Variabilities in O_3, NO, CO and CH_4 over the Indian Ocean during winter

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Under the international Indian Ocean Experiment (INDOEX), ozone and related gases were simultaneously measured during prelude cruises in 1996, 1997 and the First Field Phase (FFP) cruise in 1998 over the Indian Ocean. The observed concentrations of ozone and precursor gases are higher near the Indian coastal region and then decrease gradually toward the southern region in the open ocean. However, the gradient is minimum in methane. During these measurements, a sharp increase in the concentrations of ozone and carbon monoxide is observed in the remote Indian Ocean. Trajectory analyses show transport of continental polluted air from South Asia during these events. Ozone and nitric oxide show diurnal patterns which differ from those over any polluted region. During the 1998 cruise, the ship travelled up to about 18°S and crossed the ITCZ. The resulting effect of change in wind pattern was reflected very clearly, showing different levels of ozone concentrations at the north and south of ITCZ during onward as well as on return legs.

TROPOSPHERIC ozone is a potential greenhouse gas. It is a precursor of OH radical which decides the oxidation efficiency of the troposphere and hence modulates the budgets of many trace gases in the atmosphere. In the troposphere, ozone is not only controlled by chemical processes but also by physical and dynamical processes. Large spatial and temporal variations in ozone cause uncertainties in its contribution to radiative forcing and its budget. Recent observations of surface ozone as well as free lower tropospheric ozone show increase in its concentrations (1–2%) in many parts of the northern hemisphere[1–4]. Because of its important role in tropospheric chemistry, radiation and deleterious effect on human beings and plants[5,6], the study of tropospheric ozone and its precursor gases has now become a topic of both local and global concern.

Free tropospheric ozone is controlled by changes in the levels of ozone in the planetary boundary layer as well as transport from the stratosphere. Photochemical processes play major role in controlling the tropospheric ozone concentration[7,8]. In the lower troposphere, ozone is mainly produced by photochemistry involving pollutants which are released from various industrial and other man-made activities. Photochemical ozone production takes place by photoxidation of CH_4, CO and NMHCs in presence of sufficient amount of NO_x. In case of NO_x rich air, the production of NO_2 takes place by the reaction of NO with HO_2 or RO_2 (peroxy radicals) which ultimately helps ozone production. But in case of NO_x poor air, these peroxy radicals react with ozone and leads to ozone loss. Thus ozone chemistry is affected by the levels of NO_x as its concentrations play a critical role in either formation or destruction of ozone and has a nonlinear influence on ozone production.

Essentially an unstudied part of the globe, the tropical Indian Ocean has unique meteorology. Because of this, continental, polluted air of the northern hemisphere mixes (large scale transport, hundreds to thousands km) with the pristine air of the southern hemisphere through ITCZ (Inter-Tropical Convergence Zone). This mixing occurs during winter, when the wind blows northeasterly, allowing us to study the impact and extent of continental polluted air mass in the Indian Ocean region. The Indian Ocean's warm water triggers the deep convective cirrus cloud system in association with the ITCZ and contributes significantly to the vertical exchange of minor constituents (gases and particles) between the surface and the upper troposphere (UT)/lower stratosphere (LS). Though the tropical region experiences intense photochemical activity as well as contributes to the global OH budget (due to large water vapour content, about 80% of the global budget), detailed and systematic measurements of ozone and related species are sparse over this region.

Surface measurements of ozone and related gases were made over the Indian Ocean, as a prelude to the Indian Ocean Experiment (INDOEX) during two cruises on board ORV *Sagar Kanya* (cruises SK # 109 and # 120) in January to February 1996 and December 1996 to January 1997. Recently, similar measurements were also made during the First Field Phase (FFP) cruise in February to March 1998 (SK # 133). During this cruise, NO was measured, employing an ultra sensitive analyser; O_3, CO and CH_4 were also measured as in earlier two cruises. Now it is well understood that NO is an important gas whose measurement is vital in understanding the ozone photochemistry in the oceanic region. Results obtained during these three cruises are presented here.

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Experimental techniques

Ozone measurements were made by a Dasibi analyser (RS-1008, USA) based on the UV absorption (253.7 nm) principle. Signals with and without ozone in the air stream are measured to remove the contribution by other species and scattering effect due to air molecules. The analyser also incorporates corrections due to changes in temperature and pressure in the absorption cell.

Calibration of the system is done regularly with the help of a built-in ozone generator. Zero setting of analyser is also performed regularly. The minimum detection limit of the analyser is about 1 ppbv. This Dasibi ozone analyser was compared and calibrated with the standard calibration unit at K. F. A., Juelich, Germany. The Dasibi analyser was found to be lower by about 5 ppbv. The ozone data from this instrument are corrected for the difference.

Measurements of CO were made using a non-dispersive infrared (NDIR) gas filter correlation analyser (Monitor Labs, USA, ML 9830). The analyser operates on the principle of infrared absorption at 4.67 μm vibration–rotation band of CO. The detection limit of the analyser is about 50 ppbv with noise levels of 25 ppbv. Zeroing of the analyser was done once in a day. Calibration was performed using a known primary standard (1000 ± 7.5 ppbv; Linde, UK). The analyser was also inter-compared and calibrated by parallel measurements of CO using a gas chromatograph.

As previously mentioned, NO was measured only during the 1998 cruise with an ultra sensitive analyser (ECO–Physics, Switzerland, 780TR) based on the chemiluminescence effect. Oxidation of NO by O_3 molecules gives chemiluminescence. The light intensity generated by the chemiluminescent reaction is proportional to the mixing ratio of NO. To achieve higher sensitivity a highly sensitive PMT and a powerful vacuum pump (14 ± 4 mbar pressure in reaction chamber) were employed. A specially designed fore-chamber eliminates interferences from hydrocarbons and OH radicals. For maximum sensitivity and accuracy, pure oxygen (instead of dry air) is supplied to the ozone generator. Zero point compensation is performed automatically. This instrument is specially designed to measure the tropospheric NO in pptv levels.

As air samples were also collected, when the ship was cruising in pre-evacuated glass bottles (few air samples in SS tube) at a pressure of about 1.5 bar using a metal bellow pump to measure CH_4 and CO. These samples were analysed at the Physical Research Laboratory (PRL) by gas chromatograph (GC) coupled with a flame ionization detector (FID) (Shimadzu, GC-mini-3, Japan) and the signals were integrated by an integrator (Shimadzu, C-R6A Chromatopac, Japan). To separate the CH_4 and CO, a molecular sieve 13x packed SS column was employed. Measurements of CO were made together with CH_4 by converting it into CH_4 using a heated (325°C) Ni catalyst

after its separation. Calibrations of CH_4 and CO were performed by primary and secondary standards. Primary standards of CH_4 are obtained from NIST, USA (SRM 1658a) (1.19 ± 0.01 ppmv) and Linde, UK (0.98 ± 0.05 ppmv) and that of CO from Linde, UK (1000 ± 7.5 ppbv). The secondary standard was prepared at PRL (PRL STD # 1) which was also analysed regularly. The inlet line for various analysers was far removed from the ship's exhaust. However, we see sample contamination whenever the ship was stationary. These data were selectively discarded.

Observations and discussions

The first ship cruise (SK # 109 or INDOEX 96) was conducted during 5 January to 3 February 1996, covering the region from 16°N to 5°S and from 60°E to 76°E. It made four transect routes between 5°N and 5°S. The second ship cruise (SK # 120 or INDOEX 97) was conducted during 27 December 1996 to 29 January 1997 and covered an area of 16°N to 14°S and 71°E to 79°E. Both cruises were preludes to the INDOEX. The First Field Phase (FFP) (SK # 133 or INDOEX 98) cruise was conducted during 18 February to 30 March 1998, covering the region from 16°N to 18°S. We must mention that all these cruises occurred during the winter when the wind is northeasterly (for cruise tracks, refer to Figure 1 in Introductory Note).

Latitudinal gradients

In general, O_3, CO and NO decrease from coastal region to southern region during onward cruise and increase during return cruise with dramatic low and high values in between. Figure 1 shows a composite latitudinal variation in ozone concentrations observed during 1996, 1997 and 1998 ship cruises. In all the three cruises, ozone levels were 50–65 ppbv near the coastal region. However, during INDOEX 96, ozone levels up to about 100 ppbv were also observed near the coast in the return cruise (not shown in the figure). During this cruise, ship travelled parallel to coastal region (return route) at a distance of about 100 km for about 3 days and an ozone increase was seen in two regions. For example, on 31 January ozone concentration increased from 40 ppbv to 60 ppbv within 6 h. Ozone concentration then increased from about 60 ppbv to 100 ppbv during midnight of 2 February and remained in the range of 80–100 ppbv afterwards. These night-time high ozone values are not possible by *in situ* photochemical ozone production and thus indicate the transport of ozone–rich air to the marine region where its losses are minimum. During INDOEX 96, diurnal variation in ozone differed from the one caused by daytime photochemical ozone production processes. High ozone

concentrations (80–100 ppbv) like the one obtained during INDOEX 96 have not been reported so far in the coastal region. Ozone concentrations of only 65–75 ppbv appeared during January to February 1994 near a few coastal regions in the two global cruises of the ship *Mme Butterfly*[9]. Extensive measurements from different seasons in the Atlantic Ocean (76°S–83°N) during 32 ship cruises[10] and near the west coast of Africa (55°S–53°N)[11] did not uncover ozone concentrations higher than 50 ppbv. In the present study over the Indian Ocean, the observed higher concentrations of ozone (~ 100 ppbv) during INDOEX 96 may not be permanent features of this region and may be caused by transport from the polluted continental region.

Latitudinal gradient in ozone is estimated to be 1.5–3 ppbv/° latitude (~ 15%/° latitude). These gradients vary during three different years of observations; even in the same cruise as well, gradient changes for onward and return journeys. Evidently, the position of ITCZ is vital in these variabilities of gradients.

Figure 2 shows the latitudinal variations of CO during INDOEX 97. In addition, its concentrations decrease from north to south similar to those observed in ozone during all the three cruises. The concentrations are observed to be 300–350 ppbv near the coast and as low as 40–50 ppbv in the clean Indian Ocean. A comparison of on-line measurements (analyser-based) and GC-based analyses of air samples (collected on-board) is also shown. During INDOEX 97, CO concentrations show very high values near 10–15°S. Similar higher values are also seen in ozone. It was observed that the ITCZ shows significant movements (about 5° in a day) causing the mixing of pollutants from north of the ITCZ to the southern part of the Indian Ocean. Figure 3 shows a scatter plot between O_3 and CO and the correlation is observed to be good. A

group of data of near coastal region is visible separately with higher O_3 and CO values. During INDOEX 98, CO remains unchanged until about 5°S, particularly in the onwards route; the position of ITCZ may explain why. Very few observations of ozone precursor gases occur over the oceanic regions. For instance, measurements made by Rhoads *et al.*[12] during the 1995 ship cruise over the Indian Ocean (from Africa to Sri Lanka) reveal CO concentrations of about 140 ppbv near 6°N which decrease to about 50 ppbv near 33°S.

NO observed during INDOEX 98 exhibits very systematic latitudinal variations. Near the coast, average concentrations of NO are observed to be about 200 pptv and as low as 5–10 pptv in the open ocean (not shown here). Higher levels (50–100 pptv) of NO are also observed near Male (Maldives) and Port Louis (Mauritius). Here, it should be noted that NO levels over the clean ocean are about 3 orders lower than over any urban area. Also there are very limited observation of NO over the oceanic region due to complications in measuring its very low levels. For example, measurements made over the Indian Ocean (9°N–33°S) aboard the NOAA *RV Malcolm Baldrige*, show NO levels below 60 pptv[12].

Figure 4 shows the latitudinal variations in CH_4 observed during INDOEX 97. During all the three cruises, the gradient is observed to be minimum in CH_4 as its lifetime is very large (~ 10 years) in comparison to NO, O_3 and CO (minutes to ~ 1 month). In general, its concentration decreases from about 1.8 ppmv (near coast) to about 1.6 ppmv in the open ocean. From these results, the average gradient in methane concentrations is estimated to be about 6 ppbv/° latitude (0.006 ppmv/° latitude).
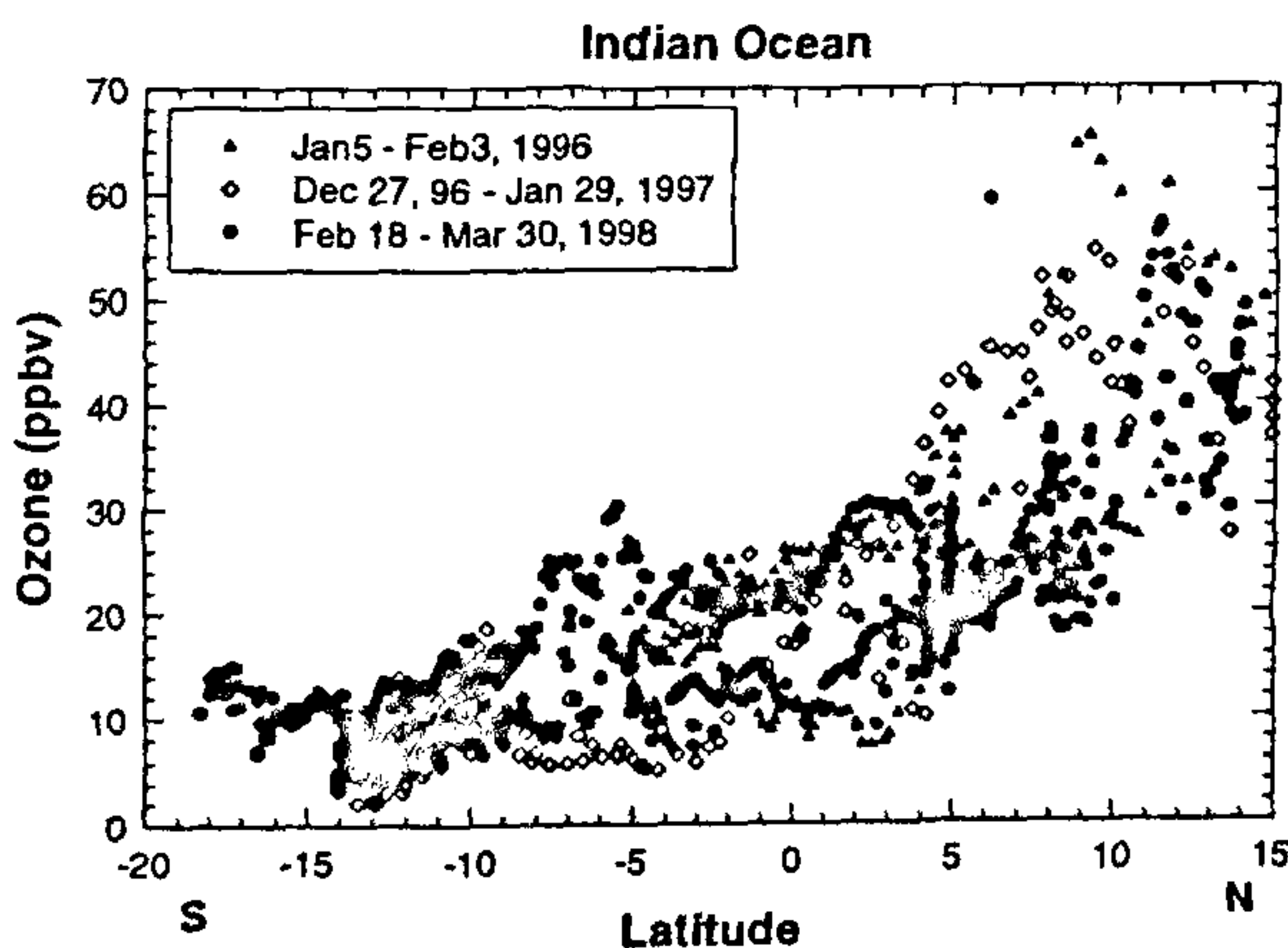

Figure 1. Latitudinal variations in ozone over the Indian Ocean during the three INDOEX ship cruises of 1996, 1997, and 1998. Data very close to the coastal region are not shown here.
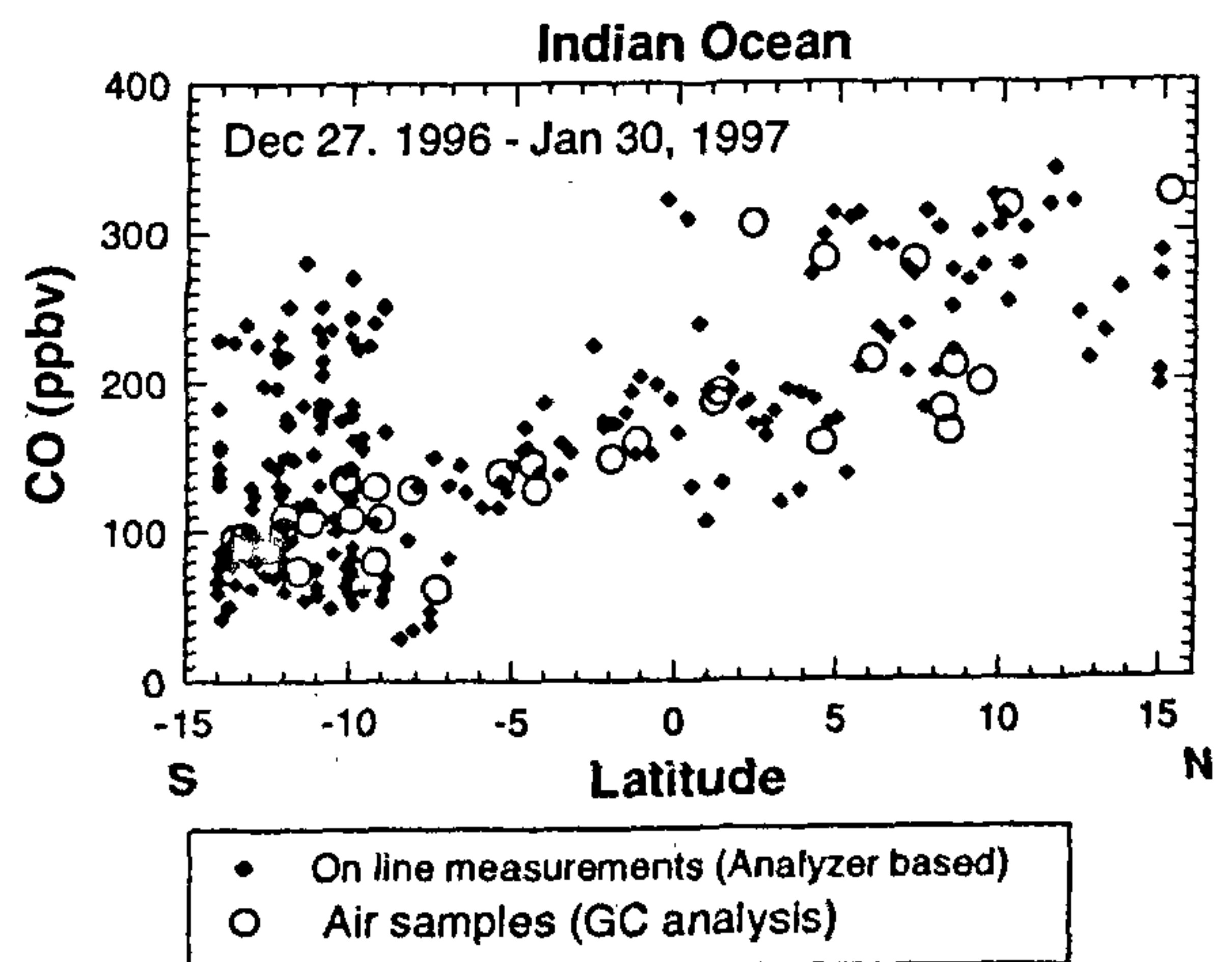

Figure 2. Latitudinal variation in carbon monoxide (CO) during the INDOEX ship cruise in 1997. A comparison with the analysis of collected air samples made using gas chromatograph is also shown. Very high concentrations of CO in 10–15°S region are observed on 10–16 January and 20–23 January 1997.

O_3, CO and CH_4 are observed to be higher during INDOEX 98, compared to the INDOEX 97 measurements. During INDOEX 97, measurements were made in December–January when the north-east wind was beginning whereas during INDOEX 98, measurements were made in February–March when this wind pattern was well established. Therefore, higher levels of ozone and precursors could be transported in the latter case.

Higher O_3 levels: Role of ITCZ

During all the three cruises, there have been events of transport of higher ozone levels in the clean oceanic region. During INDOEX 96, ozone concentrations sharply increased by about 2.5 times within about 6 h near 5°N on 20 January 1996. On this day, ozone levels rose suddenly from 14 ppbv to as high as 35 ppbv. These high levels of ozone (of about 27 ppbv) remained for about 3 days and then in the morning of 24 January, ozone levels decreased gradually[13]. Mass concentrations of sulfate increased by 6–8 times[14] and aerosol optical depth also by about 3 times[15] during this period. CO concentrations also were found to be higher. These correlated higher levels of ozone and other species are supported by air back trajectory analysis, which show the transportation of continental polluted air from the South Asian region[13].

During INDOEX 97, there have been three events (1 January, 12 and 13 January and 20–22 January) displaying higher concentrations of O_3 or CO in the deep Indian Ocean. These events of higher concentrations were associated with the dramatic movements of the ITCZ. During this period the ITCZ moved by about 5° within a day. Similar types of two events have been observed during INDOEX 98 also. During INDOEX 97 the movement of ITCZ caused the transport of 10–15 ppbv ozone in the deep Indian Ocean. Now, it is well understood that during southwest monsoon, ITCZ is generally found over the continental region about 20°N over the Indian subcontinent (about 50–100°E longitude). However, during northeast monsoon period, ITCZ moves to the southern hemisphere which extends the continental polluted air into the deep Indian Ocean.

Similar type of events of elevated ozone levels (2.5 times increase) were noted in the equatorial Pacific Ocean during the RITS (Radiatively Important Trace Species) programme in February, but out of two only one event was associated with transport from continental side whereas the other was accompanied by drastic changes in wind speed and dew-point[16]. During the SAGA 3 (Soviet-American Gas and Aerosol) cruise in the Pacific Ocean the observed elevated ozone levels from about 7 ppbv to as high as 21 ppbv were linked with the mesoscale convective system[17]. This group suggested that air rich in NO and O_3 from above the boundary layer mixed with the air inside the boundary layer.

Diurnal variations

During the measurements, some of the species (O_3 and NO) show very systematic diurnal variations. By studying the diurnal variations, particularly of O_3, one can ascertain the chemistry of the region or type of the environment. Figure 5 shows a typical example of the diurnal variation in ozone observed during INDOEX 98. In the oceanic region these variations show ozone maximum during morning hours followed by a decrease until evening
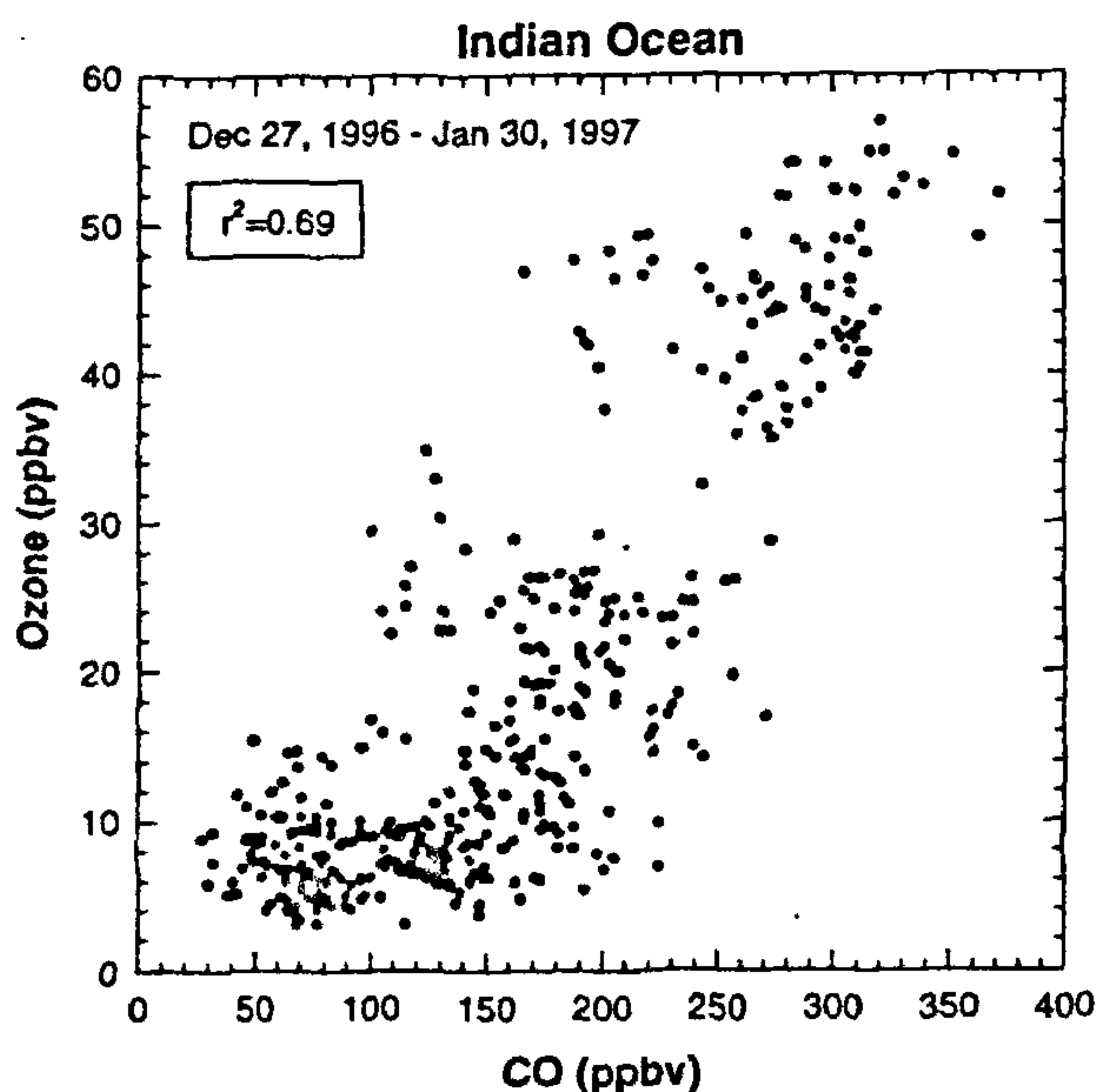
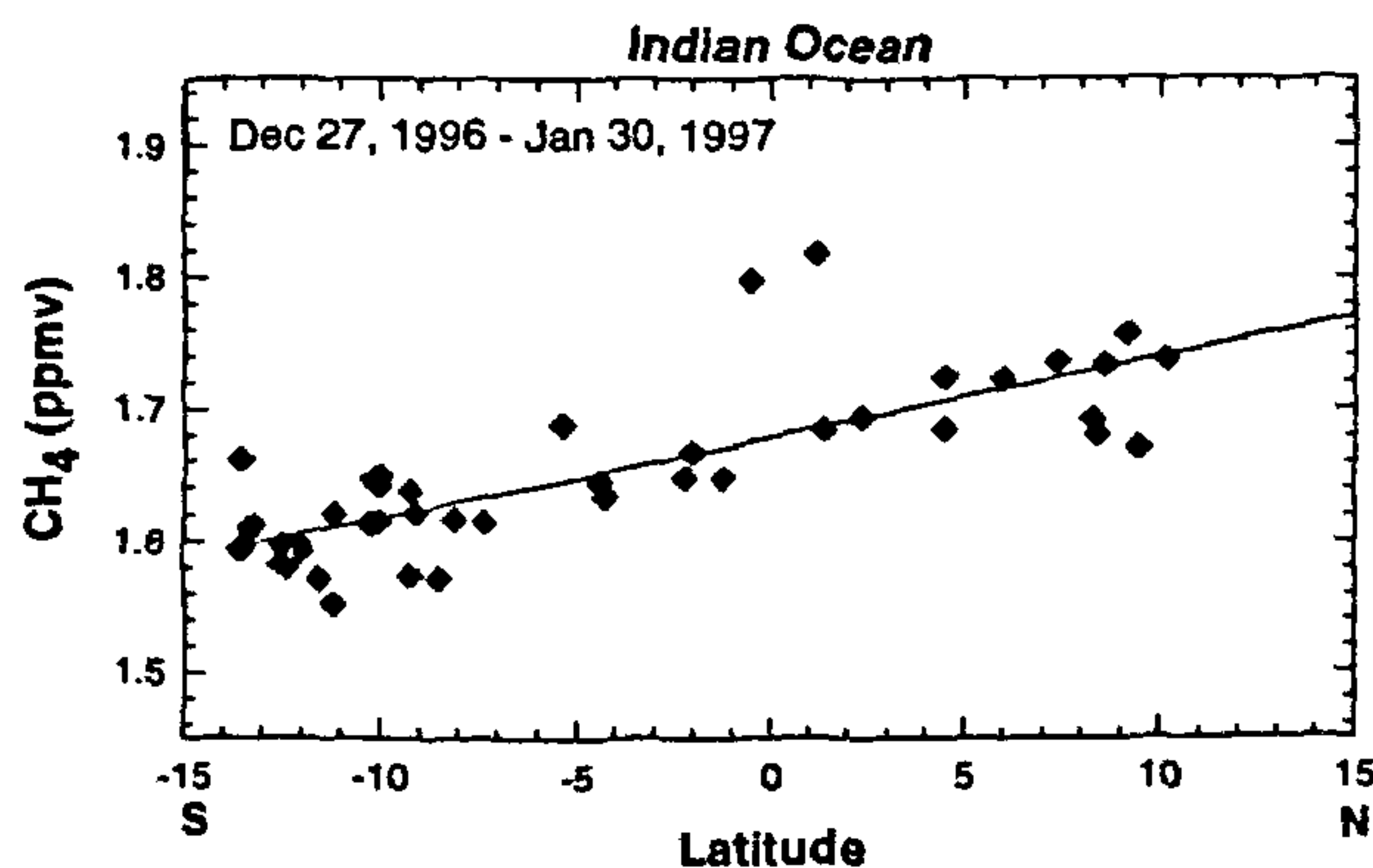**Figure 3.** Scatter plot between O_3 and CO for measurements made during INDOEX 1997.

Figure 4. Latitudinal variations in methane (CH_4) observed during the INDOEX 97 ship cruise over the Indian Ocean.

and then the ozone recovers subsequently by night and the morning of the next day. The average amplitude was estimated to be about 3 ppbv (peak-to-peak difference). During INDOEX 96 the maximum amplitude was about 7 ppbv, whereas during INDOEX 98 it was 9–10 ppbv. During INDOEX 97, the diurnal variations in ozone were not very clear and systematic; however, the maximum amplitude was 6–7 ppbv. These diurnal variations were

not very clear near coastal region during all the three cruises.

The diurnal variations in ozone over the oceanic region can be explained by the chemistry of very low levels of NO^{17-20} and exchange between the ozone-rich free tropospheric air and the ozone-poor boundary layer air, which dominates during night-time[20,21]. Over the continental side, higher concentrations of NO are well above the critical limit for ozone production which result in the ozone production during the day. For example, photoxidation cycle of CO can be represented as:

$$CO + OH + O_2 \rightarrow HO_2 + CO_2, \tag{1}$$

$$HO_2 + NO \rightarrow NO_2 + OH, \tag{2}$$

$$NO_2 + h\nu \rightarrow O + NO \ (\lambda < 410 \text{ nm}), \tag{3}$$

$$O + O_2 + M \rightarrow O_3 + M. \tag{4}$$

These diurnal cycles at continental sites are driven by photochemical ozone production in daylight with loss to surface dominating at night.

In the remote marine boundary layer, NO concentrations are generally found to be lower so that the reaction

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{5}$$

dominates over the reaction eq. (2) and loss of ozone takes place. Thus the daytime photochemical processes become net ozone destructive in the marine region.

At night, the photochemical ozone loss is absent (absence of solar radiation) and also over the oceanic sur-
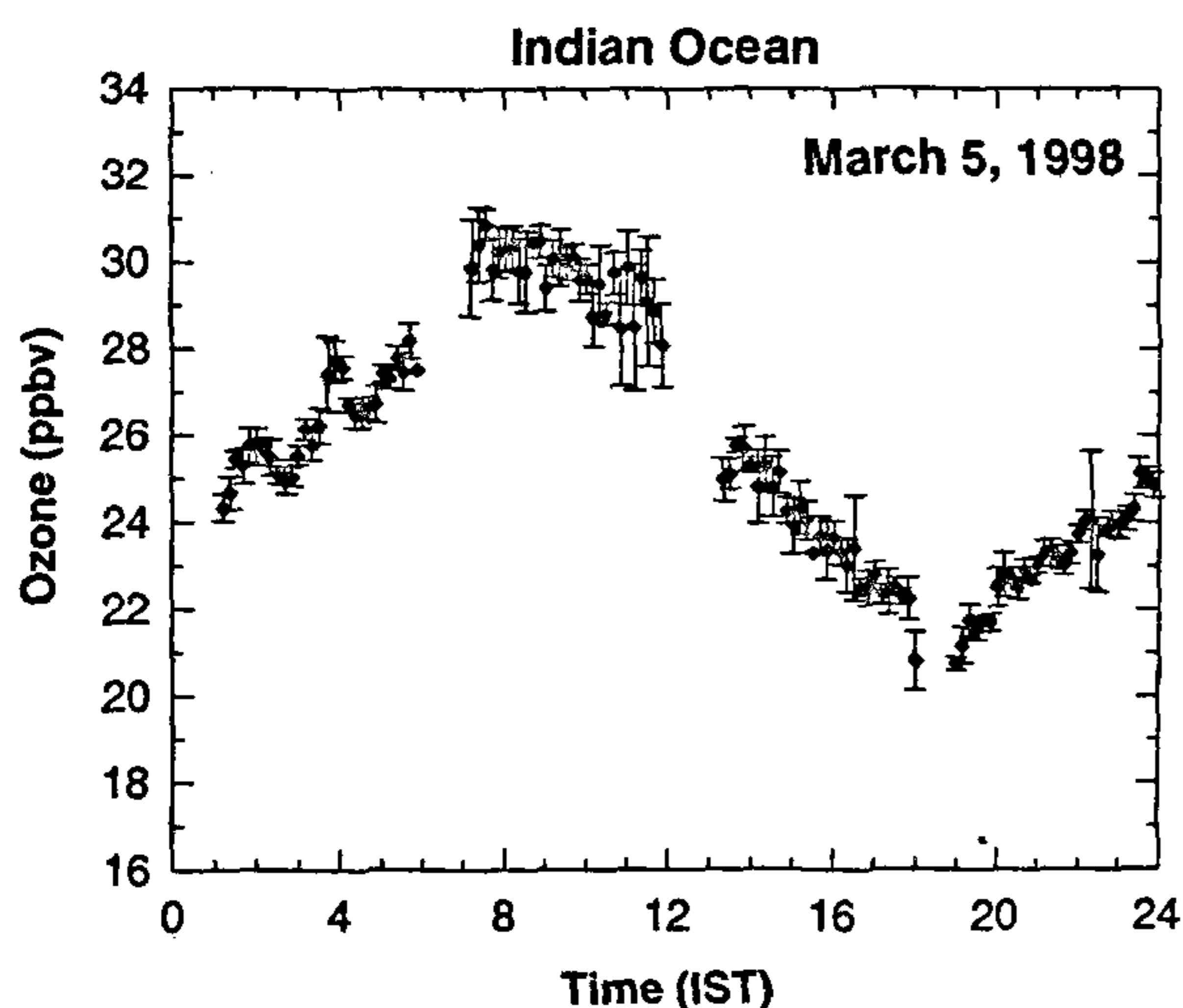

Figure 5. A typical diurnal variation (ten minutes average) in ozone (O_3) observed on 5 March 1998. Vertical bars are 1 σ variabilities.
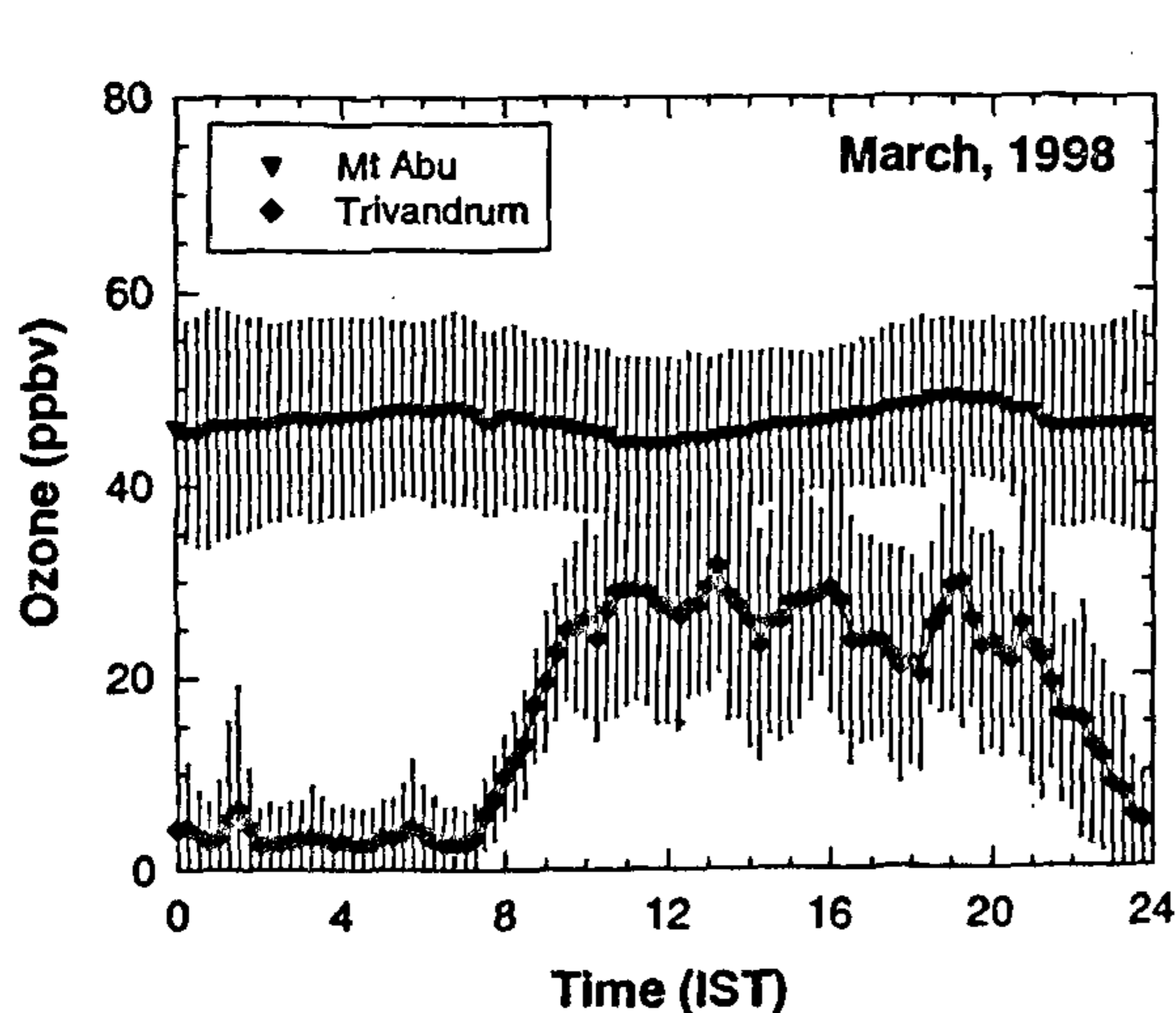

Figure 6. Average diurnal variations in ozone observed at Mt Abu and Thiruvananthapuram during March 1998. Vertical bars are 1 σ variabilities.
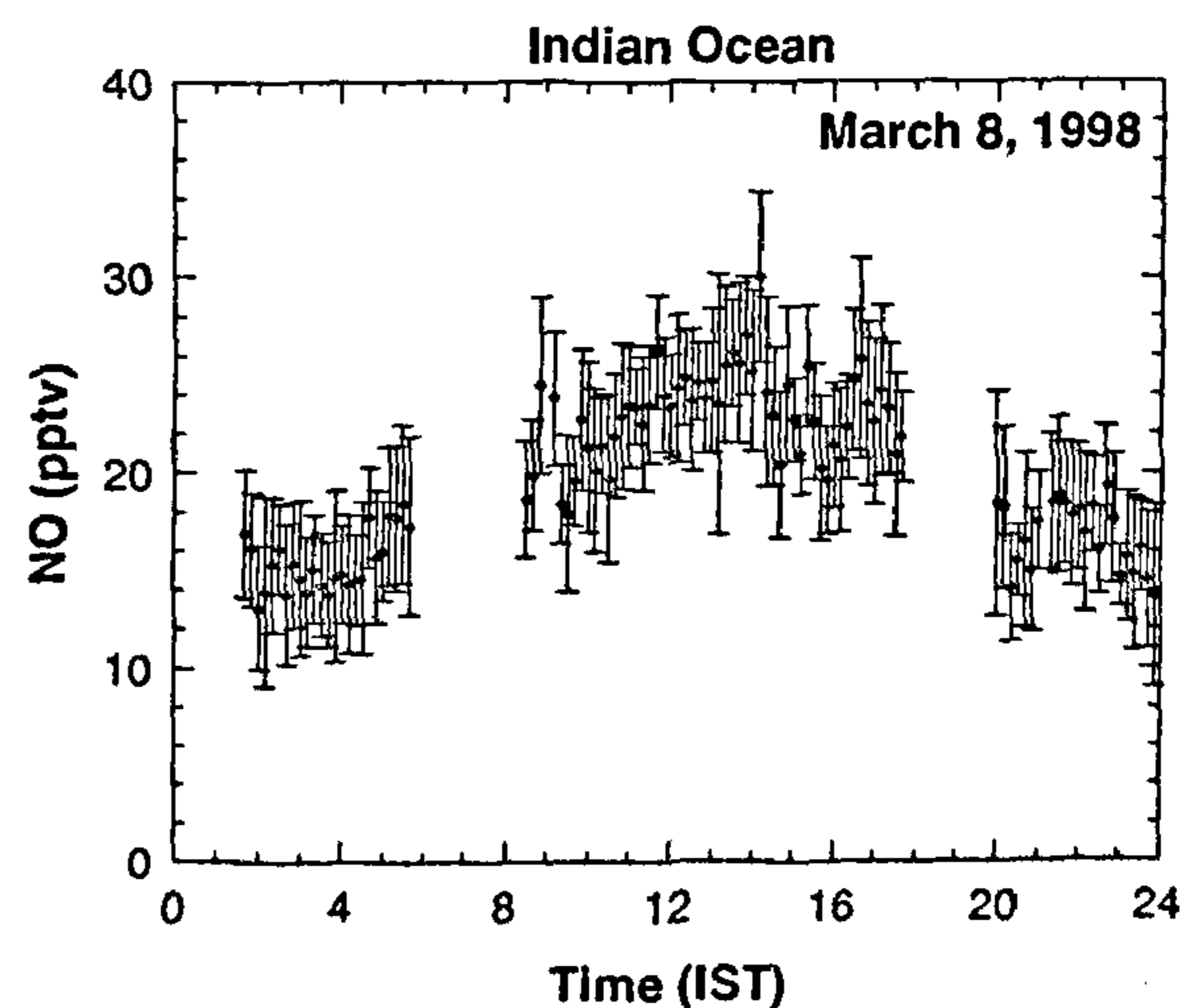

Figure 7. A typical diurnal variation (ten-minute average) in nitric oxide (NO) observed on 8 March 1998. Vertical bars are 1 σ variabilities.

face, ozone loss by surface deposition is much less than on land[22]. Hence, due to vertical mixing between the ozone-poor air near the surface and ozone-rich air of the above layer, ozone concentration increases during the night-time. An extensive model study by Bremaud et al.[21] concludes that the exchange between the ozone-rich free tropospheric air and the ozone-poor boundary layer air, which dominates during the night-time, causes the nocturnal increase in ozone concentrations.

In most of the measurements over the oceanic environments, the amplitude of diurnal variations in ozone is found to be very low or diurnal variations are not very clear[23,17,18], unlike the present study where diurnal amplitude (peak-to-peak) is observed to be as high as about 10 ppbv. The explanation of such high diurnal amplitude is the topic of debate with the present available knowledge of ozone chemistry over the marine environment. Studies made by Vogt et al.[24], Davis et al.[25] and Sander and Crutzen[26] show that sea-salt aerosols and halogen chemistry significantly control the ozone levels and variabilities in the marine boundary layer.

During the observational period of INDOEX 98, simultaneous measurements of ozone were made at Thiruvananthapuram (8.5°N, 76.6°E) and Mt Abu (24.6°N, 72.7°E). Thiruvananthapuram is a coastal site and Mt Abu is a high altitude station (1680 m), representing a free tropospheric site. Figure 6 shows the average diurnal variations in ozone observed at Thiruvananthapuram and Mt Abu during March 1998. Observations made at Thiruvananthapuram show daytime higher concentrations of ozone, caused by the photochemical ozone production initiated by the pollutants. Here levels of NO are sufficiently high (1–2 ppbv) to initiate the photochemical ozone production. This diurnal variation in ozone is similar to the one observed over any other polluted site[27]. On the other hand, Mt Abu, a free tropospheric site, does not show daytime ozone production; in fact it shows decreased ozone levels with minimum concentration during noon time. Here ozone levels are controlled by the chemistry as well as by the up slope and down slope wind patterns over the mountains[28]. Ozone measurements over the Indian Ocean also do not show diurnal variations with daytime ozone production, but ozone levels are minimum in the afternoon hours, unlike Mt Abu. We must remember that over the oceanic region the diurnal patterns are driven by chemistry and boundary layer exchange processes. Higher baseline levels of ozone at Mt Abu are basically due to the high altitude site.

Figure 7 shows typical NO diurnal variations: its levels increase during daytime from the night-time levels of about 12 pptv, peak during noon time (about 28 pptv) and then decrease. During the daytime NO is produced by the photodissociation of NO_2. Very few observations made over the Pacific and Atlantic Oceans show similar diurnal variations in NO[17,29]. The observed diurnal variation in NO over the Indian Ocean differs from a continental site
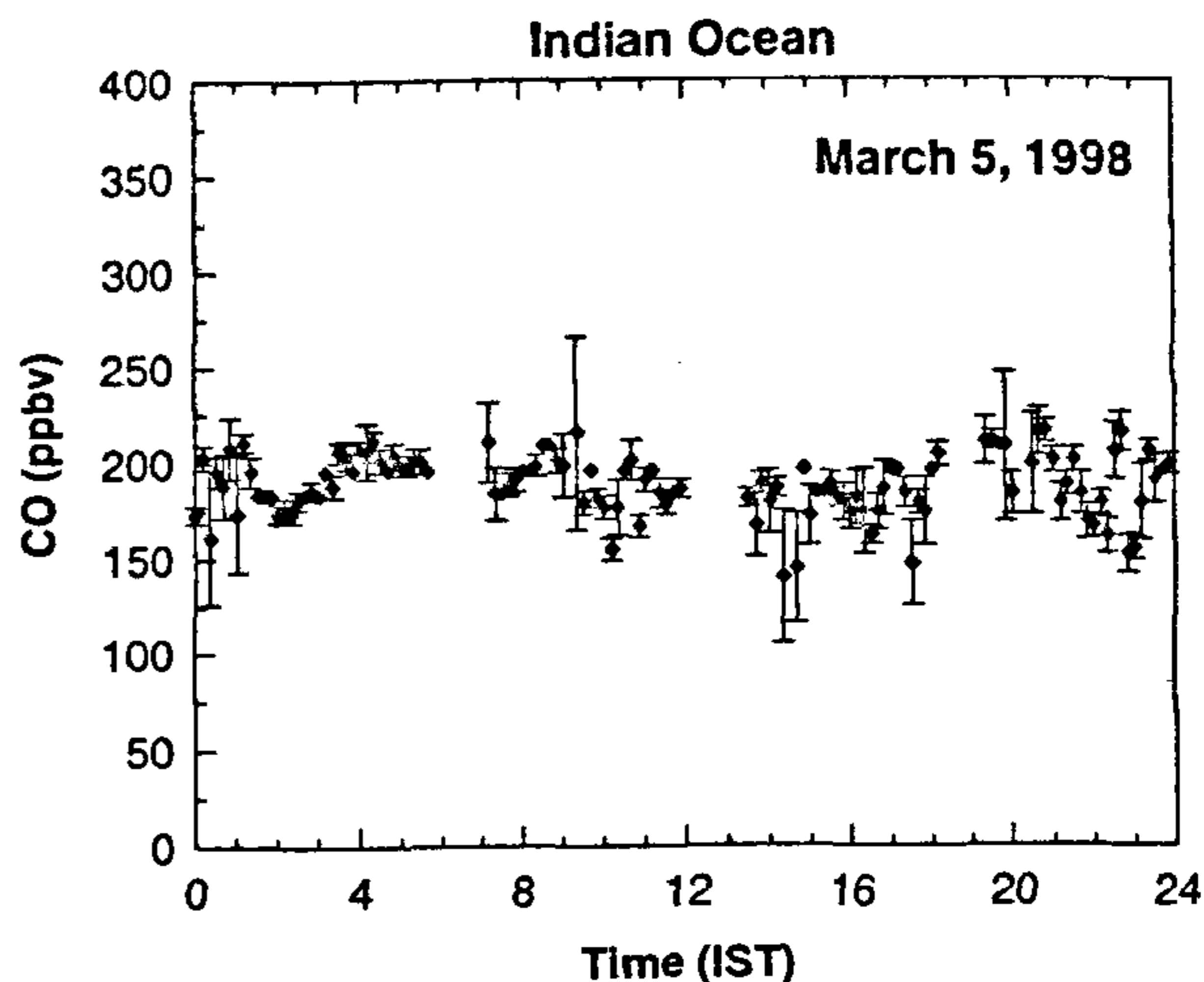

Figure 8. A typical diurnal variation (ten-minutes average) in carbon monoxide (CO) observed on 5 March 1998. Vertical bars are 1 σ variabilities.

here NO levels are low during the day and then higher during the morning and evening hours. Over the continental site, its diurnal variations are controlled by the boundary layer processes, surface emissions, chemistry, local wind patterns[28].

Figure 8 shows an example of the diurnal variation in CO over the Indian Ocean. Notably, CO does not show any clear and systematic diurnal variation during the entire cruise in the oceanic region. CO is produced mainly anthropogenically; its photochemical source is only by the photodissociation of HCHO, which does not contribute significantly to any diurnal pattern in the oceanic region. Hence, due to absence of anthropogenic sources over the oceanic region, CO does not show any systematic diurnal variation. Measurements of CO made by Rhoad et al.[27] over the Indian Ocean also lack any diurnal variations.

Summary

Measurements of O_3 and related gases (NO, CO and CH_4) made during three INDOEX ship cruises in 1996 (SK # 109), 1997 (SK # 120) and 1998 (SK # 133) are presented and discussed. During 1996, measurements were made till 5°S only, whereas during 1997 and 1998 measurements were made up to about 14°S and 8°S respectively, in the north and south of ITCZ. In general, ozone concentrations are observed to be higher near coastal region and decrease towards the southern region and gradient is estimated to be about 15%/° latitude. Ozone levels are also observed to be higher in region north of ITCZ. Similar

trends are observed in NO and CO. Methane also shows a similar trend, but the gradient is estimated to be minimum (3–4/° latitude). The extent of the continental polluted air from the northern hemisphere is observed in the deep Indian Ocean, in which ITCZ plays an important role. It was found that the movement of ITCZ can cause the transport of high ozone concentrations in the clean Indian Ocean. Only O_3 and NO show systematic diurnal variations which are not observed in CO. Ozone shows maximum concentrations during morning hours and decrease until evening, whereas NO shows maximum concentrations during noon time. These diurnal variations over oceanic region are different than observed over any polluted or clean continental region. This work provides an important data set for the Indian Ocean, since measurements are sparse over this region.

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