An estimate of changes in the tropospheric hydroxyl concentration with long-term total column CO measurements

L.N.Yurganov,¹ E.I.Grechko,² and A.V. Dzhola² ¹Physics Department, University of Toronto, Toronto M5S 1A7, Canada ²Institute of Atmospheric Physics, Russian Academy of Sciences, Moscow 109017, Russia.

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Abstract Most of non-CO₂ greenhouse gases (NCGS) are removed from the troposphere in a reaction with tropospheric hydroxyl (OH). Meanwhile, present and future trends in hydroxyl concentration are not understood at all. The main sink for OH is its reaction with carbon monoxide (CO). Total column amounts of CO were measured in Russia for 29 years. A correlation between total column amounts of CO and ozone is analyzed in this report. A positive slope of 0.55 ppb CO in the troposphere per 1 DU (Dobson Unit) of total column amount of ozone was found. It is known that ozone total column currently declines in the northern mid latitudes with a rate of -1.3 DU per year. As a result CO anthropogenic increase should be offset by -0.7 ppb per year. A hydroxyl build up of about 0.6 % per year after early 1980s due to more intense photochemical reactions initiated by increased UV was inferred. If it is the case, scenarios of long-term variations of the NCGS, removed by OH, should be reevaluated in view of total ozone trends.

1. INTRODUCTION

Hydroxyl (OH) has been known as a highly important "scavenger" of the troposphere since early 1970s (Levy 1971). Several radiatively-active trace gases are removed from the troposphere in reactions with OH. The reaction between CO and OH represents 90-95% of the CO sink (Logan *et al.* 1981) and about 75% of the removal of OH (Thompson 1992). The most important source of OH starts with the photolysis of tropospheric ozone, followed by a reaction of excited oxygen with water vapor (Logan *et al.* 1981). Recent reliable OH measurements (Mount and Williams 1997; Branderburger *et al.*

1998) have confirmed, that ozone photolysis is the primary OH production pathway during the daytime.

Both surface (Khalil and Rasmussen 1995) and total column (Dvoryashina *et al.* 1984; Zander *et al.* 1989) observations revealed growing CO concentrations in the Northern Hemisphere between the early 1950s and early 1980s with a rate of 0.8-1.5 % per year or 1.0-1.8 ppb/year. However, after 1983 a stabilisation or even a significant decrease in CO (Yurganov *et al.*, 1995; Mahieu *et al.*,1997; Rinsland *et al.* 1998; Khalil and Rasmussen 1995; Novelli *et al.* 1998) were detected (Table 1). There would be two explanations for this effect: either slowing down of CO sources or an intensification of CO consumption by OH (or a combination of both). Both US and West-European car CO emissions tend to decrease (Bakwin *et al.* 1994), but in Southeast Asia (as well as in the former Soviet Union) trends in CO emissions are still highly uncertain.



CO total column over Zvenigorod

Figure 1. Monthly mean and deseasonalyzed CO over Zvenigorod, Russia. Smoothing has been performed using 9-month running average.

Model calculations predicted a substantial impact of changes in the stratospheric UV transparency on the tropospheric chemistry and composition (Madronich and Granier 1992). The influence of UV attenuation by volcanic stratospheric aerosol on OH has been proposed to explain the CO observations right after El-Chichon eruption in Northern Hemisphere and after Pinatubo eruption in the tropics and in the southern hemisphere (Dlugokencky *et al.* 1996; Yurganov *et al.* 1997). Yurganov *et al.* (1997) noted that stratospheric aerosol and ozone after major eruptions play competitive roles in their influence on OH and CO; aerosol usually increases after eruptions, but ozone, in contrast, decreases.

Two available experimental estimates of OH trend have been based on methyl chloroform (CH₃CCl₃) measurements at five stations in both hemispheres. Prinn *et al.* (1995) inferred that the global average OH trend over the period 1978-1983 was close to zero. Krol *et al.* (1998) used an alternative statistical technique and a more detailed model to show that the positive trend may be in the range 0.4-0.5% per year. Yurganov *et al.* (1999) (also this paper) estimated the OH trend after 1980 to be +0.6 \pm 0.3 % per year. The latter estimate was based on the observed ozone trend and correlation between CO and total ozone.

2. EXPERIMENTAL TECHNIQUE

A grating spectrometer (Dianov-Klokov 1984) with a solar tracker was used. Atmospheric absorption spectra were acquired between 2153.0 cm⁻¹ and 2160.0 cm⁻¹ with a resolution of 0.2 cm⁻¹. Values of absorption inside the R(3) line of CO fundamental band (near 2158.30 cm⁻¹) were converted into CO mixing ratios or total column amounts using the algorithm described by Dianov-Klokov *et al.* (1989).

The CO mixing ratios in the calculations were assumed to be constant throughout the atmosphere. The uncertainty connected with CO line parameters was estimated to be at most $\pm 5\%$ (Yurganov *et al.* 1998); this uncertainty enters as a systematic bias.



Figure 2. Correlations between tropospheric CO and stratospheric components after major eruptions: (a) [CO] *vs* aerosol after El-Chichon event; (b) ([CO]-87 AOD) *vs* total ozone after Pinatubo event (AOD from Hansen *et al.* 1996).

As was analysed by Yurganov *et al.* (1998) spectroscopically measured CO mixing ratio can be considered as weighted average mixing ratio for the entire atmosphere. Weighting function for the R(3) line has a maximum near the ground and gradually diminishes with height. 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 tropospheric layer between 0 and 10 km.

The standard deviation of points for a day with steady conditions was typically $\pm 4-6\%$. Normally 15-25 spectra per day were observed. Monthly means were obtained over 5-20 sunny days and the day-to-day variability of CO abundance had a magnitude of $\pm 10-12\%$.

3. **RESULTS**

Monthly mean CO mixing ratios in ppb (parts per billion by volume) and corresponding total column amounts in mol/cm² for the period between February 1970 and May 1999, are presented in Figure 1 (triangles). Between October 1976 and December 1979 the measurements were not conducted, but the instrument was neither moved nor modified.

Long-term measurements are usually represented 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). To determine the seasonal cycle, we averaged all the available data by months regardless the year. Then the overall average mixing ratio, 122.2 ppb, was subtracted from the obtained monthly means, and the mean seasonal deviations from the annual average S(t) (here t is the month of the year) were determined.

The seasonal cycle S was subtracted from measured monthly mean [CO]. The thick line in the Figure 1 shows deseasonalized CO smoothed by 9-month running average. A linear trend between 1970 and the end of 1983 of 1.7 ppb per year (or 1.6 % per year) was observed. Between 1984 and the end of 1997 there were no significant trend.

CO concentration substantially varied from year to year. This partly explains disagreements in estimates of CO trend by various authors (Table 1). It is important also to count the atmospheric domain where the measurements take place. It seems that total column CO (both for the sea level station Zvenigorod and for mountain stations) was stable or slightly decreasing in the 1980s – 1990s. On the contrary, CO concentrations in the marine boundary layer were decreasing with higher rates of -1...-2 % per year.

The observed reversal of CO trend in the early 1980s requires an explanation. We analysed a sensitivity of tropospheric CO to changes in the stratospheric composition (Figure 2). During periods of time after El-Chichon (1982) and Pinatubo (1991) eruptions CO correlated to aerosol optical depth (AOD) and total ozone. The slope of the regression line "CO-aerosol" for 17 month after April 1982 (Figure 2a) was 87 ppb CO per unit of AOD at 550 nm. CO data were corrected for the aerosol influence

(Figures 3 and 2b). Correlation between the corrected values of CO mixing ratio and total ozone just before and after Pinatubo eruption (January 1991 – July 1994) is illustrated by Figure 2b: the slope is 0.55 ppb/DU.

Table 1. A review of available estimates for CO trend in % per year. Arial is for spectroscopic measurements in the total column above the site (H is the height above sea level) or columns in some layers in the atmosphere (see Layer column). *Italic* is for sampling in the surface layer (which is assumed to represent the marine boundary layer). Trend for Jungfraujoch, 1984-1997 according to WMO (1999).

Site and reference	H, km	Period	Trend, %/yr	STD,	Layer,
				%/yr	km
Zvenigorod, Russia,	0.2	1980-1995	+0.2	0.2	0.2-10
this paper		1984-1995	+0.4	0.2	
		1984-1997	+0.02	0.18	
Jungfrau., Switzer.	3.58	1984-1995	-0.18	0.16	Above
(Mahieu <i>et al.</i> 1995)		1984-1997	-0.53	0.18	3.5
Kitt Peak, USA	2.09	1978-1997	-0.27	0.17	2.1-14
(Rinsland. <i>et al.</i> 1998)					
NH, 20 sites	0-0.2	1990-1995	-2.0	0.2	MBL
(Novelli et al. 1998)					
NH, 2 sites	0-0.2	1987-1992	-1.4	0.9	MBL
(Khalil & Rasm. 1995)					

It is known (Harris *et al.* 1986) that total ozone columns over mid latitude in the northern hemisphere (Figure 3, two top traces) are declining starting with the early 1980s. This decline with the rate of -1.28 DU/yr (last



Figure 3. Deseasonalized total ozone (two top traces) and CO in Zvenigorod.

2 years were not taken in account) is evident for deseasonalysed total ozone zonally averaged for 55°N-60°N, measured by TOMS (upper trace, crosses) and also for total ozone measured at the Moscow station (lower trace, squares). Meanwhile, as we have seen, every 1 DU drop of ozone should result in 0.55 ppb drop in CO.

A simple calculation gives a contribution of changing sink into the change of CO trend: $1.28 \times 0.55 = 0.7$ ppb per yr or 0.6 % CO per yr. It



Figure 4. CO over Zvenigorod: measured and corrected for ozone and aerosol variations explains a half of CO deceleration from 1.6 % per yr down to 0-0.2 % per year (Figure 1). Figure 4 displays corrected CO concentration that would be in the case of zero aerosol and stable ozone 370 DU (the line without symbols). The deceleration of the corrected CO is much less than observed one.

A very rough estimate of a trend in OH concentration can be made if we assume that 100 % of OH and 100% of CO are destroyed in the reaction between CO and OH (in reality it is estimated to be 90-95%). In this case 1% of OH change should result in 1% of CO change. Therefore, 0.6 %/yr CO decrease would correspond to 0.6 % per yr increase of OH.

This estimate originates from 0.55 ppb/DU sensitivity and -1.3 DU/yr ozone trend. Both these values may be corrected or modified. However, at least qualitatively an influence of total ozone variations on tropospheric OH seems quite plausible. This OH positive trend probably is responsible for the most of currently observed methane deceleration (Khalil and Rasmussen 1995).

4. CONCLUSIONS

Long-term total column CO measurements over Russia revealed a CO deceleration started in the early 1980s. CO after major volcanic eruptions correlated to stratospheric aerosol and total ozone. These effects were explained in terms of OH dependence on UV radiation. Slopes of regression lines have been taken as empirical sensitivities of tropospheric CO to AOD and total O_3 . Current total ozone depletion in the Northern mid latitudes should result in increase of UV and OH, and may be responsible for a half or more of CO deceleration. Assuming OH as the only sink for CO one can expect an OH positive trend to be +0.6% per year. A role of this trend in methane slowing down should be investigated.

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