Observations of Carbon Monoxide in Antarctic Troposphere at Maitri, Antarctica

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ABSTRACT

Observations of carbon monoxide have been made using IR CO analyzer at Maitri (70°.44'S, 11°.45'E), Antarctica during 22nd Indian Scientific Expedition. A diurnal cycle was systematically observed during clear sky condition. The CO concentration was observed higher in daytime sunlight period however; during cloudy day diurnal variation was absent. It has been observed that the CO concentration increases with increase of solar elevation and decline of CO concentration correlated with the drop of the solar radiation. In present communication experimental setup and results obtained are discussed in detail.

Key Words: Infra red (IR) CO Analyzer, CO, Antarctica

INTRODUCTION

Carbon monoxide is the important trace gas in the atmosphere. It does not absorb terrestrial infrared radiation strongly enough to be counted as a direct greenhouse gas. However, it has an influence on oxidation in the atmosphere through interaction with hydroxyl radicals (OH), which react with methane and non-methane hydrocarbon and eventually brings out changes in concentrations of important greenhouse gases. CO plays an important role in determining tropospheric OH and indirectly affects the atmospheric burden of CH_4 .Fossil fuel combustion, biomass burning, methane oxidation and oxidation of non-methane hydrocarbon are main sources of CO in the atmosphere. More than half of atmospheric CO emissions today are caused by human activities, and as a result, the Northern Hemisphere contains about twice as much as the Southern Hemisphere[1]. Large amount of biomass burning can increase the concentration of CO above background levels over large areas[2]. Carbon monoxide also is the primary sink for

hydroxyl radical. Its short lifetime, about 2 months[3], together with its varied sources implies that CO concentration varies regionally. CO plays role in determining tropospheric OH and indirectly affects the atmospheric burden of CH_4 and can lead to the formation of O_3 (Ref. 4). There are no such sources of carbon monoxide at Antarctica. Whatever concentration we observed is due to transport and dynamics mechanism. However, recent measurements of snow and gas phase formaldehyde in the Arctic suggest photochemical Formaldehyde (HCHO) production at the air-snow interface, resulting in a substantial flux out of the snowpack[5]. Hutterli *et al* (1999) reported the de-gassing process for HCHO from buried winter fern layers. In any case this would be a significant source of HCHO in Polar Regions because large areas are covered with ice and snow. Formaldehyde is an important constituent in the photochemical oxidation of atmospheric hydrocarbons. Photolysis is an important sink for HCHO, which, depending on the wavelength, yields H atoms and HCO radicals or hydrogen and carbon monoxide. Production of free radicals and carbon monoxide (CO) from photolysis of HCHO from this newly discovered source is potentially important to the oxidative capacity of the polar troposphere.

In view of the above, continuous measurement of atmospheric CO using gas filter correlation non-dispersive IR absorption (NDIR) CO analyzer of Advanced Pollution Instrument Inc (API) started in the 22nd Indian Antarctic expedition. The studies at Maitri station were aimed towards the estimation of a complete diurnal variation for CO in the near-surface air in Antarctica. In the present communication salient features of the instrument, experimental technique and result obtained are discussed in detail.

EXPERIMENTAL TECHNIQUE

Observations were carried out at the Indian Antarctic Research Station Maitri during summer season from February to March 2003. The station is located on Schirmacher hill on an ice-free area, Queen Maud Land of Antarctica, 120 m above sea level. The instruments were installed in an Environmental Laboratory, which is located 300 m north of the main station. Thus, no serious contamination problem due to the main station existed. Data were taken using gas filter correlation non-dispersive IR absorption (NDIR) CO analyzer of Advanced Pollution Instrument Inc (API), which has a capability of detecting very low CO concentration in pristine environment like Antarctica. The block diagram of the instrumentations system is shown in Fig. 1. The detection and measurement of carbon monoxide is based on

the absorption of Infra Red (IR) radiation by CO molecules at wavelengths near 4.7 microns. As shown in Figure 1, IR source, a high heated element generates broadband IR light. This IR beam is passed through a rotating Gas Filter Wheel which causes the beam to alternately pass through a gas cell filled with Nitrogen, (the Measure Cell) and a cell filled with CO/Nitrogen Mixture (the Reference Cell).
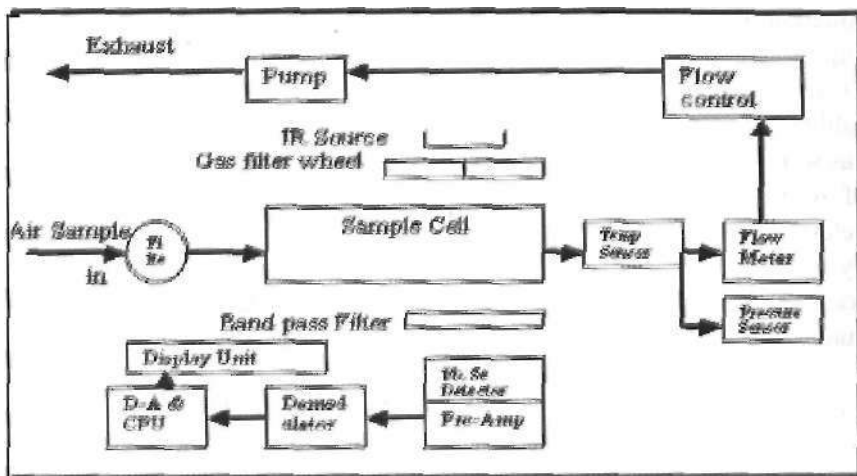

Fig. 1: Block diagram of Infra Red (IR) CO Analyzer

This alternation occurs at a rate of 30 cycles/second and causes the beam to be modulate into Reference and Measure pulse. During a reference pulse, the CO in gas filter wheel effectively strips the beam of all IR energy at wavelengths where CO can absorb. This results in a beam which is unaffected by any CO in the Sample Cell. During the Measure pulse, the nitrogen in the filter wheel does not effect the beam which can subsequently be alternated by any CO in the sample cell. The Gas Filter wheel also incorporates an optical chopping mark which superimposes a 360 Cycles/Second Light/Dark modulation on IR beam. This high frequency modulation is included to maximize detector signal-to-noise performance.

After the gas filter wheel the IR beam enters the multipass sample cell. This sample cell uses folding optics to generate a 16 meter absorption path length in order to achieve maximum sensitivity. The beam then passes through a band pass interference filter to limit the light to wavelength of interest. Finally, the detector which is thermoelectrically cooled solid-state photo-conductor detects the IR signal. The detector along with pre amplifier

convert the IR signal into a modulated electrical signal. The detector output is electronically demodulated to generate two DC voltages, CO measure and CO reference. These voltages are proportional to the light intensity striking the detector during the Measure Pulse and Reference Pulse, respectively. The measured difference is converted to an electrical signal, which is related to the concentration of CO in the measurement cell.

For data accuracy and to enhance stability for low level detection at Antarctic air, carbon monoxide measurements by aforementioned instrument require a periodic determination of the signal at zero air (clean air without CO) and periodic determination of the systems sensitivity by circulating a calibration gas through sample cell. Span calibration by 10 PPM CO standard gas were performed alternate days during the period of observation. Signals of zero air of an internal standard zero air were compared and used to determine the sensitivity of the instrument. Zero air was generated internally by passing ambient air through an internal zero air traps. CO values were sometimes close to the detection limit of the instrument therefore regular automatic zero checking, every two hours, was carried out.

The main air inlet was installed on top of the side wall of the observatory 8 m above the ground. The Teflon line between the inlet and the instrument was around 3 m long with an inner diameter of 4 mm. The inlet was protected against drifting snow with a specially designed tumbler.

RESULTS

Diurnal Variation

Fig. 2 (A) and (B) shows the diurnal variation of surface CO mixing ratios observed at Maitri station on clear sunny day of 5 February 2003 and cloudy day of 5 March 2003 respectively. A clear diurnal cycle in CO concentration was observed during clear sky condition, while diurnal variation in CO could not be observed during the overcastted days. Maximum CO concentration up to 66 ppb has been observed from 11:00 AM to 19:00 AM and minimum up to 20 ppb during nighttime hours on 5 Feb 2003. It has been observed that the CO concentration increases with increase of solar elevation and decline of CO concentration coincides with the drop of the solar radiation. This result indicates that primarily photochemical reactions influence the atmospheric concentrations of CO during the days when solar radiation are available.

Fig 3. (A) illustrates the diurnal variation of hourly averaged CO concentration for the observation period of 1 February to 11 March 2003.
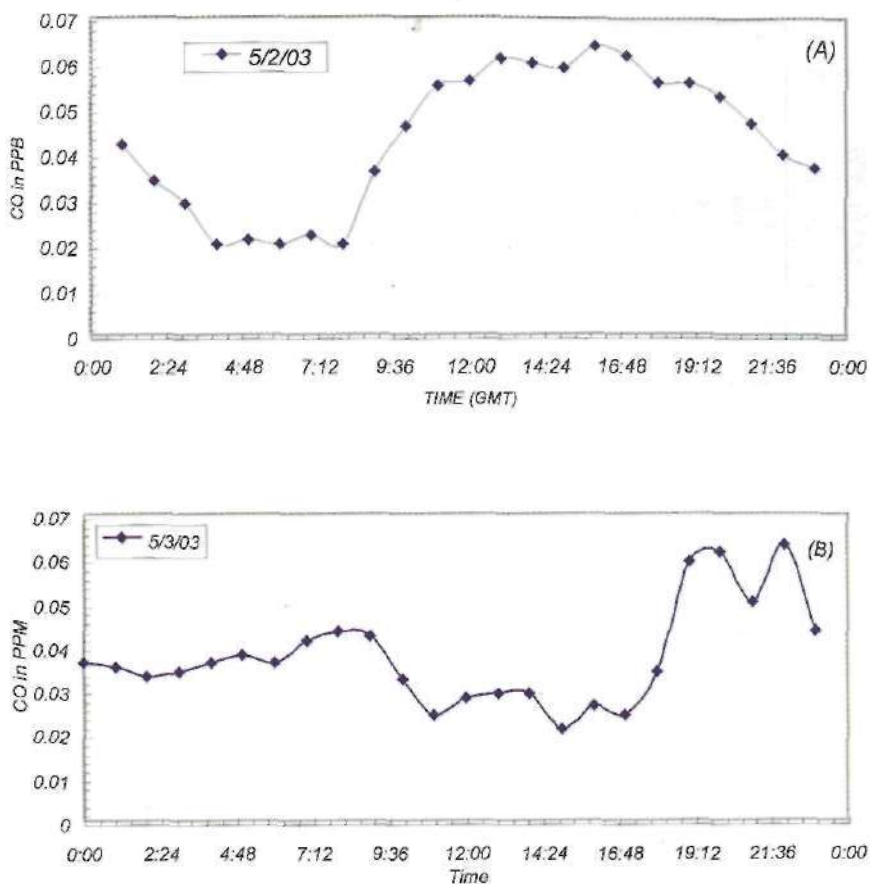
Fig. 2: *Diurnal variation of surface CO concentration at Maitri, Antarctica*
(A) Diurnal variation on 5th Feb 2003 on clear sky day.
(B) Variation in CO on cloudy day of 5th March 2003

Similarly, Fig. 3 (B) illustrates the diurnal variation of hourly mean CO concentration for the month of January, February, March and April 2004. The diurnal variability in CO concentration has been observed with hourly mixing ratios ranging from 30 ppb to 65 ppb during 1 February to 11 March 2003. Similarly, CO concentration was found to vary from 27 ppb to 50 ppb, 30 ppb to 50 ppb, 45 ppb to 63 ppb and 53 ppb to 60 ppb in January, February, March and April 2004 respectively. The mean rate of increase in CO concentration between 8:00 and 15:00 hrs has been observed 2.6 ppb, 3 ppb, 1.8 ppb and 1.1 ppb per hour in the month of January, February, March and April 2004 respectively. CO was found out to be maximum in the afternoon.
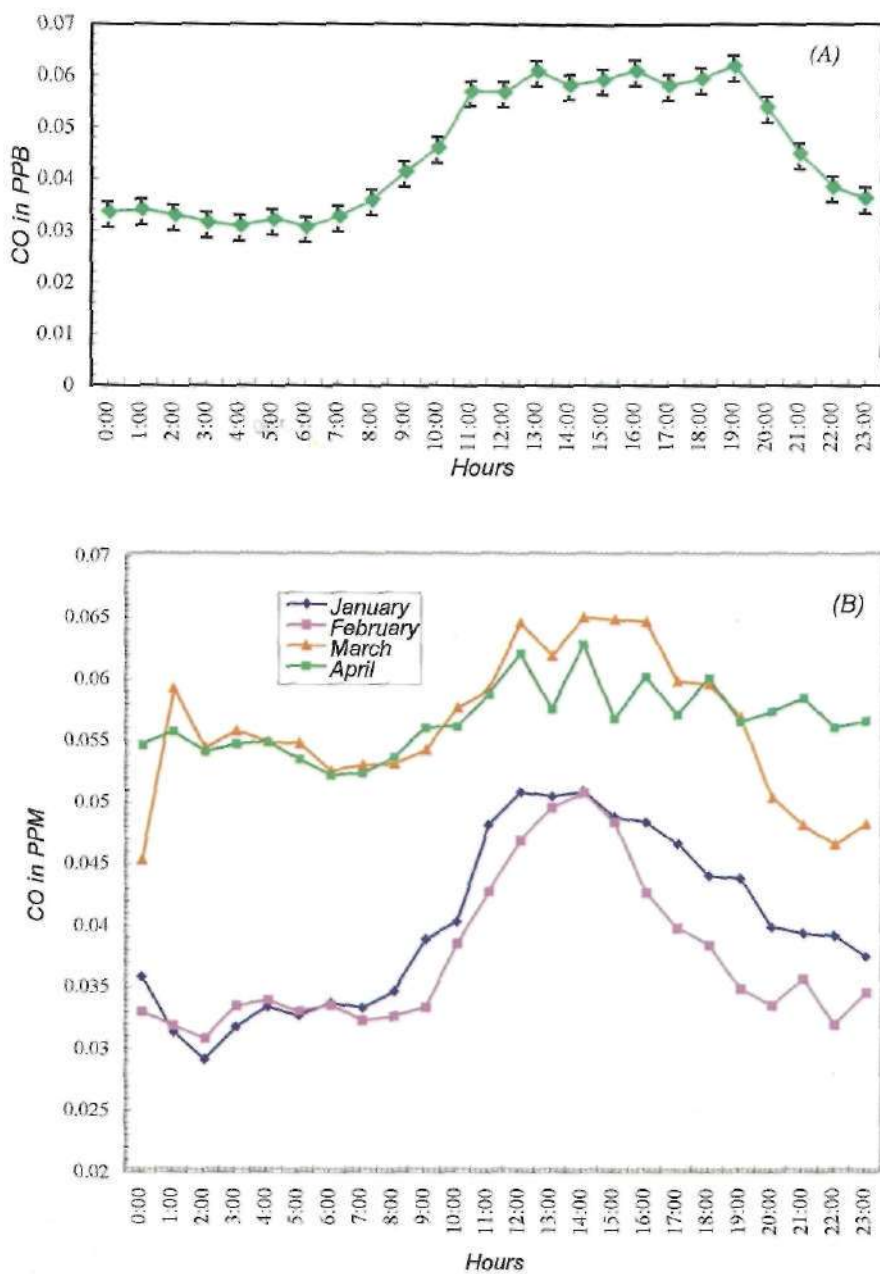
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Fig. 3: Diurnal cycle of CO concentrations
(A) Hourly mean observed from 1 Feb. to 11 March 2003
(B) Hourly mean observed in January, February, March and April, 2004

During nighttime, CO concentration declined to a minimum, which found to be correlated with the rise and drop of solar radiation. These observations show that the CO production processes in cold polar ice are activated by sunlight.

The variation in diurnal cycle and daytime increase in CO concentration can be attributed to the photochemical destruction of formaldehyde (HCHO) at Antarctica. Lowe and Schmidt (1983) showed the dominant source of HCHO in the free troposphere is the reaction of methane with OH radicals. While Sumner, Simmons et al. (1999) presume that HCHO is produced photo chemically at air-snow interface, Hutterli et al. (1999) favour a degassing process for HCHO from buried winter fern layers. Therefore polar region may be a significant source of HCHO because large areas are covered with ice and snow. Photolysis is an important sink of HCHO, which rapidly destroyed by sunlight producing carbon monoxide (CO) and HO_2 radicals as given by the following reactions.

$$HCHO + hv\ (\lambda < 325\ nm) = H + CHO \qquad (1)\ and,$$
$$HCHO + hv\ (325\ nm < \lambda < 360\ nm)\ H + CO \qquad (2)$$
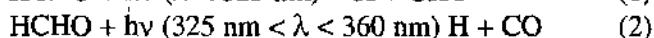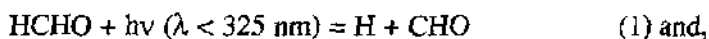
First reaction rapidly reacts with molecular oxygen to form CO as $CHO + H + 2O_2 = 2HO_2 + CO$. Under the clear sky condition during noon time 45% photolysis occurs through reaction 1 and 55% occurs through reaction. This implies that HCHO photolysis, depending on the amount of solar actinic flux yields CO and can be a significant source in the lower polar troposphere. Katja et al. (1999) investigated the annual cycle of formaldehyde (HCHO) at Antarctica and found that the diurnal and seasonal cycle of HCHO exists, with Maximum in summer and minimum in winter. Further, they investigated that the observed concentrations show daily variation on clear sunny days, with maximum in early afternoon and minimum during night. These observations show that during maximum solar radiation period positive correlation exists between CO and HCHO and the snow-covered regions may act as a source of CO.

CONCLUSION

Observations made at Maitri, Antarctica showed a systematic diurnal variation of CO concentration during observational period. The diurnal variation and daytime increase in CO concentration indicates that primarily photochemical reactions influence the atmospheric concentration of CO during the days when solar radiations are available. Finally, the observation made in extreme cold conditions in Antarctica has proved the IR CO Analyzer to

be an important tool to measure low-level surface air concentration of CO in Antarctic air.

ACKNOWLEDGEMENT

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