

## Long-term trends in tropospheric ozone over the Indian tropical region

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[1] We report a statistical regression model analysis of long-term linear trends in the ozonesonde vertical profiles in the troposphere for the period 1972–2001 from the three tropical stations in tropical India. An analysis of tropospheric column ozone (TCO) data derived from ozonesonde and Nimbus7/Earth Probe total ozone mapping spectrometer (TOMS) during the period 1979–2002 has also been done. There are no statistically significant trends over Trivandrum (8.3°N, 76.6°E, 61 m) but significant positive trend (within 2-sigma error) are found to occur in the lower troposphere over Pune (18.3°N, 73.5°E, 559 m) and throughout the entire troposphere over a heavily air-polluted urban center Delhi (28.4°N, 77.1°E, 216 m). However, over the last decade, variations in tropospheric ozone have become statistically insignificant even over Delhi in spite of increasing surface NO<sub>x</sub> concentrations. The TCO obtained by ozonesonde as well as TOMS satellite data over Trivandrum do not reveal any statistically significant trend. **INDEX TERMS:** 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 9320 Information Related to Geographic Region: Asia. **Citation:** Saraf, N., and G. Beig (2004), Long-term trends in tropospheric ozone over the Indian tropical region, *Geophys. Res. Lett.*, 31, L05101, doi:10.1029/2003GL018516.

### 1. Introduction

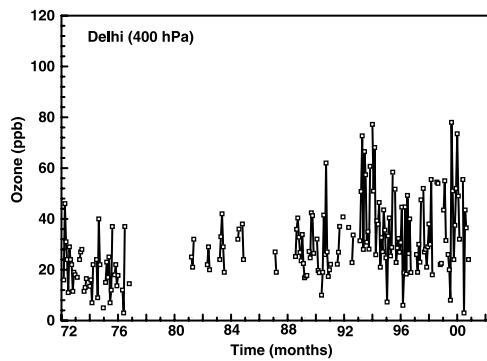
[2] Over the tropical region, stratospheric ozone depletion problem has proven not to be as serious and critical as the problem of increase in tropospheric ozone. A long-term change in tropospheric ozone has important climatic implications as it acts as a greenhouse gas and as a source of the atmospheric detergent OH. The *WMO* [1999] and Intergovernmental Panel for Climate Change [*IPCC*, 2001] assessment reports have reported large uncertainties due to anthropogenically related increases in tropospheric ozone resulting from the emissions of ozone precursors.

[3] In the recent past, most of the work on long-term variations in tropospheric ozone and its causes relied on photochemical models [Berntsen *et al.*, 2000]. This has led to predictions of marginal to high rates of increase in tropospheric ozone and thus quantitative estimates could never be ascertained with full confidence. Although we have a number of long-term data sets for the stratospheric and total integrated ozone from ground-based stations and satellites, long-term vertical profiles of tropospheric ozone concentrations are provided only by ozonesondes [Logan, 1994]. The

problem is more serious in tropical regions where not many long-term ozonesonde records are available. An analysis of ozonesonde data taken over Hawaii (20°N) [Logan, 1994; Logan *et al.*, 1999] and a few other tropical locations has reported insignificant trends in tropospheric ozone [Hudson and Thompson, 1998]. Such results are in contrast to model predictions [Berntsen *et al.*, 2000 and references therein], which unequivocally recognize the potential for anthropogenic modification of tropospheric ozone. Such discrepancies need to be resolved and understood. According to IPCC Third Assessment Report [*IPCC*, 2001], some Asian stations have indicated a possible rise in tropospheric ozone, which could be related to the increase in East Asian emissions. Tropospheric ozone can augment the global-mean radiative forcing due to well-mixed greenhouse gases by 10 to 15% and hence play a very important role in predicting future climate changes [*IPCC*, 2001]. Due to limited observed information on tropospheric ozone in the tropics particularly over the Indian subcontinent the estimate of radiative forcing due to tropospheric ozone is not ascertained accurately, which is a high priority for future IPCC assessments [*IPCC*, 2001]. The Indian tropical region is vulnerable to emissions of several pollutants like CO, NO<sub>x</sub>, volatile organic compounds (VOCs), SO<sub>2</sub> etc. In this paper, we report a first time up to date analysis of the vertical distribution of tropospheric trends in ozone using ozonesonde measurements from three different tropical stations in India from 1972–2001. We also provide the trend analyses of tropospheric column ozone (TCO) concentrations obtained by integrating these ozonesonde data and those derived from TOMS satellite measurements. The present work will be an important contribution towards achieving the goals set by *IPCC* [2001].

### 2. Data and Regression Model

[4] The ozonesonde is used to measure the vertical distribution of ozone from the surface into the lower stratosphere. In general, weekly ozonesonde soundings are made using a modified electrochemical Brewer Bubbler ozone sensor (B-M sonde) [Shreedharan, 1968]. The ozone profile ( $\mu\text{mb}$ ) after integrating vertically has been normalized to the total ozone measured by Dobson spectrophotometer. The performance of the electrochemical concentration cell (ECC) and the Indian ozonesonde were assessed in several inter-comparisons [*WMO*, 1994; Smit *et al.*, 1996] and it had concluded that the precision of a measurement at the ozone layer peak is better than  $\pm 2\%$  [*WMO*, 1994]. Juelich ozonesonde intercomparison experiment (JOSIE) in 1996 had removed the key shortcomings of earlier inter-comparisons where the major goal was to investigate the precision, accuracy and response of various ozonesonde types under controlled laboratory conditions. In the present work, such high quality ozone time series are used which has recently



**Figure 1.** Time series of ozone volume mixing ratio (ppb) over Delhi, for the period 1972–2001 for the altitude 400 hPa.

been quality checked and reported by *Beig et al.* [2002] for detecting volcanic signals. The tropospheric ozonesonde data obtained during the period 1972–2001 over Trivandrum, Pune and Delhi up to 200 hPa are used in this work. The number of soundings for each month varies typically from a total of 2 soundings per month to as large as about 4–6 in some cases. On an average there are 2 soundings available for each month that went into the calculation. In all total number of soundings included in the analysis are typically of the order of 300 for one station. The coverage of data is sparse during some years in the early and mid 1980s over all the three stations during which observations were discontinued. On some occasions, the monthly averaged data for several months are missing. However, this is the case with midpoints in time series. Obviously, trend determination depends most strongly upon the points near the beginning and end of the data set (where the data set is more complete), while the midpoints do not contribute much [*Reisin and Scheer*, 2002].

[5] A normalization factor has been used to check the quality of the data [*WMO*, 1994]. The issue of normalization of the ozonesonde data is a debatable issue, which still needs to be resolved. The Stratospheric Processes And their Role in Climate (SPARC) assessment report [*SPARC*, 1998] on sonde data quality concluded that the scaling procedure should be applied to the entire profile; however, it has been suggested that the normalization may not be suited for the tropospheric part of the profile. *Logan et al.* [1999] are of the view that the normalization does not affect the trend results if the trends in the normalizing coefficients are small for a particular location. The unnormalized data has its own shortcomings. In the present case, we have repeated the analysis using the normalized as well as unnormalized data. However, as in majority of the cases, due to the scatter in the data the  $2\sigma$  error goes beyond the critical limit with normalized data and no definite conclusions can be drawn. Whereas the normalized data analysis was found to yield results where definite inferences can be made within statistical limitations and hence preferred in the present analysis. The average normalization factor for the ozone soundings varies from 0.9–1.1. The altitude dependent corrections are made for every ozonesonde reading.

[6] The above-mentioned ozonesonde data are also integrated over the tropospheric altitudes to obtain the TCO values. We have also used the TCO time series derived from

the Nimbus7/Earth Probe – TOMS measurements for the period 1979–2002 using the cloud convective differential (CCD) technique described in detail elsewhere [*Ziemke et al.*, 1998] and available at the Web: [http://code916.gsfc.nasa.gov/Data\\_services/cloud\\_slice/](http://code916.gsfc.nasa.gov/Data_services/cloud_slice/).

[7] The regression model applied for the analysis of ozone data to remove the effects of natural signals and to separate out linear trends is an extended version of the original model of *Stolarski et al.* [1991]. For details of this model, applied to Indian ozonesonde time series, reader is referred to *Beig et al.* [2002]. Hence, model is described here briefly. The model performs multiple regression analyses of each time series at each pressure level and also for TCO separately. The general expression for the regression model equation used for the analysis can be written as follows:

$$O_3(t, z) = \alpha(z) + \beta(z) \cdot \text{Trend}(t) + \varepsilon(z) \cdot \text{ENSO}(t) + \text{res}(t) \quad (1)$$

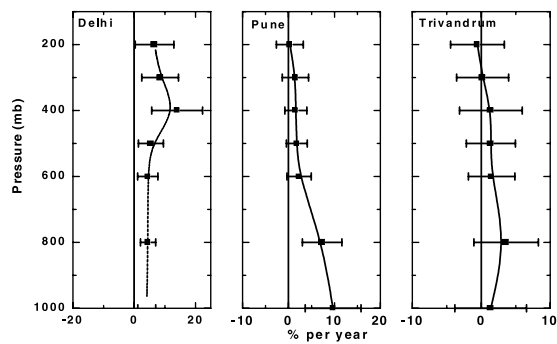
Here,  $\alpha(z)$  is the time-dependent seasonal coefficient,  $\beta(z)$  is the time-dependent seasonal trend coefficient,  $\text{res}(t)$  represents the time series of other parameters not considered in the regression analysis, including noise, and  $\varepsilon(z)$  is the time-dependent regression coefficients corresponding to the ozone driving quantity ENSO (El Nino Southern Oscillation). The influence of 11-year solar flux and QBO in the troposphere is insignificant which has been evaluated in the present analysis. Trend models often use a particular harmonic expansion to represent the seasonality of the interaction between  $O_3(t)$  and a particular surrogate (proxy). In the present statistical model, we have included the ENSO proxy time series based on the actual measured values of Southern Oscillation Index (SOI), which is the Tahiti ( $18^\circ\text{S}$ ,  $150^\circ\text{W}$ ) minus Darwin ( $13^\circ\text{S}$ ,  $131^\circ\text{E}$ ) monthly-mean sea-level pressure (hPa) [*Ziemke et al.*, 1997]. Proxy time series has been detrended and deseasonalized to avoid any tampering of the derived seasonal fits and to remove any fictional trends caused by sudden changes in the proxies on the long term variations of ozone.

### 3. Results

[8] The average surface (1000 hPa) volume-mixing ratio of ozone for the period 1972–2001 is of the order of 5–100 ppb over Delhi, 5–80 ppb over Pune and 5–60 ppb over Trivandrum thereby depicting the latitudinal gradient. Figure 1 shows the time series of ozone at 400 hPa over Delhi where the increasing trend can be noticed. Gaps represent missing data. It is known that the  $\text{SO}_2$  levels and the titration efficiency of ozone by  $\text{NO}_x$  both affect the ozone concentrations in the free troposphere, particularly at altitudes below 4 km [*Logan*, 1994]. However, over Delhi, one of the highly polluted cities in India, surface ozone volume mixing ratios do not show anticipated very low values. Hence, the error in the sonde measurements due to interference of high levels of  $\text{SO}_2$  with ozone concentrations and its effect on the detection of long-term trends might be considered insignificant.

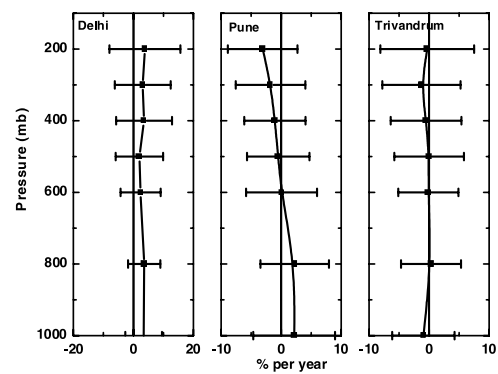
#### 3.1. Trends in the Vertical Distribution of Ozone

[9] Figure 2 shows the calculated vertical distribution of the trend regression coefficients (% per year) for the period



**Figure 2.** Vertical distribution of ozone trend coefficient (% per year) in the troposphere over Delhi, Pune and Trivandrum, for the period 1972–2001. The horizontal bars represent 2-sigma error.

1972–2001 at Delhi, Pune and Trivandrum respectively. The actual trend values along with the  $2\sigma$  standard deviation with 95% confidence limit are tabulated in Table 1a. The linear trends throughout the entire troposphere during the 30-year period over Trivandrum are statistically insignificant. The positive trend at low altitudes becomes negative in the upper troposphere (200 hPa). The trends over Pune are close to significance ( $9.7 \pm 6.1\%$  per year) in the planetary boundary layer. At and above 600 hPa, trends become statistically insignificant, although positive. The data for the Delhi station, however, show a statistically significant positive trend throughout the troposphere. The trend coefficient of  $4.3 \pm 2.5\%$  per year is found to be highly significant at and near the surface (1000–800 hPa). The maximum trend coefficient occurs at altitudes corresponding to 400–300 hPa. No distinct seasonal variation in the trend coefficients is observed over Trivandrum. In the lower (surface to 800 hPa) and mid-troposphere (600 to



**Figure 3.** Same as Figure 2 but during the period 1989–2001.

500 hPa) over Pune, the maximum trend is observed during March and June but at the pressure levels 400 to 200 hPa, no clear seasonal trend pattern can be deciphered. The lack of sunlight for the photochemical production of ozone during the summer monsoon months is a likely reason for smaller ozone change. For all altitudes, the trend coefficients are found to be at maximum during the dry winter months (January and February). In the mid and upper troposphere, the minimum trend occurs during the months of April and May.

[10] The trend regression coefficients (% per year) calculated for the period 1989–2001 are shown in Table 1b, for various tropospheric altitudes. The magnitude of the trend varies among the three stations but they all show a statistically insignificant trend extending from the surface to the upper tropospheric heights (Figure 3). A positive but insignificant trend of about 3.0% per year is found over Delhi ( $28^\circ\text{N}$ ) throughout the entire troposphere. Over Pune, the maximum trend of  $2.2 \pm 5.7\%$  per year is obtained at  $\sim 800$  hPa. The minimum trend over Pune is found at pressure levels corresponding to 300 and 200 hPa. Through the entire mid to upper troposphere over Pune, a negative trend is found all year round. No distinct seasonal pattern is observed at levels near the surface and in the upper troposphere. Different from the trends observed over Delhi and Pune, the trends over Trivandrum show no clear annual or seasonal pattern throughout the troposphere.

[11] The ozone trend regression coefficients over all the three stations show a systematic pattern above the boundary layer where magnitude of trend is found to increase with increasing latitude for the pressure level 600–200 hPa (Table 1a). The positive trend coefficient in tropospheric ozone over Delhi is significant almost at all levels whereas it is insignificant in most part of troposphere over Trivandrum and Pune. The effect of regional surface pollution is seen clearly only at altitudes corresponding to the boundary level up to about 2 km from the surface. It can be noticed from Table 1a that comparatively smaller increase is seen, near the boundary layer over Delhi which is more polluted as compared to Pune and Trivandrum. This may be due to the enhanced titration effects of ozone in the presence of higher surface  $\text{NO}_x$  levels found over Delhi as compared to Trivandrum and Pune [Garg *et al.*, 2000]. In the free troposphere, variations in tropospheric ozone are affected more by the

**Table 1.** Trend Regression Coefficients (% Per Year) (a) 1972–2001, and (b) 1989–2001, for Ozone Over the Three Tropical Stations Trivandrum, Pune, and Delhi for the Tropospheric Altitudes (1000–200 hPa) Derived Using the Statistical Regression Model

(a)	Trend coefficients (% per year) (1972–2001)		
	Trivandrum ( $8^\circ\text{N}$ , $76^\circ\text{E}$ )	Pune ( $18^\circ\text{N}$ , $73^\circ\text{E}$ )	Delhi ( $28^\circ\text{N}$ , $77^\circ\text{E}$ )
Altitude (hPa)			
1000	1.4 (3.3)	9.7 (6.1)	4.1 (2.9)
800	3.6 (4.7)	7.3 (4.3)	4.5 (2.5)
600	1.5 (3.4)	2.3 (2.6)	4.4 (3.3)
500	1.4 (3.6)	1.8 (2.3)	5.4 (4.1)
400	1.4 (4.5)	1.6 (2.4)	14.0 (8.3)
300	0.2 (3.8)	1.5 (2.8)	8.5 (6.0)
200	-0.5 (3.9)	0.3 (2.9)	6.6 (6.3)
(b)	Trend coefficients (% per year) (1989–2001)		
Altitude (hPa)	Trivandrum	Pune	Delhi
1000	-0.9 (5.2)	2.1 (6.8)	3.4 (6.1)
800	0.3 (5.0)	2.2 (5.7)	3.6 (5.4)
600	-0.1 (5.0)	0.05 (5.9)	2.3 (6.7)
500	-0.01 (5.8)	-0.5 (5.2)	2.0 (7.9)
400	-0.5 (5.9)	-1.0 (5.1)	3.5 (9.3)
300	-1.2 (6.5)	-1.7 (5.8)	3.1 (9.3)
200	-0.3 (7.8)	-3.0 (5.8)	3.8 (11.8)

Quantities in bracket represent 2-sigma error estimates.



diffused sources of  $\text{NO}_x$  rather than the more concentrated surface emissions.

### 3.2. Trends in TCO

[12] The annual mean trends (% per year) in TCO derived by integrating the vertical profiles of ozonesonde data over Delhi, Pune and Trivandrum (1972–2001) and that of TOMS data at  $7.5^\circ\text{N}$ . The ozonesonde data over Trivandrum, reveals statistically insignificant annual trend at  $0.3 \pm 2.6\%$  per year with is almost in agreement with satellite derived trend of  $0.2 \pm 0.6\%$  per year at about the same latitude. As the latitudinal extent of CCD data ranges from  $-12.5^\circ\text{S}$  to  $12.5^\circ\text{N}$  only, the comparison with ozonesonde data for latitudes corresponding to Delhi and Pune is not possible. It is also clear from the analysis that the trend in TCO over Pune is also insignificant ( $0.9 \pm 1.8\%$  per year) but it indicates a statistically significant value of  $2.7 \pm 2.3\%$  per year over Delhi. The trend regression coefficients in sonde derived TCO obtained over the three stations during the last one decade (1989–2001) is also found to be highly insignificant concomitant with the insignificant trend values found in the vertical distribution of ozone over the same period. The integrated ozonesonde tropospheric column ozone over these stations also shows increasing values in trends from Trivandrum to Delhi.

## 4. Discussion and Conclusions

[13] Most of the ozone measurements at several remote coastal and high altitude sites north of  $20^\circ\text{N}$  exhibit a positive trend significant at the 95% level [Harris *et al.*, 1997 and references therein], since 1970s. However, if these measurements were initiated in 1980s, at the time when the ozone concentration was at its peak, no significant ozone increases would have been found [Harris *et al.*, 1997] as is the case for Indian region.

[14] Ozone in the troposphere absorbs strongly at 320 nm. Photolysis rates play a key role in tropospheric chemistry. The photolysis rate of ozone is strongly determined by the stratospheric ozone amount. It is shown that the negative trend in stratospheric ozone leads to a positive trend in the ozone photolysis rates in the troposphere due to increasing UV-B radiation [WMO, 1999]. Over the Indian tropical region, significant decrease in ozone is found over Delhi but not much statistically significant ozone decrease takes place during the period 1972–2001 over the other two stations above altitudes corresponding to the tropopause ( $<100$  hPa). The increasing surface  $\text{NO}_x$  concentrations over the Indian region and particularly over Delhi during the early 1990s have been attributed mainly to the sources related to surface transportation [Garg *et al.*, 2000]. Over Pune and Trivandrum, no significant increase in surface  $\text{NO}_x$  emissions has been reported. However, the lack of increase in ozone over Delhi during the last decade (1989–2001) through the entire troposphere argues against a significant influence of  $\text{NO}_x$  emissions from surface transportation sources. It can also be argued that under the conditions of high  $\text{NO}_x$  (reaching to levels beyond 10 ppb) which is found in urban centers like Delhi,  $\text{O}_3$  can be lost or 'titrated' by the presence of large  $\text{NO}_x$  abundances via reaction  $\text{NO} +$

$\text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$  [Brasseur *et al.*, 1999]. It further implies that surface sources of  $\text{NO}_x$  are not very effective in increasing tropospheric ozone when compared to diffuse sources of  $\text{NO}_x$  like emissions from aircraft. Another factor that can be attributed to insignificant changes in ozone distribution over the previous decade may be due to the global decrease in CO concentrations since 1980s [Novelli *et al.*, 1998]. The production of tropospheric ozone is mainly from CO, VOCs, and  $\text{CH}_4$  in the presence of  $\text{NO}_x$ . The reaction of CO, VOCs, and  $\text{CH}_4$  with hydroxyl radicals is the main source of peroxy ( $\text{RO}_2$ ,  $\text{HO}_2$ ) radicals, which aids in the conversion of NO to  $\text{NO}_2$ . Hence, a decrease in the chemical fuels (CO, VOCs,  $\text{CH}_4$ ) may ultimately lead to a decrease in the production of  $\text{NO}_2$  consequently affecting the ozone production.

[15] In conclusion it can be stated that the results obtained in this paper provide first hand information on tropospheric trends over the tropical Indian region, which has the latitudinal gradient. It is significant over Delhi but relatively insignificant over the other two stations. It should be emphasized that although the present analysis using the normalized tropospheric ozone profiles might influence the magnitude of the trend coefficients, we believe that it would not affect the general qualitative nature of the trend results.

[16] **Acknowledgments.** We acknowledge the DST, New Delhi for the financial assistance. Thanks are due to Dr. G. B. Pant (Director, IITM) for his encouragement and Dr. S. K. Srivastava and Dr. S. K. Peshin for scientific help.

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