

Influence of biotic exchange and combustion sources on atmospheric CO₂ concentrations in New England from observations at a forest flux tower

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Abstract. Hourly data for concentrations and fluxes of CO₂ at 30 m in Harvard Forest (Petersham, Massachusetts) are analyzed using linear modeling to obtain regionally representative CO₂ 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 (C₂H₂)), and measurements of indicators of proximate canopy exchange (CO₂ flux and momentum flux). Results are compared to observations at Cold Bay, Alaska. Combustion contributes on average 4–5 ppm to ambient CO₂ at Harvard Forest in winter and 2–3 ppm in summer. Regional biotic emissions elevate daily mean CO₂ by 4–6 ppm in winter, and the covariance of the biotic cycle of uptake and emission with PBL height enhances daily mean CO₂ 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 CO₂ can be determined at continental sites if suitable correlates (tracers, fluxes of CO₂, and momentum) are measured simultaneously with CO₂ itself.

1. Introduction

Models simulating atmospheric transport and CO₂ exchange with the surface are often used to infer the distribution of global sources and sinks for CO₂. 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ variation over a forest, using measured concentrations to recover regional CO₂ 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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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 (C₂H₂) provide excellent correlates for regional combustion sources and that eddy covariance fluxes of CO₂ and momentum provide correlates for the local influence of exchange with the forest near the sensor. Thus we can infer regionally representative concentrations of CO₂ at canopy height, including diurnal and seasonal variations, for comparison with observations from remote stations.

2. Sources of Data

Hourly averaged concentrations of CO, CO₂, and C₂H₂ and CO₂ 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>). CO₂ 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). CO₂ flux was determined from the CO₂ 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. C₂H₂ 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 CO₂ 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

CO₂ 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 CO₂ 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 [CO₂] and [CO] denote the observed concentrations at 30 m altitude, F_p is the ratio of the vertical flux of CO₂, Φ_{CO_2} , divided by u^* , f represents time-of-day factors (denoted 0 through 7) for eight 3 hour intervals, and δ_{jf} is the Kronecker delta (= 1 if $j = f$ and zero otherwise).

Studies of pollution plumes in northeastern North America show enhancements of CO₂ and CO concentrations in reasonably consistent ratios [e.g., Wofsy *et al.*, 1994]. We assume that, during a given month, anthropogenic CO and CO₂ 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 CO₂ emissions, values of a_1 are lower in summer than in winter (see below). Sources of CO that are not correlated to CO₂ 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 CO₂ 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 Φ_{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 (Φ_{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 CO₂ 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-

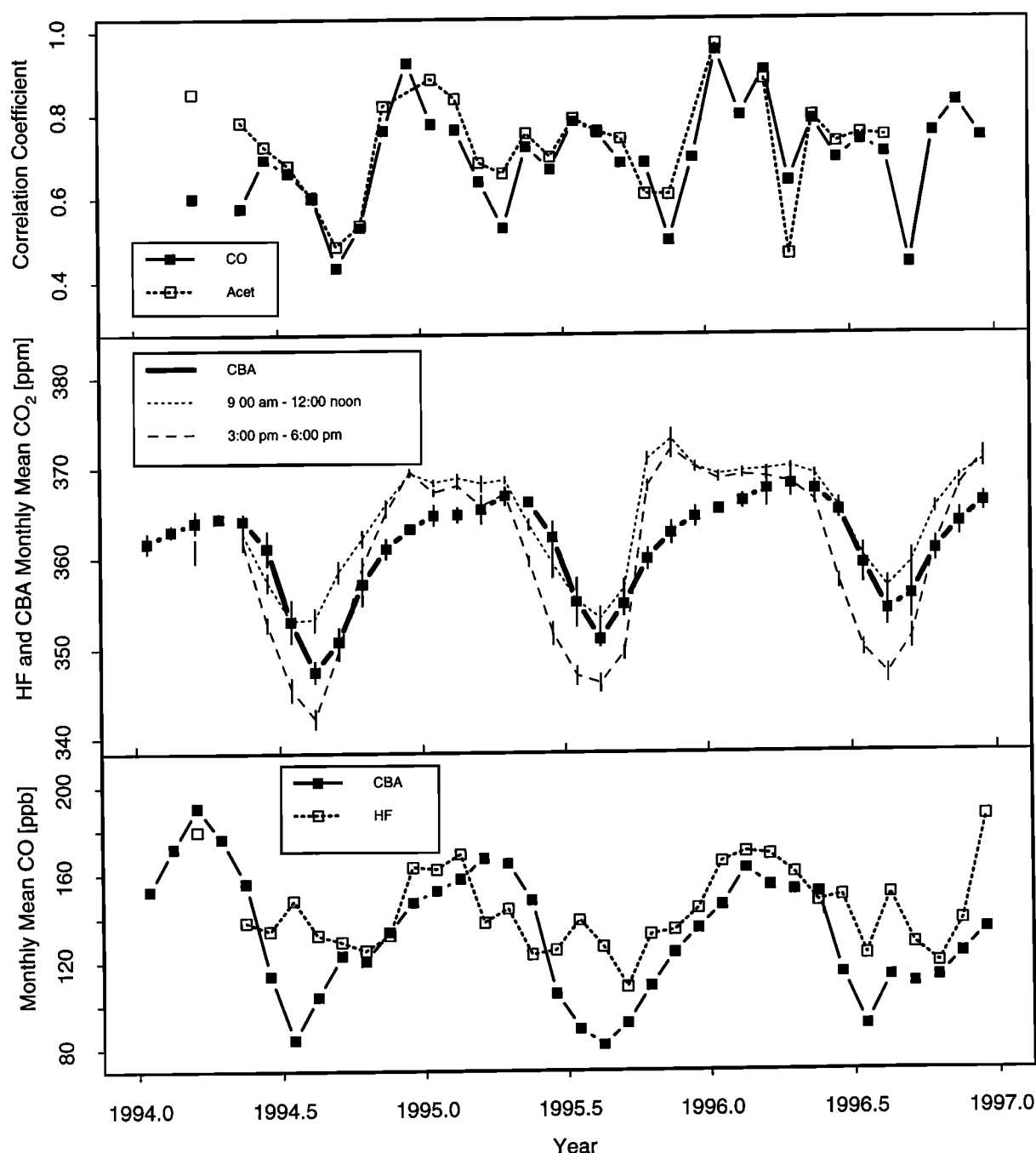


Figure 1. (top) Comparison of the model r^2 results when either CO or C₂H₂ is used as a tracer for anthropogenic CO₂. Although C₂H₂ performs better, there are large gaps in the instrument record. (middle) Comparison of monthly mean CO₂ at Cold Bay, Alaska (CBA) with derived regional monthly background 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 CO₂ 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 CO₂ in the PBL at sites with significant biological activity.

The value $a_0 + a_1\text{CO}_{\text{background}}$ gives the regional average CO₂ 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 CO₂. Since subtracting a constant does not change the regression (except for a_0), this method is equivalent to our approach. CO_{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 CO₂ 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 CO₂. 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 C₂H₂ 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 CO₂ 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 CO₂ 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 ₂ :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

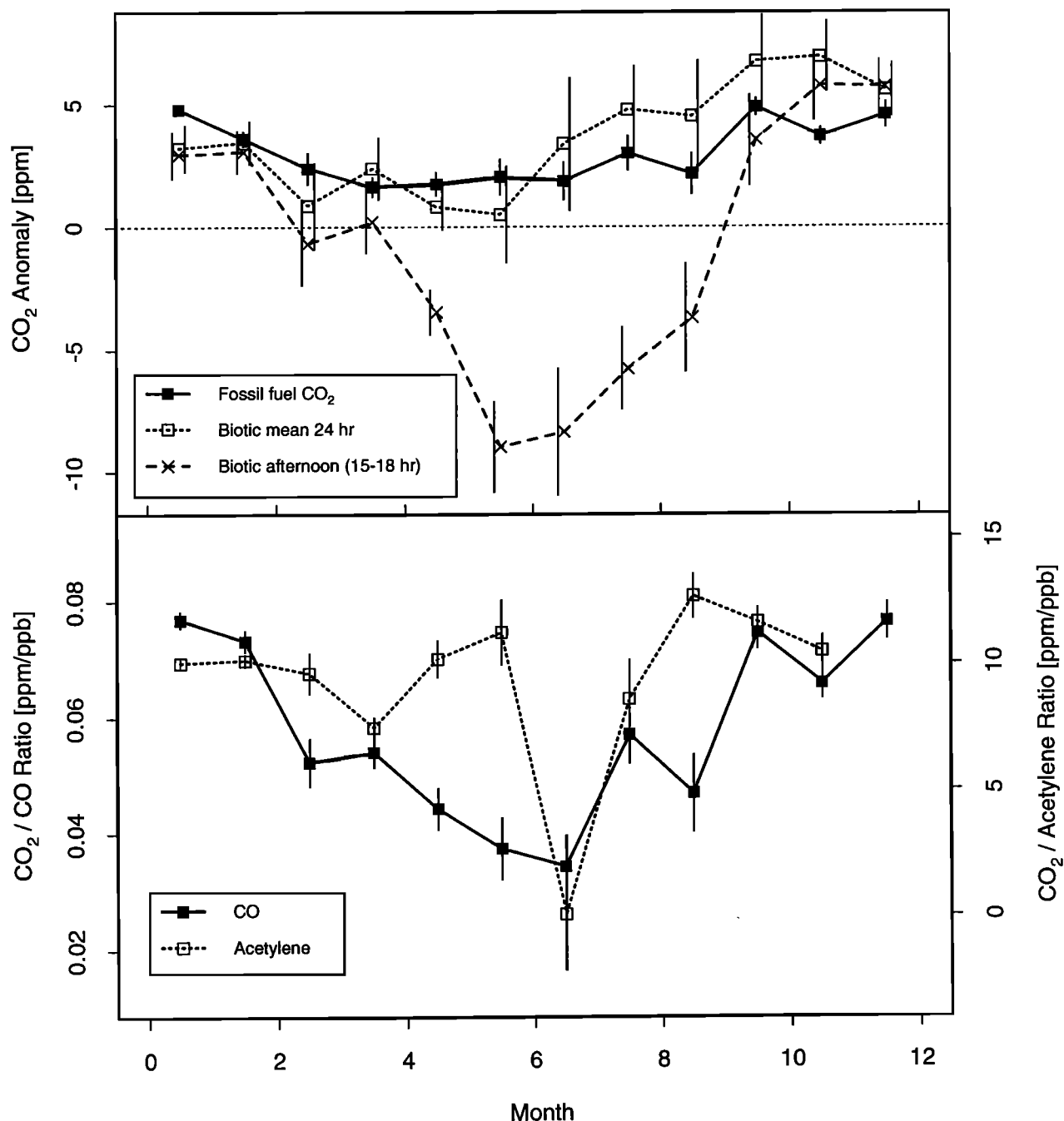


Figure 2. (top) The seasonal cycle of CO₂ contributions for Harvard Forest averaged over the 3 years of data (see text for explanation). Note the larger contribution of fossil fuel in winter versus summer, the increase of Harvard Forest over Cold Bay when averaged over 24 hours, and the late afternoon drawdown of CO₂. (bottom) The seasonal cycle in the a_1 coefficient averaged over the 3 years of data, using either CO or C₂H₂. 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 CO₂ mixing ratios, the choice of CO_{background} is important. Above, this error

was estimated as no greater than 0.3 ppm. Finally, biogenic hydrocarbons produced in regions that are CO₂ sources will affect the calculation of a_1 . This will not change the clean background signal, but some biogenic CO₂ 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. ¹⁴CO₂.

Table 2 gives coefficients and Table 3 gives derived means for 1996. The capability of the linear model to represent hourly CO₂ 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 CO₂ values match both the shape and amplitude of the measured CO₂ 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 CO₂ 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 CO₂ concentrations through terms 3 and 4. We think that the latter is likely since net CO₂ exchange and height of the PBL are both correlated with incident sunlight.

To test the hypothesis that the regression extracts the background CO₂ concentration in the PBL, both the predicted diurnal and seasonal cycles of CO₂ 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. CO₂ and CO Concentrations for 1996

Month	CO ₂ , ppm					CO, ppb	
	Raw Mean	0900–1200	1 σ	1500–1800	1 σ	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

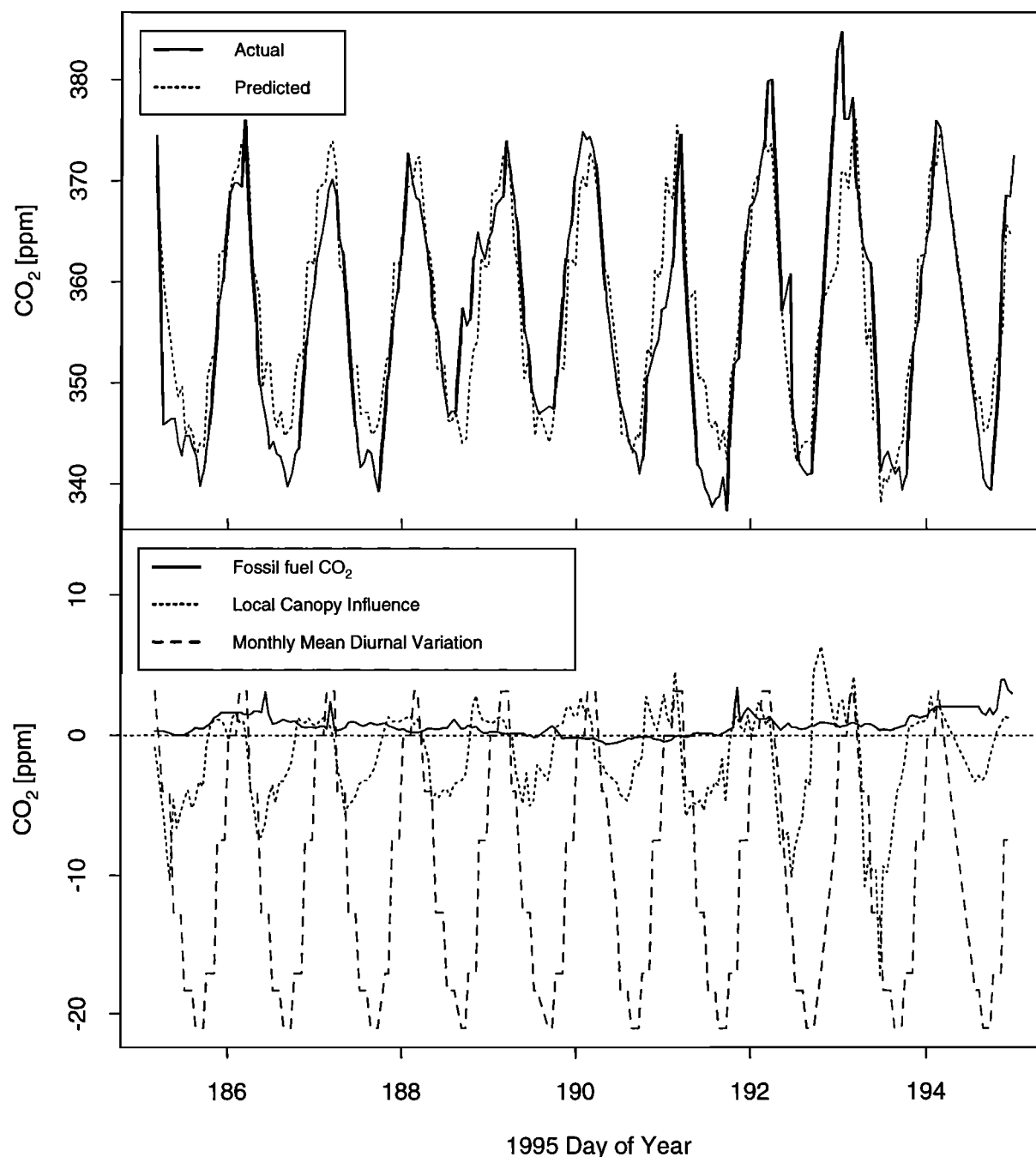


Figure 3. (top) Comparison of measured CO₂ values (solid line) with output from the linear model representation (dashed line) for 10 days in July 1995; r^2 was 0.78 for the month, typical for summer. (bottom) The three individual terms of the model (the monthly constant is not included). Contributions 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 CO₂ sources to CO₂ 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 CO₂, concentrations of

CO₂ 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 CO₂ 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 CO₂ 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 CO₂ during the months when net emission of CO₂ occurs, and the diurnal variation is much smaller. During the fall of 1995, there is a notable increase in CO₂ 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 CO₂ 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 CO₂. To test this explanation, we tried using data for C₂H₂ in place of CO in (1), since C₂H₂, 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 C₂H₂ (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 C₂H₂ influencing Harvard Forest in July.

Figure 2 (top panel, solid line) shows the monthly mean contribution of combustion CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ dominate. Combustion contributed on average 4–5 ppm to ambient CO₂ at Harvard Forest in winter and 2–3 ppm in summer. Regional biotic emissions elevate daily mean CO₂ by 4–6 ppm in winter, and the covariance of the biotic cycle of uptake and emission with PBL height enhances daily mean CO₂ 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 CO₂, 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 CO₂ budget using inverse methods.

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References

- Ciais, P., P. P. Tans, J. W. C. White, M. Troler, R. J. Francey, J. A. Berry, D. R. Random, P. J. Sellers, J. G. Collatz, and D. S. Schimel, Partitioning of ocean and land uptake of CO₂ as inferred by $\delta^{13}\text{C}$ measurements from the NOAA Climate Monitoring and Diagnostics Laboratory global air sampling network, *J. Geophys. Res.*, **100**, 5051–5070, 1995.
- Conway, T. J., P. P. Tans, L. S. Waterman, K. W. Thoning, D. R. Kitzis, K. A. Masarie, and N. Zhang, Evidence for interannual variability of the carbon cycle from the NOAA/CMDL global air sampling network, *J. Geophys. Res.*, **99**, 22831–22855, 1994.
- Denmead, O. T., M. R. Raupach, F. X. Dunin, H. A. Cleugh, and R. Leuning, Boundary layer budgets for regional estimates of scalar fluxes, *Global Change Biol.*, **2**, 255–265, 1996.
- Denning, A. S., I. Y. Fung, and D. Randall, Latitudinal gradient of atmospheric CO₂ due to seasonal exchange with land biota, *Nature*, **376**, 240–243, 1995.
- Denning, A. S., D. A. Randall, G. J. Collatz, and P. J. Sellers, Simulations of terrestrial carbon metabolism and atmospheric CO₂ in a general circulation model, 2, Simulated CO₂ concentrations, *Tellus*, **48B**, 543–567, 1996.
- Enting, I. G., C. M. Trudinger, R. J. Francey, and H. Granek, Synthesis inversion of atmospheric CO₂ using the GISS tracer transport model, *Div. of Atmos. Res. Tech. Pap.*, **29**, pp. 1–44, Commonw. Sci. and Ind. Res. Org., Melbourne, Victoria, Australia, 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.
- Goldstein, A. H., C. M. Spivakovsky, and S. C. Wofsy, Seasonal variations of nonmethane 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 deciduous forest: Response to interannual climate variability, *Science*, **271**, 1576–1578, 1996.
- Komhyr, W. D., R. H. Gammon, T. B. Harris, L. S. Waterman, T. J. Conway, W. R. Taylor, and K. W. Thoning, Global atmospheric CO₂ distribution and variations from 1968–1982 NOAA/GMCC CO₂ flask sample data, *J. Geophys. Res.*, **90**, 5567–5596, 1985.
- Law, R. M., et al., Variations in modeled atmospheric transport of carbon dioxide and the consequences for CO₂ inversions, *Global Biogeochem. Cycles*, **10**, 783–796, 1996.
- Novelli, P. C., L. P. Steele, and P. P. Tans, Mixing ratios of carbon monoxide in the troposphere, *J. Geophys. Res.*, **97**, 20731–20750, 1992.
- Raupach, M. R., O. T. Denmead, and F. X. Dunin, Challenges in linking atmospheric CO₂ concentrations to fluxes at local and regional scales, *Aust. J. of Bot.*, **40**, 697–716, 1992.
- U.S. Environmental Protection Agency, National air pollution emissions trends, 1900–1994, *Rep. EPA-454/R-95-011*, Research Triangle Park, N.C., 1995.
- Venables, W. N., and B. D. Ripley, *Modern Applied Statistics With S-Plus*, Springer-Verlag, New York, 1994.
- Wofsy, S. C., M. L. Goulden, and J. W. Munger, Net exchange of CO₂ in a mid-latitude forest, *Science*, **260**, 1314–1317, 1993.
- Wofsy, S. C., S.-M. Fan, D. R. Blake, J. D. Bradshaw, S. T. Sandholm, H. B. Singh, G. W. Sachse, and R. C. Harriss, Factors influencing atmospheric composition over subarctic America during summer, *J. Geophys. Res.*, **99**, 1887–1897, 1994.

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