station values, will require high-accuracy measurements at fine spatial and temporal resolutions in and around the boundary layer. The required accuracies and precisions for CO_2 are on the order of a few tenths of a ppm (see Figure 2), while the requirements for CO are approximately 50 times as strict. Although such measurements are far from trivial on an aircraft platform, available instruments can measure CO_2 with an accuracy of 0.1 ppm at 0.5 Hz [B. Daube, personal communication] and CO with an accuracy of 1.5 ppb at 1 Hz [*Gerbig et al.*, 1999]. Measurements of O_2 concentration would need to have a precision of 1-2 per meg, approximately equivalent to 0.2-0.4 ppm CO_2, to provide additional constraints. While airborne O_2 measurements at this level may be possible using an ultraviolet absorption technique [*Stephens*, 1999], presently they are limited to flask-sampling methods.

4. HARVARD FOREST DATA

To test the ability of CO data to distinguish CO_2 signals from fossil fuel emissions and terrestrial vegetation,

we can use concentrations of CO_2 and CO, and vertical fluxes for CO_2 and momentum measured continuously for several years at Harvard Forest, Massachusetts (42.5°N, 72.2°W). *Potosnak et al.* [1999] have carried out such an analysis. Here we briefly present a subset of their results that are most relevant to measuring rectifiers. Figure 3 shows hourly CO_2 data for January and July 1996, with monthly fits to the form

$$[CO_2] = a_0 + a_1[CO] + a_2F_p + \sum_{j=0}^{7} a_{3j}\delta_{jf} \qquad (1)$$

The term a_0 is the monthly-mean regional background concentration from 0000 to 0300 local time, and F_p is a flux parameter that accounts for CO_2 gradients that develop within the PBL from local exchange with the underlying canopy: $F_p = \phi/u^*$ where ϕ is the CO_2 vertical flux measured by eddy correlation and u^* is the friction velocity. This assumed scaling implies that at zero local CO_2 flux, or infinite local momentum flux, the tower CO_2 concentration would equal that of the regional boundary-layer. The variables $a_{3j}\delta_{jf}$ represent diurnal CO_2 variations in the regional boundary layer, resulting from diurnal variations in regional CO_2 flux and boundary-layer height. The data are binned into 3-hour intervals corresponding to f = 0 through 7 and δ_{jf} is set to 1 when j = f and otherwise to 0. The time-of-day parameters a_{3j} are derived for each interval using a generalized linear model [*Venables and Ripley*, 1994], thus allowing the model to fit an arbitrary shape to the monthly-mean diurnal cycle [*Potosnak et al.*, 1999].

Table 1 shows the results of the statistical fits from Figures 3a and 3b. The model fits the hourly data very well in every month with r^2 values typically between 0.7 and 0.9. The coefficient multiplying the local flux parameter (a_2), and the range of the day factors ($amp(a_{3j})$), both reflect the dominant influence of biospheric exchange during summer and its relatively small influence during winter. The CO_2:CO slopes shown in Figures 3b and 3d are fairly reproducible, but are slightly lower in summer due to the oxidation of hydrocarbons co-located with CO_2 emissions.

We have removed the influence of combustion on the CO_2 variance at Harvard Forest by substituting into equation (1) the CO concentration at the 20th percentile for the month, which gives a good estimate for the zonal mean background [*Goldstein et al.*, 1995]. We removed proximate effects of surface exchange by inserting zero for the local flux parameter. Figure 4a shows results given by the fitted formula for two different times of day with these parameters. These monthly values represent
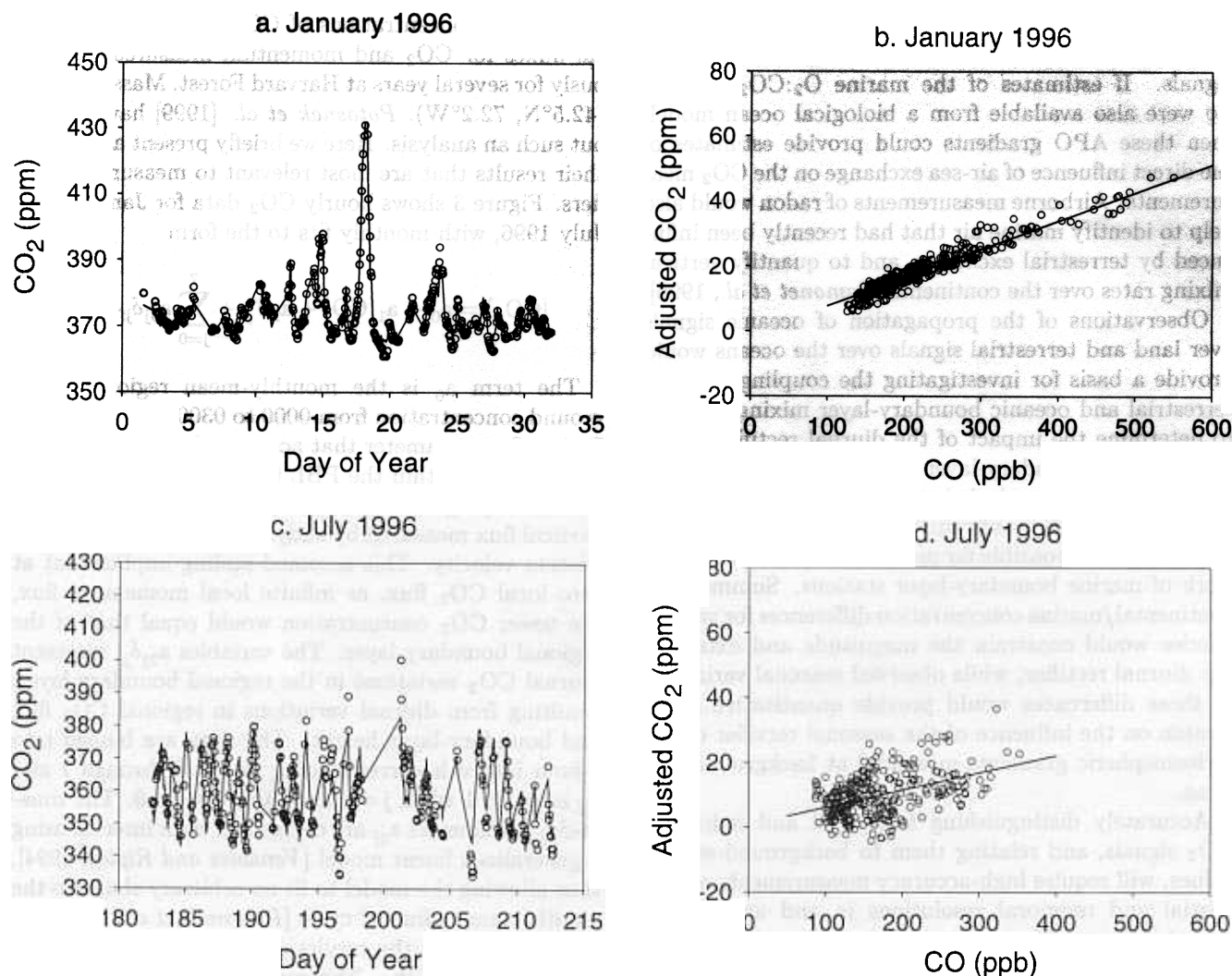
Figure 3. CO$_2$ and CO measurements from Harvard Forest. (a) Hourly CO$_2$ concentrations at 30 m during January 1996, shown with a fit to the form of equation (1). (b) Hourly CO$_2$ versus CO at 30 m during January 1996 with the first, third, and fourth terms in equation (1) subtracted from the CO$_2$ data, thus leaving only the fossil fuel component and the residual to the fit. (c) and (d) Same as (a) and (b) for July 1996 [*Potosnak et al.*, 1999].

the background concentrations in the PBL plus the influence of the monthly-mean regional diurnal cycle due to variations in biotic exchange and PBL height. We have compared these derived concentrations to CMDL data from Cold Bay, Alaska (55.2°N, 162.7°W), an upstream marine boundary-layer site of comparable latitude. As Figure 4a shows, this method of removing the effects of industrial and local canopy exchange using monthly statistical fits produces plausible background seasonal CO$_2$ cycles for a continental station [*Potosnak et al.*, 1999].

Wintertime CO$_2$ in the PBL over Harvard Forest appears to be slightly higher than at Cold Bay at all times of day (Figure 4a), as expected due to net respiration. During summer when the terrestrial biota have more of an influence, early morning CO$_2$ values are higher and afternoon values are lower at Harvard Forest than at Cold Bay (Figure 4a). Figure 4b compares the observed background differences between Harvard Forest and Cold Bay to differences predicted by the TM2 model. Even though the biota are a strong net sink at this time, the 24-hour mean concentrations at 30 m in

Table 1. Coefficients from fit of Equation (1) to Harvard Forest data.

parameter	January 1996	July 1996
a_0	354.9	358.7
a_1	0.083	0.059
a_2	0.005	0.030
$amp(a_{3j})$	0.85	19.45
r^2	0.95	0.74

Harvard Forest appear higher than at Cold Bay. The model predicts a depression of 7 ppm in 24-hour mean CO_2 at this height in midsummer, which is considerably different than the observations. This discrepancy is likely the result of a strong diurnal rectifier that is not reproduced in the TM2 model.

These analyses are encouraging for the use of CO data to account for industrial influences on airborne CO_2 data. However, there are still considerable uncertainties concerning the sources for CO at Harvard Forest [Potasnak et al., 1999], as well as the regional variability of industrial CO_2:CO ratios that would be encountered during continental scale measurements. The ability to derive continental background CO_2 concentrations from tower measurements would allow significant improvements to global inversion calculations. However, airborne measurements at different times of year over Harvard Forest would first be needed to investigate the spatial and temporal representativeness of the a_0 values calculated by Potasnak et al. [1999].

5. AMAZON DATA

Data obtained in the Amazon region from 1982-87 provide additional preliminary insights into rectifier effects, and information to guide future measurements. Figure 5 [Keller and Wofsy, unpublished data, 1983-84] shows flask measurements from November, 1983 to July, 1984 obtained in the interior of Amazonia near Manaus and at the same latitude (3°S) at the coast near Fortaleza. Samples were obtained in mid-morning or mid-afternoon in well-ventilated conditions. The data for CO_2 show higher concentrations in the interior (downwind), similar to the observations for CH_4 and N_2O, even though these gases are emitted in the region while CO_2 is being taken up at the time of sampling. This appears to be a manifestation of the diurnal rectifier, however as noted above, the possibility of an inland CO_2 source cannot be ruled out from surface data alone.

Figure 6 shows airborne observations of CO_2 over Amazonia made during the Atmospheric Boundary Layer Experiment 2B (ABLE2B). We have aggregated data from 15 flights near Manaus. The surface CO_2 excess in the morning was as high as 20 ppm [Wofsy et al., 1988], which was well simulated by the model of Denning et al. [1996]. As Figure 6 shows, the low values that characterize altitudes above 1 km were generated in the PBL in late afternoon, when the PBL height was maximum and CO_2 concentrations minimum (compare to Figure 1). These low concentrations are stranded aloft when PBL mixing ceases in the evening. The mean concentration was lower than Christmas Island, an equatorial marine boundary-layer site, at most altitudes, but CO_2 concentrations were higher than adjacent coastal regions below 2 km [Wofsy et al., 1988], consistent with a strong diurnal rectifier.

We can again test the ability to separate the influence of combustion from canopy exchange on CO_2 variability using a statistical model fit to the 9500 simultaneous CO and CO_2 measurements in this data set. We binned the data from all 15 flights by altitude ($\Delta z = 0.2$ km, range 0.2-6 km) and time ($\Delta t = 1$ hr, range 8-17 hr) to obtain data classified with a factor $(a_{2j}\delta_{jf})$ having 300 possible values. There were ample measurements to define the diurnal variation at altitudes below 3 km, but more sparse diurnal coverage above. The overall fit to the form

$$[CO_2] = a_0 + a_1[CO] + \sum_{j=0}^{299} a_{2j}\delta_{jf} \qquad (2)$$

has residual standard error of 2 ppm and an r^2 of 0.6, with about half of the residual error due to sensor variance inherent to this early instrument. The accurate representation of the ABLE2B data by this linear model can again provide a basis for separating background (a_0), combustion-derived $(a_0 + a_1[CO])$, and biogenic (setting [CO] to background value) CO_2.

The fit to equation (2) provides an estimate for the CO_2 from combustion and other oxidation processes of 71 ± 2 mol CO_2:mol CO, similar to the values obtained from Harvard Forest data (Table 1). This is likely a result of variable mixing of Northern Hemisphere air at a time when fossil fuel burning dominates the interhemispheric gradient. Harriss et al. [1990] inferred that much of the CO variance in ABLE2B was associated with episodic influx of polluted air from the Northern Hemisphere, and it is likely that the urban region of Manaus also contributed to the observed signal. The
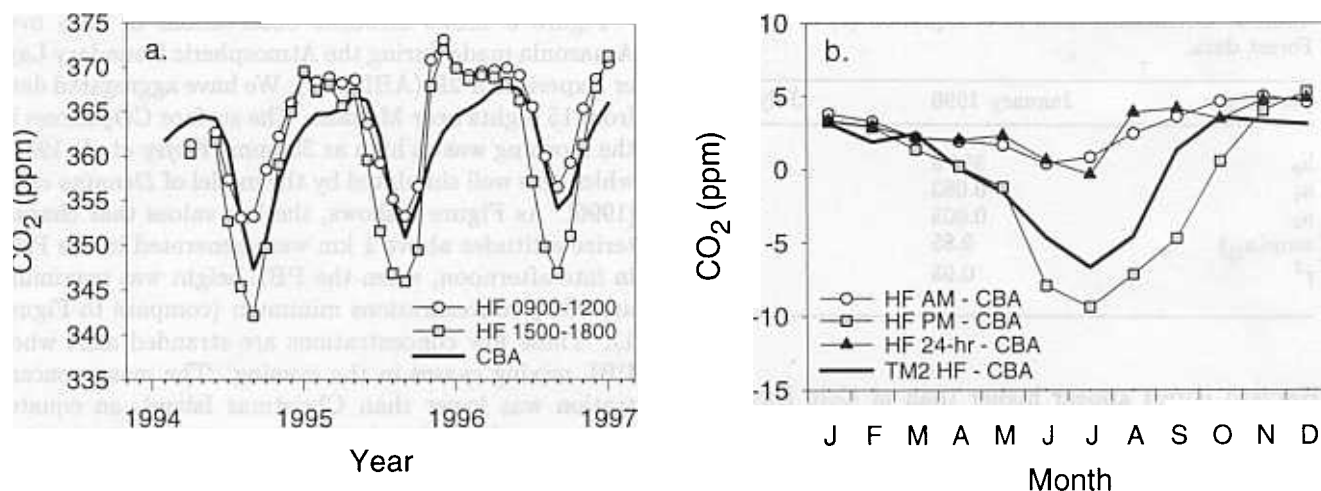
Figure 4. Comparison between background CO_2 concentrations at Harvard Forest, Massachusetts and Cold Bay, Alaska (CBA). (a) Monthly Cold Bay values (thick line) compared to monthly-mean Harvard Forest values, derived from equation (1) by setting the local flux parameter to zero, setting the CO concentration to its 20th percentile value, and selecting time of day factors corresponding to late morning (0900-1200 local time, open circles) and late afternoon (1500-1800 local time, gray squares) [Potosnak et al., 1999]. (b) Differences between derived Harvard Forest values and Cold Bay measurements for 12 months in 1996. Differences are shown for the two times of day in (a) and for a 24-hour mean (black triangles) [Potosnak et al., 1999]. For comparison, Harvard Forest - Cold Bay differences predicted by the TM2 model are also plotted (thick line).

observed CO_2:CO ratio is notably higher than the value of 11.7 obtained from biomass burning plumes in the region during ABLE2A [Andreae et al., 1987], however ABLE2B took place during the wet season when there was very little biomass burning in the region. The other major source identified for CO during this period, oxidation of isoprene, produces about 1:1 CO_2:CO and appears to have a negligible effect on the correlated variance of CO_2.

6. A SIMPLE BOUNDARY-LAYER MODEL

Intensive airborne measurements such as the ABLE-2B data just shown can provide reliable estimates of regional CO_2 and CO fluxes. *Wofsy et al.* [1988] used a direct mass-balance approach for the CO_2 column amount in the lower atmosphere to compute a midday uptake of 9 ± 4 kgC/ha/hr, indistinguishable from measurements by eddy correlation obtained in a subsequent experiment [Fan et al., 1990]. Future attempts at measuring regional fluxes would benefit from measurements of additional PBL parameters such as heights, entrainment rates, and buoyancy fluxes, as well as from the implementation of an improved conceptual framework.

Following the work of *Tennekes* [1973], *McNaughton and Spriggs* [1986], *Raupach et al.* [1992], *Raupach and*

Finnigan [1995], *Denmead et al.* [1996], and others, we express the variation of CO_2 in a well-mixed PBL over time by:

$$h \frac{\partial C_{bl}}{\partial t} =$$

$$(\frac{\partial h}{\partial t} - \langle w \rangle)(C_u - C_{bl}) + S \quad \text{for} \quad (\frac{\partial h}{\partial t} - \langle w \rangle) > 0$$

$$S \quad \text{for} \quad (\frac{\partial h}{\partial t} - \langle w \rangle) \leq 0$$

$$(3)$$

where h is the boundary-layer height, C_{bl} is the CO_2 concentration in the boundary layer, t is time, $\langle w \rangle$ is the regional-mean vertical wind component, C_u is the background CO_2 concentration, and S is the surface exchange flux. This model is two-dimensionally Lagrangian in the sense that it tracks the horizontal motion of a column of air, but accounts for the effect of vertical advection ($\langle w \rangle$) across the concentration jump at the top of the boundary layer. In a typical continental high-pressure air mass, $\langle w \rangle$ represents the mean subsidence velocity and, as demonstrated by Raupach and *Finnigan* [1995], can be a significant term in boundary-
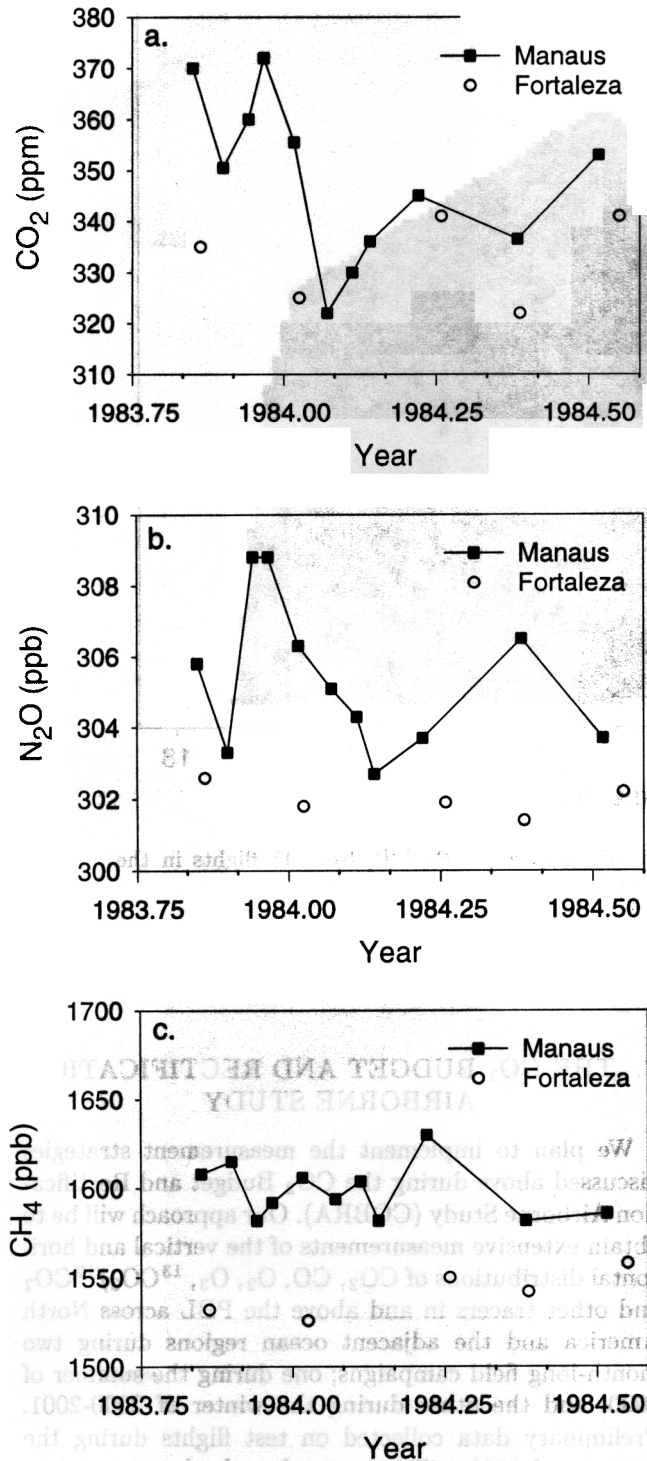
Figure 5. Concentrations of (a) CO_2, (b) N_2O, and (c) CH_4 observed in the Amazon. Measurements are shown from flasks collected during 1983-4 on the east coast of Brazil in Fortaleza (open circles) and 1000 km downwind at the same latitude (3°S), near Manaus (black squares) [*Keller and Wofsy, unpublished data,* 1983-84].

layer budgeting. The lower condition in Equation (3) represents times when either uplifting velocities exceed the rate of boundary-layer growth or boundary-layer collapse occurs faster than the rate of subsidence, during which the background CO_2 concentration can not influence that in the boundary layer.

Figure 7a shows variations in h and S over a 24 hour period, estimated from CO_2 (Figure 6), O_3, and H_2O measurements made during ABLE2B. The timing of both these parameters is linked to daily variations in solar intensity; CO_2 uptake is roughly proportional to the amount of photosynthetically active radiation and the PBL grows and shrinks with solar-driven buoyancy flux variations. It is this naturally tight correlation which drives the diurnal, and the seasonal, rectifiers.

Figure 7b shows the CO_2 concentration predicted at several heights by equation (3) using the values in Figure 7a as input. C_{bl} increases throughout the night, then decreases rapidly with the onset of photosynthesis. As the PBL grows, air from increasing heights is entrained as indicated by the concentration jumps in Figure 7b. Even for a net balanced source, C_{bl} only drops slightly below the background concentration for 6 hours in the afternoon. It is easy to see from Figure 7b how the 24-hour mean surface concentration could be much higher than background, and how difficult it could be to estimate net fluxes from surface data alone.

Airborne data provides the advantage of being able to monitor concentration variations in total or partial atmospheric columns. Figure 7c shows results from equation (3) for the CO_2 concentration, C_{max}, averaged from the surface to the height of daily maximum PBL growth. By comparison, C_{bl} is averaged from the surface to the instantaneous PBL height. This column-averaged concentration is not affected by variations in PBL height, and reflects primarily the integral of the exchange rate, S:

$$h_{max} \frac{\partial C_{max}}{\partial t} = - \langle w \rangle (C_u - C_{max}) + S \qquad (4)$$

assuming $\langle w \rangle$ is negative and that the subsiding air spreads equally at all heights below h_{max}. While the significance of the subsidence term ($\langle w \rangle$) to C_{bl} in Equation (3) depends on its magnitude relative to the change in boundary-layer height ($\partial h/\partial t$), $\langle w \rangle$ is the only thing other than the surface flux (S) that can modify C_{max} in Equation (4). By integrating equation (4) over 24 hours we get
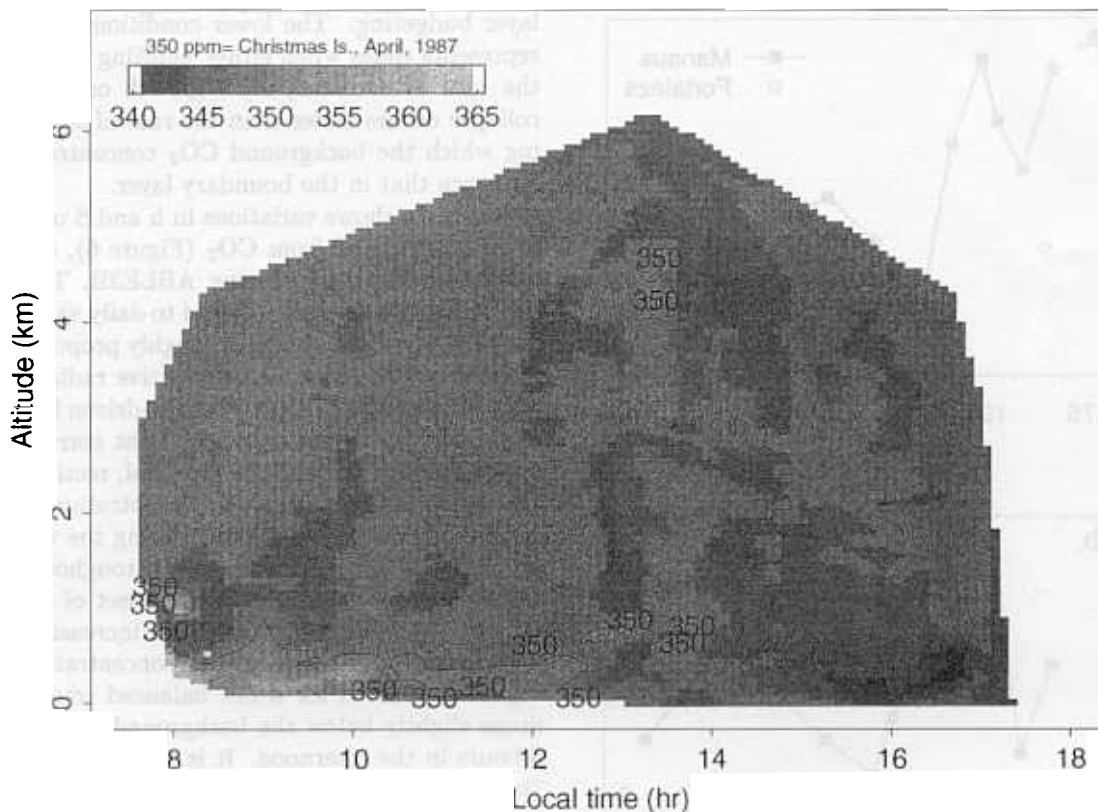
Figure 6. Time-height cross section of CO_2 concentrations during ABLE2B, from 15 flights in the central Amazon Basin ($0°$-$3°$S) near Manaus, in April 1987.

$$\langle C_{max} \rangle - \langle C_u \rangle = -\frac{\langle S \rangle}{\langle w \rangle} \qquad (5)$$

which demonstrates that straightforward estimates of the net exchange flux, $\langle S \rangle$, may be made by measuring the average subsidence rate and the column abundance of CO_2. Furthermore, as Figure 7c shows, this doesn't necessarily require intensive 24-hour monitoring; a reasonable estimate of $\langle C_{max} \rangle$ might be obtained by interpolating column averages made at sunrise and sunset. The application of this 1-D model is subject to uncertainties regarding the assumption of consistent subsidence into and lateral spreading within the boundary layer. While extensive airborne CO_2 measurements would benefit from this conceptual framework, at the same time they would provide important data for validating various flux-estimate techniques [*Denmead et al.*, 1996].

7. THE CO₂ BUDGET AND RECTIFICATION AIRBORNE STUDY

We plan to implement the measurement strategies discussed above during the CO_2 Budget and Rectification Airborne Study (COBRA). Our approach will be to obtain extensive measurements of the vertical and horizontal distributions of CO_2, CO, O_2, O_3, $^{13}CO_2/^{12}CO_2$ and other tracers in and above the PBL across North America and the adjacent ocean regions during two month-long field campaigns; one during the summer of 2000, and the other during the winter of 2000-2001. Preliminary data collected on test flights during the summer of 1999 will help to plan the later measurements. The platform will be the University of North Dakota Citation II aircraft. We plan continuous measurements of CO_2 using an infra-red analyzer [*Boering et al.*, 1994], of CO using a resonance fluorescence instrument [*Gerbig et al.*, 1999], and of O_3 using a UV
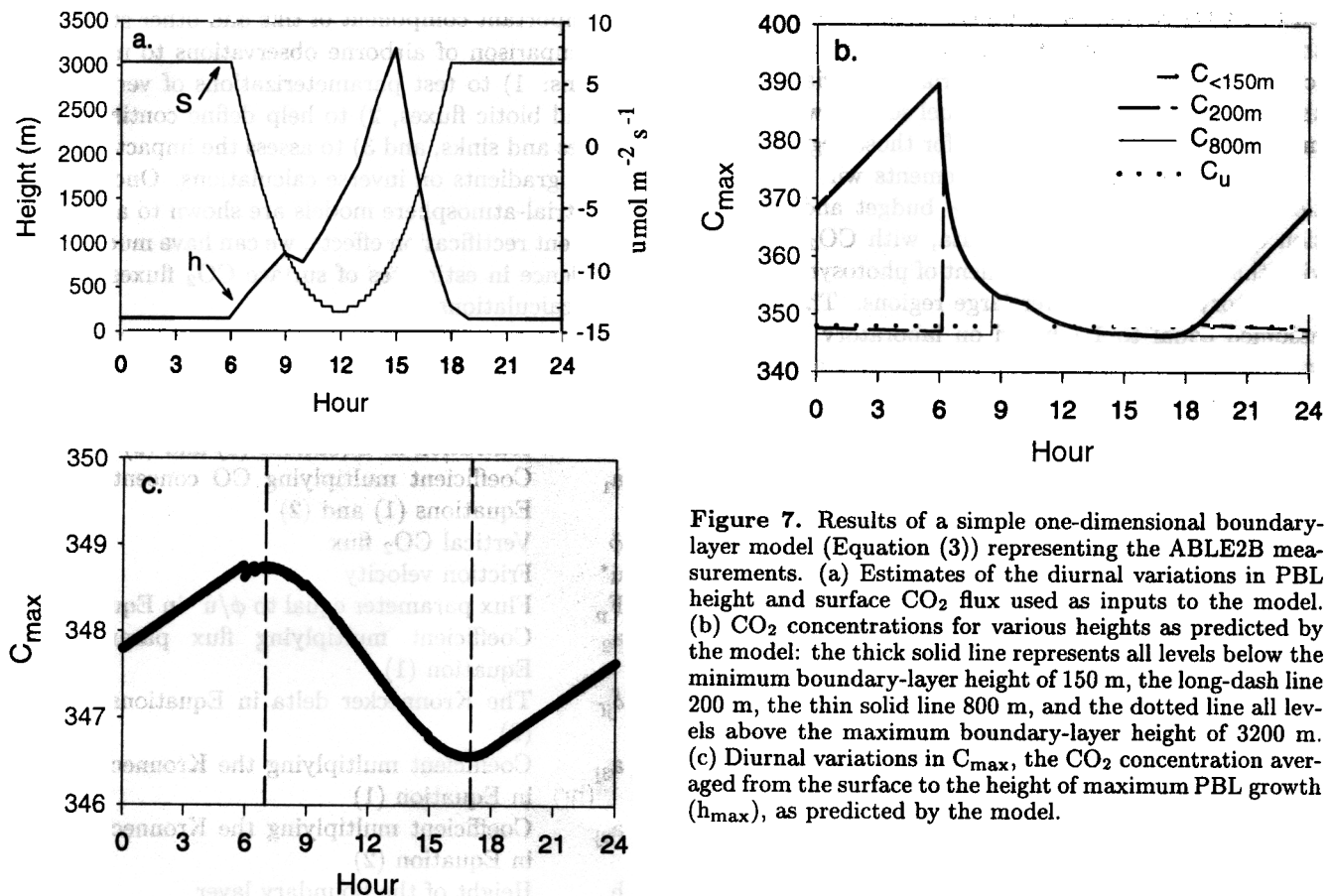
Figure 7. Results of a simple one-dimensional boundary-layer model (Equation (3)) representing the ABLE2B measurements. (a) Estimates of the diurnal variations in PBL height and surface CO_2 flux used as inputs to the model. (b) CO_2 concentrations for various heights as predicted by the model: the thick solid line represents all levels below the minimum boundary-layer height of 150 m, the long-dash line 200 m, the thin solid line 800 m, and the dotted line all levels above the maximum boundary-layer height of 3200 m. (c) Diurnal variations in C_{max}, the CO_2 concentration averaged from the surface to the height of maximum PBL growth (h_{max}), as predicted by the model.

instrument [L. Avallone, personal communication] with approximate vertical and horizontal resolutions of 5 and 150 meters respectively. We will take flask samples for the measurement of CO_2 and O_2/N_2 ratios at Scripps and for the measurement of CO_2, CH_4, CO, H_2, SF_6, N_2O, $^{13}CO_2/^{12}CO_2$, and $C^{18}O^{16}O/C^{16}O_2$ at CMDL.

As for the Harvard Forest and ABLE2B analyses above, we plan to develop statistical models of our data that enable the use of tracer-tracer correlations to separate the influence of terrestrial biotic exchange, fossil fuel combustion, and oceanic exchange on the observed CO_2 variations. The resulting summertime continental-scale terrestrial CO_2 signals will quantitatively measure the diurnal rectifier, while comparisons between our summer and winter measurements will constrain the seasonal rectifier. We plan to use output from the *Denning et al.* [1996] model and other coupled terrestrial-atmospheric models to help plan our flight patterns and interpret the resulting data.

In addition to spatially extensive continental-survey flights, we also plan temporally intensive diurnal ob-

servations in and above the planetary boundary layer in selected regions. These flights will extend over 100-300 km, centered above the WLEF tower in Wisconsin [*Bakwin et al.*, 1998] and Harvard Forest [*Goulden et al.*, 1996], where continuous measurements of flux and concentrations of CO_2 and CO are currently made. At the WLEF tower we will have measurements of all the terms in equations (3)-(5), providing an ideal framework to elucidate the functioning of the diurnal rectifier, to investigate the feasibility of determining regional fluxes using aircraft observations, and to define the optimal suite of tracer and ancillary data.

Together, the continental-survey and diurnal studies will characterize the spatial and temporal variability of CO_2 concentrations over North America. This information will aid in assessing the design and feasibility of an airborne, flask-based, carbon cycle observing network such as Carbon America [*Tans et al.*, 1996]. It will also allow us to investigate other protocols for calculating regional to continental scale CO_2 fluxes. For example, by vertically integrating the observed terrestrial and fos-

sil fuel CO_2 components, we can define ratios between these influences for specified regions across North America. By multiplying these terrestrial:industrial ratios by the relatively well known fossil fuel source, we can estimate net terrestrial CO_2 fluxes for those regions.

Our planned suite of measurements will have additional applications beyond CO_2 budget and rectification questions. The O_2/N_2 data, with CO_2, will provide the first direct measurement of photosynthetic and respiratory quotients over large regions. These ratios, assumed equal to 1.1 based on laboratory incubation studies [*Severinghaus*, 1995], are significant for ecosystem studies and critical to the inversion of CO_2 and O_2 data to obtain regional and global carbon budgets [*Keeling et al.*, 1996]. The observed $^{13}CO_2/^{12}CO_2$ and $C^{18}O^{16}O/C^{16}O_2$ gradients will provide new measurements of the isotopic signatures of terrestrial CO_2 exchange on continental scales. The CH_4, N_2O, and O_3 measurements will help to improve our current understanding of the global budgets for these species.

8. CONCLUSION

Inverse calculations of surface CO_2 fluxes are currently subject to significant uncertainties associated with the representation of seasonal and diurnal rectifier effects. The data from Harvard Forest and the Amazon presented here suggest that even during times of net CO_2 uptake, the diurnal rectifier maintains continental surface concentrations higher than those at marine boundary-layer sites. However, additional measurements are clearly needed to quantify vertical and horizontal CO_2 gradients resulting from both the diurnal and seasonal rectifier effects. We have shown that airborne measurements of CO_2, CO, O_2, and other tracers might allow the independent identification of continental-scale terrestrial CO_2 signals. We have also presented a simple boundary-layer model that may provide a framework for using airborne measurements to calculate regional CO_2 fluxes, and to investigate rectification processes.

Airborne measurements have the potential to bridge the gap between tower-based flux measurements and global scale carbon budget constraints, and to reduce large uncertainties in the relationships between surface CO_2 concentrations, rates of mixing and advection, and surface CO_2 fluxes, which currently limit our ability to define the present carbon cycle. Such measurements can also contribute to designing optimal strategies for measuring regional and continental scale fluxes. We have outlined plans for the CO_2 Budget and Rectification Airborne Study, which incorporates these goals.

An important component of this and other studies will be comparison of airborne observations to model predictions: 1) to test parameterizations of vertical mixing and biotic fluxes, 2) to help define continental net sources and sinks, and 3) to assess the impact of rectification gradients on inverse calculations. Once coupled terrestrial-atmosphere models are shown to adequately represent rectification effects, we can have much greater confidence in estimates of surface CO_2 fluxes from inverse calculations.

NOTATION

a_0	Monthly-mean regional background CO_2 concentration in Equations (1) and (2)
a_1	Coefficient multiplying CO concentration in Equations (1) and (2)
ϕ	Vertical CO_2 flux
u^*	Friction velocity
F_p	Flux parameter equal to ϕ/u^* in Equation (1)
a_2	Coefficient multiplying flux parameter in Equation (1)
δ_{jf}	The Kronnecker delta in Equations (1) and (2)
a_{3j}	Coefficient multiplying the Kronnecker delta in Equation (1)
a_{2j}	Coefficient multiplying the Kronnecker delta in Equation (2)
h	Height of the boundary layer
t	Time
C_{bl}	Average CO_2 concentration within the boundary-layer.
C_u	Background CO_2 concentration
$\langle w \rangle$	Regional-mean vertical wind component
S	Surface CO_2 flux
h_{max}	Daily maximum height of the boundary-layer
C_{max}	Average CO_2 concentration below h_{max}

REFERENCES

Andreae, M. O., E. V. Browell, P. L. Silva Dias, M. Garstang, G. L. Gregory, R. C. Harriss, G. F. Hill, D. J. Jacob, M. C. Pereira, G. W. Sachse, A. W. Setzer, R. W. Talbot, and A. L. Torres, Biomass Burning Emissions and Associated Haze Layers Over Amazonia, *J. Geophys. Res., 93*, 1509-1527, 1987.

Baker, D., An inversion method for determining time dependent surface CO_2 fluxes, this volume, 1999, American Geophysical Union.

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

Boering, K. A., B. C. Daube, S. C. Wofsy, Jr., M. Loewenstein, J. R. Podolske, and E. R. Keim, Tracer-tracer relationships and lower stratospheric dynamics - CO$_2$ and N$_2$O correlations during SPADE, Geophys. Res. Lett. 21, 2567-2570, 1994.

Ciais, P., P. P. Tans, J. W. C. White, M. Trolier, R. J. Francey, J. A. Berry, D. R. Random, P. J. Sellers, G. J. Collatz, and D. S. Schimel, Partitioning of ocean and land uptake of CO$_2$ as inferred by δ^{13}C measurements from the NOAA Climate Monitoring and Diagnostics Laboratory global air sampling network, J. Geophys. Res., 100, 5051-5070, 1995.

Dargaville, R.J., and Simmonds, I., Calculating CO$_2$ fluxes by data assimilation coupled to a three dimensional mass balance inversion, this volume, 1999, American Geophysical Union.

Denmead, O. T., M. R. Raupach, F. X. Dunin, H. A. Cleugh, and R. Leuning, Boundary layer budgets for regional estimates of scalar fluxes, Glob. Change Bio., 2, 255-264, 1996.

Denning, A. S., I. Y. Fung, and D. A. Randall, Latitudinal gradient of atmospheric CO$_2$ due to seasonal exchange with land biota, Nature, 376, 240-243, 1995.

Denning, A. S., D. A. Random, G. J. Collatz, and P. J. Sellers, Simulations of terrestrial carbon metabolism and atmospheric CO$_2$ in a general circulation model. Part 2: Simulated CO$_2$ concentrations, Tellus, 48B, 543-567, 1996.

Denning, A. S., T. Takahashi, and P. Friedlingstein, Can a strong atmospheric CO$_2$ rectifier be reconciled with a "reasonable" carbon budget, Tellus, 51B, 249-253, 1999.

Enting, I. G., and J. V. Mansbridge, Seasonal sources and sinks of atmospheric CO$_2$. Direct inversion of filtered data, Tellus, 39B, 318-325, 1989.

Enting, I. G., C. M. Trudinger, R. J. Francey, and H. Granek, Synthesis inversion of atmospheric CO$_2$ using the GISS tracer transport model, Division of Atmospheric Research Technical Paper No. 29. CSIRO Australia, pp. 1-44, 1993.

Fan, S., M. Gloor, J. Mahlman, S. Pacala, J. Sarmiento, T. Takahashi, and P. Tans, A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models, Science, 282, 442-446, 1998.

Fan, S.-M., S. C. Wofsy, P. S. Bakwin, D. J. Jacob, and D. R. Fitzjarrald, Atmosphere-biosphere exchange of CO$_2$ and O3 in the Central-Amazon-Forest, J. Geophys. Res., 95, 16851-16864, 1990.

Gerbig, C., S. Schmitgen, D. Kley, A. Volz-Thomas, K. Dewey, and D. Haaks, An improved fast-response vacuum-UV resonance fluorescence CO instrument, J. Geophys. Res., 104, 1699-1704, 1999.

Goldstein, A. H., C. M. Spivakovsky, and S. C. Wofsy. Seasonal variations of non-methane hydrocarbons in rural New England: Constraints on OH concentrations in northern midlatitudes, J. Geophys. Res., 100, 21023-21033, 1995.

Goulden, M. L., J. W. Munger, S.-M. Fan, B. C. Daube, and S. C. Wofsy, Exchange of carbon dioxide by a decid-

uous forest: Response to interannual climate variability, Science, 271, 1576-1578, 1996.

Harriss, R. C., M. Garstang, S. C. Wofsy, S. M. Beck, R. J. Bendura, J. R. B. Coelho, J. W. Drewry, J. M. Hoell, P. A. Matson, R. J. McNeal, L. C. B. Molion, R. L. Navarro, V. Rabine, and R. L. Snell, The Amazon Boundary Layer Experiment - wet season 1987, J. Geophys. Res., 95, 16721-16736, 1990.

Heimann, M. The global atmospheric tracer model TM2, Technical Report No. 10 (ISSN 0940-9327). Deutsches Klimarechenzentrum, Hamburg, pp. 1-53, 1995.

Keeling, C. D., S. C. Piper, and M. Heimann, A three-dimensional model of atmospheric CO$_2$ transport based on observed winds, 4, Mean annual gradients and interannual variations, in Aspects of Climate Variability in the Pacific and Western Americas, Geophys. Monogr. Ser., vol. 55, edited by D. H. Peterson, pp. 305-363, AGU, Washington D. C., 1989.

Keeling, R. F., Development of an interferometric oxygen analyzer for precise measurement of the atmospheric O$_2$ mole fraction, Ph.D. thesis, 178 pp., Harvard Univ., Cambridge, Mass., 1988.

Keeling, R. F., S. C. Piper, and M. Heimann, Global and hemispheric CO$_2$ sinks deduced from changes in atmospheric O$_2$ concentration, Nature, 381, 218-221, 1996.

Law, R. M., P. J. Rayner, A. S. Denning, D. J. Erickson, I. Y. Fung, M. Heimann, S. C. Piper, M. Ramonet, S. Taguchi, J. A. Taylor, C. M. Trudinger, and I. G. Watterson, Variations in modeled atmospheric transport of carbon dioxide and the consequences for CO$_2$ inversions., Global Biogeochem. Cycles, 10, 783-796, 1996.

McNaughton, K. G., and T. W. Spriggs, A mixed-layer model for regional evaporation, Boundary-Layer Meteorol., 34, 243-262, 1986.

Pearman, G. I., and P. Hyson, Activities of the global biosphere as reflected in atmospheric CO$_2$ records, J. Geophys. Res., 85, 4468-4474, 1980.

Peylin, P., Bousquet P., Ciais, P., and Monfray P., Differences of CO$_2$ flux estimates based on a "time-independent" versus a "time-independent" inversion method, this volume, 1999, American Geophysical Union.

Potosnak, M. J., S. C. Wofsy, A. S. Denning, T. J. Conway, J. W. Munger, and D. H. Barnes, Influence of biotic exchange and combustion sources on atmospheric CO$_2$ concentrations in New England from observations at a forest flux tower, J. Geophys. Res., 104, 9561-9569, 1999.

Ramonet, M., J. C. Le Roulley, P. Bousquet, and P. Monfray, Radon-222 measurements during the Tropoz II campaign and comparison with a global atmospheric transport model, J. Atm. Chem., 23, 107-136, 1996.

Raupach, M. R., O. T. Denmead, and F. X. Dunin, Challenges in linking atmospheric CO$_2$ concentrations to fluxes at local and regional scales, Aust. J. Bot., 40, 697-716, 1992.

Raupach, M. R., and J. J. Finnigan, Scale issues in boundary layer meteorology: Surface energy balances in heterogeneous terrain, Hydrol. Proc., 9, 589-612, 1995.

Schimel, D., I. G. Enting, M. Heimann, T. M. L. Wigley, D. Raynaud, D. Alves, and U. Siegenthaler, CO$_2$ and the carbon cycle, in Climate Change 1994, Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92

Emission Scenarios (Houghton, J.T., L.G. Meira Filho, J. Bruce, et al., eds.), Cambridge University Press, Cambridge, pp. 35-71, 1995.

Severinghaus, J. P., Studies of Terrestrial O$_2$ and Carbon Cycles in Sand Dune Gases and in Biosphere 2, Ph. D. Thesis, Columbia University, 1995.

Stephens, B. B., R. F. Keeling, M. Heimann, K. D. Six, R. Murnane, and K. Caldeira, Testing global ocean carbon cycle models using measurements of atmospheric O$_2$ and CO$_2$ concentration, *Global Biogeochem. Cycles, 12*, 213-230, 1998.

Stephens, B. B., Field-based Atmospheric O$_2$ Measurements and the Ocean Carbon Cycle, Ph. D. Thesis, 221 pp., Scripps Institution of Oceanography, La Jolla, California, 1999.

Taguchi, S., Synthesis inversion of atmospheric CO$_2$ using the NIRE chemical transport model, this volume, 1999, American Geophysical Union.

Tans, P. P., P. S. Bakwin and D. W. Guenther, A feasible global carbon cycle observing system: A plan to decipher today's carbon cycle based on observations, *Global Change Biology, 2*, 309-318, 1996.

Tennekes, H., A model for the dynamics of the inversion above a convective boundary layer, *J. Atmos. Sci., 30*, 558-567, 1973.

Venables, W., and B. Ripley, *Modern Applied Statistics using Splus, Springer-Verlag*, New York, 1994.

Wofsy, S. C., R. C. Harriss and W. A. Kaplan, Carbon dioxide in the atmosphere over the Amazon Basin, *J. Geophys. Res., 93*, 1377-1387, 1988.

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