Zvenigorod carbon monoxide total column time series: 27 yr of measurements

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Importance of this Paper: Is the oxidizing capacity of the atmosphere, which is controlled mainly by hydroxyl, stable or not? Tropospheric OH is the main sink for carbon monoxide. Here is one of the longest consistent series of CO measurements in the total atmospheric column. After a period of increase total column amount of CO stabilized. We compared our data to available data on total ozone and stratospheric aerosol, which influence tropospheric OH. We concluded that the apparent CO stabilization after 1983 seems to be a result of growth both in its source and sink – OH concentration.

Abstract

The analysis of total column spectroscopic CO (carbon monoxide) observations over Russia between 1970 and 1996 revealed an upward trend, with a rate of 0.96 ppb/yr or 0.9%/yr. A similar trend has been reported over Switzerland between 1950 and 1987. This rate of CO growth is almost three times higher than the rate between 1920 and 1950, obtained from ice core data. However, after 1982, CO above Zvenigorod varied from year-to-year with no apparent long-term trend. The inter-annual variations in the data set were associated with vast forest and peat fires in the central Russia in 1972 and major volcanic eruptions after 1982. It was proposed, that the slowing down of the CO increase was caused mainly by changes in CO consumption by OH. Sensitivities of CO mixing ratio in the troposphere to changes in total ozone and stratospheric aerosol have been assessed from the smoothed monthly measurements. Corrections due to unstable aerosol and total ozone were introduced into the experimental data. The CO trend over the entire measurement period which would be expected under conditions of constant "undisturbed" total ozone and no stratospheric aerosol would be 1.3 ppb/yr, or 30% higher, than the observed trend. A positive trend in OH concentrations between 1980 and 1995 was estimated to be 0.6 ± 0.3%/yr. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Carbon monoxide (CO) concentrations have been measured by many researchers, both in the surface layer (e.g., Seiler, 1974; Novelli et al., 1992 and references therein), and in the total atmospheric column using IR spectroscopy with the

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Sun as a light source (Migeotte, 1949; Dianov-Klokov et al., 1989; Zander et al., 1989; Pougatchev and Rinsland, 1995; Yonemura and Iwagami, 1996). Both kinds of observations revealed growing CO concentrations on a hemispheric scale between the early 1950s and early 1980s, with a rate of 0.8–1.5%/yr or 1.0–1.8 ppb/yr (Dvoryashina et al., 1984; Khalil and Rasmussen, 1988; Zander et al., 1989). However, after 1983 a stabilisation (Yurganov et al., 1995) or even a decrease in CO (Khalil and Rasmussen, 1994; Novelli et al., 1998) was detected. The influence of UV attenuation by volcanic stratospheric aerosol on OH, the main CO scavenger, has been proposed to explain the CO observations (Dlugokencky et al., 1996; Yurganov et al., 1997). Model calculations predict that the tropospheric composition is highly dependant on stratospheric transparency (Madronich and Granier, 1992; Bekki et al., 1994). A positive trend in the atmospheric CO concentration during the period between 1850 and 1950 has been inferred from analysis of the air bubbles enclosed in Greenland polar ice cores; the rate of growth after 1920 amounted to 0.35 ppb/yr (Haan et al., 1996).

The annual cycle of CO is driven by both natural and artificial processes (Logan et al., 1981; Mueller and Brasseur, 1995). Fuel combustion, biomass burning and photochemical oxidation of hydrocarbons are principal sources of CO. The reaction between CO and OH is the main sink for both species in the troposphere. The average lifetime of atmospheric CO is about two months (Mueller and Brasseur, 1995), but it is strongly dependent on latitude and season. In the fall–winter period a reduction in OH concentrations results in the accumulation of CO in the Northern Hemisphere (NH). In the spring, CO mixing ratios begin to drop, due to increased solar radiation and OH production, and a minimum is reached in late summer. Because of its relatively long lifetime, especially in winter, long-range transport of CO is an important mechanism for its spatial distribution and temporal variations.

The vertical distribution of CO in the troposphere is highly variable and often complicated (Conway et al., 1993; Harris et al., 1994; Yurganov et al., 1998). As a result, measurements inside the atmospheric boundary layer do not always characterise CO variations in the troposphere as a whole. However, the measurement of CO by IR spectroscopic techniques allows the determination of the mean mixing ratio of the whole troposphere. Such a technique has been used since 1970 in Zvenigorod Russia, near Moscow (55°42'N, 37°36'E, 200 m above sea level (asl)) (Yurganov et al., 1997). The main objective of this paper was to analyse causes of CO changes. In particular, it was studied if the slowing down of CO build up in the NH – during 1980–1990s – has been caused by a decrease in the CO production or by an increase in the CO sink.

2. Experimental technique

All CO spectroscopic measurements that are analysed in this paper were made using an 855 mm focal length Ebert/Fastie-type grating spectrometer, with a 300 grooves/mm grating and a solar tracker. Atmospheric absorption spectra were acquired between 2153.0 cm^{-1} and 2160.0 cm^{-1}, with a resolution of 0.2 cm^{-1} (Dianov-Klokov, 1984).

The initial retrieval technique used with this spectrometer involved the manual determination of values of absorption inside the $R(3)$ line of CO fundamental band (near 2158.30 cm^{-1}), which were then converted into CO mixing ratios using the algorithm described by Dianov-Klokov et al. (1989). Briefly, the measured spectrum was compared to a spectrum calculated using the HITRAN-86 database (Rothman et al., 1987) and typical atmospheric temperature profiles. The CO mixing ratios in the calculations were assumed to be constant throughout the atmosphere. This value of mixing ratio was presented as a result of measurement. A correction for an overlapping weak water vapor line (near 2158.15 cm^{-1}) was made for the cases with total H_2O content higher than 1.2 g/cm^2. The H_2O total column, used for this correction, was estimated using an adjacent water vapor line near 2156.56 cm^1. The uncertainty connected with an inaccurate knowledge of CO line parameters was estimated to be at most ±5% (Yurganov et al., 1998); this uncertainty enters as a systematic bias.

As was analysed by Yurganov et al. (1998) (and, more generally, by Rodgers (1990), Pougatchev and Rinsland (1995), and references therein), spectroscopically measured CO mixing ratio should be considered as weighted average mixing ratio for the entire atmosphere. For typical mid-latitudinal vertical CO profiles the weighted average is very close (deviations are less than 5%) to the mixing ratio, averaged over the entire troposphere (Dianov-Klokov and Yurganov, 1989; Yurganov et al., 1998).

Yurganov et al. (1998) developed another technique, which used a newer version of the HITRAN database (Rothman et al., 1992) and spectra, recorded by the computer. The "original" manual algorithm was simulated in computer code as well. A difference in retrieved values of CO mixing ratio in the Alaskan troposphere during the period between March and August of 1995 between these two procedures was less than 6%.

The precision of a single measurement (i.e., the standard deviation of points for a day with steady conditions) is typically ±4–6%. Normally 15–25 spectra per day were observed, therefore a statistical 1-sigma uncertainty of the daily average was around ±1%. Monthly means were obtained over 5–20 sunny days and the day-to-day variability of CO abundance had a magnitude of ±10–12% (Yurganov et al., 1995). Statistical uncertainty in the monthly mean amounted to ±3–5%.

The influence of CO emissions from Moscow on CO observations in Zvenigorod have been discussed in the early papers by Dianov-Klokov et al. (1979) and Dianov-Klokov and Yurganov (1981). No significant dependence of CO abundance on wind direction was found. Slightly higher CO values (appr. 7%) were, however, observed on days when the wind was from the North (Moscow being to the East from Zvenigorod). Presumably this is a result of CO background latitudinal distribution. A study is now underway to determine if the contribution of Moscow to Zvenigorod data has increased during more recent 20 yr. However, direct measurements of the CO total column above the Moscow centre have not found any increase of the urban surplus to the background for the last 15 yr (Fokeeva et al., 1997; also Fokeeva et al., 1998, personal communication).

3. Results

3.1. Long-term trends

Monthly mean CO mixing ratios in ppb for the period between February 1970 and December 1996, are presented in Fig. 1 (triangles). Between October 1976 and December 1979 the measurements were not conducted, but the instrument was neither moved nor modified. The data was modelled as a superposition of a linear trend $T(t)$, a seasonal variations $S(t)$ and an irregular disturbance $D(t)$, which is not described by the trend and seasonal cycle (Khalil and Rasmussen, 1995):

$$[CO](t) = T(t) + S(t) + D(t). \tag{1}$$

First, a simple 12-month running average was applied to exclude the seasonal cycle (thick curve in Fig. 1). This procedure probably is not quite correct because measurements were not possible during some months (e.g., November and December) because of weather and/or short daylight period during the day. The annual averages of the data therefore depend on which and how many months were missing. Thus, another procedure for excluding seasonal variations was also utilised.

To determine the seasonal cycle, all the available data were averaged by months regardless the year.
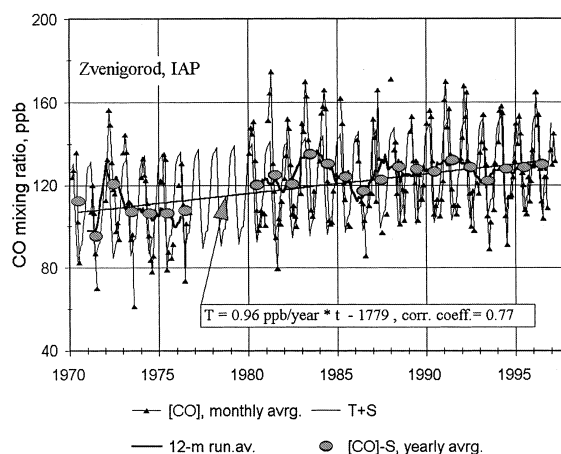

Fig. 1. Total column CO abundance over Zvenigorod, Russia, presented as weighted mean mixing ratio ([CO]) for the tropospheric depth. In the box is linear trend $T(t)$, S is the seasonal cycle (see text).

Then the overall average mixing ratio, 122.2 ppb (parts per billion by volume), was subtracted from the obtained monthly means, and the mean seasonal deviations from the annual average $S(t)$ (here t is a month of the year) were determined. In this approach we assume that the seasonal cycle was the same for the entire period of measurements.

Deseasonalized monthly means ([CO]-S) were analysed further. The filled circles in Fig. 1 correspond to the annual averages of [CO]-S, representing $T + D$ (see Eq. (1)). It should be noted that the circles do not significantly deviate from the simple running averages (thick curve); therefore, both procedures can be used in this case. The straight line in Fig. 1 is the simple linear regression derived from the annual means (the trend T). The thin periodical broken line is $T + S$, calculated as described above.

Fig. 1 clearly demonstrates an upward trend for both the deseasonalized yearly means (circles) and for the simplest 12-months running average data (thick curve). The slope and standard deviation [STD] of the regression line calculated from the annual means is 0.96 ± 0.17 ppb/yr. This rate corresponds to 0.90 ± 0.16%/yr if we divide it by the mean [CO] in 1970, i.e., 106.2 ppb. It can be noted that the trend of total column CO over Russia for 1970–1996 is in excellent agreement with the trend of total column CO amount, spectroscopically measured by Zander et al. (1989) over Jungfraujoch Germany for the period 1950–1987: 0.85 ± 0.20%/yr.

However, this CO growth is three times faster than that between 1920 and 1950 (0.35 ppb/yr), assessed from the analysis of air preserved in Greenland ice (Haan et al., 1996). This apparent acceleration is speculated to be due to the enormous economic growth after World War II (similar features exist in the carbon dioxide and methane time series, Khalil and Rasmussen, 1995). After 1982, the CO growth slowed down again (see below).

3.2. Interannual variations and sensitivities of CO to changes in total ozone and stratospheric aerosol

The seasonal cycle S was subtracted from measured monthly mean [CO] (Fig. 2, points). The
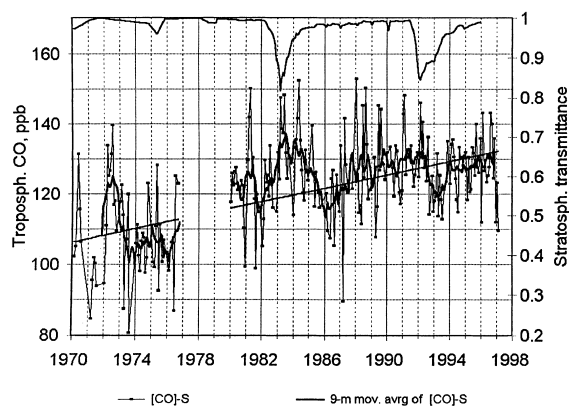

Fig. 2. Monthly mean deseasonalized mixing ratios [CO]-S (points) and 9-months running average (solid curve). Upper curve is the zenith transmittance of stratospheric aerosol at wavelength 550 nm, calculated from optical depths τ for 58.7° N, which were taken from Hansen et al. (1996).

thick line shows a 9-month running average; 12-month smoothing was not necessary because the seasonal cycle had been removed already.

The unusually high CO values in summer of 1972 have been discussed by Dvoryashina et al. (1984) and explained by emissions from catastrophic forest and peat fires in the European part of Russia caused by a strong drought (Kats, 1974).

Volcanic eruptions of Mt. El-Chichon in April 1982 and Mt. Pinatubo in June 1991 resulted in the injection of large quantities of aerosols into the stratosphere on a global scale. Atmospheric transmittance at the wavelength of 550 nm for the latitudinal belt near 58.7°N is plotted at the top of Fig. 2 (compiled by Hansen et al., 1996). This data shows that visible (and, obviously, UV) solar radiation was similarly attenuated by the stratospheric aerosol after these eruptions. On the contrary, variations of CO after the eruptions differed not only in magnitude, but even in sign: CO increased after the Mt. El-Chichon eruption and decreased after the Mt. Pinatubo eruption.

Solar UV radiation in the spectral range 290–330 nm determines the rate of OH formation in the troposphere. Attenuated UV after the El-Chichon eruption could be a cause of CO increase in the same period of time. However, a similar variation of aerosol after the Pinatubo eruption

resulted in quite different behaviour of CO. This leads to a conclusion, that there should be another mechanism, probably connected with volcanic eruptions, which influences tropospheric CO.

As was shown by Solomon et al. (1996) (and references therein), volcanic aerosol particles trigger photochemical heterogeneous reactions, which destroy ozone molecules in the lower stratosphere. Ozone depletion after the Pinatubo eruption turned out to be much more pronounced, than after the El-Chichon eruption because of higher levels of ozone-destructing man-made chlorine in the stratosphere in 1990s. Both aerosol and ozone attenuate solar UV; these two mechanisms compete in the net effect on UV changes.

We considered three total ozone data sets for a comparison to the CO data (Fig. 3), two of which being measured in Russia. The first one was collected near Moscow (Dolgoprudny) using M83/M124 ozone filter photometers; the second data set was obtained near St. Petersburg (Voyeykovo) by a Dobson spectrophotometer (both archived at the World Ozone and Ultraviolet Radiation Data Centre, WOUDC; WWW site http://www.tor.-ec.gc.ca/woudc/woudc.htm). The third data set was measured by TOMS instruments (version 7) on NIMBUS-7 (NASA, 1996a) and METEOR-3 (NASA, 1996b), complemented by recent measurements on the EARTH PROBE spacecraft between August 1996 and January 1998 (personal communication, R. McPeters, 1998). These raw data were deseasonalised and smoothed by the same procedure applied to the CO data (see above). A very fine correlation can be seen between these three ozone curves (Fig. 3), both for interannual variations and for the long-term trends. In particular, all three data sets show a drop in ozone with two minima (or a "double hollow") during 1991–1993 after the Pinatubo event. The slopes of the regression lines in Dobson Units (DU)/yr were TOMS (-1.28 ± 0.15); St. Petersburg (-1.91 ± 0.12); Moscow (-1.51 ± 0.12). A detailed discussion of the decline in total ozone after 1980 and interannual variations can be found in Harris et al. (1997). In our analysis, we have used the TOMS satellite data set, but the results that would be obtained using other data sets are expected to be similar.

The quasi-linear ozone decline after 1980 could influence CO tropospheric mixing ratios through an increase in tropospheric UV and OH. What is the sensitivity of tropospheric CO to changes in the total ozone? It can be assessed from a correlation between the detrended and the deseasonalized CO and ozone monthly means. But first it is necessary to correct CO values to remove the effects of the stratospheric aerosol. A convenient time period to assess how much CO is effected by changes in aerosol occurred just after the El-Chichon eruption between April 1982 and August 1983 (Fig. 4). During this time, the total ozone was relatively constant (Fig. 3). The slope of regression line is 86 ± 10 ppb per unit of optical depth (τ) (dimensionless). The r^2 correlation coefficient is 0.86.

Fig. 5 illustrates the time series of measured deviations of CO (points) and TOMS ozone (triangles) from their trends. The bottom curve is the mean zonal optical depth (τ) of the stratospheric aerosol at the wavelength 550 nm for the latitude 58.7°N (Hansen et al., 1996). CO, corrected for aerosol (open circles), is derived by subtracting the
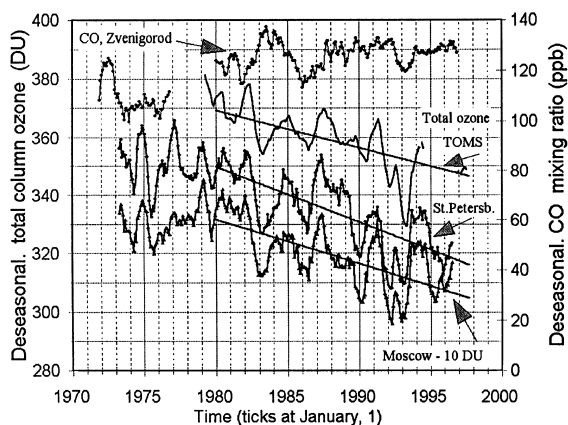

Fig. 3. Monthly averaged and deseasonalized (not detrended) total column ozone in Dobson units (DU) measured from the surface at two sites in Russia (St. Petersburg, 60°N and Moscow, 56°N) and from satellites by TOMS instruments. Note that Moscow trace is shifted down by 10 DU for clarity. Satellite data are zonal averages for the latitudinal belt 55–60°N. CO curve is plotted for comparison.

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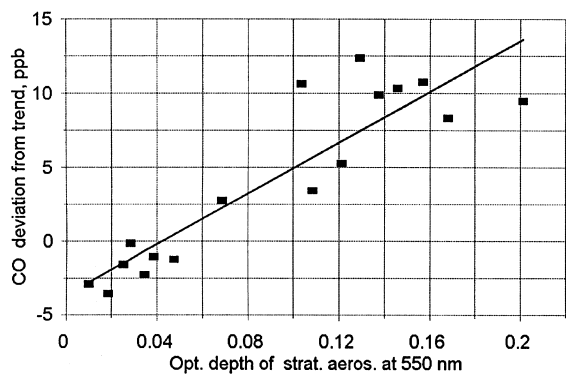stratospheric aerosol and total ozone. Now we can reduce the measured CO to some constant levels of these two parameters: namely to zero aerosol and to mean total column amount of ozone before 1980. Unfortunately, there were no TOMS data before 1979. Available ground based measurements revealed no trend between 1973 and 1980 (Fig. 3). Therefore, we have assumed 370 DU to represent "undisturbed" zonal ozone annual level at 55°N.

Grey circles in Fig. 7 relate to measured, deseasonalized and smoothed (but not detrended) CO mixing ratios. The slope of the regression line is 0.94 ± 0.06 ppb/yr ($r^2 = 0.48$). The triangles correspond to the measured CO subtracted by a "contribution from ozone": ([O$_3$]-370 DU) × 0.53 ppb/DU. This curve represents CO variations assuming stable total ozone. We see in this data two peaks after both great volcanic eruptions; measured CO has had just one peak. The regression line corresponding to this case has a slope of 1.45 ± 0.07 ppb/yr and $r^2 = 0.67$.

After the subtraction of a "contribution from aerosol" ($\tau \times 86$) we obtain the thick line, which corresponds to CO mixing ratio in an assumption of an "aerosol-free stratosphere" and stable an-

Fig. 8. The same as Fig. 7 (without triangles), but regression lines were drawn separately for the first and second parts of the entire period.

nual average of total ozone of 370 DU. In this case, the peaks induced by aerosol disappeared. The slope of regression line is 1.27 ± 0.06 ppb/yr ($r^2 = 0.67$). The residual CO variations, however, are significant. They should be attributed to other factors influencing tropospheric CO (e.g., production rates) and/or imperfect correction for ozone and aerosol effects.

Therefore, the trend in tropospheric CO between 1971 and 1995 was influenced by stratospheric ozone and aerosol variations. It seems helpful to look at the stabilisation of CO in 1980–1990s, which was probably caused by the decline in ozone (Fig. 8). The slope of regression line, STD and r^2 correlation coefficient for actual CO mixing ratios between 1980 and 1995 are $+0.25 \pm 0.10$ ppb/yr, $r^2 = 0.04$ (i.e., CO is practically stable). The same parameters calculated for CO mixing ratios, corrected for variable ozone and aerosol are 0.94 ± 0.09 ppb/yr, $r^2 = 0.40$. For the period between 1971 and 1982 (with a gap in the middle) the slopes are 1.26 and 1.14 ppb/yr with STDs being 0.2 ppb/yr (i.e., almost the same). Thus, the correction for unstable stratospheric composition during 1980–1995 restored the CO trend to a value that is close to 1 ppb/yr. However, it is evident from Fig. 8, that residual interannual variations are still significant. These variations most likely should be attributed to changes in CO production in the NH.
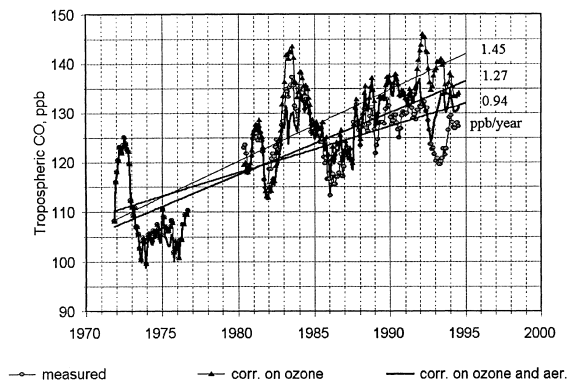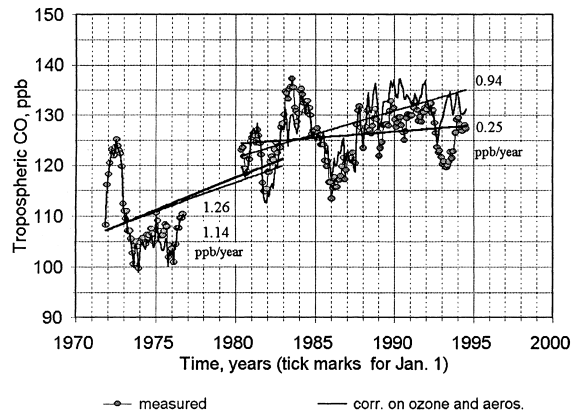

Fig. 7. Deseasonalized and smoothed CO mixing ratios and corresponding regression lines. Grey circles and the line with a slope 0.94 ppb/year relate to measured values. Triangles and the line with a slope of 1.45 ppb/year relate to CO in assumption of constant total ozone of 370 DU. Thick broken line and regression with a slope 1.27 ppb/year correspond to CO reduced to constant ozone and zero aerosol ("no eruptions/no ozone trend" case).

3.4. Comparison to concurrent free tropospheric Colorado flask data.

How representative are the total column data obtained in Zvenigorod and the conclusions made above? As it has been already found by Yurganov et al. (1998), the correlation between spectroscopic and surface measurements even at the same place is quite poor. The most extensive and precise data on worldwide surface-level atmospheric CO have been collected by the NOAA/CMDL (Novelli et al., 1998). Moreover, those are mostly measured within the marine boundary layer. Only a few stations supply data on CO mixing ratio in the free troposphere. Fig. 9 illustrates a comparison of spectroscopic CO data, collected at Zvenigorod, Russia, to CO mixing ratios, measured in Niwot Ridge, Colorado (40°03'N, 105°35'W at the height of 3475 m asl) (Novelli et al., 1998) (the data was obtained from the WWW-site http://www.cmdl.noaa.gov/).

One can see a good correlation between the two data sets ($r^2 = 0.74$), especially after January 1991, when the calibration technique, used for flask analysis, was improved (Novelli et al., 1998). This appears to be evidence of a good horizontal mixing for the troposphere as a whole in mid latitudes (much better than for the boundary layer). It is

also worth noting the CO decline after 1991 at both sites, treated in this paper as a result of the Pinatubo eruption. Mean mixing ratios for the entire 7-yr period of concurrent measurements were 127.8 ppb in Zvenigorod and 121.8 ppb in Niwot Ridge. It is not very surprising, that mixing ratios averaged over total tropospheric depth turned out to be close to mixing ratio measured at the height of 3.5 km. However, additional co-located measurements should be carried out to check this hypothesis.

4. Discussion

Seven years of simultaneous measurements at Zvenigorod, Russia and at Niwot Ridge, Colorado revealed a very good correspondence of data. This allows us to extrapolate the conclusions presented above onto the mid-latitude zonal band. Mean tropospheric CO mixing ratio, measured by solar spectroscopy in Zvenigorod, increased during last 27 yr from 100–110 ppb up to 120–130 ppb.

The increase was not steady. After a peak in 1983 two drops were observed, thus no significant trend was observed for the period 1980–1995. The tropospheric CO was found to correlate to total ozone and stratospheric aerosol. Both these high-altitude species impact on transmission of solar incoming UV radiation into the troposphere and, therefore, on OH generation in the troposphere. Sensitivities of CO to changes in ozone and aerosol were assessed from these correlations: 0.53 ± 0.06 ppb CO per 1 DU change of total ozone and 86 ± 10 ppb CO per 1 optical aerosol depth.

The changes in the UV radiation result not just in inter-annual CO variations, but also in its long-term trend. The latter effect is associated mainly with a -1.28 DU/yr depletion of zonally averaged total ozone near 55°N after 1980. When the measured CO values were reduced to stable annual level of 370 DU of total ozone, the CO positive trend restored.

A conclusion was drawn that the observed stabilisation in the CO total column is associated with an intensification of photochemical sink rather than with a stabilisation (or even decrease) in the anthropogenic production.
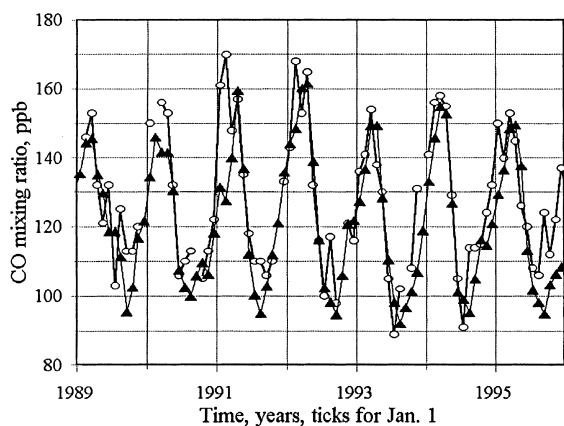

Fig. 9. Weighted average CO mixing ratio (mainly tropospheric average), measured in Zvenigorod (○), in comparison to free tropospheric mixing ratio, sampled at the altitude of 3475 m in Niwot Ridge, Colorado, USA (▲).

Extensive measurements in the marine boundary layer (Novelli et al., 1998; Khalil and Rasmussen, 1994) indicated a global decrease of CO mixing ratio with a rate -2 to -3 ppb/yr after 1987. There could be several reasons for the apparent disagreement with our data. First, the boundary layer is more strongly influenced by surface CO sources than the total column amount. Second, some conclusions on CO decline (e.g., Novelli et al., 1994) have been made for a relatively short period of time after the Pinatubo eruption. Total column CO above Zvenigorod underwent a decrease between 1991 and 1993 also. Third, a possibility of a change in vertical CO distribution, caused by the global surface temperature warming and more intensive vertical transport can not be ruled out. Anyway, this difference seems to be objective and should be taken into account in a treatment of CO global trends.

What was the rate of OH increase, which was necessary to explain the change in CO trend? The 0.25 ± 0.10 and 0.94 ± 0.09 ppb CO/yr slopes (Fig. 8) converted into exponential growth correspond to 0.20% and 0.77%/yr. Thus the change of CO trend is 0.57 ± 0.19%/yr. Assuming that the reaction with OH is the only tropospheric sink for CO, a similar per year rate of [OH] increase between 1980 and 1995 would be expected. The rate was estimated to be 0.6 ± 0.3%/yr (the precision should include also uncertainty because of rather poor correlation between CO and ozone). It is interesting that a very similar estimate of 0.46%/yr for OH build up with the range of estimate between -0.1 and $+1.1$%/yr was recently published on the basis of reevaluation of global methylchloroform measurements between 1978 and 1993 (Krol et al., 1998).

Acknowledgements

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