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Carbon monoxide in the U.S. Mid-Atlantic troposphere: Evidence for a decreasing trend

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Abstract. Nearly continuous measurements of carbon monoxide (CO) were made at Shenandoah National Park-Big Meadows in rural Virginia, a site considered representative of regional air quality, from December 1994 to November 1997. Similar observations were also made at this location from October 1988 to October 1989. These observations combine to indicate a decreasing trend in CO concentration over the U.S. mid-Atlantic region of about 5.0 ppbv yr^{-1}, with greater than 95% confidence that the slope is significantly different from zero. The decrease suggests U.S. reductions in anthropogenic CO emissions have been effective in reducing pollutant levels. The observed trend is consistent with the U.S. EPA reported trend in emissions and the decrease in Northern Hemisphere tropospheric background CO mixing ratios observed by other researchers.

Introduction.

Carbon monoxide (CO) is a trace pollutant and key contributor to the chemistry of the troposphere. Released directly into the atmosphere by the combustion of fossil fuels and biomass burning and produced in the troposphere by the oxidation of methane (CH_4) and other non-methane hydrocarbons (NMHC) (*Logan et al.*, 1981), CO has a tropospheric residence time on the order of months. The dominant sink for CO is reaction with the hydroxyl radical (OH) (*Levy*, 1971), accounting for 90-95% of the removal of tropospheric CO (*Logan et al.*, 1981). Oxidation of CO can lead to photochemical ozone (O_3) production or destruction depending on the availability of nitrogen oxides (*Crutzen*, 1974). The close relationship between CO, OH, and O_3 establishes CO as an important link in controlling the oxidizing capacity of the atmosphere.

Long term CO measurements prior to the early 1990's indicated a Northern Hemisphere increase (*Khalil and Rasmussen*, 1988; *Dainov-Klokov and Yurganov*, 1989; *Novelli et al.*, 1992). More recent studies indicate the CO global background decreased from the late 1980's to 1992 (*Khalil and Rasmussen*, 1994; *Novelli et al.*, 1994). Since 1993, global CO trend studies have yielded different results. *Novelli et al.* (1998a) present evidence from the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) flask sampling network that from 1990 to 1995, globally averaged CO decreased by 2 ppbv yr^{-1} and in the Northern Hemisphere decreased by 2.6 ± 0.3 ppbv yr^{-1}. *Hard et al.* (1998) conclude there has been no significant change in globally averaged CO over the most recent decade.

Here we present nearly continuous measurements of CO made at Shenandoah National Park-Big Meadows (SNP) in rural Virginia from December 1994 through November 1997. Measurements made at the same location from 1988-1989 (*Poulida et al.*, 1991) are teamed with the more recent results to provide evidence of a decrease in tropospheric CO in the U.S. mid-Atlantic region. Although the trend is based on observations from only one mid-Atlantic location, past research from this monitoring station (*Poulida et al.*, 1991; *Doddridge et al.*, 1992) supports the assertion that the site is removed from local sources of pollution and is representative of regional air quality. The SNP monitoring site is located at 38.5°N, 78.5°W and 1100 m elevation. Other observations include meteorological variables, UV radiative flux, ozone, sulfur dioxide, and reactive nitrogen species (to be presented elsewhere).

The trend in boundary layer CO can be approximated by the following expression.

$$d[CO]/dt = V_I + A_I + P_A + P_N + P_{BHC} + P_{AHC} - A_O - V_O - L_{OH} - L_S \qquad (1)$$

where V_I is the vertical flux into the boundary layer, A_I is advection into the region, P_A is direct anthropogenic emission, P_N is direct biogenic emission, P_{BHC} is production from biogenic hydrocarbon oxidation, P_{AHC} is production from anthropogenic hydrocarbon oxidation, A_O is advection out of the region, V_O is vertical flux out of the boundary layer, L_{OH} is loss from reaction with OH, and L_S is deposition at the surface.

Here we assume the trend is due to changes in regional emissions and a decreasing Northern Hemisphere background CO level (*Novelli et al.*, 1998a). We assume that (1) deposition (L_S) and direct natural emission (P_N) represent reasonably small fluxes, (2) changes in P_{AHC} and P_{BHC} are minor contributors to the trend, and (3) the meteorology controlling the vertical and advective terms shows no significant trend from 1989-1997.

An increase in tropospheric OH would impact the CO budget, however for this paper we assume no change in OH (L_{OH}). *Krol et al.* (1998) estimate a 0.46% yr^{-1} increase in global OH abundance from 1978 to 1993; *Prinn et al.* (1995) found none. A 0.46% yr^{-1} change in OH is expected to produce less than a 0.46% yr^{-1} change in CO (*Thompson*, 1992).

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Experimental Technique.

The sample stream (1.0 L min^{-1}) for CO measurements during the 1994-1997 study was drawn through a 0.5 µm Teflon filter located atop a 10-m tower at slightly above canopy height. Detectors were housed in a temperature controlled shelter; all data were archived as 60 s averages. The CO detector used was a non-dispersive infrared gas filter correlation analyzer. The analyzer, modifications, and sampling protocols have been described previously (*Dickerson and Delany,* 1988; *Doddridge et al.,* 1994). Diagnostic checks were performed weekly and the detector was calibrated at regular intervals (at least 4 per year) using a compressed CO/N$_2$ mixture. This secondary calibration standard was referenced to a National Institute of Standards and Technology (NIST) traceable standard (NIST/SRM 1677c, 9.970 ppbv CO/N$_2$). During the 1994-1997 study, the instrument calibration showed no significant trend. The range in the calibration factor varied by less than 3.5% with a standard deviation of 1%. Based on instrument noise, calibration protocol, working calibration standard, batch to batch variability in the NIST primary standard, and calibration drift, the absolute accuracy of the measurements is estimated at ± 8.3% (95% confidence). Previous intercomparisons with NOAA/CMDL (*Doddridge et al.,* 1994, 1998; *Novelli et al.,* 1998b) show agreement to within 5%.

The 60 s data were processed into longer averages after removal of spikes from obvious local contamination, instrument malfunction, and calibrations. For the period December 1, 1994 to November 31, 1997 presented here, data collection exceeded 80%. The analytical method, data reduction, and calibration techniques were consistent with those of the 1988-1989 study. Mixing ratios following are expressed in ppbv (parts per 10^9 by volume) in dry air.

Results and Discussion.

The 1994-1997 CO hourly averages varied from 51 ppbv to 652 ppbv. Annual mean (median) values were 188 (186) ppbv, 176 (173) ppbv, and 166 (163) ppbv for 1995, 1996, and 1997 respectively. For the October 1988-October 1989 study, *Poulida et al.* (1991) report an annual mean (median) of 204 (202) ppbv, 22.9% higher than the annual mean in 1997. The annual means indicate a -4.8 ppbv yr^{-1} decrease in CO over the 9-year period, in total, considerably higher than the standard deviation of available detrended annual means ($1\sigma \sim 6$ ppbv). The annual frequency distributions (Figure 1) show a progressive shift toward lower CO mixing ratios and tighter distribution. The U.S. Environmental Protection Agency estimates of CO emissions from anthropogenic sources show a 18.3% decrease over the same period, with reduction in on-road vehicle emissions accounting for most of the change (*U.S. EPA,* 1998). The observed decrease at SNP is greater than estimated emissions reductions by 4.6%. Referring to equation (1), assuming P_A accounts for 50% of the CO source, the observed trend is consistent with a 2-3 ppbv yr^{-1} decrease attributable to anthropogenic emission reductions and the 2.6 ppbv yr^{-1} decrease in Northern Hemisphere background documented by *Novelli et al.* (1998a).

To further investigate the decrease in CO and determine the significance of the trend, a number of statistical methods were employed. Seasonal, monthly, and daily means were fit with "least squares" regression lines. Seasons were defined as winter (Dec-Jan-Feb), spring (Mar-April-May), summer (June-July-Aug) and fall (Sept-Oct-Nov). All regression line slopes presented here are accompanied by 95% confidence intervals (*Moore and McCabe,* 1989). The significance of the trend as indicated by the slopes was determined with two-tailed "t" tests. The calculated values of the "t" statistic were compared to published tables (*Moore and McCabe,* 1989) of "t" critical values to determine the level of significance. For seasonal and monthly data, the number of degrees of freedom used in determining the appropriate critical value was taken as the number of seasons or months minus two degrees lost in calculating the regression line.

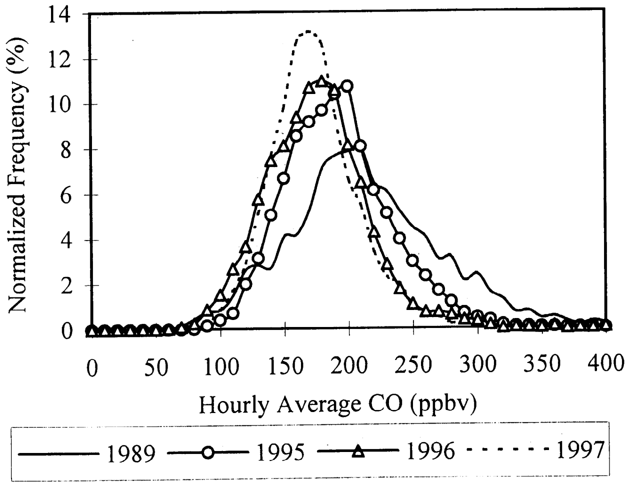

Figure 1. Annual CO frequency distributions expressed as a percentage of the total number of possible hourly observations during a single year. 1989 data adapted from *Poulida et al.* (1991).

The average CO seasonal trend was removed from the 1995-1997 data by calculating residuals. Monthly residuals were calculated by subtracting the average monthly mean over the entire measurement period from each month. Daily residuals were derived by subtracting three-year monthly means from each daily mean within a given month.

To determine the persistence of air mass chemical character with respect to CO, an autocorrelation function was calculated for the daily residuals, lagging the correlation by zero to seven days. A minimum coefficient (R= 0.18) was found after a four day lag. The number of different synoptic events per year was, therefore, estimated at 365/4, and 91 degrees of freedom were used when testing the significance of the daily trend.

The combined 1988-1989 and 1994-1997 CO seasonal means are presented in Figure 2. Seasonal mean mixing ratios indicate a decreasing slope of -5.1 ± 1.9 ppbv yr^{-1} with greater than 95% confidence that the slope is significantly different from zero. Examining the 1994-1997 data only, a gradual decrease in the CO time series superimposed on a modest seasonal cycle is evident. The 1994-1997 monthly means (Figure 3a) indicate a decrease in CO of -14.0 ± 7.8 ppbv yr^{-1} with greater than 95% confidence that the slope is significantly different from zero. When the average seasonal trend is removed, the resulting residuals (Figure 3b) display a slower decrease of -10.0 ± 5.5 ppbv yr^{-1}, suggesting the CO seasonal

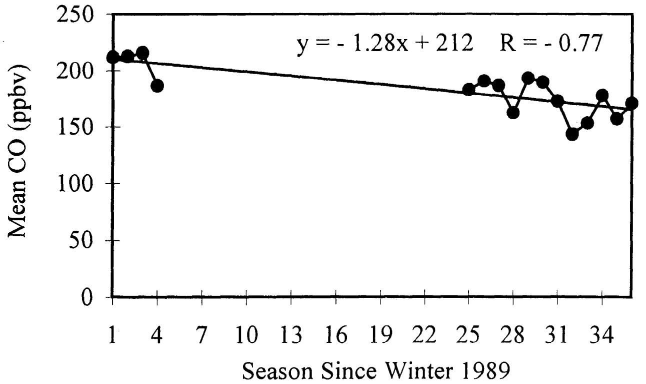

Figure 2. Seasonal mean CO mixing ratios (in ppbv) at SNP for the period Winter 1989 through Fall 1997. The slope has units of ppbv season^{-1}. 1989 data adapted from *Poulida et al.* (1991).

cycle introduces a 4.0 ppbv yr^{-1} artifact in the trend. A higher level of confidence was achieved by increasing the temporal resolution used in calculating the significance of the trend to days. Daily residuals (Figure 3c) show a decrease of -9.5 ± 2.1 ppbv yr^{-1}. This slope is significantly different from zero, with the calculated value of "t" a factor of 4.6 greater than the critical value for 95% significance. Although the 1995-1997 data show a trend with strong statistical significance, the large difference between the 3-year trend and the trend calculated with the 1988-1989 data included, intimates interannual variability in advection and vertical flux may dominate over changes in emissions during the shorter observation period. A full-scale study of transport and mixing patterns would require an analysis of advection and convection (*Thompson et al.,* 1994) and is beyond the scope of this paper.

Another eastern U.S. regional air quality site is the NOAA/CMDL site in Grifton, NC (35.21°N, 77.23°W, and 500 m) (*Novelli et al.,* 1998a). For the available period of simultaneous observations (December 1994 to November 1997), measurements from the two sites agreed well (*P. Novelli,* NOAA/CMDL, personal communication, 1999). The mean from SNP was 177 ppbv (1σ = 23) while that from Grifton was 171 ppbv (1σ = 32); the rms difference for monthly means was 25 ppbv. The trends over this period were also similar, -13.2 ± 12.0 ppbv yr^{-1} at Grifton and –14.0 ± 7.8 ppbv yr^{-1} at SNP.

The data recorded at Grifton may be too short to determine a trend due to changes in emissions. For the longer observational period, (July 1992 to November 1997) there was no statistically significant trend (-0.9 ± 4.7 ppbv yr^{-1}) at Grifton. The sample size at Grifton is much smaller than at SNP, NOAA takes approximately weekly grab samples, reducing the confidence in the trend determined from the NC site. A more detailed statistical analysis of all available Eastern U.S. data would be beneficial for better defining the trend.

We find no evidence for an increase in OH at SNP or the region. *Fiore et al.* (1998) found no significant trend in median O_3 over the continental U.S. and SNP O_3 data (to be presented elsewhere) show no significant trend from 1983 to 1997. Water vapor shows no statistically significant increase over the region (*W. Ryan,* University of Maryland, personal communication, 1999). Estimated increases in UV flux at Northern mid-latitudes are small and highly uncertain (*WMO,* 1999). Emissions estimates of anthropogenic hydrocarbons show a 15.9% decrease (*U.S. EPA,* 1998) which if anything should lead to decreased OH. Determination of changes in biogenic hydrocarbons is difficult due to uncertainty in existing emission estimates and sparsity of data. A comparison of SNP 1995-1997 NO data with 1989 observations indicates no substantial change in NO mixing ratios. EPA also estimates no change in anthropogenic nitrogen oxide emissions (*U.S. EPA,* 1998).

Conclusions.

Comparison of 1988-1989 measurements over Shenandoah National Park-Big Meadows with more recent measurements at this location from 1994-1997 indicates a decline in CO

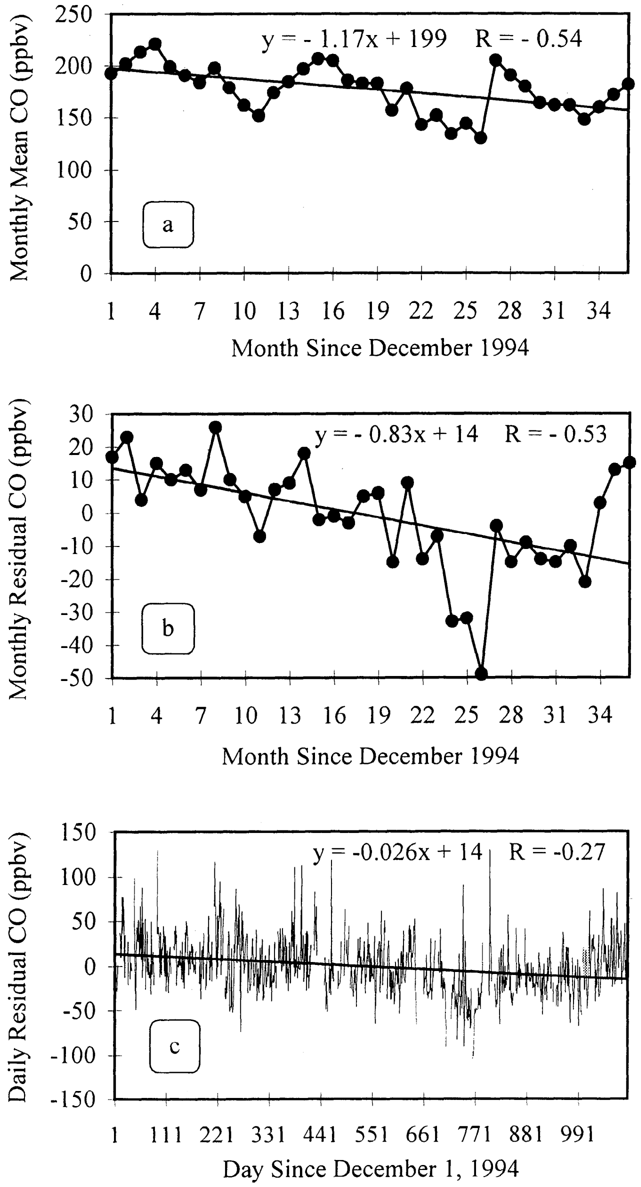

Figure 3. (a) Monthly mean CO mixing ratios (in ppbv) at SNP. (b) Monthly residual differences in CO mixing ratios (in ppbv). (c) Daily residual differences in CO mixing ratios (in ppbv). Slopes have units of (a) ppbv month^{-1}, (b) ppbv month^{-1}, and (c) ppbv day^{-1}.

mixing ratios of -5.1 ± 1.9 ppbv yr^{-1}. The deseasonalized data from 1994-1997 indicate a decrease of about 10 ppbv yr^{-1}, however, interannual variability in transport patterns may dominate over changes in emissions during short observation periods. A 9-year sampling period appears adequate for determining trends in CO and the best estimate of the trend is that calculated over 1989-1997. These data are consistent with EPA estimated anthropogenic emission reductions and the reported decrease in global background CO levels.

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