Continuous measurement of ambient carbon monoxide at a tropical coastal station

G.Mohan Kumar, S.Sampath and V.S.Jeena

Atmospheric Sciences Division, Centre for Earth Science Studies PB 7250, Akkulam, Thiruvananthapuram - 695 031

ABSTRACT

Carbon monoxide (CO) is a toxic gas formed in all burning processes under insufficient oxygen conditions. Accumulation of CO in the atmosphere is of concern to us, as its accumulation degrades the ambient air quality. Measurement of ambient CO was carried out using a standard CO Analyser (Monitor Europe Model 9830B) in Thiruvananthapuram, a tropical coastal station (8.5° N, 77.6° E). CO was measured from January till June 2003 only during the daytime and on a continuous mode from August 2003 onwards after using an uninterrupted power supply. The site of measurement is close to a water body (Akkulam Lake) adjoining the Arabian Sea. Preliminary results indicate that the ambient CO values are close to 100 ppb and indicate agreement with the MOPITT satellite data for the surface. Ambient CO shows a diurnal variation and its response to sea and land breeze is evident. During this measurement in 2003, there were two local events associated with firewood burning in open areas. Enhanced CO values were noticed associated with the events and the dissipation of this enhancement with time was also seen. The ambient levels of CO, its diurnal variation and its links with meteorological parameters are presented and discussed.

INTRODUCTION

CO is a toxic gas present normally in ppb levels in the Earth's atmosphere. It gets into the atmosphere through all processes of burning biotic material at insufficient oxygen levels. In a clean atmosphere, typically the CO amount at the surface of the Earth is about 100 ppb (MOPITT satellite data). The importance of atmospheric CO lies in the fact that (i) it is a well-mixed gas with air, as its molecular weight is closer to that of air, (ii) its loss is biotical through the respiratory cycle of warm-blooded animals and (iii) the only known chemical sink in the upper troposphere and in the lower stratosphere involves the hydroxyl (OH) radical. The reduction in OH radical by CO makes less OH available for methane destruction, leading eventually to green house warming. Also, presence of OH in the upper troposphere and lower stratosphere by photolysis of water vapour on a long-term causes concern due to probable water loss from the atmosphere.

CO is a colourless, odourless gas and an important reactive trace gas in the troposphere. CO has both natural and anthropogenic sources, the total source strength of 2850 Tg/yr. Manmade sources are chiefly

the gaseous byproduct of incomplete combustion of fossil fuels, industry and automobiles aggregating to 1350 Tg/yr. Natural sources, about 800 Tg/yr, include photochemical conversion of methane and hydrocarbons (IPCC 2001). Its effect regarding health is that it has great affinity to hemoglobin in blood and forms a macromolecule, carboxyhemoglobin. Carboxyhemoglobin inhibits the transference of oxygen by blood to the heart and brain causing oxygen starvation that affects the body. The related atmospheric effect is that elevated levels of CO will reduce the tropospheric OH, thus reducing removal rates of many other pollutants. In the unpolluted troposphere 70% of OH disappear through reaction with CO (Jockel, Brenninkmeijer & Crutzen 2002). Reaction with OH is the major sink for CO, while continental soils, microbial oxidation to CO2 and oceans act only as its minor sinks (Yurganov 2000). The global soil sink for atmospheric CO was estimated to be 115 -230 Tg/yr and this forms only 5% of the global CO sink. Temperate forests are significant sinks of atmospheric CO (Sanhuesa et al. 1998).

OH radical reacts with CO and CH₄ providing their only chemical sink in the atmosphere. The rate of OH reacting with CO is faster than that with CH₄

Possibly this could be the reason for net CO stabilization or even decrease over northern hemisphere for the period after 1983-87. The approximate residence time of CO is two months in the upper troposphere and because of its short lifetime, the changes in sources or sinks rapidly reflect in atmospheric CO concentration (Khalil & Rasmussen 1994; Khalil 1995). Therefore, making measurements to obtain a base level of CO is very useful and important.

A scientific objective of this study is to estimate a baseline CO in the air at a tropical coastal site. For this pollution prone areas are avoided, as instantaneous CO injection from point sources such as the vehicular traffic exhausts could be very high. Thiruvananthapuram is a coastal city -adjoining the Arabian Sea and air-sea interaction signal, if any, could also be attempted, as oceans contribute about 100 Tg/yr (Meszaros 1981, Climate Change- 2001 IPCC Report). Therefore, monitoring of CO at such a site for a long duration will help us to understand the ambient levels of CO and its variability with time.

METHOD OF MEASUREMENT

The CO Analyser measures by spectroscopic absorption at the IR wavelength 4.6 μ m. The analyser measures CO from 0-200 ppm in four ranges, with 0-50 as the default range and has an auto-ranging facility. The lowest CO level detectability is close to 10 ppb full range and the accuracy of measurement is 1% of measured value in the lowest range. The sampling period is selectable from 1 minute to 1 hour. Here a data interval of 5 min. was selected considering the response of ambient air to wind speed changes and direction, location of the instrument, storable duration in the analyser memory module and the data length. The instrument displays Time in IST, instantaneous CO and its average value over 5 samples. The event log describes 20 events of instrument operation such as power failure, restoration etc. Also, there is an instrument status menu with regard to the components behaviour such as the heater, scrubber gas, CO₂, valves operation, electronic status,

At the time of installation, this instrument is internally calibrated against a known source of CO gas that is traceable to a National Institute of Standards and Technology, USA. This calibration is valid till the

analyser characteristics (such as CO Timed span, span comparison or CO span ratio) do not show a change from the initial calibration. Such a change is indicated in the calibration menu of the CO monitor. The system was put into continuous operation from July 30, 2003 using a 1-KVA on-line sine wave UPS (with < 3% Total Harmonic Distortion). The laboratory where the instrument is installed is under a canopy in a region with ample vegetation. Air for CO analysis is drawn from under the canopy.

RESULTS AND DISCUSSION

Measurements of CO in the ambient air for deriving a baseline for a region are few, especially the tropics. However, satellites monitor CO in the troposphere. Measurement of Pollution in The Troposphere (MOPITT) is an instrument aboard NASA's Terra satellite launched on December 18, 1999. Preliminary CO data measured here are close to 100 ppb and they compare well with MOPITT satellite data retrieved from the NCAR MOPITT website (http:// www.eos.ucar.edu/mopitt/). From the CO monitored in the ambient air, its diurnal variation and the possible links with meteorological parameters have been studied. These results are presented here. An Automatic Weather Station (AWS) operational here records meteorological parameters such as air temperature (T, °C), diurnal pressure (p, mb), RH (%), Rainfall (mm), wind speed (m/s) and wind direction (0-360° off N). The CO data was examined for dependence on all the measured meteorological parameters. Temperature, pressure, RH and rainfall did not show any consistent association with the measured CO. But wind direction seemed to affect the CO diurnal pattern, even at low wind speeds (0-5 kmph denoted as calm). The role of vertical circulation in affecting the diurnal variation of CO is being examined.

The diurnal pattern of CO on a fair weather day, with wind speeds less than 5 kmph, (August. 27, 2003) is shown in Fig.1. CO levels are about 0.05ppm from midnight to 06:00 hrs IST. Then, a steady increase in CO is seen with a maximum of 0.10ppm close to 08:00 hrs IST. Then the CO decreases to a steady low value during the day. CO level increases from 20:00 hrs to reach a maximum at about 22:00 hrs and then decreases. Thus, the diurnal variation of CO on a fair weather day shows two enhancements.

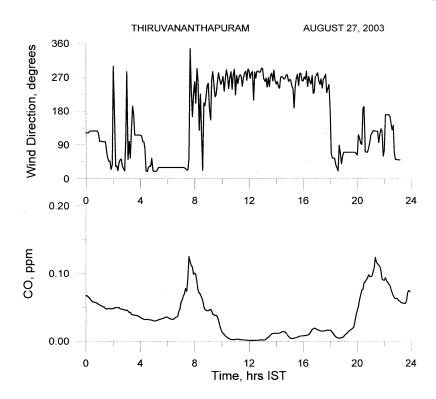


Figure 1. Variation of CO and wind direction during the course of a day, August 27, 2003, shown against time.

Let us examine the mechanism of CO diurnal pattern. In Fig.1, wind direction is seen hovering around 90° till 08:00 hrs, indicating easterly winds. From 08:00 hrs when the sea breeze sets in and operational up to 20:00 hrs, the winds are westerly (270°). The changes in wind direction from easterly to westerly and back coincide with the CO enhancements. Thus the morning and late evening increase in CO are due to sea breeze and land breeze respectively. A change in wind direction brings fresh air over the site of observation and this affects the CO distribution. Air over the sea surface is pushed towards land with the onset of sea breeze after the sunrise. Due to sea breeze, a peak in CO (0.1 ppm) at about 8:00 hrs is observed. There is evidence that the sea surface is rich in CO, though the levels are low (Keiichi Ohta 1997). Between 10:00 and 18:00 hrs, the wind blows landward and it appears that CO accumulated over the site is transported away. After sunset the air over the land blows towards sea (land breeze) and this creates another CO peak after 20:00 hrs. Disturbances to CO are primarily anthropogenic (vehicular exhausts and events of fossil fuel burning).

Fig. 2 shows the wind speed and CO for four days of measurements. The ambient CO does not seem to have any direct relation with wind speed. A study

on CO emissions conducted in Oklahoma (USA) for the temperate region monitored continuously CO with wind speed, traffic density and the 8-hr CO toxicity limit. The study revealed that anthropogenic CO (vehicular exhausts) gets dissipated in high wind regimes and at low wind speeds CO accumulates after sunset hours in the dense traffic conditions (Oklahoma Dept. of Environment Quality, May 2001). The study presented here discusses the ambient CO levels and not those due to traffic. Hence, the effect of wind speeds on the ambient CO, far away from the traffic, may not be evident.

Apart from wind, local production of CO too affects the ambient CO. There were two local events associated with religious festivals (*Pongala*) when massive biomass burning took place in the open. They were on Feb 17th and Feb 26th. The second event was closer to the site of observation. The CO data for the second event are shown in Fig.3. Wind speeds were less than 5 kmph that day. CO showed an enhancement associated with the event and then the CO values decreased to the background level. This also indicates that accumulation of CO over a site does not normally occur. The effect of temperature, RH and pressure on the diurnal variation of CO on a normal day (*Aug 02, 2003*) seems to be negligible, as shown in Fig.4.

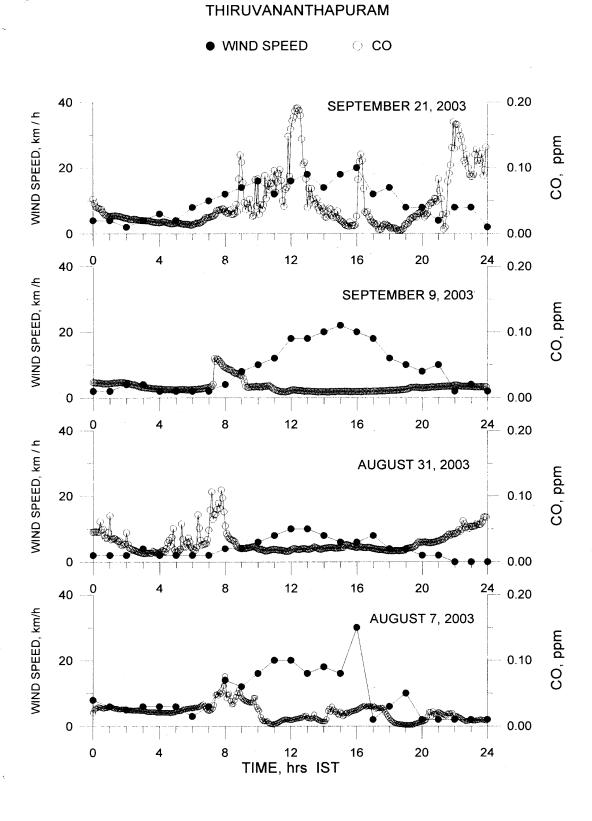


Figure 2. Variation of CO and wind speed shown against time on four days

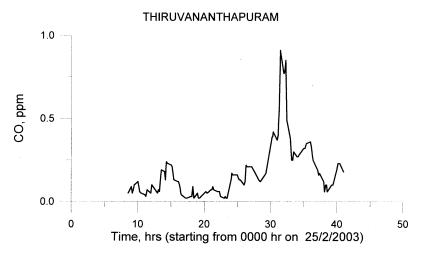


Figure 3. Variation of CO with time during a local festival (Pongala) associated with open fossil fuel (fire wood) burning

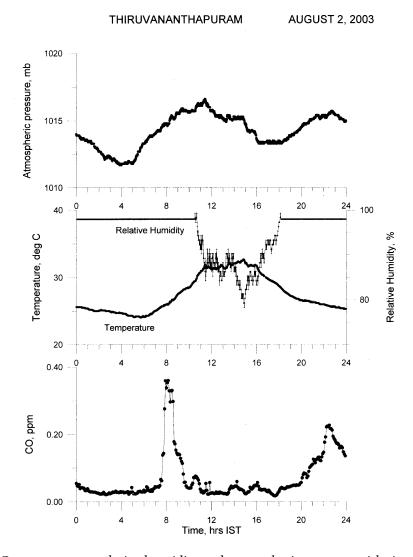


Figure 4. Variation of CO, temperature, relative humidity and atmospheric pressure with time, shown for a typical day.

CONCLUSIONS

CO measured in the ambient air at a tropical coastal site at ground level indicates that the ambient CO levels are in agreement with satellite data, which is indicative of the preliminary baseline accuracy.

Meteorological links of CO with pressure, RH, temperature and rainfall have been examined. Significant modulations of these parameters on CO have not been noted.

Wind direction has significant effect on CO. The effects of sea and land breeze on the diurnal variation of CO have been detected.

Local production of CO is detectable but it dissipates with time, indicating no accumulation.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Indian Space Research Organization (Department of Space, Govt. of India) for funding this project under their Geosphere Biosphere Programme through the Space Physics Laboratory, Vikram Sarabhai Space Centre, Thiruvananthapuram. The authors thank the Director, CESS for the support.

REFERENCES

Climate Change-2001, IPCC Report 2001. The scientific Basis. Contribution of Working Group

- 1 to the Third Assessment Report of the Intergovernmental Panel on Climate change, Cambridge University Press, New York.
- Jockel, P., Brenninkmeijer, C.A.M. & Crutzen, P.J., 2002: A discussion on the determination of atmospheric OH & its trends? Atmos. Chem. Phys. Disc., 2, 1261-1286.
- Keiichi Ohta, 1997. Diurnal Variation of Carbon Monoxide Concentration in the Equatorial Pacific Region., J. Oceanography, 53,173-178.
- Khalil, M.A.K. & Rasmussen, R.A., 1994. Global decrease in atmospheric Carbon Monoxide Concentration. Nature, 370,639-641.
- Khalil, M.A.K., 1995: Decline in Atmospheric Carbon Monoxide Raises Questions About Its Cause, Earth in Space, 8, No.3, November, p.7.
- Meszaros, 1981. Atmospheric cycle of trace constituents. In Atmospheric Chemistry, Elsevier, New York, 29-90 pp.
- NCAR MOPITT website (http://www.eos.ucar.edu/mopitt/).
- Report of the Dept. of Environment Quality, Oklahoma, USA, May 2001.
- Sanhueza, E., Dong,Y., Scharffe,D., Lobert J.M. & Crutzen, P.J., 1998. Carbon monxide uptake by temperate forest soils: the effect of leaves and humus layers., Tellus B, 50, February p.51.
- Yurganov, L., 2000. Carbon monoxide inter-annual variations and trends in the Northern Hemisphere: Role of OH, IGACtivities Newsletter, Sept., 15-18.

(Accepted 2004 April 24. Received 2004 April 21; in original form 2004 February 17)