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Latitudinal trends in O_3, CO, CH_4 and SF_6 over the Indian Ocean during the INDOEX IFP-1999 ship cruise

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Surface measurements of ozone (O_3), carbon monoxide (CO), methane (CH_4) and sulfur hexafluoride (SF_6) were made over the Arabian Sea and the Indian Ocean during the INDOEX field experiment in January–March 1999 covering the latitude range from 17°N to 20°S. Observations show decreasing trends in all these trace gases from the Indian coastal region to the open Indian Ocean. Ozone with a lifetime of few days, shortest among the species presented here, shows large variations while SF_6, which has relatively longer lifetime, shows smaller variations. Ozone also shows clearly the effect of ITCZ and its movement. These observations show higher ozone near the Indian coastal region in January 1999 than in March 1999 and also compared to the observed ozone during the INDOEX-1998 cruise. This is believed to be due to strong anti-cyclonic conditions in January 1999 bringing more polluted air from the Indian continent. A decrease in the latitudinal gradient in CH_4 was observed in 1999 compared to that in 1998 in the same region, indicating slower growth rate in 1998–1999 period.

THE tropospheric ozone is very important since its higher concentration at surface is harmful to humans and plants[1,2] and it is a potential greenhouse gas[3]. In addition, it is the only source of OH radicals in the troposphere which controls the chemistry of the atmosphere. In the troposphere, ozone is controlled by chemical, physical and dynamical processes. Recent observations at surface and in the free lower troposphere show increase in ozone concentration in many parts of the Northern Hemisphere[4–7] and there has been reports of linear increase of about 1 to 3% per year in the past two or three decades[8–10]. Ozone in the free troposphere is controlled by changes in the levels of ozone in the planetary boundary layer and transport from the stratosphere[11]. Photochemical production of ozone takes place by photo-oxidation of CO, CH_4 and NMHC in presence of sufficient amount of NO_x. Elevated ozone concentrations observed during the Indonesian forest fires confirm the impact of bio-mass burning on tropospheric O_3 in the South Asian region[12].

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Sulfur hexafluoride (SF_6) is an extremely stable gas that has received considerable attention recently. Its unique physico-chemical properties make this gas ideally suited for many applications, predominantly in electrical insulation and switching. Due to its growing industrial production and long lifetime in the range of 2000–3000 years[13,14], it is rapidly accumulating in the atmosphere. Atmospheric SF_6 concentration has increased by two orders of magnitude since 1970 (refs 15, 16). Though SF_6 is one of the strongest greenhouse gases, with its low ambient mixing ratio, its effect on climate forcing is insignificant at present[17]. Its greater stability and high growth rate make SF_6 a valuable atmospheric tracer.

The Indian Ocean bordered in the south by one of the most sparsely populated areas and in the north by the densely populated and rapidly developing subcontinent, is a unique environment to study the large-scale impact of air pollutants on marine tropospheric chemistry and its impact on climate. During the northern hemispheric winter, large-scale cooling of the Tibetan Plateau is associated with the development of a high pressure over the Asian continent. The north-easterly outflow from this high-pressure area transports polluted air masses from Asia to the Indian Ocean. The important question is to what extent the growing south Asian pollutant emissions affect the composition of this relatively pristine atmosphere[18,19]. The warm water from the Indian Ocean triggers the deep convective cirrus clouds in association with the Inter-Tropical Convergence Zone (ITCZ) and contributes significantly to the vertical exchange of minor constituents (gases and particles) between the surface and the upper troposphere/lower stratosphere. Due to the intense and deep convectivity together with higher solar radiation flux along the ITCZ, there is a large production of OH radicals. The INDOEX offers an excellent opportunity to study the transport of various trace gases from the Indian continent to the Indian Ocean and the role of ITCZ in the inter-hemispheric transport of trace gases.

Surface measurements of O_3, CO, CH_4 and SF_6 have been made over the Indian Ocean during the Intensive Field Phase (IFP) of INDOEX in 1999. In this paper, we present the latitudinal distributions of O_3, CO, CH_4 and SF_6 over the Indian Ocean along with a comparison of

the measurements with the INDOEX-1998 cruise results. Inter-hemispheric exchange time and growth rate of SF_6 are calculated over the Indian Ocean using SF_6 data from the INDOEX-1999 and INDOEX-1998 cruises and other available data.

Experimental details

The INDOEX IFP (cruise no. SK-141) was conducted from 20 January to 12 March 1999 and the INDOEX First Field Phase (FFP) was conducted during 18 February to 30 March 1998 (cruise no. SK-133). Ozone and CO were measured on-board the ship and air samples were collected from the front of the ship when it was cruising. Ozone was measured by a Dasibi analyser (RS-1008, USA) based on UV absorption at 253.7 nm, while CO was measured using a non-dispersive infrared (NDIR) gas filter correlation analyser (Monitor Labs, USA, ML 9830) based on the principle of absorption of infrared radiation at 4.67 μm in its vibrational–rotational bands. Air samples were collected during both the cruises in pre-evacuated glass bottles at a pressure of about 1.5 bar using a metal bellow compressor. These samples were analysed at Physical Research Laboratory (PRL) using gas chromatograph (GC-Varian Vista 6000, USA) coupled with flame ionization detector (FID) for CH_4 and electron capturing detector (ECD) for SF_6. The signals were integrated using an integrator (Varian 4270, USA). For SF_6, 2 ml of air sample was pre-concentrated and injected into a 3 m long (3.2 mm OD) molecular sieve 5 Å stainless steel (SS) column and for CH_4, 5 ml of air sample was directly injected into a 5.5 m long (3.2 mm OD) SS column filled with molecular sieve 13X. Nitrogen is used as a carrier gas for both SF_6 and CH_4 analyses. Further details of the measurement techniques and calibration procedures for O_3, CO and CH_4 are given elsewhere[19,20]. The precision of analyses for SF_6 was about 2%, while the CH_4 measurements were made with a precision of about 5%. SF_6 was calibrated with a gravimetrically prepared standard[21] at the Institut fur Umweltphysik, University of Heidelberg, Germany.

Observations

The cruise track of the INDOEX IFP-1999 is given in the Introductory Note. The ship travelled parallel to the Indian coastal region from 15°N to 8°N latitudes and then almost meridionally towards the open Indian Ocean. During INDOEX IFP-1999 and INDOEX FFP-1998, air samples were collected throughout the cruise tracks at an interval of less than one degree.

The latitudinal variations of ozone measured during the INDOEX IFP-1999 and INDOEX FFP-1998 are shown in Figure 1. During the onward journey in 1999 the daily average ozone was observed to be around 57 ppbv in 14–15°N region. This increased to about 62 ppbv in the 9–12°N region. Thereafter there was a sharp decrease in ozone mixing ratios. At 6°N, the ozone mixing ratio sharply decreased to about 38 ppbv. Another sudden decrease was observed in the 3–5°S region. However, this is the region of ITCZ. Lowest ozone mixing ratios were observed around 8°S with a value of about 4 ppbv. Ozone values were higher (10–16 ppbv) again at Port Louis. Ozone mixing ratios in the 5–15°S region are higher (12–15 ppbv) in the return journey than during the onward journey in the same latitude region. However, the longitudes are different. During the return leg, even though the ITCZ was observed around the equator, the ozone mixing ratios were lower in the region north of 4°S than during the onward leg even near the coastal region of India. This is due to weakening of the anti-cyclonic conditions which prevailed over the Indian continent during January 1999 (ref. 22). The anti-cyclonic conditions brought more polluted air over the Indian Ocean in January. Partially the difference in ozone mixing ratios could also be due to the longitude difference between the onward and return journeys (see the cruise track INDOEX-1999). The maximum difference was around 8–12°N when the ozone mixing ratios were in the range of 25–35 ppbv during the return leg and 52–62 ppbv during the onward leg. O_3 mixing ratios were higher north of 4°S during the onward leg of INDOEX IFP-1999 than those observed during INDOEX FFP-1998. The INDOEX FFP-1998 results have been discussed in detail in Naja *et al.*[20].

The daily average carbon monoxide (CO) measured during the INDOEX IFP-1999 cruise is shown in Figure 2 along with results of the FFP-1998 for comparison. Highest CO concentrations (about 300 ppbv) are observed in the 8–12°N during the onward journey. There was a gradual decrease in its mixing ratios towards the south. At Port Louis, CO concentration was observed in the range of 60–100 ppbv. There was no clear difference in the CO mixing ratios during the two legs except north of 8°N, i.e. near the Indian continent. This could be due to longer

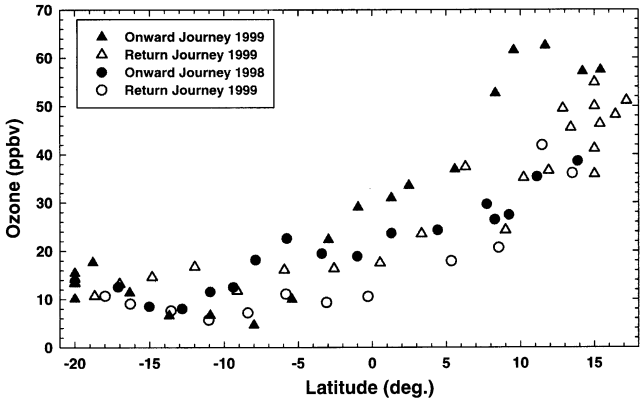

Figure 1. Latitudinal variations of daily average ozone during onward and return journeys of INDOEX FFP-1998 and INDOEX IFP-1999 cruises.

lifetime (~ 2–3 months) of CO than that of ozone which is only few days in the marine region. However, in the vicinity of the Indian continent, the differences in CO mixing ratios in the two legs are similar to that of ozone. The average latitudinal gradient was about 4 ppbv/°lat. As observed during the previous cruises, there is a correlation ($r^2 = 0.7$) of ozone with CO during this cruise also. However, in the clean region of the Indian Ocean where NO values are very low, ozone does not increase even if CO increases. Measurements made by Rhoads *et al.*[18] during the 1995 ship cruise over the Indian ocean from Africa to Sri Lanka, revealed CO concentration of about 140 ppbv near 6°N which decreased to about 50 ppbv near 33°S. There is no systematic difference in CO mixing ratios observed in IFP-1999 and FFP-1998 cruises.

The latitudinal distributions of methane mixing ratios obtained from the air samples collected during FFP-1998 and IFP-1999 are shown in Figure 3. Its mixing ratio decreases from an average value of about 1.75 ppmv near the Indian coast to about 1.65 ppmv at 20°S. There is a scatter of about ± 0.08 ppmv about the mean values in the total data of both the legs. The average gradient is about 2.3 ppbv/°lat. This latitude gradient is lower than that observed during INDOEX-1998, which was 4.3 ppbv/°lat. However, there is no appreciable difference in the average mixing ratios during the two years (Figure 4). This indicates that the growth rate of methane is decreasing and it is trying to redistribute uniformly in the two hemispheres. Lower or almost no growth rate of CH_4 in the recent past has been a point of discussion[10].

Figure 5 shows distribution of SF_6 observed during onward and return legs of IFP-1999. SF_6 mixing ratios of about 4.4 pptv were observed in the northern region and lower in the southern region. However, the lowest levels (~ 3.9 pptv) were observed in the 5–15°S latitude region. SF_6 mixing ratios increase slightly near the Port Louis during the onward leg. There is a positive gradient from south to north like in other gases. The average gradient is of about 9×10^{-3} pptv/°lat. The scatter in the mixing ratios was observed both during onward and during return journeys. However, the spread was beyond the measurement errors. Higher mixing ratios in the northern region

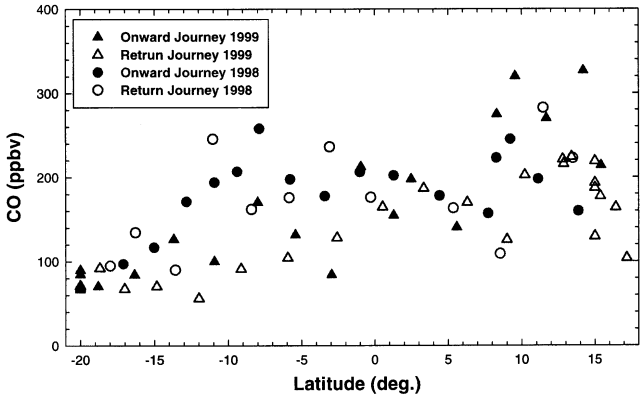

Figure 2. Latitudinal variations of daily average CO during onward and return journeys of INDOEX FFP-1998 and INDOEX IFP-1999 cruises.

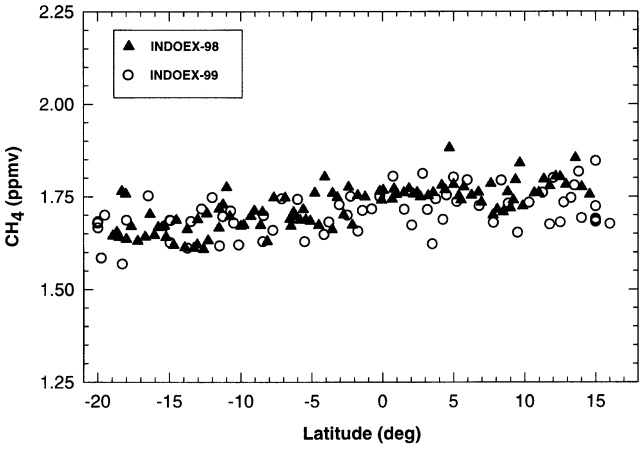

Figure 4. Latitudinal variation of CH_4 during the INDOEX IFP-1999 and INDOEX FFP-1998 cruises.

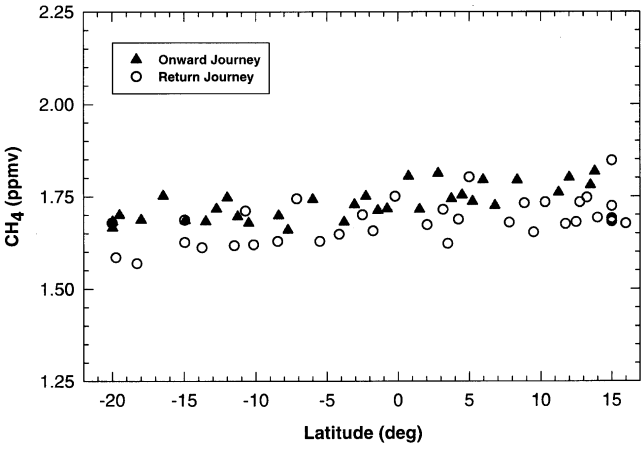

Figure 3. Latitudinal variation of CH_4 during the INDOEX IFP-1999 cruise during onward and return journeys.

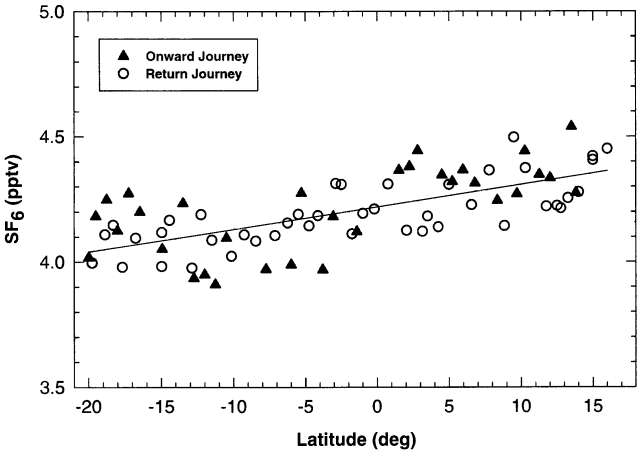

Figure 5. Latitudinal variation of SF_6 during INDOEX IFP-1999 cruise during onward and return journeys.

have been observed in the earlier cruise data also. This is due to its dominant source in the Northern Hemisphere. Even though the lifetime of SF_6 is much higher, in the range of 2000–3000 years, the latitudinal gradient in its distribution is mainly caused by the anthropogenic source in the Northern Hemisphere with its high growth rate.

Figure 6 shows a comparison of SF_6 measurements with similar measurements made in 1998 during the INDOEX FFP and also with measurements made in the Pacific and Atlantic Oceans in January 1994 and October 1994 respectively[23]. These later measurements are presented here only for the latitude range covered by the INDOEX cruises. These observations show an increase in SF_6 mixing ratios from INDOEX-1998 to INDOEX-1999 by about 4%/yr. Using the observations made in the Pacific Ocean and the INDOEX-1998 data, we infer a linear growth rate of about 9%/yr during 1994–1999 period. The average global growth rate in SF_6 is reported to be 6.9%[10,21,23]. The INDOEX data show a slower growth rate. The average latitudinal gradients of SF_6 measured during the two INDOEX cruises are in the range of $7–9 \times 10^{-3}$ pptv/lat.

Mixing of a trace gas between the two hemispheres depends on inter-hemispheric exchange time[24,25]. The inter-hemispheric exchange time varies with the season and further depends on the position of the ITCZ. The ITCZ oscillates with a time period of one year due to the earth's tilt on its axis and its orbital motion around the sun. The position of the ITCZ based on surface streamlines given by Jha and Krishnamurty[22] during the period of INDOEX-1999 is observed to move from 5°S to 1°S. Due to this movement of ITCZ, the extent of transportation of pollutants from NH to SH during onward journey was relatively more than during the return journey.

Inter-hemispheric exchange time (t_{ex}) is a very important parameter to characterize the global atmospheric transport models. t_{ex} expresses the strength of the ITCZ acting as a major resistance of air mass exchange between the two hemispheres[26,27]. We have used the present measurements of SF_6 over the Indian Ocean to estimate t_{ex}. The region of measurements is divided into two parts 0–15°N and 0–15°S. The following equation based on the two-box model of Singh *et al.*[27] is used to calculate t_{ex}.

$$t_{ex} = \frac{\frac{C_{NH}}{C_{NH}} - 1}{b + \frac{1}{t_s}}, \quad (1)$$

where C_{NH} and C_{SH} are the average mixing ratios of SF_6 in the NH and the SH respectively, t_s is the SF_6 atmospheric residence time which is taken as 3000 years[13,14] and b is its growth rate. Using the INDOEX-99 and 98 cruises data and taking b as computed, 4%/yr, we calculate an inter-hemispheric exchange time of 1.5 ± 0.1 year. Similar models were used by others[21,23,24] using data from other regions of the globe and estimated t_{ex} values as 1.7 years, 1.5 years and 1.3 years respectively. This shows that the inter-hemispheric exchange time over the Indian Ocean is in the range of the average global exchange time.

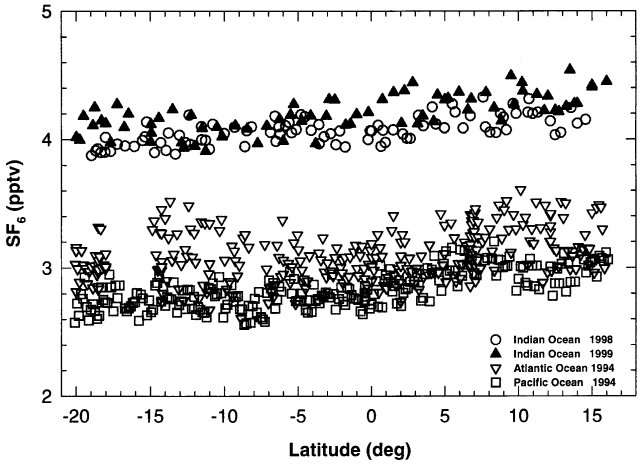

Figure 6. Latitudinal variation of SF_6 during INDOEX IFP-1999 and INDOEX FFP-1998 cruises compared with measurements from the Pacific and Atlantic Ocean cruises taken from Geller *et al.*[22].

Summary

Measurements of O_3, CO, SF_6, CH_4 and other trace gases are made between 17°N and 20°S over the Indian Ocean during INDOEX-1999 and 1998 ship cruises to study the transportation of trace gases over the Indian Ocean and across the ITCZ. Concentrations of all the measured trace gases are found higher near the Indian coastal region. Highest levels of ozone of about 62 ppbv near 12°N and a minimum of about 4 ppbv at 8°S, both during the onward journey in 1999, are observed. Ozone levels are higher (12–16 ppbv) in the latitude range of 5–15°S during the return leg. However, ozone values are lower in the north of ITCZ during the return journey when compared to onward journey values. The effect of ITCZ is clearly reflected in the distribution of ozone. In general, CO values also show similar latitudinal gradient with high values (around 300 ppbv) in the north and low values (around 50 ppbv) in the south. Similar to ozone, CO values are also lower near the coast in March when compared to that in January. This specific feature is attributed to the higher transport of pollutants in January 1999 due to the anti-cyclonic conditions observed during that period[22]. A uniform gradient with high values in north and low values in south is observed in the long-lived gases like CH_4 and SF_6. A comparison of the gradients in methane distribution observed in the two INDOEX cruises clearly shows the effect of decrease in its growth rate during 1998–1999. The results of SF_6 from these two INDOEX cruises give a growth rate of about 4%/yr during the 1998–1999 period

which is lower than the earlier estimates[10,21,23] for the 1994–1996 period.

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