CO_2 budget and atmospheric rectification over North America (CO_2BAR):

Comprehensive airborne measurements of CO_2, CO, tracers, and O_2 on the continental scale

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Project Summary

Motivation for the proposed study:
Studies of the global carbon cycle are motivated by the need to predict future trends in atmospheric CO_2, to define responses of the terrestrial biosphere and oceans to changing CO_2 and climate, and to determine permissible emissions for selected future levels of atmospheric CO_2. The confidence in predictions of future CO_2 is limited by uncertainties in the magnitude of terrestrial and oceanic sinks and associated biophysical mechanisms. Currently the best constraints on marine and terrestrial fluxes are derived by inverse analysis of concentration data for CO_2, $^{13}CO_2/^{12}CO_2$, and O_2 from the global surface observing network, using global biophysical/transport models. One of the largest sources of uncertainty for inverse studies is the "rectification" of seasonal and diurnal oscillations of CO_2 fluxes, atmospheric concentration gradients caused by correlation between biophysical fluxes and rates for transport that are difficult for models to simulate, and for which validation data are currently unavailable. The proposed study will measure the CO_2 gradients due to rectification phenomena over North America and will separate the influence of biogenic and combustion fluxes on CO_2 distributions at continental scale, using measurements of CO_2, CO, O_2, $^{13}CO_2$ SF_6, and other tracers. The goal is to provide unique, valuable new constraints on the global carbon cycle.

Objectives of the proposed measurements:
• Obtain **comprehensive extensive** measurements of the vertical and horizontal distributions of CO_2, CO, O_2, $^{13}CO_2$ SF_6, and other tracers in and above the planetary boundary layer (PBL) across North America and adjacent ocean regions in two seasons (summer, winter) using airborne *in situ* instrumentation and grab samples.

• Obtain **intensive diurnal** observations in and above the planetary boundary layer in selected regions to complement the **extensive** measurements, to quantify the effect of the diurnal rectifier on distributions of these tracers over land, and to obtain regional flux estimates.

Deliverables:
• **Extensive** and **intensive** tracer distributions and covariances will be analyzed to determine the influence on observed concentrations over North America of each of the three primary processes in the global carbon cycle: *fossil fuel burning, terrestrial biotic exchange,* and *oceanic exchange.*
• The data from **intensive** regional studies will be analyzed to define regional emission rates.
• Analysis of data from the proposed experiments will define the magnitude of gradients over the continent of North America associated with both the seasonal and diurnal rectifiers, and will determine the influence of rectification on concentrations measured at marine boundary layer stations by comparison of our airborne data to concentrations measured at remote stations at the same time.
• The measurements will be compared to model predictions to test parameterizations of mixing and rectification, to help define continental source and sink distributions/magnitudes, and to assess the impact of rectification phenomena on inverse analyses of the global carbon cycle. The work will provide primary data to aid in assessing the design of a carbon cycle observing network, such as Carbon America, that expands upon current surface measurements. The data will provide the first direct measurement of photosynthetic and respiratory quotients over large regions, essential parameters for understanding the relationship between global CO_2 and O_2 cycles currently available only from laboratory measurements.
• We plan to examine the accuracy of continental fluxes derived by scaling the observed ratios of CO_2 concentration changes associated with terrestrial fluxes vs. fossil fuel emissions by accounting for the influence of rectification on observed concentration gradients, using the known magnitude of the fossil fuel combustion.

I. Introduction

The inventory of sources of atmospheric carbon dioxide (CO_2), including fossil fuel combustion and biomass burning, appears to exceed the sum of atmospheric build up, oceanic uptake, and terrestrial sinks by 1 - 2 Gtons of carbon/year (*e.g.* Schimel *et al.*, 1995), 15-30% of the total. To predict future atmospheric CO_2 trends for specified emission scenarios, or to assess future responses of ecosystems to changes in CO_2 or climate, it is critical to determine where excess carbon is being stored and to define the mechanisms for sequestration.

The best available estimates of large scale oceanic and terrestrial CO_2 fluxes have been made by inverse analysis of measurements at background stations of atmospheric concentrations of CO_2, $^{13}CO_2/^{12}CO_2$ (Enting *et al.*, 1993; Ciais *et al.*, 1995) or O_2 (Keeling *et al.*, 1996), using numerical biophysical/transport models. Background monitoring is carried out exclusively at the earth's surface. Stations are located, and protocols selected, to obtain data representing the largest spatial scales, to facilitate determination of global trends. Thus most stations are remote from source/sink regions and protocols stress sampling of air "uncontaminated" by surface processes. Unfortunately, since the network design deliberately minimizes influence of surface exchange, the station data are not ideal for determining the loci and magnitudes of major surface fluxes, nor 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. Denning *et al.* (1996) showed that covariations between terrestrial CO_2 fluxes and rates of vertical mixing through the planetary boundary layer (PBL) can produce vertical and horizontal CO_2 gradients greater than those due to net industrial, terrestrial, or oceanic exchanges. Sharp gradients were computed due to correlation between CO_2 diurnal uptake and growth of the PBL during the day, the **diurnal rectifier effect**; the calculated effect was validated using airborne data over Amazonia (Wofsy *et al.*, 1988)[see Figs. I-1a-b]. Gradients with smaller magnitude, but larger horizontal scales, were associated with seasonal correlation between CO_2 net uptake and enhanced PBL heights during summer, the **seasonal rectifier effect** [Fig. I-2].

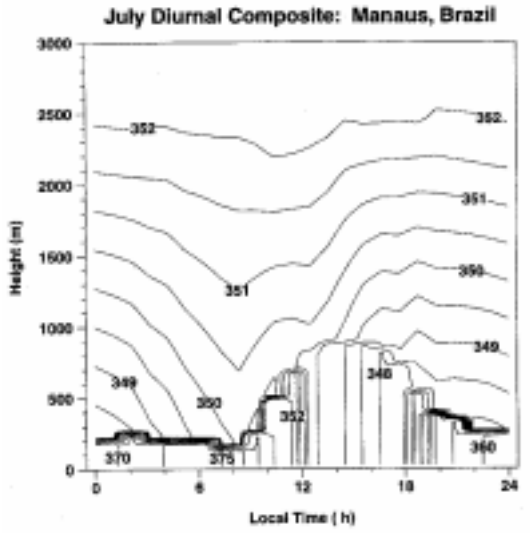


Fig. I-1a Computed diurnal variation of CO_2 concentrations over the tropical forest near Manaus, Brazil, in June, 1985 (Denning, 1995); note the prevalence of low concentrations at the highest levels attained by the PBL growth, and high concentrations at lower altitudes, an example of the *diurnal rectifier*.

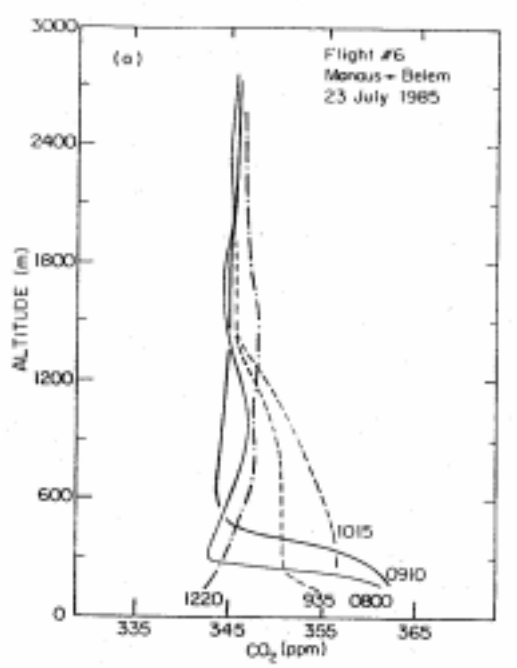


Fig. I-1b Observed concentrations of CO_2 over the tropical forest near Manaus on July 21, 1985 (Wofsy et al., 1988), used to validate model results in Fig. I-1a (Denning (1995) and Denning et al. (1996).

There have been no observations defining gradients from rectification of diurnal and seasonal cycles over North America. Denning et al. (1996) argued that the seasonal rectifier would have a larger impact than the diurnal rectifier on island stations, and hence on inverse calculations. However, data from Harvard Forest and Amazonia (see below) suggest that both rectifiers may be stronger than computed by Denning et al. Inverse analysis using a

model that inaccurately represents rectifier effects can produce spurious source and sink patterns by fitting incorrect gradients to real data; errors cannot be readily detected because of the remoteness of stations from source/sink regions. The recent TRANSCOM study *(vide infra)* confirms that models with various representations for the PBL predict markedly different meridional gradients, likely due to rectification.

The present proposal addresses these issues for the North American continent by obtaining comprehensive tracer and CO_2 data in and above the PBL.

•• The study is intended ***to define the impact of rectifier effects on large scale CO_2 distributions, and consequently on model-derived global CO_2 flux estimates****;*

•it will be a ***pilot study to determine how to measure CO_2 fluxes on regional, continental and global scales***.

We plan to install on the University of North Dakota's Citation II aircraft continuous CO_2 and CO analyzers and a flask collection system for analysis of CO_2, $^{13}CO_2$, and O_2. Two airborne surveys are planned, in summer and in winter, each consisting of 4 weeks of numerous vertical profiles from near the surface to 40 kft. over North America and coastal oceans. The influence of CO_2 fluxes from the terrestrial biosphere, fossil fuel combustion, and the oceans will be distinguished using the suite of tracers as described below. The proposed study will characterize the spatial variability of CO_2 concentrations over North America, which will assist in planning of long-term CO_2 observations above the surface (e.g Tans' "Carbon America") and will provide the information to develop measurement protocols for terrestrial CO_2 fluxes at regional scales. Results will be compared to biosphere-atmosphere model predictions to test representations of mixing in the PBL and representations of biospheric exchange fluxes.

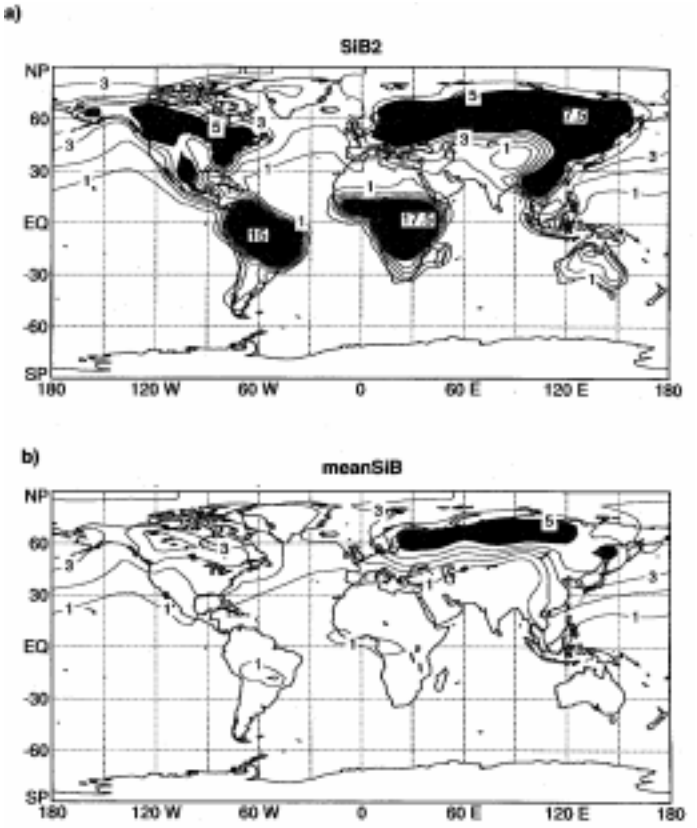


Fig. I-2. Annual mean horizontal gradients for a model with the diurnal and seasonal rectifiers (upper panel), and with the diurnal rectifier omitted (lower panel). Values represent the annual mean difference at the surface in each location vs South Pole. Note the seasonal rectifier alone is predicted to produce the most important gradients at remote Pacific stations, while the diurnal rectifier produces large apparent excesses over continents, even in the annual mean (Denning et al., 1996).

II. Scientific Background

A. The Mechanisms for Rectifier Effects

Figure II-1a (Denning *et al.*, 1996) shows a schematic of the biophysical covariance leading to the seasonal rectifier effect. During the 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 is mitigated by dilution in the deep PBL. In contrast, during the winter the PBL is shallow and the increase in CO_2 due to 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 signal propagates over the oceans to island stations (see Fig. I-2.) *This annual signal cannot be distinguished from a net terrestrial CO_2 source if measurements are obtained only at the surface.*

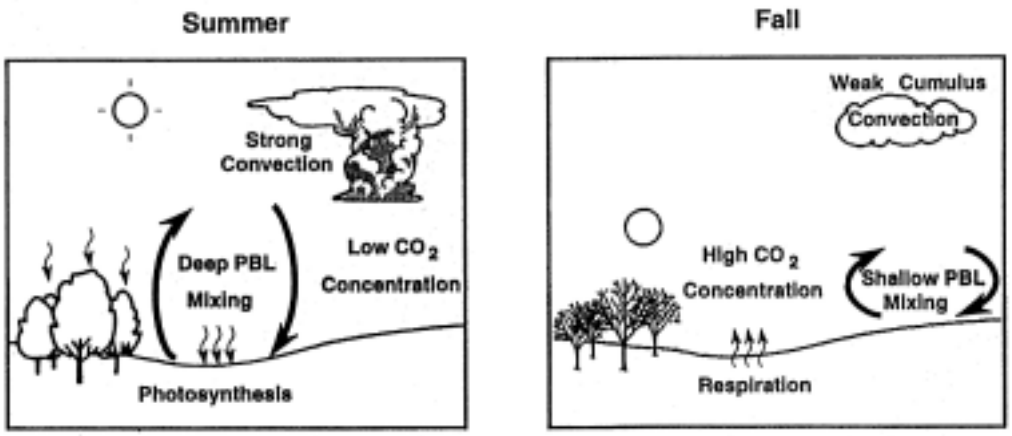


Figure II-1a. Schematic of the seasonal rectifier effect (from Denning *et al.*, 1996).

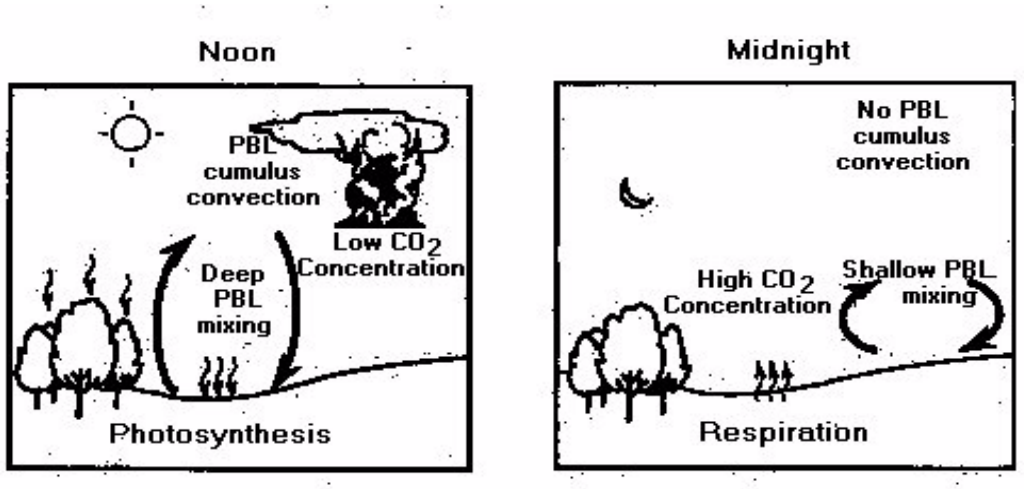


Figure II-1b. Schematic of the diurnal rectifier effect (from Denning *et al.*, 1996).

A similar mechanism operates on diurnal time scales (Figure II-1b; Denning *et al.*, 1996). In daytime during summer photosynthetic uptake is distributed through a deep atmospheric layer, due the deep PBL in the afternoon. 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 absence of net continental CO_2 uptake. Seasonal and diurnal rectifiers have large effects on inverse studies.

Figure II-2 shows the zonal annual mean CO_2 variations at the surface computed by 12 models all using specified, seasonally-varying, annually-balanced terrestrial exchange (TRANSCOM study; Law *et al.*, 1996). The disparities in Northern Hemisphere surface concentrations result from different treatments of the PBL. If natural rectifiers produce an interhemispheric difference on the order of 2 ppm, as some models show, 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. Even greater uncertainty may be associated with the diurnal rectifier, as it produces even higher concentrations at the surface over the continents (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. High resolution measurements of vertical profiles in CO_2 and tracers will be needed to characterize and account for potential rectifier effects.

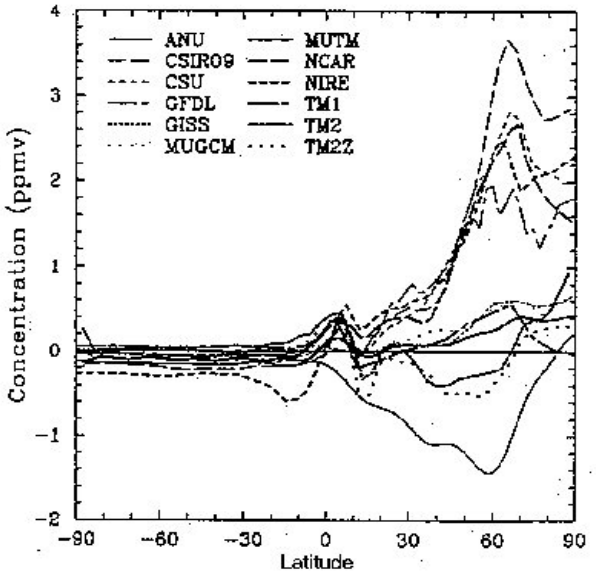


Figure II-2. Annual zonal mean CO_2 concentrations as a function of latitude resulting from a seasonally balanced biospheric source, providing a measure of the gradients produced by rectification. Note the gross differences among as the 12 transport models used in the TRANSCOM study, even for identical realizations of biospheric exchange fluxes (from Law *et al.*, 1996).

Figure II-3 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 during winter and summer. Our high resolution measurements of CO_2 will produce comparable cross sections. Because combustion sources release CO in reproducible ratios to CO_2 (see below), we will measure CO in addition to CO_2 to quantify the fossil fuel component and to separate it from the terrestrial component of CO_2, providing a direct test of model simulations of these components. The longitudinal patterns in Figure II-3 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 the winter and a sink during the summer.

TM2 lacks the diurnal rectifier and consequently predicts a drawdown of CO_2 near the continental surface during summer. Depending on the degree of rectification, and the sampling design (surface vs altitude data, 24-hour means vs grad sampling), measurements may actually show enhanced CO_2 concentrations in this region, evidently a serious consequence for inversion calculations using such a model. Thus our proposed measurements will provide a key test of the magnitude of diurnal rectification predicted by current and future models. Furthermore, it is the seasonal difference in the efficiency of mixing through the PBL which drives the seasonal rectifier. Thus our observations of the vertical propagation, with longitude, of these continental signals will provide additional tests for model representations of the seasonal rectifier.

B. Feasibility of the Proposed Study: Previous Observations

The use of CO data to distinguish CO_2 due to fossil fuel from CO_2 due to terrestrial vegetation can be tested using concentrations of CO_2 and CO, and vertical fluxes for CO_2, heat, and momentum, measured continuously for several years at Harvard Forest (42.5N, 72.2W). Figure II-4 shows CO_2 data for January and August 1995, selected for moderate or strong mixing (friction velocity U* > 0.3 m/s), with a fit to the form

$$[CO_2] = a_0 + a_1 [CO] + a_2 F_p + \sum_j a_3^j f_d^j \qquad \textbf{(1)}$$

where a_0 is the intercept and F_p is a flux parameter that accounts for the influence of CO_2 net exchange ($F_p = \Phi/U^*$, where Φ is the CO_2 vertical flux and U* is the friction velocity) with the underlying canopy. The variables f_d^j represent diurnal variations in the PBL: the data are binned into3-hour intervals and parameters $\{a_3^j\}$ derived for each interval using a generalized linear model (Venables and Ripley, 1994)(i.e, times of day are treated as factors). (Table II-1). Excellent fits to hourly data are obtained in each month (r^2 = 0.6 - 0.9). The CO_2 :CO slopes (~57(±17) moles CO_2/mole CO) are reproducible, slightly lower in summer due to oxidation of hydrocarbons co-located with CO_2 emissions (Table II-1). The CO_2 associated with CO in these data represents primarily regional

mean fossil fuel emissions for the northeast corridor (Potosnak, Wofsy, et al., 1997), with small contributions from oxidation of atmospheric hydrocarbons. The analysis will be checked using data for another urban tracer, SF_6, to be measured by Tans et al. from their flask samples. Possible influence of CO_2 from power plants not co-located with CO sources (e.g. western coal-burning stations) will be examined, and corrections made if necessary.

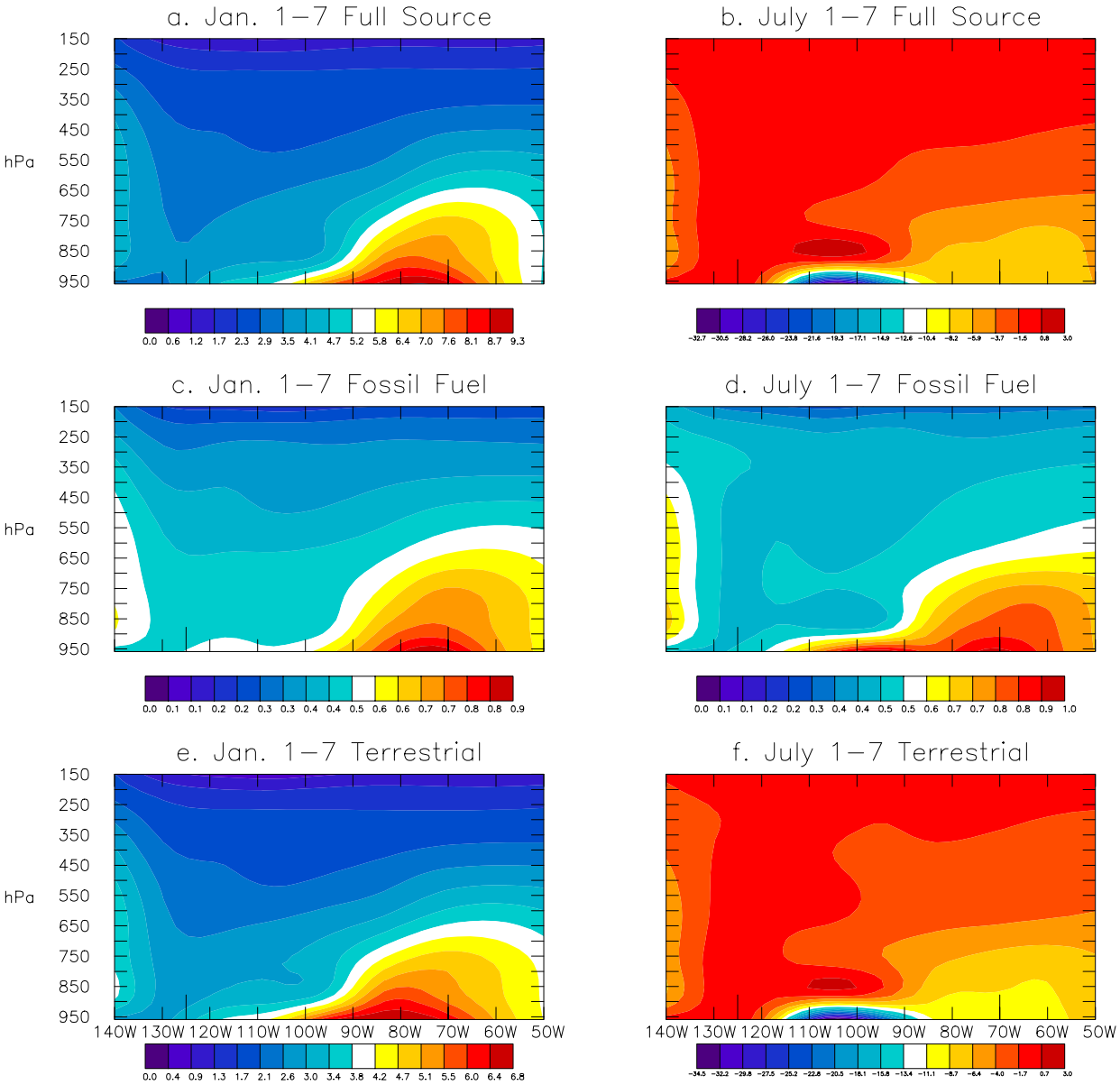


Figure 3. Vertical and longitudinal variations in CO_2 (ppm) as predicted by TM2 for composite, fossil fuel, and terrestrial sources. Plots show 7 day averages in early January and July at 43° N. Large tick marks indicate the edges of North America.

Figure II-3

Month	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Sep-96	Oct-96	Nov-96	Dec-96
(Intercept)	356.3411	362.9660	358.4205	360.6521	364.1233	365.7329	355.4550	363.0805	349.0309	353.4740	359.7105	351.6529
co	0.0764	0.0403	0.0666	0.0667	0.0519	0.0349	0.0498	0.0293	0.0606	0.0637	0.0603	0.0910
phi.uu	-0.1703	0.6662	1.9000	5.5491	4.2383	2.3972	3.1534	2.5865	3.2795	5.5381	3.5921	0.2947
dayf.fact1	0.3318	0.0413	0.4370	0.6160	2.1163	4.7704	2.8556	3.1564	10.4032	1.9728	0.0285	-0.0258
dayf.fact2	0.6589	-0.6445	0.5148	0.1215	1.8994	-3.6567	3.3541	1.3529	9.3982	1.1544	0.1199	0.1093
dayf.fact3	0.3481	0.9678	-0.6150	-1.7380	-3.0276	-10.5029	-0.8559	-12.8318	6.9206	0.2855	-0.1664	1.4234
dayf.fact4	-0.4601	-0.5951	-1.7334	-3.5389	-4.9134	-12.2051	-11.7753	-17.8989	2.9357	-2.4257	-1.8768	1.5369
dayf.fact5	-0.1896	-0.4977	-1.5511	-3.4567	-4.8620	-17.5423	-16.9286	-22.3202	-12.2331	-5.3346	-2.1691	1.9064
dayf.fact6	-0.6031	-0.4232	-0.3616	-2.3379	-3.7783	-14.2478	-16.9181	-18.4279	-12.2856	-2.1903	-1.2225	1.1243
dayf.fact7	-0.7160	-0.4139	-0.0166	-0.9048	-1.4793	-3.8255	-5.5755	-8.6056	-8.8783	-1.9299	-0.8704	1.0200
R squared	0.9358	0.6612	0.8994	0.6471	0.7355	0.6956	0.7127	0.7266	0.5956	0.8440	0.6822	0.7872
Mean	374.0263	372.9284	373.2005	372.5606	373.8542	368.0959	362.8630	364.1301	362.5561	365.6900	374.7508	376.4215
Std Dev	8.4551	5.0999	4.8720	4.2770	6.5298	11.0784	12.0255	15.1613	13.7612	5.1271	5.9620	6.8156
Morning	367.7737	369.7792	367.4652	368.5891	368.6200	360.2940	361.8157	354.4933	364.7445	362.9949	368.2906	366.2709
Afternoon	367.2360	368.3136	366.5291	366.8704	366.7857	353.2546	345.7429	345.0049	345.5908	357.3748	366.2879	366.7539

Table II-1. Regressions for CO_2 at Harvard Forest for 1996, using Eq. **(1)**.The fits show greater significance for CO in winter, reflecting the dominant contribution of combustion sources to variance in CO_2 at this site in January; biospheric exchange (phi.uu) and diurnal changes in the depth of the boundary layer (day.fact) dominate in summer.

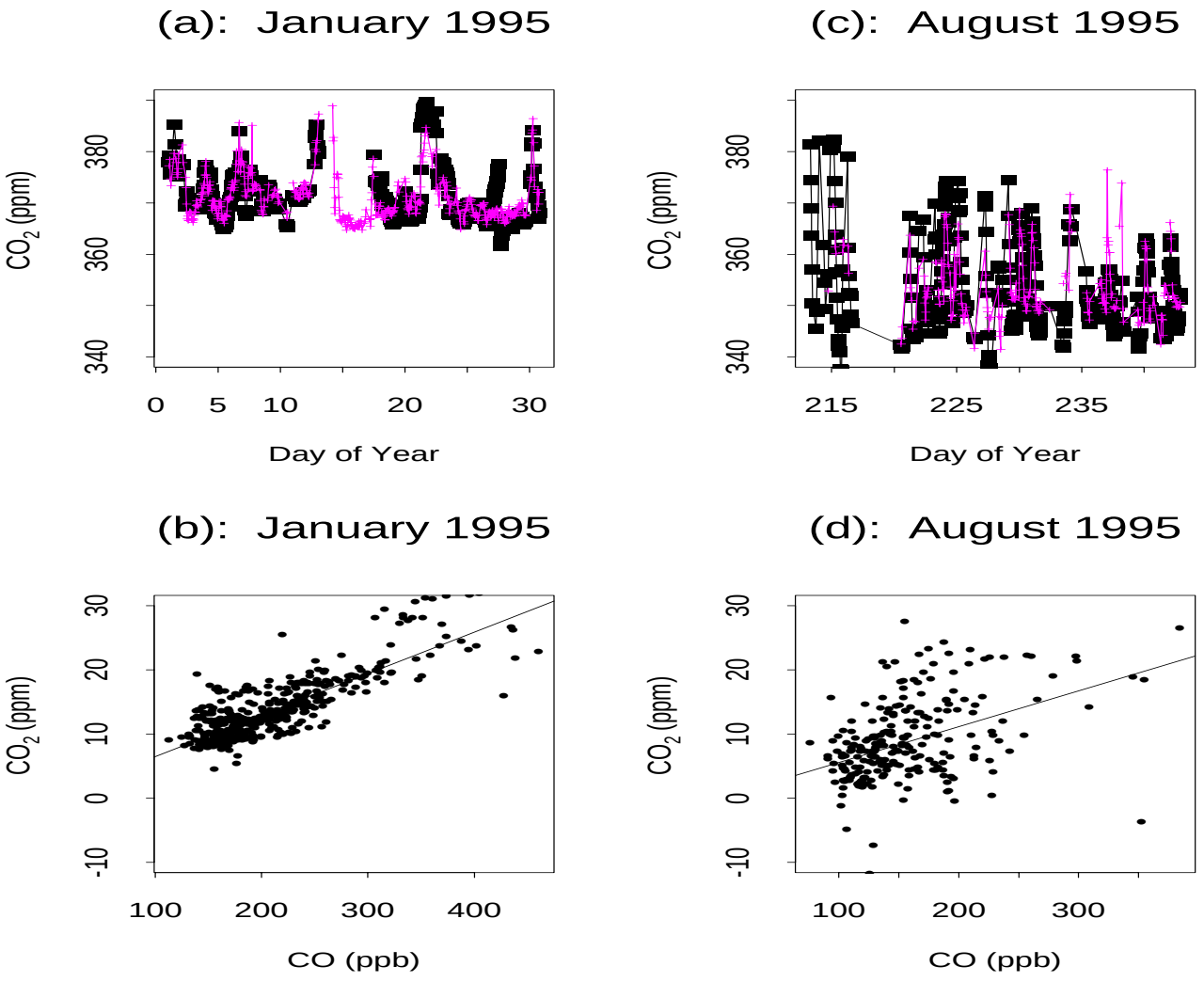


Figure II-4. Carbon dioxide concentrations at Harvard Forest in January and July, 1995, conditionally sampled for periods with significant momentum exchange (U* > .3 m/s).
Upper: Data (black) with fit to { CO, (F-CO2/U*), time-of-day } (red);
Lower, Concentrations accounting for { (F-CO2/U*), time-of-day } plotted vs. CO.

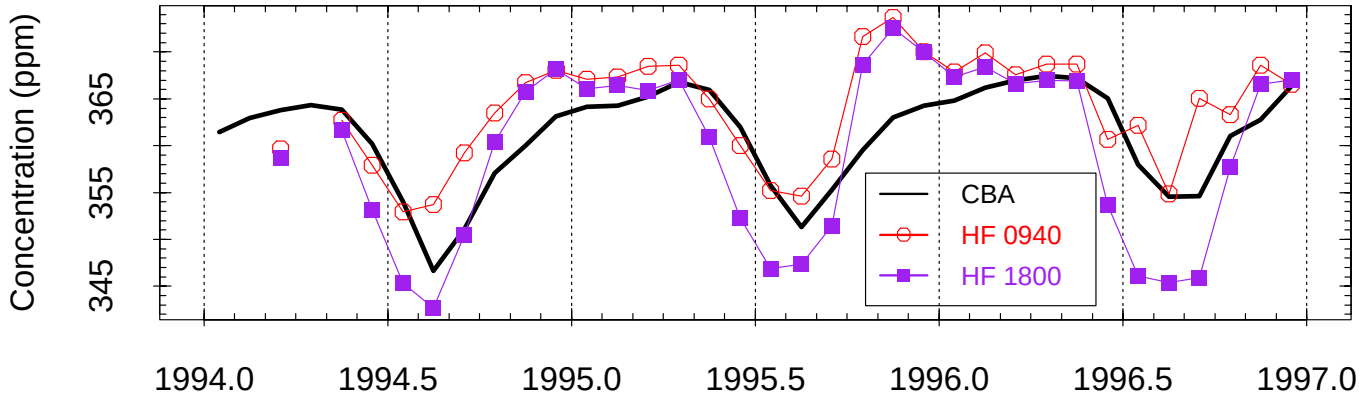


Figure II-5.
Carbon dioxide concentrations in the continental boundary layer at Harvard Forest (42.5 N, 72.2 W). Effects of combustion and forest atmosphere exchange removed by conditionally sampling for strong momentum exchange (U* >.3 m/s) and fitting to Eq. 1, corrected to zonal mean CO (20%ile, Goldstein e and zero flux parameter, for morning and afternoon.
The black heavy line shows data from Cold Bay (CBA) in the Pacific Ocean (55.2 N, 162.7 W).

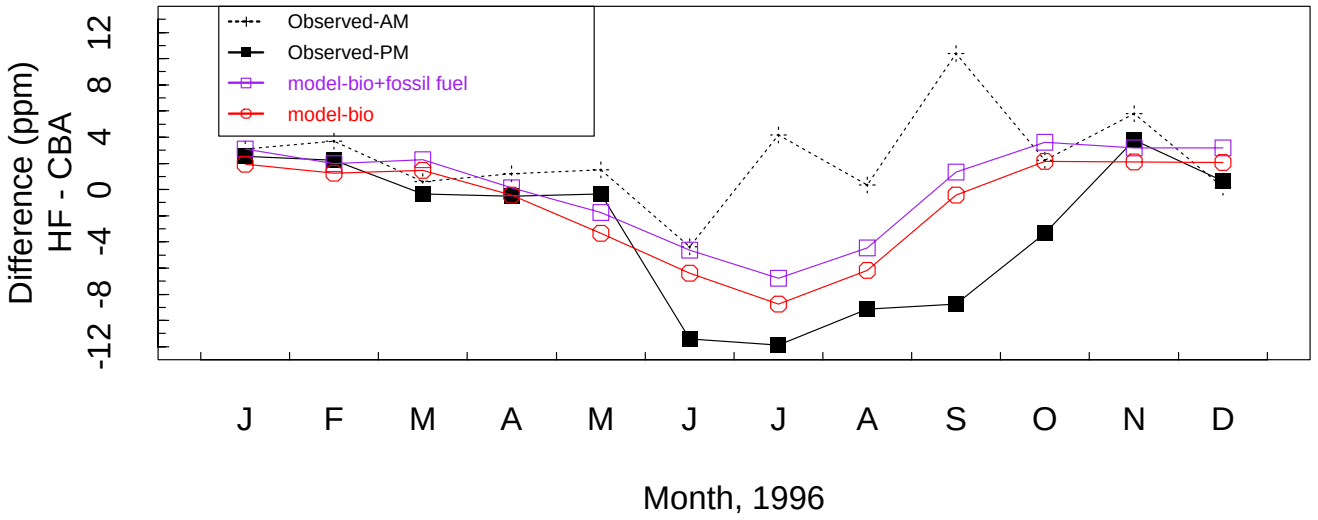


Figure II-6. Comparison of observed and modeled differences in background concentrations of carbon dioxide at Harvard Forest (MA) and Cold Bay, Alaska.
Model (TCM-2) used global observed winds and mechanistic biosphere.

We removed the influence of combustion on CO_2 the variance at Harvard Forest by substituting into the regression equation 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 flux parameter, correcting for the small gradients that develop in the PBL due to local canopy uptake or release. Figure II-5 shows results given by the fitted formula for various hours of the day with these parameters, representing the background concentrations in the PBL plus the influence of biotic exchange in the lower part of the PBL. Comparison to CMDL data from Cold Bay, AK (55N, 162.7W) shows that wintertime CO_2 in the PBL over Harvard Forest is slightly higher than at Cold Bay at all times of day, as expected due to net respiration. However, summertime mean concentrations at 30 m are higher than CBA, due to high values all night and through the morning, . Figure II-6 compares observed Harvard Forest - Cold Bay differences to the TM2 model. The model

predicts depression of 8 ppm near the surface in midsummer, comparable to observations late in the day. However, 24-hour mean concentrations show excess CO_2 all year round, even though we have used only data from well-ventilated periods. The proposed experiments will measure the low CO_2 values found at high altitudes over the continents, and, in combination with surface data from remote stations and from forested sites, will define the magnitude of the diurnal rectifier.

Observations of biogenic and combustion CO_2 over Amazonia in ABLE-2B

Data obtained in the Amazon region in 1982-87 provide direct tests of the proposed experimental design. Figure II-7 (Keller and Wofsy, unpublished data, 1983) shows flask measurements obtained in the interior of Amazonia from November, 1982 - July, 1983 near Manaus, AM and at the same latitude (3 S) at the coast (Fortaleza, PA). Samples were obtained in mid-morning or mid-afternoon in well-ventilated conditions The data for CO_2, show higher concentrations in the interior, 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. We now know that this similarity is an artifact of the diurnal rectifier.

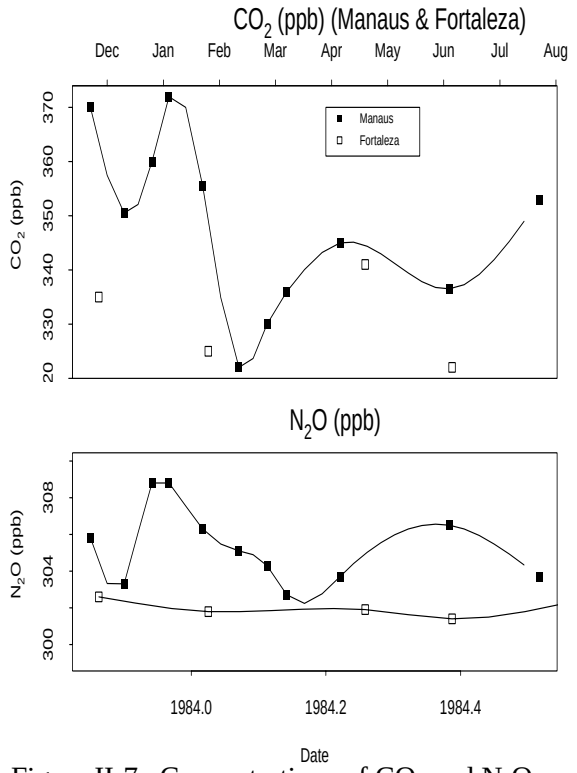


Figure II-7. Concentrations of CO_2 and N_2O observed in interior Amazonia in mid-morning (3 S, near Manaus, AM) and on the beach in Fortaleza at the same time of day during 1982-83 (Keller and Wofsy, unpublished, 1983). The excess CO_2 in the morning was 10-30 ppm, even after vigorous development of the PBL had been proceeding for several hours, a consequence of the diurnal rectifier effect..

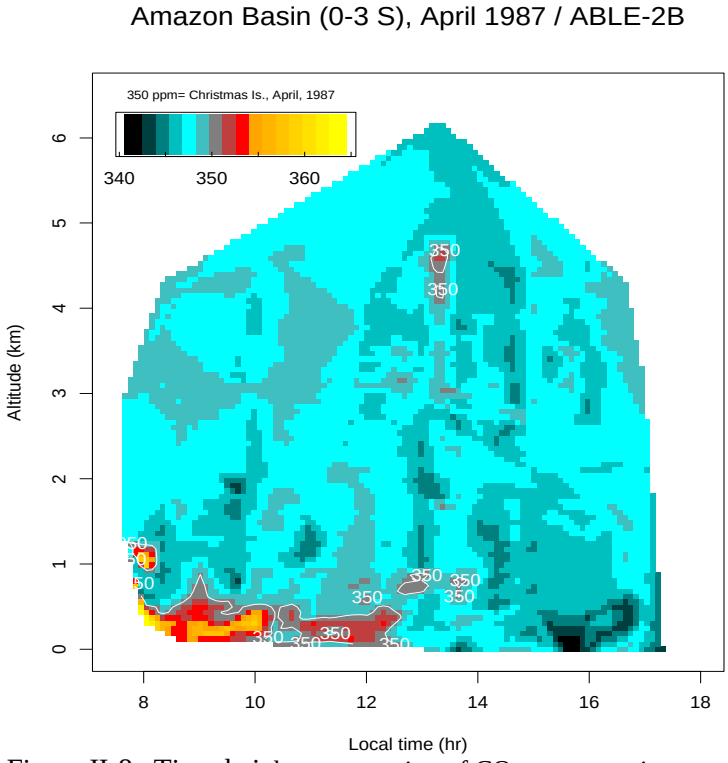


Figure II-8. Time-height cross section of CO_2 concentrations during ABLE2B, from 15 flights in the central Amazon Basin (0-3 S latitude) in April 1987. Note the development of the CO_2-rich PBL, with low concentrations aloft. In late afternoon the low values develop in the PBL when it is at its maximum thickness; these low values are supplied by the rectification process to the higher altitudes and adjacent oceans (Wofsy and Harriss, 1987, unpublished [available at ftp:// ftp-gte.larc.nasa.gov]).

Figure II-8 shows airborne observations of CO_2 over Amazonia similar to those that proposed here for North America, although the prototype CO_2 sensor had much lower precision (±0.6 ppm). Data were aggregated from 15 flights near Manaus. The excess CO_2 in the morning was 20-30 ppm (cf. Fig. II-7 and Wofsy *et al.*, 1988), which was well simulated by the model of Denning *et al.* (1996). The low values that characterize altitudes

above 1 km were generated in the PBL in late afternoon, when the PBL height is maximum and CO_2 concentrations minimum, and these anomalous concentrations were left behind as PBL mixing ceased in evening. The mean concentration was lower than Christmas Is. at most altitudes (Fig. II-9a), but CO_2 concentrations were higher than adjacent coastal regions below 2 km (Fig. II-9b; confirmed in Figs. II-7 and in aircraft data in Wofsy et al., 1988)

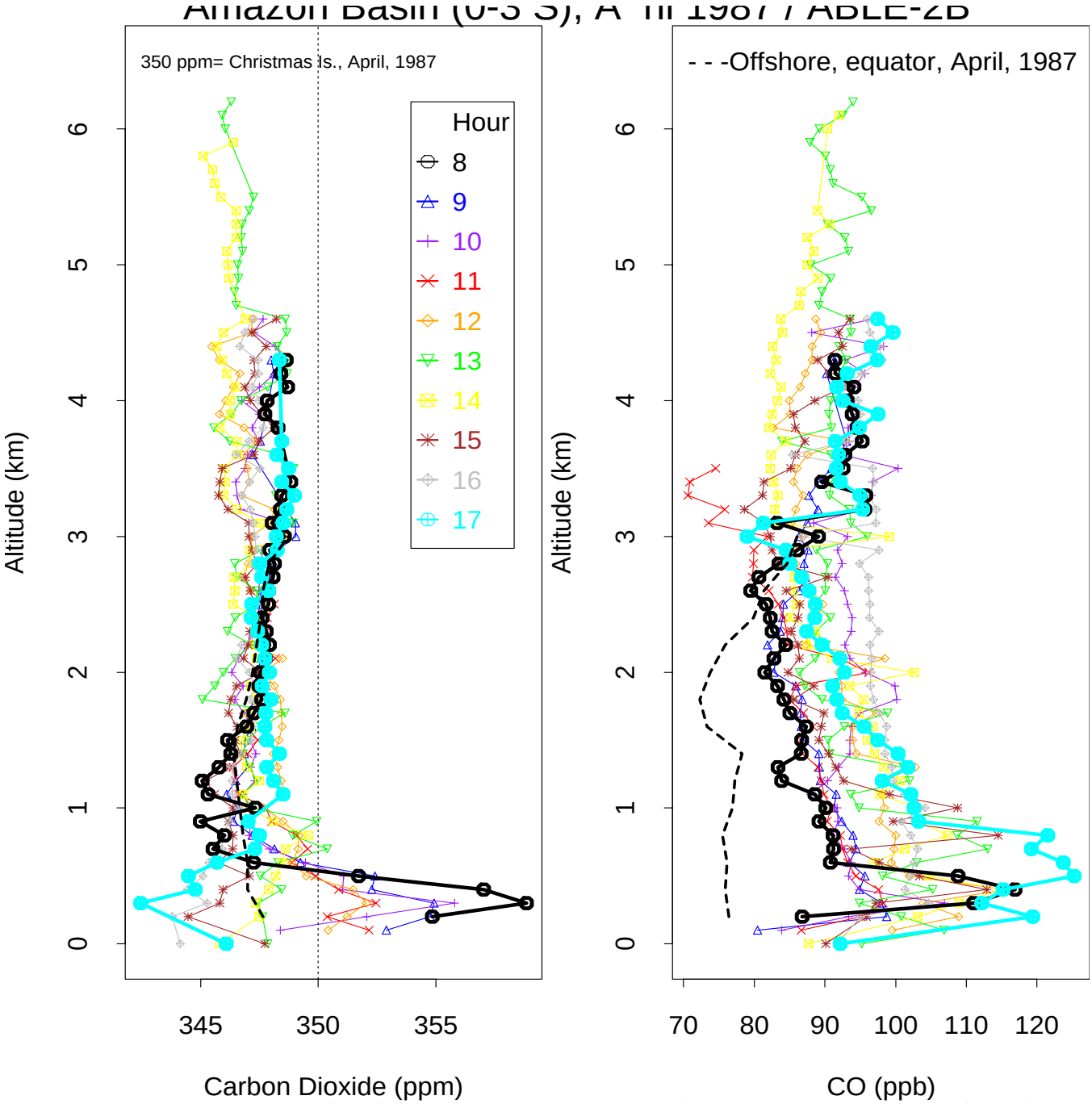
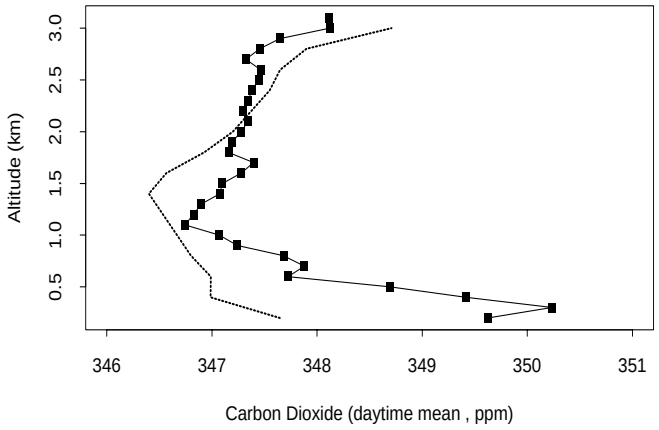


Figure II-9a. Hourly average vertical profiles of CO_2 and CO over the Amazon Basin for 8 - 17 hours local time, from 15 flights of the Electra during ABLE-2B. Data for CO_2 (left panel) show diurnal variations similar to observations in ABLE2A (Fig. I-1b), with a phase reversal near 1 km representing the upward propagation of the diurnal signal (the PBL is not perfectly mixed). All data above 1km lie below the values observed at Christmas Island at the same time, a measure of the diurnal rectifier. For CO (right panel), the net source is evident from the excess observed throughout the day between 0 and 3 km. Note marked difference between the CO_2 time/height variations and the variations for CO.



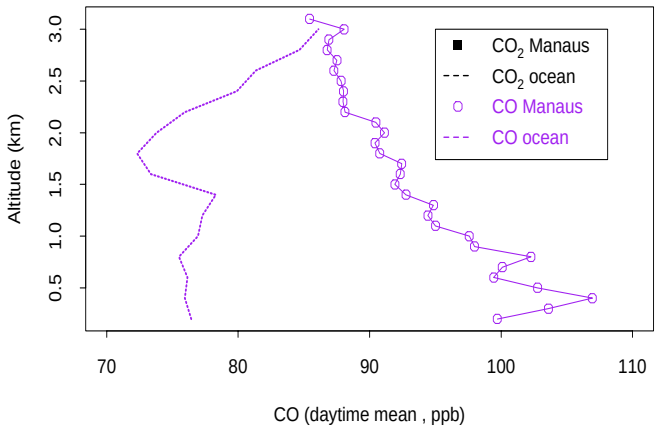


Figure 9b. Vertical profiles of CO_2 (upper)and CO (lower) over the Amazon basin averaged over the time period 8-17 hrs. local time (points), and profiles obtained off the Atlantic Coast, at the equator, during the same mission (ABLE2B). Note the marked differences, especially below 2 km. The minimum in CO_2 in the mixed layer displays the influence of the diurnal rectifier, which is absent for CO, for which the surface is a net source at all times of day. increasing concentrations between 2 and 3 km appear to represent intrusion of air from the northern hemisphere.

We can test the capability to separate the influence of combustion from canopy exchange on the variance of CO_2 using the 9500 simultaneous CO and CO_2 measurements in this data set. We binned the data from all 15 flights by altitude (0.2 km = Δz, range 0.2-6 km)) and time (1 hr = Δt, range 8-17 hr) to obtain data classified with a factor (f_{dz}) having 300 possible values; there were ample measurements to define the diurnal variation at altitudes below 3 km, but sparse coverage of times of day above. The overall fit to the form

$$[CO_2] = a_0 + a_1 [CO] + \sum_j a_2^j f_{dz}^j \qquad \textbf{(2)}$$

has residual standard error of 2 ppm and r^2 of 0.6, with about half of the residual error due to sensor variance (this early instrument was affected by aircraft motions by at least ±0.6 ppm with additional variance due to changes in cabin temperature). Accurate representation of the data by this linear model provides the basis for separating background, biogenic, and combustion-derived CO_2, as shown in Figure II-9c.

The linear model provides an estimate for the CO_2 from combustion and other oxidation processes, 71 (±2) moles per mole of CO, very similar to the value obtained from Harvard Forest data (Table II-1) and notably higher than the value of 11.7 obtained from biomass burning plumes in the region during ABLE2A (Andreae et al, 1988). ABLE2B took place during the wet season, and there was very little biomass burning in the region. Harriss et al. (1990) inferred that much of the CO variance in ABLE2B (during the wet season) was associated with episodic influx of polluted air from the northern hemisphere, and no doubt the urban region of Manaus contributed to the observed signal. The other major source identified for CO during this period, oxidation of isoprene, produces about 1:1 CO_2:CO and hence negligible correlated variance of CO_2. This kind of source blending contributes some uncertainty to the attribution of combustion-derived CO_2 of the linear model. We expect biogenic and anthropogenic combustion sources to dominate the variance of CO_2 over North America, and that CO production from oxidation of hydrocarbons to be readily folded in to the analysis as at Harvard Forest. The proposed work will examine a variety of urban and industrial tracers and O_2 to constrain and check this determination.

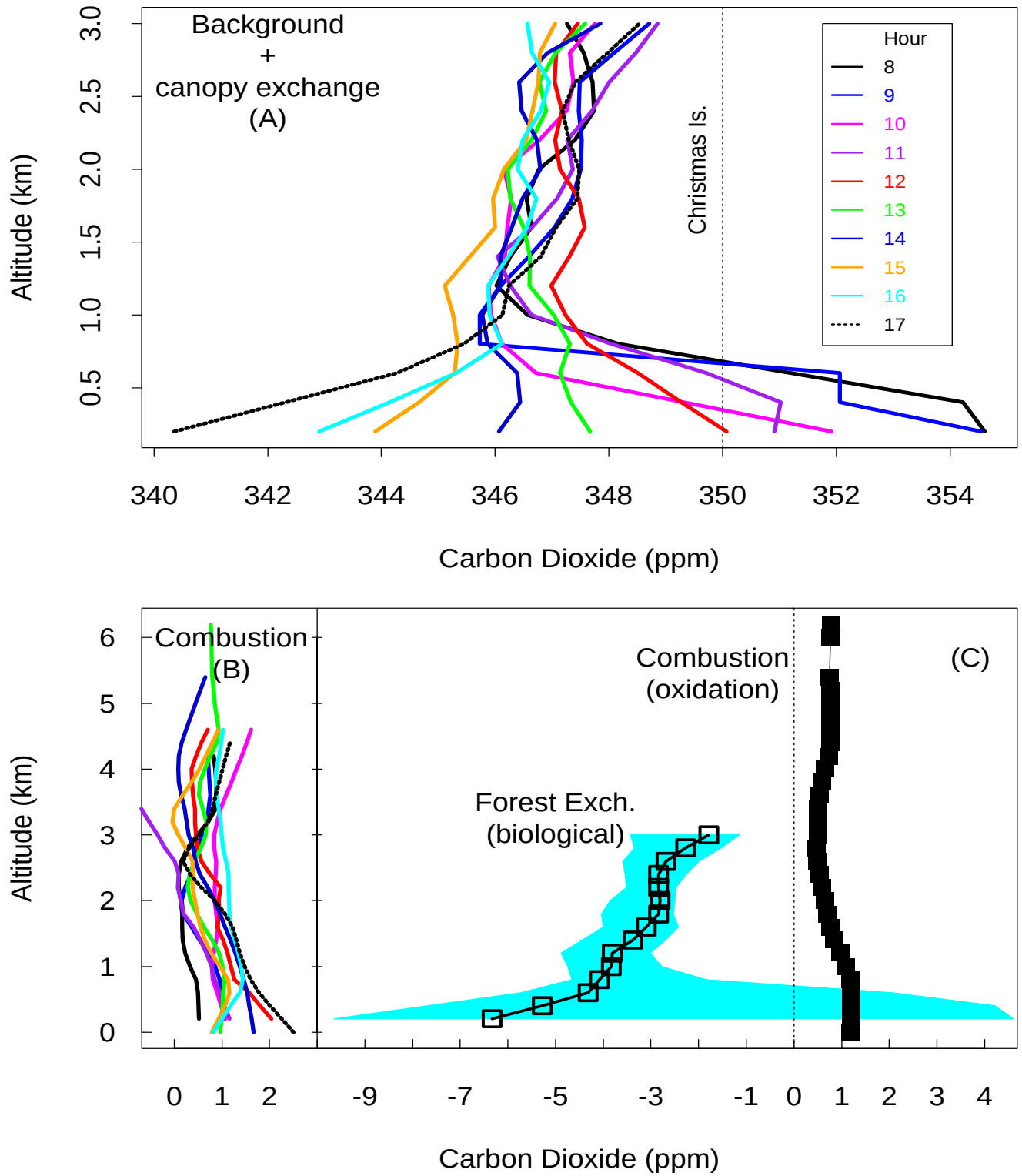


Figure II-9c Linear model representation of ABLE2B data for CO_2 and CO over Amazonia. (panel A) Mean vertical profiles for CO_2 with CO set equal to the 20th percentile, representing the background + biogenic CO_2. (panel B) Vertical profile of combustion-derived CO_2, using the CO_2:CO ratio from the fit (71(±2):1 mole/mole) and observed CO; the molar ratios over Amazonia were very similar in ABLE2A (Andreae et al., 1988). (panel C) Vertical profiles of CO_2, averaged over 24 hours, differenced against the value observed at a background tropical site (Christmas Is.). The 24-hour means (■, combustion; □, biogenic) were constructed assuming that profiles at night (between 17 hr and 8 hr) were the same as the profile at 17 hr, as noted during night flights in ABLE2A (Wofsy et al, 1988). The observed 24-hour mean CO_2 at 41 m from our tower site was 362.4 ppm, or +12.4 ppm relative to Christmas Is. The uncertainty in absolute calibration, using Standard Reference Materials from the National Bureau of Standards, is estimated to be about ±2 ppm.

III. Proposed work

III-A. Instrumentation and Sampling Strategy

A continuous CO_2 instrument with 1 Hz resolution, identical to our ER-2 and balloon-borne instruments (Boering *et al.*, 1994) is currently under construction supported by NOAA OGP. The ER-2 instrument has demonstrated long-term precision for more than 126 flights from 1992-97 better than 0.05 ppm (Boering et al., 1994, 1995). We maintain standards traceable to Scripps and CMDL scales to the best accuracy attainable (~0.2 ppm). Current instruments have resolution 5-10x better than the prototype used in ABLE-2 (Fig. II-8), more than adequate to resolve the gradients (1-10 ppm) in this study. The NCAR Tunable Diode Laser Spectrometer measures CO continuously. It has been successfully test flown to demonstrate long-term precision better than ±1%; additional test flights are planned to fine-tune the sensor. We will measure CO and CO_2 continuously at 1 Hz, giving approximate vertical and horizontal resolutions of 5 and 150 meters respectively. The capability to measure the O_2:N_2 ratio with a precision better than 2.5 per meg (equivalent to ~0.5 ppm CO_2) in flask samples has been demonstrated (Keeling and Shertz, 1992); we will also measure CO and CO_2 in each of these flasks.

NOAA/CMDL has developed an automated flask sampling system (Tans *et al.*, 1996) which collects 20 flasks per package, in an automated procedure, with rapid automated measurements in the laboratory of $^{13}CO_2$ ratios, CO_2, CH_4, CO, N_2O, and SF_6. We propose construction of two such packages for use in the current study in combination with the two existing samplers at CMDL. By turning these around rapidly during the mission, we will provide fairly complete coverage of the proposed flights. These flasks extend the suite of tracers considerably and they provide independent, reliable, traceable standardization relative to the CMDL measurements at the network of remote stations, a key part of the plan.

The aircraft currently under consideration is the University of North Dakota Citation, a small jet plane with capability for cruise at 340 kts with a duration of approximately 4 hrs. We plan transcontinental *survey flights* at northern and southern latitudes over the US, each comprised of 4 flight segments over land plus two over the ocean from each coast. Cruise altitudes will be primarily in the range 3-6 km, with a total of 12-18 vertical profiles on each transect covering the height range 150-13,000m (300-13000 m at night). These flights are intended to provide cross-sections similar to Fig. II-8, but with significantly more extensive spatial and temporal coverage, to define both horizontal and vertical gradients at continental scales at all times of day.

Survey flights will be complemented by 2-3 *intensive diurnal studies*, in which selected areas extending over 100-300 km are studied over a full day cycle or several cycles, including a region with extensive forest cover, another with intensive agriculture, and possibly an urban complex. These flights will elucidate the functioning of the diurnal rectifier and provide pilot data to define regional-scale sources/sinks of CO_2, CO, and O_2. Both intensive and extensive flights will emphasize relatively undisturbed meteorological conditions, avoiding strong fronts and synoptic disturbances.

We will obtain vertical profiles as often as possible over ground based observation stations, such as La Jolla, CA, Niwot Ridge, CO, WLEF (WI), Harvard Forest, MA, WITN (NC), and Bermuda (if it is with range for the aircraft and payload). At La Jolla, we are making continuous CO_2 and O_2 measurements in the marine boundary layer, and the variability in these measurements as well as the wind direction gives an indication of the relative fossil fuel influence. Over Carr, Colorado, NOAA/CMDL has an ongoing program of vertical profiles by Cessna aircraft, while nearby Niwot Ridge is a long term flask sampling station in the NOAA/CMDL network. The WLEF and WITN locations are very tall tower sites where PBL mixing processes and CO_2 fluxes are being studied by NOAA/CMDL (Bakwin *et al.*, 1995). At Harvard Forest, we have an ongoing eddy-flux measurement program (Goulden *et al.*, 1996), which includes continuous measurements of CO_2, CO, halocarbons, and hydrocarbons (e.g. CH_4, C_2H_2) for the identification of fossil fuel influence, and many other gases. Both tower sites, along with Bermuda, are long term flask sampling stations in the NOAA/CMDL network. The inclusion of these sites provides a rich set of ancillary data for interpretation of the airborne measurements and for cross-checking tracer concentration data for accuracy and precision. Our study will benefit from an understanding of the natural variability and local sources for CO_2 at these stations, and the ongoing ground based investigations will benefit from our characterization of vertical CO_2 and tracer patterns above their associated stations.

We plan a summer study and a winter study (July and January). The primary objective of the summer flights will be to define the diurnal rectifier and to demonstrate the feasibility of determining net CO_2 fluxes from fossil fuel burning and from the terrestrial biosphere on continental and regional scales. The goal of the winter study is to define the magnitude of the seasonal rectifier by comparison with summer data.

III-B. Analysis of the Proposed Observations

We will use our continuous airborne data for CO, supplemented by flask data for urban tracers such as SF_6, to measure, then subtract, the fossil fuel component from observed CO_2 concentrations (as done at Harvard Forest, Fig. II-4-6). To define CO/CO_2 ratios from major source regions and to assess associated variances, we will sample polluted air masses, such as the nocturnal boundary layer and plumes from major urban/population complexes. The main areas of interest for analysis of terrestrial biogenic fluxes are rural and forested areas remote from large population centers. We will therefore emphasize observations at moderately large distances from source regions, where inputs of primary CO and CO_2 from automobiles, CO from oxidation of anthropogenic hydrocarbons, and CO_2 from power plants, have blended to define a homogeneous regional mean $CO:CO_2$ ratio (as found at Harvard Forest, 250 km from the NY-Connecticut urban complex). The work will be closely coordinated with ongoing monitoring at Harvard Forest (MA), the WITN tower (WI), and Niwot Ridge (CO).

In regions remote from oceanic influence, we will verify our correction for fossil fuel using O_2 data using differences in the oxidation quotient: Terrestrial photosynthesis and respiration exchange O_2 and CO_2 in the ratio 1.1:1.0 whereas fossil fuel oxidation ratios average approximately 1.4:1.0 due to combustion of CH_4 and other hydrogenated fuels, but with notably lower values for coal-burning power plants. Measurement of $O_2:CO_2$ and O_2:CO ratios will therefore provide strong checks on this separation and will help identify anomalies or errors.

The O_2 measurements will also be important for identifying regions affected by air-sea exchange and for distinguishing marine and terrestrial influences. We can define a derived tracer, $(O_2 + 1.1\ CO_2) \equiv$PAO (Potential Atmospheric Oxygen), that is conserved with respect to terrestrial biotic flux (Keeling and Shertz, 1992). After removing the fossil fuel influence using CO correlations, variations of PAO should reflect only oceanic exchange. We will interpret data for PAO to estimate the direct influence of air-sea exchange on CO_2 over the continents, with the help of biological ocean models and available surface ocean data to define the marine O_2: CO_2 flux ratio. Comparisons between observed distributions of PAO, which has an oceanic source, fossil fuel CO_2 with a relatively constant land source, and terrestrial biotic CO_2 with diurnally and seasonally cycling land sources, will provide quantitative information about the global patterns of CO_2 and the factors that influence global CO_2.

The continuous CO and CO_2 measurements, in combination with the flask data, will enable us to produce height versus longitude maps for the fossil fuel and terrestrial CO_2 components, and compare directly to predictions of models (e.g. Figures II-3c, d, e, and f). Atmospheric mixing acts differently on tracers with temporally and spatially distinct sources. For example, the predicted CO variations (or fossil fuel CO_2 patterns shown in Figure II-3) are distinctly different from the predicted terrestrial CO_2 patterns (Fig. II-9), and these patterns will be compared to predictions and observations for a variety tracers such as $^{13}CO_2$, SF_6, in addition to CO and CO_2.

In particular, the diurnal rectifier is responsible for the major differences between distributions of CO, fossil fuel CO_2 and terrestrial biotic CO_2 in summer. The magnitude of changes in CO_2 in the PBL at different times of day and at different locations, as well as the longitudinal gradients of CO_2, at different altitudes and integrated through the atmosphere and within the PBL, provide direct measures of CO_2 continental-scale fluxes. In addition, the observed propagation of the oceanic signals over land and the terrestrial signals over the oceans will provide a basis for investigating the coupling between terrestrial and oceanic boundary layer mixing, helping to determine the impact of the diurnal rectifier on the background stations. Summer/winter differences for CO, CO_2, and PAO, interpreted in terms of continental concentrations and continent/remote station differences, will provide the first quantitative information on the magnitude of the influence of the seasonal rectifier on interhemispheric gradients measured at background stations.

Once models are shown to adequately represent rectification effects, we can have greatly improved confidence in estimates of terrestrial, fossil fuel, and oceanic CO_2 fluxes by combining airborne measurements with data from background stations. Observational determination of fossil fuel sources from large regions may become important in providing emissions verification under future international agreements. Furthermore, the same models and data should be capable of separately determining the terrestrial biospheric contribution to a nation's net emissions, providing valuable information for policy decisions based on total carbon management.

We will use our measurements to investigate the feasibility of determining regional CO_2 fluxes from a network of small aircraft collecting flasks as proposed by Tans, *et al*., 1996). Our data will indicate the degree of variability in CO_2 profiles over diurnal and synoptic time scales, and from very small to continental spatial scales. These results will provide unique insight into sampling design for future airborne sampling. We will also

investigate other for calculating regional fluxes. For example, by vertically integrating terrestrial and fossil fuel components, we can define a ratio between these influences over a region and can multiply this ratio by the relatively well-known fossil fuel source to estimate net terrestrial CO_2 flux for that region. This technique might be applicable on continental scales.

Our intensive studies in the boundary layer should provide reliable estimates of regional CO_2 and CO fluxes, as already demonstrated over the Amazon basin. Wofsy et al. (1988) used a direct mass-balance approach for the CO_2 column amount in the lower atmosphere, to compute the midday uptake of 9±4 kgC/ha/hr, indistinguishable from measurements by eddy correlation obtained in a subsequent experiment (Fan et al., 1990). We implement a strong conceptual framework for these observations by focusing on the WITN tower where fluxes and concentrations up to 600 m and parameters of the PBL (heights, entrainment rates, buoyancy fluxes) are measured. The variation of CO_2 in the planetary boundary layer over time is given by

$$h\,\partial C/\partial t + (\partial h/\partial t - \langle w \rangle)\,\Delta C + \{\text{advective terms}\} = S \qquad (3)$$

where h is the boundary layer height, t is time, <w> is the mean regional subsidence velocity (obtainable from analyzed meteorological fields, e.g. NCEP or ECMWF), ΔC is the concentration difference across the top of the boundary layer, and S is the surface exchange flux. At the WITN tower we will have measurements of all except the advective terms, providing an ideal framework to demonstrate the feasibility of determining regional fluxes (S) using aircraft observations of tracers , and to define the optimal suite of tracer and ancillary data.

The proposed study will provide new measurements of CO_2, CO, and O_2 in regions with few existing data, with unique spatial and temporal resolution, increasing our knowledge of atmospheric CO_2 variability due to heterogeneities in sources and mixing processes. The experiment will link ground-based observations to the vertical and longitudinal structure of CO_2 concentrations.. The new measurements will have wide application beyond those outlined above. For example, O_2 has never been measured at altitude above a continent. In areas where the fossil fuel and oceanic influences are small, we will be able to use these measurements to determine the oxidative ratios for terrestrial biotic processes, known as the photosynthetic and respiratory quotients, on much larger scales than previously possible. These ratios, assumed equal to 1.1 based on laboratory incubation studies (Severinghaus, 1995), are significant for ecosystem studies and are critical to inversion of CO_2 and O_2 data to obtain regional and global carbon budgets (Keeling *et al.*, 1996).

Deliverables

Data product	Ancillary data	Derived quantity	Analysis Product
CO distribution over North America	CMDL stations and tower monitoring data	CO excess relative to remote station	CO budget for North America
$\Delta CO_2 : \Delta CO$ $\Delta CO_2 : \Delta SF_6$	CMDL stations and tower monitoring data	Mean combustion CO yield, hydrocarbon role	Distribution of combustion-derived CO_2
$^{13}CO_2$: $^{12}CO_2$	CMDL stations and tower monitoring data; $\Delta CO_2 : \Delta CO$	Vertical, horizontal and temporal distributions of isotopic anomalies	Isotopic signatures for principal CO_2 sources on continental scale
$\Delta CO_2 : \Delta O_2$	SIO stations and tower monitoring data	Mean respiration and photosynthesis ratios	Respiratory coefficient, continental O_2 budget, and ocean influence
CO_2 and tracer continental cross sections	CMDL and tower data	Distribution of biogenic CO_2, O_2	Diurnal rectifier
CO_2, O_2 diurnal profiles (intensive)	tower fluxes, concn's.; $\Delta CO_2 : \Delta CO$	Surface layer, PBL, and tropospheric profiles, time-resolved	Regional fluxes of CO_2, O_2

Table II-2

Conclusion

The proposed measurement campaign will reduce the large uncertainties in the relationships between atmospheric CO_2 concentrations at surface stations, rates of mixing and advection, and surface CO_2 fluxes, which current limit our ability to define the present carbon cycle. The measurements will demonstrate the ability to resolve the primary influences on the large scale distributions of CO_2 (fossil fuel burning, and terrestrial and oceanic exchange), providing critical quantitative tests for the representations of diurnal and seasonal rectifiers and other transport effects in atmosphere-biosphere models. The work will contribute to designing optimal strategies for measuring regional and continental scale fluxes. The study is also designed to provide unique information on the budgets for CO and O_2 over North America, to define for the first time photosynthesis and respiration quotients and $^{13}CO_2$:$^{12}CO_2$ isotopic signatures for biotic and anthropogenic CO_2, and to demonstrate the capability for determination of regional CO_2 fluxes. We expect the results to lead directly to better estimates of the processes currently responsible for the observed sequestration of anthropogenic CO_2, and to improved experimental strategies for trace gas monitoring of key trace gases at regional, continental and global scales.

Work Plan

Year 1: 1998 -

1. Build and test instrumentation, sampler, and integrated payload.
2. Assemble CO_2 instrument at Harvard (funded by NOAA Office of Global Programs);
3. Assemble and test flask collection system at SIO;
4. Assemble 6 suitcase samplers at CMDL, each with 20 flasks;
5. Additional test flights of NCAR CO instrument on the WB-57F (funded by NCAR);
6. Test flights of the package including CO_2, CO (NCAR) and flask systems to check performance and obtain pilot regional data (test April-May 1999); approximate 30 hrs of flight time including
   - shakedown and certification flight
   - payload and concept test flights
     a) Diurnal series over the Harvard Forest and/or Wisconsin towers (where continuous data for flux and concentrations of CO_2 and CO are made).
     b) limited (regional) survey flight.
     c) urban and power plant plumes, compare to CO/CO_2 data from towers, test fossil fuel/terrestrial biosphere separation).
     d) coastal flight (test terrestrial/ocean separation)

We plan to engage modelers in analysis of the preliminary data set, to make testable/quantifiable predictions, and to help select where to measure during the main field campaigns.

Year 2: 1999 - Summer Campaign (July-August, 4 weeks) (125 hours total). We assume the platform will be the UND Citation (340 kts).

1. Four transcontinental transects at two latitudes (repeat each) with 12-16 vertical profiles in each plus flights off-shore (80 hours).
2. Two regional diurnal studies (20 hours).
3. Contingency time (ATC and weather delays; 10 hours) plus North/South transits (15 hours for 4 transits).

There will be 70 vertical profiles in total, collect 10 flasks for O_2 50, using 500 flasks. Collect 10-15 CMDL suitcase flasks per profile, plus several flasks along track, using the available 480 flasks each 3 times over the month.

Year 3: 2000 Winter flight series.

Basic flight scenarios will be similar to summer campaign.
Data analysis and writing of scientific papers.

Budget
put proper budgets here

Year 1: SIO—(sub) 1 graduate student, full year + 75k for flasks = 120k + travel 10k = 130k
HU—(prime)--1 student + 1 engineer, each for 4 months = 75k + standards = 10k + 10 k travel = 95k
UND purchase via Harvard sub Flight hours 30@1200 = 36k
CMDL (sub) 6 suitcase samplers $120k + shipping
Total year 1: $xxxk
NCAR (collaborators, separate)
Year 2: SIO – 1 graduate student, full year + 1 other 3 months = 75k + travel $20k = $95k
HU -- 1 graduate student, full year + 1 other 3 months = 75k + travel $20k = $95k
Flight hours 125@1200 = $150k
Total year 2: $330k
?other NCAR + CMDL?
Year 3: SIO – 1 graduate student, full year + 1 other 3 months = 75k + travel $20k = $95k
HU -- 1 graduate student, full year + 1 other 3 months = 75k + travel $20k = $95k
Flight hours 125@1200 = $150k
Total year 3: $330k

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