

# Influence of biotic exchange and combustion sources on atmospheric CO<sub>2</sub> concentrations in New England from observations at a forest flux tower

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**Abstract.** Hourly data for concentrations and fluxes of CO<sub>2</sub> at 30 m in Harvard Forest (Petersham, Massachusetts) are analyzed using linear modeling to obtain regionally representative CO<sub>2</sub> concentrations at a continental site. The time series is decomposed into contributions due to regional combustion, local canopy exchange, monthly average regional biotic exchange (as modulated by the daily cycle of growth and decay of the planetary boundary layer (PBL)), and the regional monthly background concentration. Attributions are derived using time series analysis, data for a tracer for combustion (CO or acetylene (C<sub>2</sub>H<sub>2</sub>)), and measurements of indicators of proximate canopy exchange (CO<sub>2</sub> flux and momentum flux). Results are compared to observations at Cold Bay, Alaska. Combustion contributes on average 4–5 ppm to ambient CO<sub>2</sub> at Harvard Forest in winter and 2–3 ppm in summer. Regional biotic emissions elevate daily mean CO<sub>2</sub> by 4–6 ppm in winter, and the covariance of the biotic cycle of uptake and emission with PBL height enhances daily mean CO<sub>2</sub> by 1–2 ppm in summer; minimum values in late afternoon average 10 ppm lower than at Cold Bay in summer. The study shows that regionally representative concentrations of CO<sub>2</sub> can be determined at continental sites if suitable correlates (tracers, fluxes of CO<sub>2</sub>, and momentum) are measured simultaneously with CO<sub>2</sub> itself.

## 1. Introduction

Models simulating atmospheric transport and CO<sub>2</sub> exchange with the surface are often used to infer the distribution of global sources and sinks for CO<sub>2</sub>. Inverse methods attempt to use atmospheric concentration data directly to obtain results for a limited number of aggregated source regions [e.g., *Enting et al.*, 1993; *Ciais et al.*, 1995; *Fan et al.*, 1998]. Forward models incorporate more detailed representation of exchange processes and compare observed and computed CO<sub>2</sub> concentrations to help constrain unknown parameters in the formulation [e.g., *Denning et al.*, 1995, 1996]. Global models

can in principle resolve sources, sinks, transport processes, and concentrations at the scale of a few grid elements (~ 1000 km). Most model studies, however, only use CO<sub>2</sub> concentration measurements from remote stations, mainly the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) air sampling network, to avoid confounding influences of subgrid scale processes such as local or regional combustion, proximate effects of vegetation, etc., but these “clean” sites are necessarily far removed from source or sink regions for which information is sought.

One way to interpret CO<sub>2</sub> data from a forest site is to explicitly model biological and planetary boundary layer (PBL) processes [cf. *Raupach et al.*, 1992; *Denmead et al.*, 1996], requiring detailed knowledge of atmospheric structure and transport over the site that may be difficult or impossible to obtain. This study applies a linear modeling approach to infer statistically the contributions of dominant source and sink processes to CO<sub>2</sub> variation over a forest, using measured concentrations to recover regional CO<sub>2</sub> signals over a continent by removing the influence of nearby sources and sinks. Since contributions from each source or sink superimpose, a linear model can distinguish contributions from various processes if suitable correlates are measured simultaneously. We analyze data from an eddy covariance

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Paper number 1999JD900102.  
0148-0227/99/1999JD900102\$09.00

flux tower in a forest in central New England where a large suite of potentially useful tracers is measured continuously. We show that combustion products such as CO and acetylene (C<sub>2</sub>H<sub>2</sub>) provide excellent correlates for regional combustion sources and that eddy covariance fluxes of CO<sub>2</sub> and momentum provide correlates for the local influence of exchange with the forest near the sensor. Thus we can infer regionally representative concentrations of CO<sub>2</sub> at canopy height, including diurnal and seasonal variations, for comparison with observations from remote stations.

## 2. Sources of Data

Hourly averaged concentrations of CO, CO<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> flux and momentum flux (expressed as friction velocity  $u^*$ , the square root of the momentum flux divided by air density) are from the long-term eddy covariance flux site at Harvard Forest (42° 32' N latitude, 72° 11' W longitude, elevation 340 m) [Wofsy *et al.*, 1993; Goulden *et al.*, 1996]. The data for this study were collected from spring 1994 to the end of 1996 (available at <http://www-as.harvard.edu>). CO<sub>2</sub> was measured with LiCOR models 6252 and 6262 infrared gas analyzers in fast response mode using standards traceable to the Scripps x95 mole fraction scale. An intercomparison of this scale with the NOAA CMDL scale produced differences under 0.20 ppm (Jim Peterson, NOAA CMDL, Boulder, Colorado). CO<sub>2</sub> flux was determined from the CO<sub>2</sub> measurements combined with vertical wind data from an Applied Technologies three axis sonic anemometer.

CO concentrations were measured using a Dasibi gas filter correlation infrared absorbance instrument. Ambient air was drawn from an inlet at the top of the sampling tower (30 m) through Dekoron tubing. The air was dried by passage through a Nafion dryer followed by a -40° cold trap. In order to achieve adequate sensitivity for measuring ambient concentrations at this rural site the instrument gains were turned up to their maximum settings. The instrumental zero was determined by passing ambient air through a Pt/Pd catalyst heated to 200°. In order to track baseline drift we used a measurement cycle of 6 min ambient sample followed by 6 min of zeroing. The CO instrument was calibrated by substituting a 500 ppb CO in zero air (Scott-Marrin) working standard several times a day. C<sub>2</sub>H<sub>2</sub> and additional CO data were measured by automated gas chromatography with flame ionization and electron capture detectors, respectively. We compare the results to concentrations of CO<sub>2</sub> and CO from a remote site in NOAA's CMDL air sampling network [Komhyr *et al.*, 1985; Novelli *et al.*, 1992; Conway *et al.*, 1994].

## 3. Model Rationale and Description

We constructed a linear model to represent the following environmental, physical, and biological influences on

CO<sub>2</sub> concentrations for each month: (1) the monthly average regional background, (2) combustion, (3) proximate forest canopy and soil fluxes, and (4) the daily cycle of regional biotic sources and the growth and decay of the planetary boundary layer (PBL). In the absence of direct observations of PBL structure, we use instead time of day to construct monthly mean diurnal cycles.

A simple fitting procedure was carried out to find the best coefficients to represent hourly CO<sub>2</sub> data for a month:

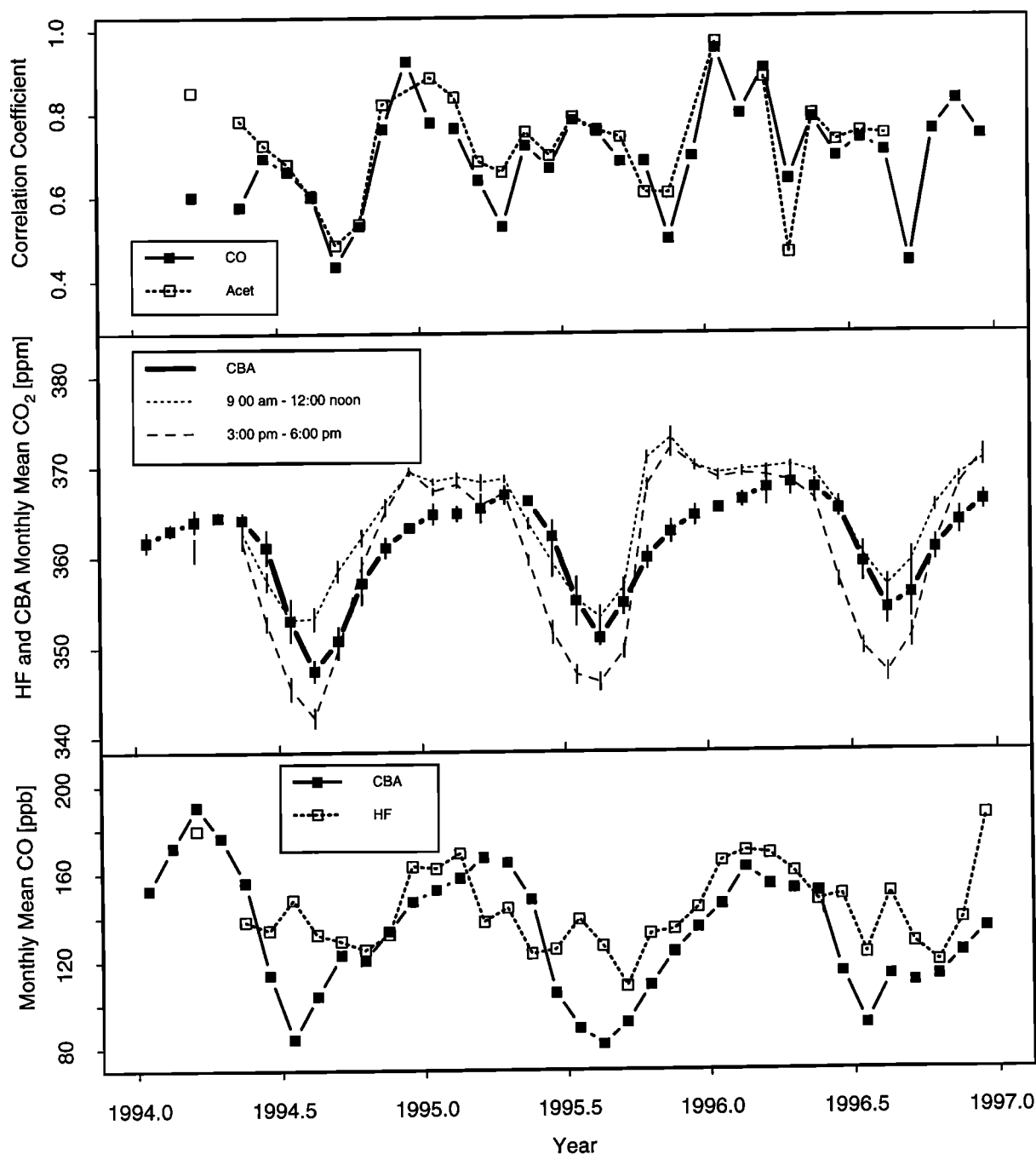
$$[\text{CO}_2] = \underbrace{a_0}_{(1)} + \underbrace{a_1[\text{CO}]}_{(2)} + \underbrace{a_2 F_p}_{(3)} + \underbrace{\sum_{j=0}^7 a_{3j} \delta_{jf}}_{(4)} \quad (1)$$

Here [CO<sub>2</sub>] and [CO] denote the observed concentrations at 30 m altitude,  $F_p$  is the ratio of the vertical flux of CO<sub>2</sub>,  $\Phi_{\text{CO}_2}$ , divided by  $u^*$ ,  $f$  represents time-of-day factors (denoted 0 through 7) for eight 3 hour intervals, and  $\delta_{jf}$  is the Kronecker delta (= 1 if  $j = f$  and zero otherwise).

Studies of pollution plumes in northeastern North America show enhancements of CO<sub>2</sub> and CO concentrations in reasonably consistent ratios [e.g., Wofsy *et al.*, 1994]. We assume that, during a given month, anthropogenic CO and CO<sub>2</sub> are emitted on average in a given ratio ( $\equiv a_1$ ) from colocated sources in the region (this assumption is examined further in the results section). Since significant CO is produced in summer from oxidation of anthropogenic and biogenic hydrocarbons, and some of this CO is produced proximate to anthropogenic CO<sub>2</sub> emissions, values of  $a_1$  are lower in summer than in winter (see below). Sources of CO that are not correlated to CO<sub>2</sub> emissions (e.g., local CO production from biogenic hydrocarbons) do not affect the magnitude of the emissions ratio.

The third term uses the parameter  $F_p (\equiv \Phi_{\text{CO}_2}/u^*)$  to represent the deviation between CO<sub>2</sub> at top of the tower and the monthly mean value for that time of day in the PBL (given by term 4) due to the influence of local canopy exchanges. The choice of  $\Phi_{\text{CO}_2}/u^*$  as the correlate reflects the view that the deviation of the concentration at 30 m from the PBL mean is directly proportional to the exchange flux ( $\Phi_{\text{CO}_2}$ ) and inversely proportional to the rate of turbulent mixing ( $u^*$ ) (cf. equations (7) and (8) of Denmead *et al.* [1996] for the physical basis behind this approach). This term has a small but significant effect on the analysis. During the summer months, about 65% of the variance of hourly data is explained by the other three terms; including this term raised  $r^2$  to 0.70, that is, removing about 15% of the residual variance.

The fourth term of the linear model is the sum of seven factors representing the monthly mean diurnal variation of regional CO<sub>2</sub> concentrations due to the combined effects of biotic exchange and the daily growth and decay of the PBL. The data used in fitting this term are binned into 3 hour intervals, and a constant is de-



**Figure 1.** (top) Comparison of the model  $r^2$  results when either CO or C<sub>2</sub>H<sub>2</sub> is used as a tracer for anthropogenic CO<sub>2</sub>. Although C<sub>2</sub>H<sub>2</sub> performs better, there are large gaps in the instrument record. (middle) Comparison of monthly mean CO<sub>2</sub> at Cold Bay, Alaska (CBA) with derived regional monthly background at Harvard Forest. Harvard Forest values are calculated by using the monthly constant from the regression and then adding term 2 of (1) with CO set to the twentieth percentile of CO for the month for 0900–1200 and 1500–1800 local time. Vertical thin lines denote 1 standard error of the mean (68% confidence interval). (bottom) Background concentrations of CO at Harvard Forest (HF) (twentieth percentile for the month) compared to the CO at Cold Bay, Alaska.

terminated for each of the last seven bins, equivalent to assigning eight time-of-day factors [Venables and Ripley, 1994] (the factor for the first bin is captured by  $a_0$ ). This approach allows an arbitrary shape for the diurnal cycle, and the number of degrees of freedom remains

high, usually above 250 per month. If diurnal variations are modeled with only two terms (sine and cosine), the goodness of fit does not change appreciably.

The diurnal variation described by term 4 is somewhat related to term 3 because the CO<sub>2</sub> flux and the

diurnal variation of the PBL are both driven by solar radiation. We assume that the processes are distinct, however, with term 4 describing the monthly mean variation due to combined PBL and biotic diurnal cycles and term 3 using the  $F_p$  correlate to describe deviations from the mean due to day-to-day variability and to the deviation of the surface layer from the PBL. This assumption has an important effect on the derived diurnal cycles. Even though the  $r^2$  for the regressions does not change much when term 3 is removed, the amplitude of the diurnal curve is increased significantly (by 5 ppm for the 0900–1200 time slice during June–September). Since the two terms are not linearly independent, term 4 accounts for some variation previously covered by term 3. If our interpretation of the partition between the two terms is correct, then flux measurements are necessary for estimating regional cycles of CO<sub>2</sub> in the PBL at sites with significant biological activity.

The value  $a_0 + a_1\text{CO}_{\text{background}}$  gives the regional average CO<sub>2</sub> concentration at the bottom of the PBL for 0000–0300 local time, except with effects of regional anthropogenic sources and local biology removed. Similar values for other times of day may be obtained by adding the appropriate factor (e.g.,  $a_0 + a_1\text{CO}_{\text{background}} + a_{35}$  for 1200–1500). All CO values could have been adjusted to remove the background CO. Then the term  $a_1$  alone would give the background CO<sub>2</sub>. Since subtracting a constant does not change the regression (expect for  $a_0$ ), this method is equivalent to our approach.  $\text{CO}_{\text{background}}$  is taken as the twentieth percentile of CO for the month [Goldstein *et al.*, 1995]. During the winter, the twentieth percentile of CO reasonably matches the values at Cold Bay (see Figure 1, bottom panel), so this assumption seems reasonable. Also, the sensitivity of the results was tested by comparing the twentieth percentile of CO with the fifteenth and 25th percentiles. The differences for background CO<sub>2</sub> were smaller than 0.3 ppm. Finally, the correlation between time of day and the CO concentrations was considered. If this were important, then the predicted diurnal cycles could be contaminated by contributions from anthropogenic CO<sub>2</sub>. To test this, we considered the covariance of the  $a_1$  term between the combined  $a_{3j}$  terms. The average was 0.03 with a maximum of 0.13, so the covariance is small and therefore has a small effect on the diurnal

cycles. These conclusions are supported by using C<sub>2</sub>H<sub>2</sub> as an alternative tracer for combustion (see below).

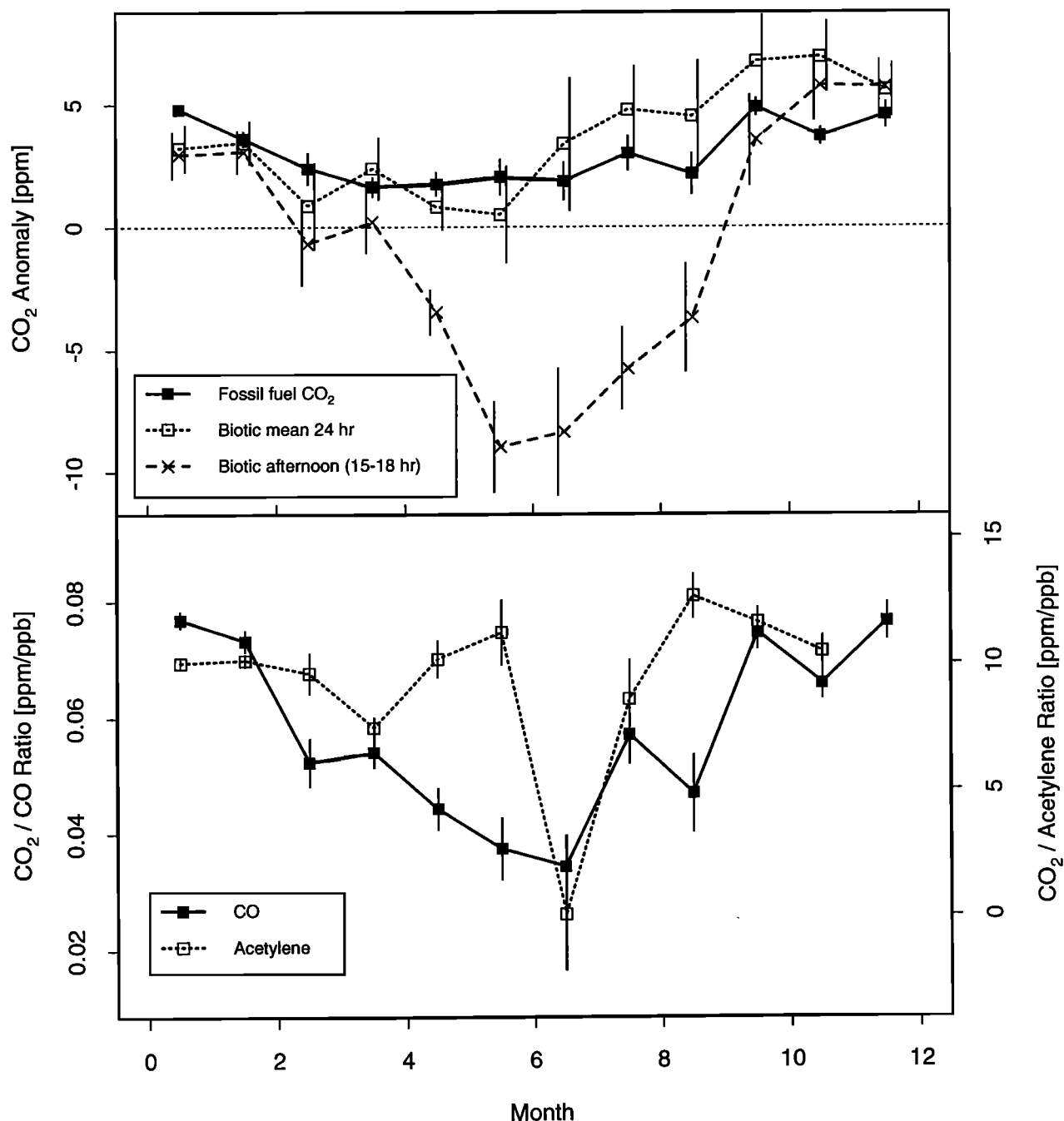
Table 1 summarizes the correspondence of each of the coefficients with physical processes and dimensional scales. The timescales for the terms are defined by the model (i.e., how often they change). The horizontal scales are estimates based on typical transport rates, except for the anthropogenic emissions ratio, which was constrained by examining flask data from the CMDL network. A subset of the model was applied to five sites: CBA (55° 12' N latitude, 162° 43' W longitude, elevation 25 m), NWR (40° 03' N latitude, 105° 35' W longitude, elevation 3749 m), IZO (28° 18' N latitude, 16° 29' W longitude, elevation 2300 m), BME (32° 22' N latitude, 64° 39' W longitude, elevation 30 m), and BMW (32° 16' N latitude, 64° 53' W longitude, elevation 30 m). For application to these data sets, only terms 1 and 2 were included in the model. Term 3 was assumed to be zero since these are remote sites with no local biological sources. This implies a small diurnal cycle, and also since the samples are generally taken at the same time of day, term 4 can be neglected. The contribution of anthropogenic CO<sub>2</sub> was calculated as  $a_1[\text{CO}_{\text{mean}} - \text{CO}_{\text{background}}]$  (see discussion of Figure 2 for rationale). At each of the sites except for NWR, the annual mean contribution of fossil fuel CO<sub>2</sub> was less than 0.25 ppm and individual months were below 1 ppm a majority of the time. At Harvard Forest, the contribution ranged from 2 to 4 ppm (see Figure 2 (top panel, solid line)). NWR, which occasionally comes under the influence of air from the Denver metropolitan area, had an intermediate annual average of 0.5 ppm. From this we surmise that the length scale for this term is constrained by the proximity of source regions to Harvard Forest, < 100 km, and to the other sites, > 500 km (except for NWR).

## 4. Results

All errors reported in the figures and the tables are 1 standard deviation of the mean from the linear regression model (calculated with S-Plus, MathSoft, Inc.). Since the number of degrees of freedom is above 90 for all of the months, the confidence interval is 68% for the true value lying within 1 standard deviation of the esti-

**Table 1.** Explanation of Terms

| Term                              | Timescale | Horizontal Scale         | Interpretation                          |
|-----------------------------------|-----------|--------------------------|---|
| $a_0$                             | 1 month   | 1000 km NS, 10,000 km EW | regional continental background         |
| $a_1[\text{CO}]$                  | 1 hour    | 500 km                   | anthropogenic CO <sub>2</sub> :CO ratio |
| $a_2F_p$                          | 1 hour    | 1 km                     | flux-concentration relationship         |
| $\sum_{j=0}^7 a_{3j} \delta_{jf}$ | 1 day     | 100 km                   | mean diurnal cycle in the PBL           |



**Figure 2.** (top) The seasonal cycle of CO<sub>2</sub> contributions for Harvard Forest averaged over the 3 years of data (see text for explanation). Note the larger contribution of fossil fuel in winter versus summer, the increase of Harvard Forest over Cold Bay when averaged over 24 hours, and the late afternoon drawdown of CO<sub>2</sub>. (bottom) The seasonal cycle in the  $a_1$  coefficient averaged over the 3 years of data, using either CO or C<sub>2</sub>H<sub>2</sub>. Values for  $a_1$  using CO are consistently lower in summer most likely due to production of CO from hydrocarbon oxidation. Vertical thin lines denote 1 standard error of the mean (68% confidence interval).

mate. In addition to statistical errors, several sources of systematic error exist. First, the measurements at Harvard Forest have some error associated with calibration, for which a conservative estimate is 0.5 ppm. Second, for the predicted monthly mean CO<sub>2</sub> mixing ratios, the choice of CO<sub>background</sub> is important. Above, this error

was estimated as no greater than 0.3 ppm. Finally, biogenic hydrocarbons produced in regions that are CO<sub>2</sub> sources will affect the calculation of  $a_1$ . This will not change the clean background signal, but some biogenic CO<sub>2</sub> may incorrectly be labeled anthropogenic. The magnitude of this error is impossible to determine with-

**Table 2.** Regression Results for 1996

| Month | $a_0$ | $a_1$ | $a_2$ | $a_{31}$ | $a_{32}$ | $a_{33}$ | $a_{34}$ | $a_{35}$ | $a_{36}$ | $a_{37}$ | $r^2$ |
|-------|-------|-------|-------|----------|----------|----------|----------|----------|----------|----------|-------|
| Jan.  | 354.9 | 0.083 | 0.005 | 0.03     | 0.48     | 0.45     | -0.34    | -0.09    | -0.37    | -0.24    | 0.95  |
| Feb.  | 355.1 | 0.083 | 0.011 | -0.08    | -0.31    | 0.27     | -0.07    | -0.13    | -0.05    | -0.12    | 0.80  |
| March | 357.4 | 0.075 | 0.017 | 0.46     | 0.57     | -0.40    | -1.41    | -1.24    | -0.32    | -0.27    | 0.90  |
| April | 360.6 | 0.068 | 0.057 | 0.54     | 0.19     | -1.51    | -3.06    | -3.26    | -2.15    | -0.81    | 0.64  |
| May   | 363.6 | 0.059 | 0.042 | 2.00     | 1.56     | -3.10    | -5.08    | -5.98    | -5.13    | -1.86    | 0.79  |
| June  | 369.1 | 0.024 | 0.032 | 2.74     | -1.94    | -7.10    | -11.47   | -15.42   | -12.26   | -3.55    | 0.69  |
| July  | 358.7 | 0.059 | 0.030 | 3.27     | -0.09    | -5.98    | -12.31   | -16.18   | -12.92   | -5.82    | 0.74  |
| Aug.  | 357.8 | 0.061 | 0.018 | 4.32     | 0.04     | -10.40   | -16.56   | -20.02   | -14.75   | -5.84    | 0.71  |
| Sep.  | 361.9 | 0.038 | 0.028 | 2.18     | 0.87     | -7.38    | -11.34   | -15.66   | -10.57   | -6.43    | 0.44  |
| Oct.  | 355.3 | 0.092 | 0.039 | 0.38     | 0.39     | -0.90    | -4.10    | -5.00    | -3.47    | -2.01    | 0.76  |
| Nov.  | 358.2 | 0.079 | 0.042 | -0.13    | 0.07     | -0.48    | -1.27    | -1.48    | -0.94    | -0.70    | 0.83  |
| Dec.  | 355.4 | 0.077 | 0.006 | 0.88     | 0.90     | 0.91     | 1.89     | 1.64     | 1.20     | 0.14     | 0.74  |

out more detailed studies of the source regions and/or a different correlate, e.g. <sup>14</sup>CO<sub>2</sub>.

Table 2 gives coefficients and Table 3 gives derived means for 1996. The capability of the linear model to represent hourly CO<sub>2</sub> data is illustrated in Figure 3, which shows the fit (top panel) and the contributions of each term (bottom panel) for a 10-day period in a summer month for which  $r^2 = 0.78$  overall. Predicted CO<sub>2</sub> values match both the shape and amplitude of the measured CO<sub>2</sub> data. The local canopy term is important mainly in early morning, when the PBL is shallow; contributions from fossil fuel range from 1–3 ppm, significantly smaller than biotic terms (this term is relatively more important in winter).

Values of  $r^2$  are generally 0.6 or better, with lowest values in spring and fall when phenological changes during a month add variance to the diurnal cycle. During summer and winter (when the canopy is not contributing), values of  $r^2$  often approach 0.8; synoptic weather events that import air with different background CO<sub>2</sub> values may account for a significant fraction of the unexplained variance.

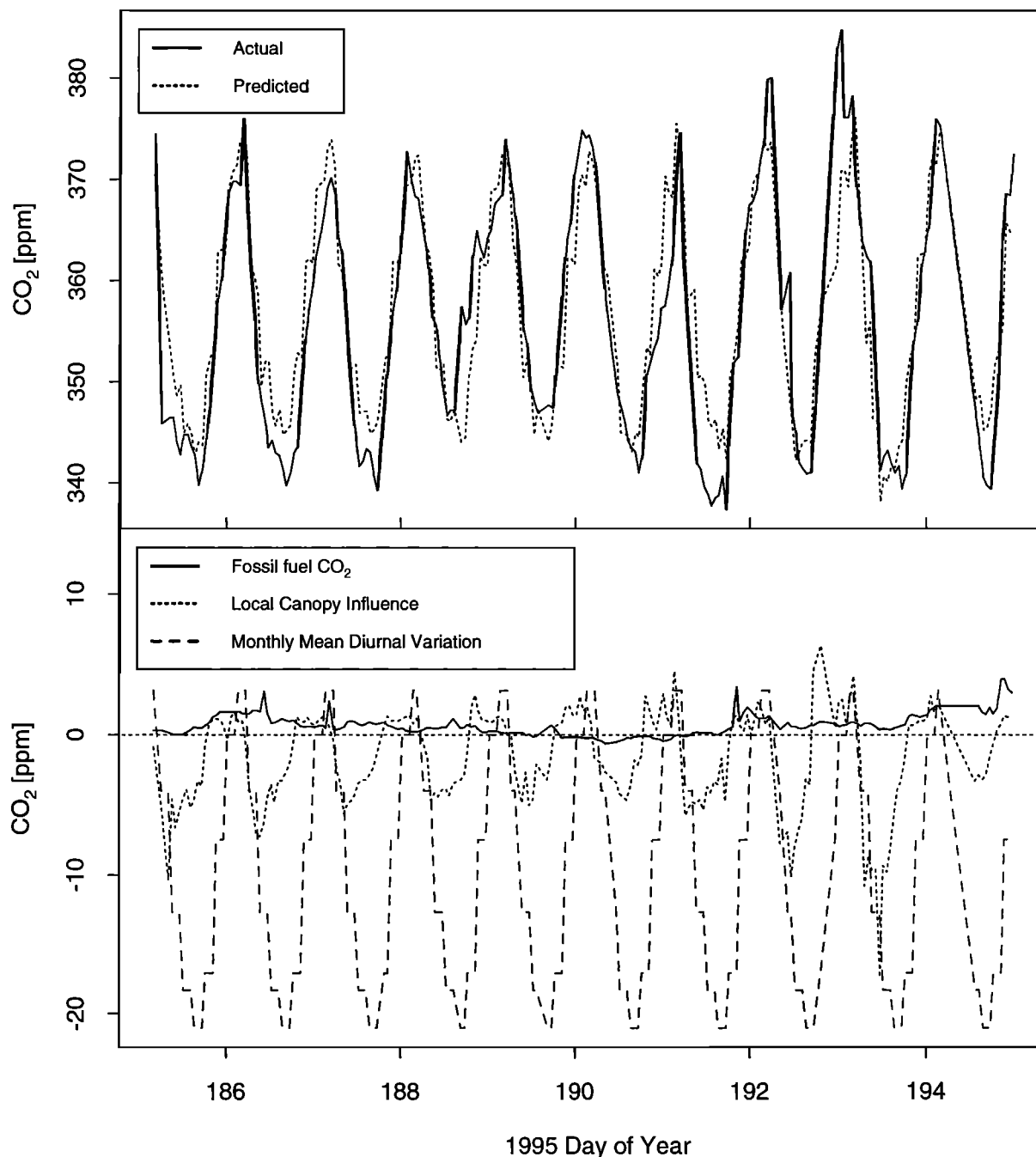
The possibility that daily fluctuations in the height of

the PBL is an important independent variable was examined by correlating the residuals of the linear model with two proxies of boundary layer height from a NOAA Automatic Surface Observing System station in Orange, Massachusetts (42° 34' 18" N latitude, 72° 16' 39" W longitude, elevation 164 m), ~ 7 km from Harvard Forest (J. M. Freedman, private communication, 1997). Comparing the residuals against both lifting condensation level and the height of the first cloud base showed no significant correlation. Either these quantities are inadequate correlates or the model captured most of the effect of PBL height on CO<sub>2</sub> concentrations through terms 3 and 4. We think that the latter is likely since net CO<sub>2</sub> exchange and height of the PBL are both correlated with incident sunlight.

To test the hypothesis that the regression extracts the background CO<sub>2</sub> concentration in the PBL, both the predicted diurnal and seasonal cycles of CO<sub>2</sub> would need to be compared to actual data from the PBL. Extensive aircraft sampling could be used to obtain these data, but since this would require both diurnal and seasonal measurements, the cost is prohibitive. In the future, we will compare our representation of diurnal cy-

**Table 3.** CO<sub>2</sub> and CO Concentrations for 1996

| Month | CO <sub>2</sub> , ppm |           |            |           |            | CO, ppb |          |
|-------|-----------------------|-----------|------------|-----------|------------|---------|----------|
|       | Raw Mean              | 0900–1200 | 1 $\sigma$ | 1500–1800 | 1 $\sigma$ | 20th    | Raw Mean |
| Jan.  | 374.4                 | 369.1     | 0.28       | 368.6     | 0.26       | 165.1   | 234.0    |
| Feb.  | 373.1                 | 369.4     | 0.31       | 369.1     | 0.29       | 169.5   | 216.4    |
| March | 373.2                 | 369.7     | 0.22       | 368.8     | 0.21       | 168.2   | 211.8    |
| April | 372.8                 | 370.0     | 0.30       | 368.2     | 0.30       | 160.0   | 188.4    |
| May   | 373.0                 | 369.1     | 0.41       | 366.2     | 0.38       | 146.9   | 185.5    |
| June  | 365.9                 | 365.5     | 0.91       | 357.2     | 0.77       | 149.4   | 196.2    |
| July  | 361.4                 | 360.0     | 1.00       | 349.8     | 0.85       | 122.6   | 171.8    |
| Aug.  | 362.2                 | 356.5     | 1.16       | 346.9     | 0.99       | 150.3   | 198.0    |
| Sep.  | 360.8                 | 359.3     | 1.42       | 351.0     | 1.31       | 127.4   | 161.5    |
| Oct.  | 369.7                 | 365.3     | 0.63       | 361.2     | 0.59       | 118.6   | 175.1    |
| Nov.  | 372.8                 | 368.7     | 0.29       | 367.7     | 0.29       | 138.0   | 180.7    |
| Dec.  | 375.5                 | 370.5     | 0.80       | 371.2     | 0.82       | 185.5   | 250.0    |



**Figure 3.** (top) Comparison of measured CO<sub>2</sub> values (solid line) with output from the linear model representation (dashed line) for 10 days in July 1995;  $r^2$  was 0.78 for the month, typical for summer. (bottom) The three individual terms of the model (the monthly constant is not included). Contributions due to combustion were relatively small, as usual in summer. Significant variation in the local canopy term allows the model to simulate the large diurnal swings during days 192 and 193.

cles to output from a general circulation model (GCM) that resolves the PBL, and in this paper the seasonal cycle will be compared to measurements from the CMDL network. The difference between our representation and a remote location should reflect the influence of the intervening sources. If the calculated contributions are reasonable, this provides support for our approach.

Our results can be compared to data from the NOAA

CMDL site in Cold Bay, Alaska (CBA, see above for location) to infer the contribution of CO<sub>2</sub> sources to CO<sub>2</sub> concentrations over the continent. Ideally, the comparison site would be at the same latitude and altitude with no anthropogenic or biogenic local sources and have no terrestrial source up fetch for some distance. Cold Bay lies at 55°N latitude; according to CMDL's Globalview index of marine boundary layer CO<sub>2</sub>, concentrations of

CO<sub>2</sub> at 42°N differ by less than 0.5 ppm from Cold Bay. Other possible sites were either affected by continental sources, had poor data coverage, or were at high altitude. In addition, the availability of CO data from CBA allowed us to confirm that anthropogenic contamination was small (< 0.25 ppm, see end of section 3).

Figure 1 (middle panel) compares computed CO<sub>2</sub> concentrations in the PBL at Harvard Forest from the linear model for 0900–1200 and 1500–1800 local time (brackets for the midday values) to Cold Bay data. The regional CO<sub>2</sub> concentrations at Harvard Forest show remarkably consistent relationships with data from CBA on a seasonal basis. Midday values are higher at Harvard Forest than at Cold Bay during the period of biotic uptake (May–September), and only late in the day is a relative drawdown observed. Harvard Forest has notably higher CO<sub>2</sub> during the months when net emission of CO<sub>2</sub> occurs, and the diurnal variation is much smaller. During the fall of 1995, there is a notable increase in CO<sub>2</sub> values at Harvard Forest, which might be associated with increased respiration due to wetting up of the regional ecosystem after an extremely severe dry period (the driest summer in ~ 100 years). Note that the error bars indicate that the late 1995 increase is not a statistical anomaly.

Figure 2 (bottom panel, solid line) shows the seasonal variation of the anthropogenic emissions ratio ( $a_1$ ). During the winter months, values range from 0.08 to 0.07 ppm/ppb and are larger than the national average of 0.037 based on emissions inventories [*U.S. Environmental Protection Agency*, 1995]. Since emissions from power plants have relatively little CO, the higher emissions ratios measured at Harvard Forest site may indicate greater influence of that source.

The robustness of CO as a predictor of anthropogenic CO<sub>2</sub> can be investigated by observing the variation of CO (Figure 1, bottom panel) and the coefficient  $a_1$  over the year (Figure 2, bottom panel, solid line). During summer, CO concentrations are seasonally low due to the hemispheric annual cycle, but the background CO at Harvard Forest is significantly higher than at Cold Bay and values for  $a_1$  are low. This pattern suggests a contribution to regional CO due to oxidation of hydrocarbons that enhances CO levels without significantly increasing CO<sub>2</sub>. To test this explanation, we tried using data for C<sub>2</sub>H<sub>2</sub> in place of CO in (1), since C<sub>2</sub>H<sub>2</sub>, like CO, is produced primarily by automobiles, but unlike CO, it is not produced in the atmosphere. Monthly  $r^2$  values were slightly higher for C<sub>2</sub>H<sub>2</sub> (Figure 1, top panel), and there was no annual variation in the associated coefficient (Figure 2, bottom panel) except for a puzzling dip in July reproduced in each of three years; possibly there is a biogenic or other source for C<sub>2</sub>H<sub>2</sub> influencing Harvard Forest in July.

Figure 2 (top panel, solid line) shows the monthly mean contribution of combustion CO<sub>2</sub> to the ambient concentrations at Harvard Forest ( $a_1[\text{CO}_{\text{mean}} - \text{CO}_{\text{background}}]$ ). The curve dips significantly during the

summer months, possibly reflecting the increased height of the PBL diluting the anthropogenic CO<sub>2</sub> signal. The 2–4 ppm annual mean contribution from fossil fuel combustion is comparable to predictions from GCM model results [e.g., *Law et al.*, 1996, Figure 4]. If we remove the effects of regional fossil fuel combustion and average over 24 hours for Harvard Forest and subtract the Cold Bay concentrations (short dashed line), the CO<sub>2</sub> concentration due only to regional biota at Harvard Forest is slightly higher all year long (1–7 ppm), which reflects respiration in the winter and covariance of CO<sub>2</sub> flux with PBL height in summer (see discussion by *Denning et al.* [1996] for an explanation of this effect and a GCM estimate (their Figure 17) that is in line with our results). The seasonal cycles of daytime respiration in the dormant season and uptake of CO<sub>2</sub> in the growing season are evident in afternoon differences of +5 to –10 ppm, respectively (long dashed line).

## 5. Conclusions

Linear modeling applied to the Harvard Forest data allowed us to determine quantitatively the influences on CO<sub>2</sub> concentrations at 30 m due to local anthropogenic sources, local and regional biology, and the regional background concentration. All of the processes are significant and have a seasonal dependence: during the summer, the differences between Harvard Forest and Cold Bay are mostly due to regional biological activity, but during the winter, local sources of anthropogenic CO<sub>2</sub> dominate. Combustion contributed on average 4–5 ppm to ambient CO<sub>2</sub> at Harvard Forest in winter and 2–3 ppm in summer. Regional biotic emissions elevate daily mean CO<sub>2</sub> by 4–6 ppm in winter, and the covariance of the biotic cycle of uptake and emission with PBL height enhances daily mean CO<sub>2</sub> at 30 m by 1–2 ppm in summer; minimum values in late afternoon average 10 ppm lower than at Cold Bay in summer.

Data from continental tower sites are potentially extremely valuable in refining our understanding of global sources and sinks, provided that high-frequency measurements are available and accurate data are obtained for a representative suite of correlates (tracers of combustion, fluxes of CO<sub>2</sub>, and momentum or buoyancy). Perhaps the most important additional information would be provided by data giving PBL depth. Observations at continental sites like Harvard Forest can provide strong constraints on models and on analyses of the global CO<sub>2</sub> budget using inverse methods.

**Acknowledgments.** We would like to graciously thank P. C. Novelli (CMDL) for unpublished Cold Bay CO data; J. M. Freedman, D. R. Fitzjarrald, and K. E. Moore (SUNY-Albany) for processed ceilometer data; and P. M. Czepiel (Harvard University) and A. H. Goldstein (University of California, Berkeley) for C<sub>2</sub>H<sub>2</sub> data. This work was supported by grants to Harvard University from the Department of Energy (DEFG95ER62002 and through the National Institute for Global Environmental Change), from



NASA (NAGW-3082), and from NOAA (NA56GP0229). A. S. Denning was funded by the U.S. Department of Energy's (DOE) National Institute of Global Environmental Change (NIGEC) through the NIGEC Western Regional Center at the University of California, Davis (DOE Cooperative Agreement DE-FC03-90ER61010).

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(Received June 13, 1998; revised February 1, 1999; accepted February 12, 1999.)