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Is the biomass burning source of CO decreasing?

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Importance of this Paper: This paper is a preliminary analysis of CO and methane mixing ratios measured by NOAA–CMDL global cooperative flask sampling network. From the seasonality of recent trends in these gases, we infer that most of the observed decrease in tropospheric CO during the early 1990s can be attributed to a decrease in biomass burning.

Abstract

To investigate secular changes in CO and CH_4, we examined monthly means of tropospheric measurements made from samples collected at 19 fixed sites in the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) global cooperative flask sampling network. The CH_4 data are available for the period 1984–1995. A somewhat shorter time series is available for CO (1989–1995). The data were analyzed to extract a consistent pattern of change in time and in latitude. The most important preliminary finding is that the patterns of CO and CH_4 change appear to resemble that of biomass burning. That is, there is maximum change during local spring in both northern and southern hemispheres. If we attribute a significant part of the change in CH_4 trend (3–6 ppb/yr) to biomass burning, the corresponding change in CO is approximately 2–5 ppb/yr. This would explain the bulk of the observed change in CO (4–7 ppb/yr).

Keywords: Carbon monoxide; Methane; Trend; Biomass burning

1. Introduction

One of the most important roles of the earth's troposphere is its oxidative capacity, the ability to oxidize a large number of chemical species, thereby removing them from the atmosphere. The species that are oxidized in the troposphere include CH_4, CH_3Cl, CH_3Br, CO, substituted chlorofluorocarbons (e.g., $CHClF_2$ (HCFC-22)), non-methane hydrocarbons (e.g., C_2H_6) and oxides of nitrogen. Any change in the oxidative capacity of the atmosphere would result in a change in the lifetimes of the above mentioned species which are important in regulating the ozone layer and/or are important greenhouse molecules (e.g. Thompson, 1992).

The oxidative capacity of the troposphere is strongly influenced by CO and CH_4 (e.g. Crutzen,

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1995). Although the primary oxidant, OH, is produced by the reaction of H_2O with $O(^1D)$ (Levy, 1972; Logan et al., 1981; Crutzen and Zimmermann, 1991), CO and CH_4 play fundamental roles in the chemistry of OH because of the two key reactions:

$$CO + OH \rightarrow CO_2 + H$$
$$CH_4 + OH \rightarrow CH_3 + H_2O.$$

The former reaction recycles OH to HO_2, another member of the odd hydrogen family (HO_x), and plays a crucial role in determining the partitioning of HO_x. The latter reaction is ultimately a net source of CO and HO_x (e.g. Logan et al., 1981; Crutzen, 1995). Indeed, OH, CO, and CH_4 form a strongly coupled system such that the response to any perturbation is non-linear and may take a much longer time to recover than that of a decoupled system (Sze, 1977; Prather, 1994). CO is also important to atmospheric chemistry by playing a role in tropospheric O_3 production and destruction (e.g. Fishman and Crutzen, 1978; Seiler and Fishman, 1981; Crutzen, 1995). In low NO_x environments, CO oxidation leads to O_3 destruction. O_3 reacts with HO_2 to create OH, but the CO oxidation reaction shown above recycles HO_2. However, in high NO_x environments, oxidation of CO, CH_4, or non-methane hydrocarbons leads to O_3 production (e.g. Crutzen, 1995). HO_2 reacts rapidly with NO instead of O_3. Both HO_2 and RO_2 convert NO to NO_2, and subsequent photolysis of NO_2 leads to production of O_3. According to Crutzen (1995) the globally averaged vertically integrated rate for the destruction of CO by OH and that for the destruction of CH_4 by OH are 3.5×10^{11} and 10^{11} molecules cm^{-2} s^{-1}, respectively. These values are greater than the rate at which ozone is transported from the stratosphere, 4×10^{10} molecules cm^{-2} s^{-1}. Thus the sources and sinks of tropospheric ozone are dominated by photochemistry that requires the presence of CO or hydrocarbons.

A recent overview of the composition of the troposphere described decreases in the trends of CO and CH_4 (Khalil and Rasmussen, 1995). Recent measurements (from 1979 to 1994) presented there indicate that CO mixing ratios in the atmosphere decreased by approximately 4–7 parts per billion per year (ppb/yr) over that time period. At the same time, the growth trend of CH_4 has decreased from about 12 ppb/yr in 1984–1988 to roughly 6 ppb/yr a decade later. These changes are of considerable importance to the oxidative capacity of our global atmosphere. The key questions are what drives these changes and whether the changes in CO and CH_4 are related to a common cause?

To investigate changes in CO and CH_4, we examined monthly means of tropospheric measurements made from samples collected at six of the nineteen fixed sites in the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) global cooperative flask sampling network (Dlugokencky et al., 1996). The CH_4 data are available for the period 1984–1995. A somewhat shorter time series is available for CO (1989–1995). The data were analyzed to extract a consistent pattern of change in time and in latitude.

2. Data analysis

We shall first illustrate our method of analysis using the NOAA–CMDL measurements of CO and CH_4 from the Mauna Loa Observatory (19.5 N, 155.5 W), Hawaii, hereafter referred to as MLO. Although our primary goal is to understand the trend in CO, we shall use the CH_4 data as additional support for our conclusion because of the longer time record of CH_4. It is reasonable to expect that CH_4 and CO abundances are related because CH_4 oxidation provides a major source of CO (e.g. Logan et al., 1981), and because the biomass burning sources of CO and CH_4 appear to be proportional (e.g. Andreae et al., 1996; Blake et al., 1996). At the end of this section, we will examine CO and CH_4 data from other oceanic NOAA–CMDL stations.

2.1. Carbon monoxide

Fig. 1(a) shows the monthly mean NOAA–CMDL measurements of CO (ppb) at MLO from 1990 to 1995. The data from four other stations

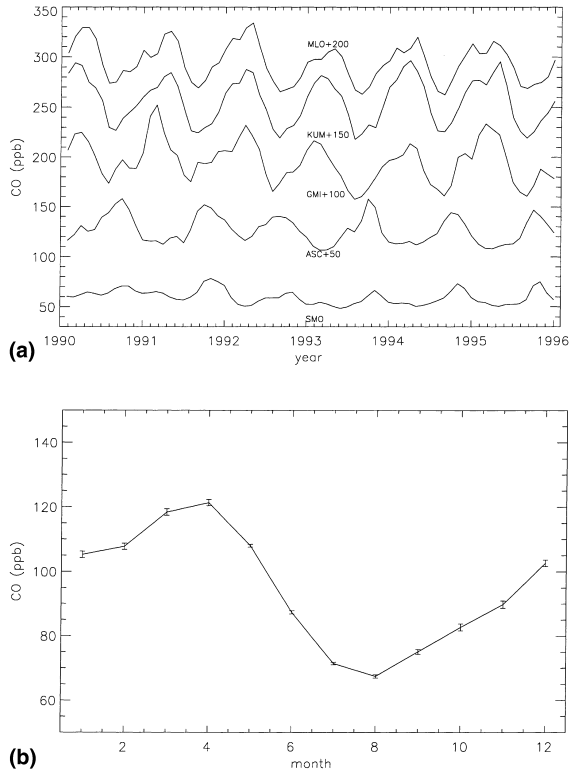

Fig. 1. (a) Monthly mean CO mixing ratios (ppb) at Mauna Loa Observatory (MLO), Hawaii (19.5 N, 155.5 W) and four other remote sites listed in Table 1. Data were obtained by the NOAA–CMDL global cooperative flask sampling network. (b) Mean seasonal cycle of CO (ppb) at MLO derived from the average of the data from 1990 to 1995 (shown in Fig. 1(a)). Error bars represent ±1 standard deviation.

(chosen to be remote sites) are shown for comparison (see Table 1 for the locations of the stations). The most prominent feature of this figure is the large seasonal cycle with maximum CO in late winter to early spring and minimum CO in summer. Fig. 1(b) shows the seasonal cycle of CO at MLO, obtained from the arithmetic mean of six years of data in Fig. 1(a). The error bars are standard deviations based on the six-year dataset. Minimum CO mixing ratios in summer are determined by a balance between CO loss via the CO + OH reaction and CO production from oxidation of CH_4 and non-methane hydrocarbons (e.g. Logan et al., 1981). The concentrations of OH are greatest in the summer because of enhanced solar insolation and more water vapor in the atmosphere.

In order to obtain a monthly-dependent trend at MLO, we separate the CO data by month and fit a least-squares linear regression through the six-year time series for each month. Representative monthly trends for the months of March, June, September, and December are shown in Figs. 2(a)–(d). The slopes of the linear fits to these monthly trends are shown in Fig. 3. The mean slope is −2 ppb/yr. However, the slopes of the monthly trends are significantly steeper in spring, with values of approximately −4 ppb/yr. Monthly trends are much smaller in the other seasons. We will show next that this pattern of change is consistent with that deduced for trends in CH_4 mixing ratios.

2.2. Methane

Fig. 4 shows monthly mean NOAA–CMDL measurements of CH_4 (ppb) at MLO, South Pole Station (SPO) and four other remote sites (see Table 1 for location of sites) for the years 1984–1995. The most prominent features in this figure are the long-term growth trend of CH_4 and the seasonal cycle, but the most interesting aspect of these data is the change in the growth trend. There

Table 1
NOAA–CMDL stations used in the CO and CH_4 data analysis

Station	Full name	Lat., Lon.	Years for CO data	Years for CH_4 data
MLO	Mauna Loa	19.5 N, 155.5 W	1990–95	1984–95
KUM	Cape Kumukahi	19.5 N, 155.8 W	1990–95	1984–95
GMI	Guam	13.4 N, 144.8 W	1990–95	1984–95
ASC	Ascension	7.6 S, 14.2 W	1990–95	1984–95
SMO	American Samoa	14.2 S, 170.3 W	1989–95	1984–95
SPO	South Pole	90.0 S, 24.8 W	Not used	1984–95

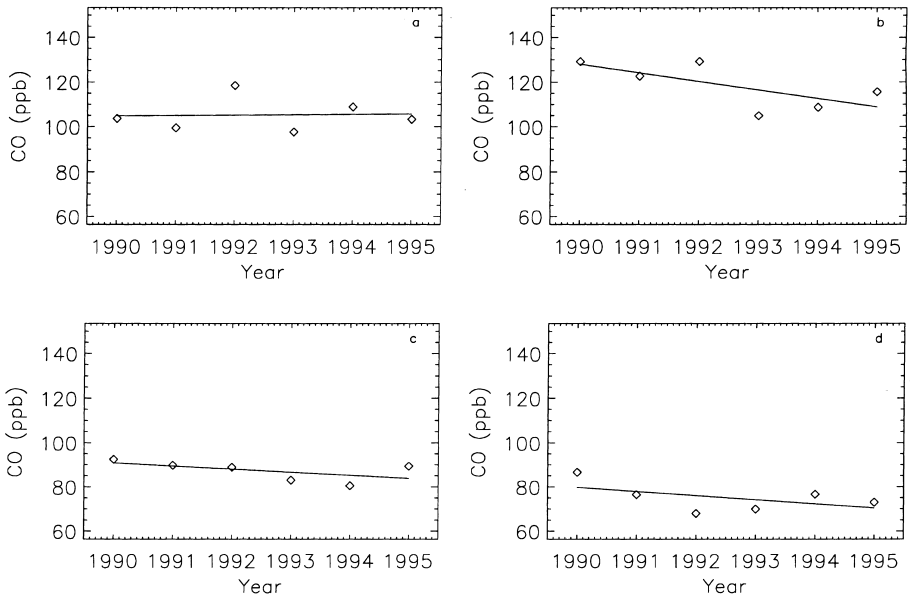

Fig. 2. Monthly trends of monthly mean CO mixing ratios (ppb) at MLO for the months of March (a), June (b), September (c) and December (d). Solid lines are least-squares linear regressions to the monthly mean data.

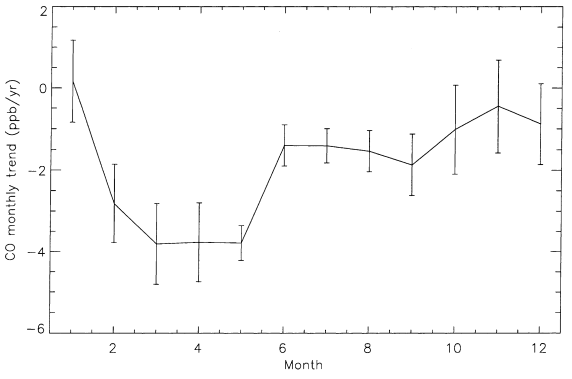

Fig. 3. Slopes of CO monthly trends (ppb/yr) at MLO, derived from CO measurements from 1990 to 1995, using the method described in the text. Error bars represent ±1 standard deviation.

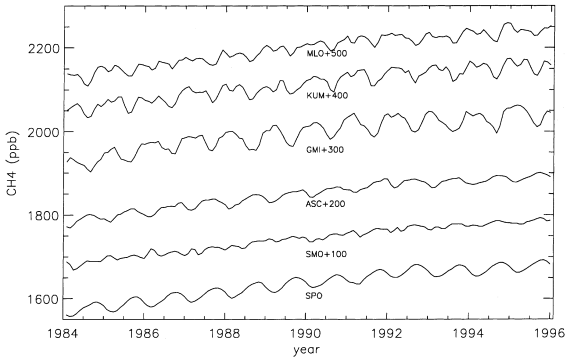

Fig. 4. Monthly mean CH_4 mixing ratios (ppb) measured by the NOAA–CMDL flask sampling network for the six stations listed in Table 1.

is a noticeable change in the slope of the data in the later period as compared with that in the earlier years (e.g. Khalil and Rasmussen, 1995; Dlugokencky et al., 1996).

First, we analyze the CH_4 data from MLO. For convenience, we divide the 12 yr of data into three overlapping six-year periods: (a) 1984–1989, (b) 1987–1992, and (c) 1990–1995. Applying the same technique as we have done with the CO data, we obtain the monthly trends for the three periods, as shown in Fig. 5. The earlier period (a) has a much larger trend (about 12 ppb/yr) than the later period (c) (about 6 ppb/yr). However, the seasonal pattern of the trend has also changed, as can be seen by taking the differences between the monthly trends of each period (Fig. 6). The difference be-

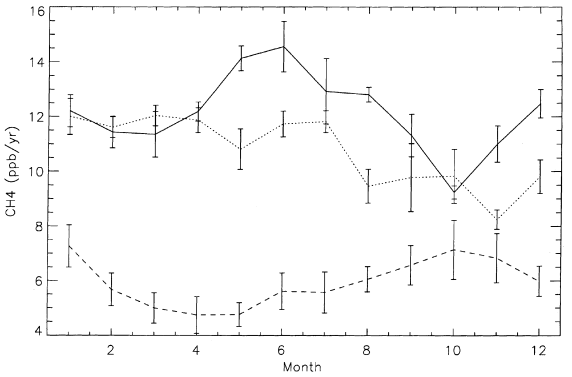

Fig. 5. Monthly trends in CH_4 (ppb/yr) at MLO. Solid line: period (a) from 1984 to 1989; Dotted line: period (b) from 1987 to 1992; Dashed line: period (c) from 1990 to 1995. Error bars represent ±1 standard deviation.

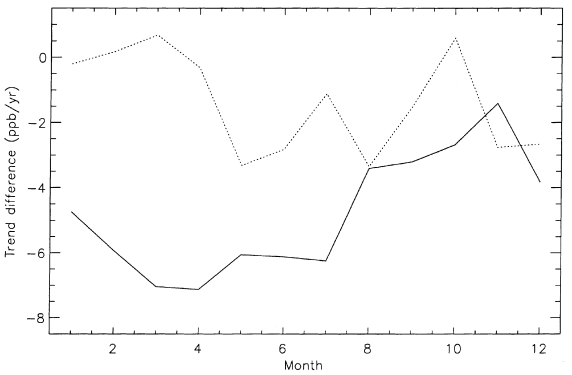

Fig. 6. Difference in CH_4 trends between periods (ppb/yr) at MLO. Dotted line: difference between periods (b) and (a); Solid line: difference between periods (c) and (b).

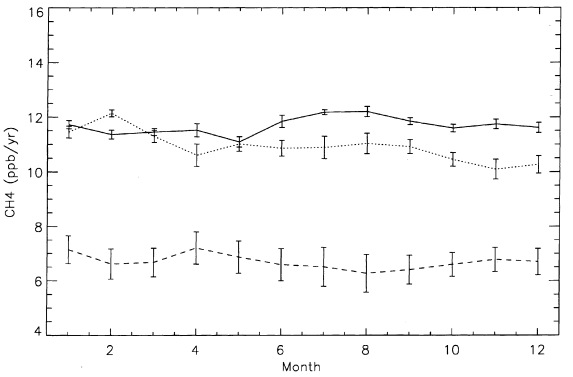

Fig. 7. Monthly trends in CH_4 (ppb/yr) at SPO. Solid line: period (a) from 1984 to 1989; Dotted line: period (b) from 1987 to 1992; Dashed line: period (c) from 1990 to 1995. Error bars represent ±1 standard deviation.

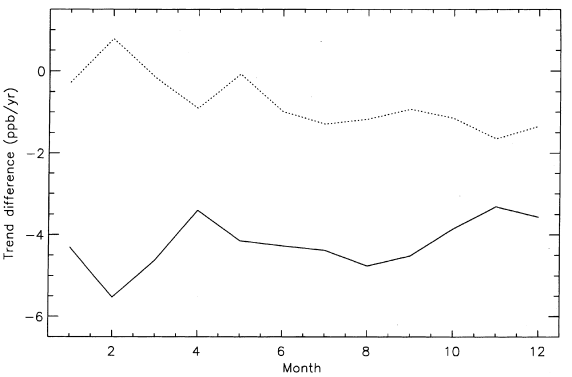

Fig. 8. Difference in CH_4 trends between periods (ppb/yr) at SPO. Dotted line: difference between periods (b) and (a); Solid line: difference between periods (c) and (b).

tween periods (b) and (a) (dotted line) does not show a clear seasonal dependence. However, the difference between periods (c) and (b) (solid line) shows a pronounced change in spring that resembles the springtime CO monthly trends (Fig. 3).

The change in CH_4 trends at SPO stands in contrast to that at MLO. Applying the same analysis to the SPO data, the CH_4 monthly trends for the periods (a), (b), and (c) are presented in Fig. 7. Compared to Fig. 5, there is much less seasonal variation in these data. The differences in trends between periods (b) and (a) (dotted line) and between periods (c) and (b) (solid line) are shown in Fig. 8. Again, the SPO data show much less seasonal variation than the MLO data in Fig. 6. The reason is that SPO is an extremely remote site, so the CH_4 that reaches there has been averaged over months in transit. The small level of variation in this difference between derivatives of SPO data, more than anything else, demonstrates the high precision of the NOAA–CMDL measurements.

2.3. Spatial and seasonal patterns of change

In order to derive a spatial and seasonal pattern of change for CO, we selected five NOAA–CMDL stations: MLO, KUM, GMI, ASC, and SMO. The

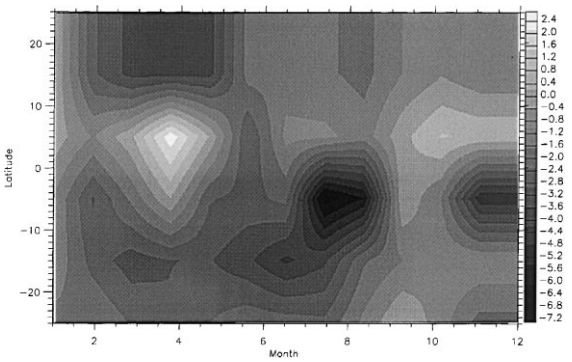

Fig. 9. Contour plot of monthly trends in CO (ppb/yr) for each month from 25 S to 25 N. The data used in this plot are from NOAA–CMDL stations SMO, ASC, GMI, KUM, and MLO.

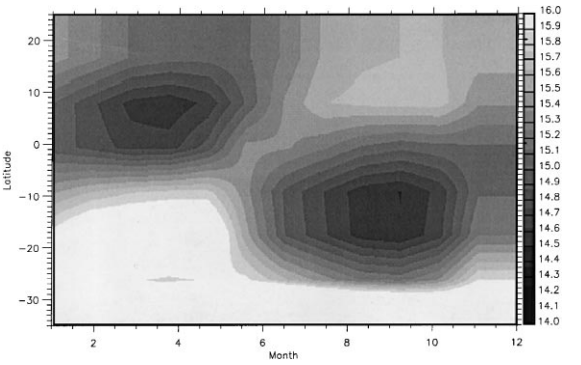

Fig. 10. Contour plot of the rate, R, of biomass burning (g C/yr) in each month from 35 S to 25 N, based on Hao and Liu (1994). The contours are $\log_{10}(R)$.

station locations and time periods of available CO data are summarized in Table 1. These stations have been chosen because they are oceanic sites unlikely to be contaminated by continental or local sources of CO. The signal we wish to extract is so small that it will be completely masked by local fluctuations. We also need a sufficient number of years of data to have confidence in the monthly trends. The method of extracting a monthly trend for each data set is the same as described earlier for CH_4. Monthly trends of CO from these five stations are shown in Fig. 9.

The CO monthly trends are generally negative (0 to -7 ppb/yr) over the time period 1990–1995, except at Ascension Island (ASC), which may be influenced by continental sources of CO. There appears to be a strong seasonal dependence in the monthly trends. This may be compared with the spatial and temporal pattern of biomass burning, as shown in Fig. 10 on the basis of data compiled by Hao and Liu (1994). Some cautionary statements would be in order. The model of Hao and Liu tends to have too much burning late in the dry period and too little in the early part of the dry season (M.O. Andreae, pers. comm.). Thus the spatial and temporal pattern of biomass mass burning shown in Fig. 10 is suggestive rather than definitive.

To provide additional evidence for the relation between CO change and biomass burning, we analyzed CH_4 data from six CMDL stations: MLO, KUM, GMI, ASC, SMO, and SPO. Station locations and time periods of available data are summarized in Table 1. Following the method described earlier, we divided the 12 yr of data from 1984 to 1995 into three periods: (a), (b), and (c). The trends for each six-year period were computed as before. The difference in trends (ppb/yr) between periods (b) and (a) is shown in Fig. 11. Aside from a large negative trend in the tropics during the early part of the year, there seems to be no simple consistent pattern to the difference between periods (b) and (a). In contrast, the difference in trends between periods (c) and (b) (Fig. 12) shows maximum changes during local spring in

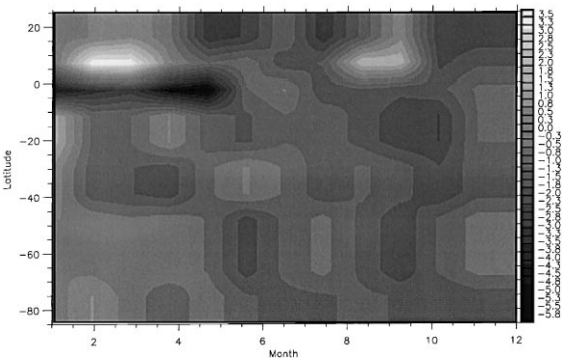

Fig. 11. Contour plot of the difference in CH_4 trends in each month (ppb/yr) between periods (b) and (a) from 85 S to 25 N. Data used in this plot are from NOAA–CMDL stations SMO, ASC, GMI, KUM, MLO, and SPO.

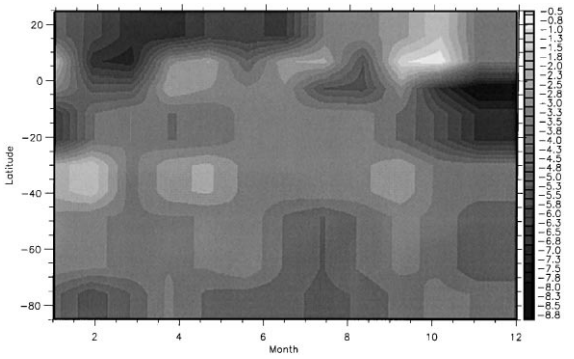

Fig. 12. Same as Fig. 11 (ppb/yr), between periods (c) and (b).

both northern and southern hemispheres. This pattern of change is similar to the pattern of biomass burning (Fig. 10). We therefore conclude that the most likely explanation for the change in CH_4 trends in the period 1984–1995 is a change in the rate of biomass burning.

3. Discussion

The temporal pattern of change for both CO and CH_4 at MLO suggests that there has been a decreasing source during spring in the northern hemisphere. A similar analysis carried out for data from several NOAA–CMDL stations suggests that there has been a similar decreasing source during spring in the southern hemisphere. This pattern of change is consistent with a decrease in biomass burning, which peaks in the spring season of each hemisphere (Hao and Liu, 1994). If we attribute a significant part of the declining upward trend in CH_4 (3–6 ppb/yr) to biomass burning, we can estimate the corresponding change in CO using the empirically determined ratio of 0.1 (v/v) for CH_4/CO release in biomass burning (Blake et al., 1996). The inferred decline in the trend for CO is 2–5 ppb/yr. This would explain the bulk of the observed change of 4–7 ppb/yr in the CO trend. The remainder of the observed change could be due to a combination of factors, including changes in column O_3 or tropospheric temperatures (Granier et al., 1996). Our results are consistent with earlier suggestions of changes in the biomass burning source of CO on the basis of ^{13}C data (Lowe et al., 1994, 1997) and a recent three-dimensional modeling study (Granier et al., 1996), but this appears to be the first attempt to extract information from the observed seasonal pattern. In the future, this analysis will be expanded by using CO measurements from more oceanic stations over a longer time period. In this way, we hope to gain a better understanding of the impact of biomass burning on the global atmosphere, particularly its impact on O_3 (e.g. Jiang and Yung, 1996).

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