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A Comparative Study of the Variability in the Observed Ozone and that Obtained from a Statistical Model of Catalytic Destruction over Antarctica

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Abstract

In this paper, day-to-day fluctuations in total ozone during the "ozone hole" period (using the TOMS data) over the Indian Antarctic Station, Maitri have been studied. First, a statistical correlation analysis is performed on the fluctuations to reveal a characteristic correlation period (T_o) in the fluctuations. The extent of the effective data sample (T) to be analysed is also made known. The rms variability in the, mean ozone level σ_T is then given in terms of the rms scatter of the observed total ozone values (σ i), T_o and T. A value σ_T of during the "ozone hole" period of September 1987 is found to be about 6 D.U., which is 3 D.U. above the "noise" rms uncertainty associated with the TOMS data. Next, this "signal" rms variability of 3 D.U. estimated in the "ozone hole" period is compared with the statistical fluctuations inherent in the process of destruction of ozone through chlorine and bromine catalysis in the lower stratosphere.

In the applications of stochastic theory to chemical kinetics, a catalytic process is represented by a "death process". Accordingly, model estimates of the variabilities associated with chlorine and bromine catalysis ($\approx$ 87.5 % and 12.5 %, respectively) are made. The resultant rms variability in the mean ozone level requires the values of T_o and T, and is also shown to be about 3 D.U. Finally, the fluctuations in total ozone in other non- "ozone hole" months have been analysed.

Introduction

Mean values of total ozone using the TOMS data are available since 1979, and show an yearly decreasing trend over Antarctica. The phenomenon of "ozone hole" refers to a decrease in the values of total ozone over Antarctica in the local spring compared to that in the winter period (Farman *et al,* 1985). This ozone depletion is spread over an altitude range of about 12 to 22 km, in the lower stratosphere. Further, large "Characteristic" fluctuations are observed in the values of total ozone on day-to-day time scales during the "ozone hole" period.

It is now well-accepted that the depletion of ozone in the stratosphere during the spring is explained by (i) formation of a polar vortex in the Antarctic winter, with the consequent formation of Polar Stratospheric Clouds (PSCs) and (ii) heterogeneous catalytic destruction of ozone with enhanced species of chlorine, in the presence of particulate matter on PSCs (Solomon *et al.,* 1986; McElroy *et al.,* 1986a, b; Anderson *et al.,* 1991).

In the present paper, the "characteristic" fluctuations in total ozone on day-to-day time scales during the "ozone hole" period are explained as due to statistical fluctuations inherent

in the catalytic destruction of ozone. First, the fluctuations in total ozone are non-random in nature and, therefore, the rms variability in the mean ozone level obtained by ordinary statistical methods needs to be suitably modified to account for "persistence" in a "time series" (Bartels, 1935; Bloomfield *etal,* 1983; Forbush ef a/., 1983; Pasrichaef *al,* 1991). Persistence damps out any harmonic relationship that might exist between successive data points. A model correlation analysis is performed on the fluctuations in total ozone over a period of five years (1987 to 1991), as reported in the TOMS data, over the Indian Antarctic Station Maitri (70°S, 12° E). Next, the application of the stochastic theory to chemical kinetics indicates inherent statistical fluctuations in the mean density in a catalytic (first order kinetics) process. (Bharucha-Reid, 1960; McQuarrie, 1969). The rms variability in the mean ozone level during the "ozone hole" period estimated by the two approaches is compared. Further, estimates of the rms variabilities in the mean ozone levels in other non-"ozone hole" months are analysed.

Observed Variance in the Total Ozone Values over Antarctica

Autocorrelation functions of the fluctuations in total ozone in various months are computed, except for the period from May to June for which no data are available. A sample of fluctuations in total ozone analysed represents an autocorrelated time series in which individual data points are not independent of one another. A measure of persistence in the autocorrelated time series is the correlation period (T_0), which may be evaluated through suitable statistical models. Data points spaced T_0 apart are thus uncorrelated. The corrected variance *al* in the observed values of total ozone (after removing persistence and making them random) is related to the variance of of the scatter in the observed ozone values themselves (obtained by ordinary methods) through the relation;

$$o_c^2 = T_0 / Stc? \qquad ...(1)$$

where T_0 is measured in units of the sampling interval St (a day in the present study). The variance of is increased/decreased because the number of data points in a time series is increased/decreased by a factor of To/St. Consequently, the variance $o|^2$ needs to be reduced/increased by a factor of To/8t. Finally, the variance $0"T^2$ in the mean ozone level in a given month is given by:

$$O\,T = O\,i\,\frac{T^2}{OLT} \qquad ...(2)$$

where T is a sufficiently long period of the sample analysed. The rms variability in a mean ozone level is thus proportional to $T_0/\sqrt{\delta_{tT}}$ ($8_t = 1$); T_0=l and a-r/ai ***a*** 1 /VT~ for independent data.

The correlation period T_0 in a time series of the fluctuations in total ozone values may be evaluated through" certain statistical methods (Kendall and Stuart, 1966). The time series of the fluctuations may be given in terms of the autocorrelation values ps. The autocorrelation function of the fluctuations in the "ozone hole" period in September 1987, for instance, may be represented by a Markov process. In a Markov process, an autocorrelation value at a 1-day lag (i.e., pi) is sufficient to represent the autocorrelation function of the measured

fluctuations. In general, autocorrelation values up to 9-days lags have been used to represent the measured autocorrelation functions through statistical methods in various months. A set of Yule-Walker equations in terms of the autocorrelation values ps are then solved to obtain the coefficients as forming the time series of the fluctuations in the total ozone values themselves.

The set of equations for, say, 3 lags are:

$$\alpha_1 + \rho_1 \alpha_2 + \rho_2 \alpha_3 + \rho_1 = 0$$

$$\rho_1 \alpha_1 + \alpha_2 + \rho_1 \alpha_3 + \mu_2 = 0$$

$$\rho_2 \alpha_1 + \rho_1 \alpha_2 + \alpha_3 + \rho_3 = 0 \quad \text{...(3)}$$

Next, a polynomial in terms of as is solved to obtain pair(s) of complex conjugate roots (Pi,6i). The computed autocorrelation function ρk of the fluctuations is represented as the

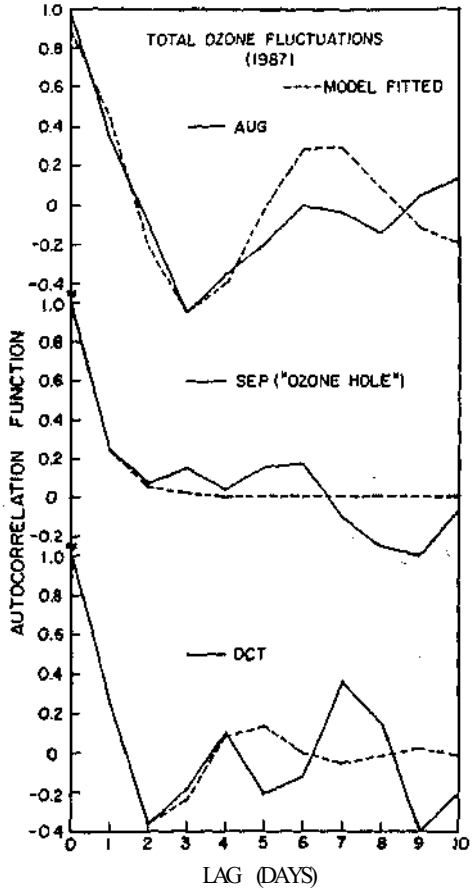

Fig. 1. A representative set of autocorrelation functions of the fluctuations in total ozone values using the TOMS data for the month of August, September ("ozone hole" period) and October 1987.

sum of terms as $\beta i\ Pi^k \sin(k\theta i + \phi i)$, where k = 1,2,. ..,n, and the coefficients βi and φi (i=l,2,,..,m) obtained by a general least-square fitting algorithm. Finally, the correlation period T_o is given by

$$T_o = 2 \sum_{k=0}^{k=T} (1-k/T)\, \rho k \qquad ...(4)$$

The value of T_o may be obtained by computing T_o for a number of values of T, and choosing the appropriate value of T_o at a sufficiently large value of T.

A representative set of autocorrelation functions of the fluctuations for the months of August, September ("ozone hole" period) and October are fitted with model functions, using autocorrelation values up to three, one and two lags, respectively (Fig.l). The correlation period T_o for the fluctuations in different months is then obtained (from expression 4), and are shown as a set of plots of T_o vs T in Fig.2. The values of T_o for the the months of August, September and October may be adopted for large values of the sampling period T of 60, 15 and 60 days, respectively. (A value of T = 60 days, say, means that total ozone values over 2 "similar" months should have been averaged, and then subtracted from individual total ozone values to obtain the variability). Values of the ratio $T_o/\sqrt{T}$, observed rms variability in the scatter of total ozone values (σi) and the estimated rms variability in the mean ozone level (σT) for various months are presented in Fig.3. An approximate change inthe mean ozone level (δO3) for different months are also included in this figure. The "ozone hole" periods of 1987 and 1989 are marked by low values of σi (≈ 15 D.U.) and large values of both $T_o / \sqrt{T}$ (≈0.4) and σT (≈ 6 D.U.). The fluctuations in total ozone in the "ozone hole" period of 1988, as well as in the months of October to December of all the years, show large

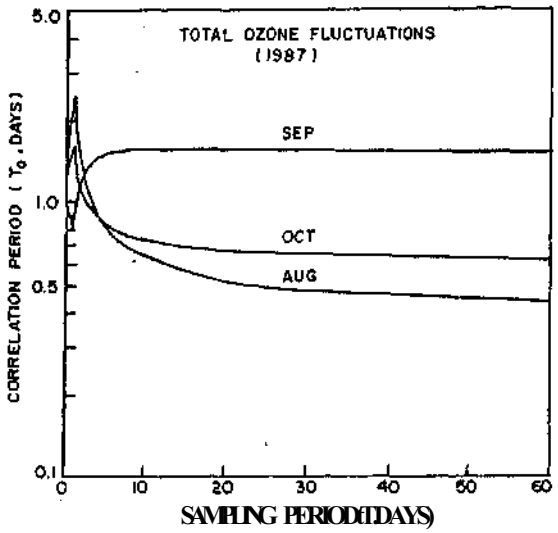

Fig. 2, A set of curves of T_o vs T for the months of August, September ("ozone hole" period) and October 1987.

values of σi (=40 D.U.). The corresponding values of $T_o / \sqrt{T}$ and σ_T are rather low =0.1 and 3, respectively. The "ozone hole" months of August and September of 1990 and 1991, as well as the month of August for other years (except 1988), are marked by low values of $T_o / \sqrt{T}$, σ_i and σ_T of =0.1, 15 D.U. and 2 D.U., respectively. The ozone variability in these months is similar to that observed in the non-"ozone hole" months of January to April in various years.

The rms variability in the mean ozone level in the "ozone hole" period has been estimated as =6 D.U. Now, the relative experimental uncertainty (rms/mean) in total ozone measurements themselves due to atmospheric variations (such as, absorption due to ozone and other species, variability in aerosol content etc.) amounts to about 5 % (Komhyr, 1980). It refers to the uncertainty measured at the 3-sigma (or rms) point in statistical terms. Therefore, the rms uncertainty at the 1-sigma point is about 1.7 %, i.e., 1.7 D.U. at a mean ozone level of 100 D.U. At the mean ozone levels ≈ 175 D.U. in an "ozone hole" period, the rms uncertainty in the TOMS measurements itself becomes =3 D.U. Thus, the "signal" rms variability in the fluctuations in total ozone above the atmospheric "noise" is about 3 D.U. It is next compared with the rms variability obtained in the stochastic treatment of catalytic destruction of ozone.

Estimation of the Variability in Total Ozone due to Chlorine and Bromine Catalysis

Two sets of catalytic cycles involving chlorine and bromine that lead to a destruction of ozone upto 75 % and 25 %, respectively, over Antarctica have been formulated (McElroy *et al.,* 1986a, b; Molina and Molina, 1987; Anderson *et al.,* 1991). Reactions, such as, C1+, O3 → C1O + O2 and Br + O3 → BrO + O2 represent unimolecular decomposition of ozone catalysed by a fixed concentration of chlorine and bromine, respectively. Unlike in the "deterministic" approach to chemical kinetics, the concentration of a reactant is considered a random variable at a given time in the "stochastic" approach. A set of probability criterions describe the temporal distribution of the concentrations. The mean concentration in both the approaches, however, remains the same. In the stochastic approach, the variance about the mean concentration represents inherent statistical fluctuations. It has been shown that large fluctuations exist in unimolecular reactions alone. The fluctuations in higher order reactions are rather negligibly small. Accordingly, the mean and (magnitude of) variance in the total ozone values in the catalytic reactions involving chlorine and bromine may be represented by a "death process", given by

$$x = x_o e^{-kt} \qquad ,.(5)$$

$$\sigma_x^2 = | x_o | e^{-kt} (1 - e^{-kt}) \qquad ...(6)$$

where $x_o(x)$ is the value of total ozone at the beginning (end) of the "ozone hole" period, t = 30 days and k the reaction rate constant for chlorine and bromine catalysis, given by, $2.9 \times 10^{-11} \times e^{-260/TK} \times [Cl]/10^6$ and $1.4 \times 10^{-11} \times e^{-750/TK} \times [Br]/ 10^6$, respectively. The total ozone values roughly pertain to the lower stratosphere from 12.5 to 22.5 km, and TK is the corresponding mean temperature. [C1] and [Br] are the columnar (of height 10 km or 10^6 cm) concentrations of chlorine and bromine (cm^{-2}). Model estimates of the variance in total ozone (σ_x^2) would be $\sigma_x^2 \simeq \sigma_{xCl}^2$, where σ_{xCl}^2 is the variance in total ozone due to chlorine

catalysis and $\sigma_{x_{Br}}^2$ the variance due to bromine catalysis. The variances $a_{x_{Cl}}^2$ and $a_{x_{Br}}^2$ are computed (for the "ozone hole" in September 1987) by considering an observed loss in total ozone from 240 to 180 D,U. (i.e., about 87.5 %) and from 180 to 170 D.U. (i.e., about 12.5 %), respectively. The columnar concentrations of chlorine and bromine corresponding to the modelled losses in total ozone, from expression (5), are approximately 10^{10} and 4×10^{10} (cm^{-2}), respectively. From expression (6), the variances (in the scatter of values) $a_{x_{Cl}}^2$ and $a_{x_{Br}}^2$ and σ_x^2 are 45, 9 and 54 (D.U.)^2, respectively. Finally, the rms variability in the mean total ozone level due to statistical fluctuations inherent in the process of catalysis is $\sigma_x T_0 / VT = 7.3 \times 0.4 = 3$ D.U., where $T_0 / VT = 0.4$ as shown in Fig. 3.

Other reactions in chlorine catalysis obeying the first order kinetics that may also be treated by stochastic approach are those of photolysis of Cl_2O_2 (Ishida, 1960) and unimolecular decomposition of ClOO in the presence of a large neutral number density. The rms variabilities in the production of chlorine (of statistical nature) through these reactions, however, do not contribute significantly to the rms variability in the destruction of ozone through chlorine catalysis. This is due to the statistical formulation that rms of an rms-variability (CT) is $a / \sqrt{2T}$, assuming a normal population.

Conclusions

The fluctuations in the daily values of total ozone observed using the TOMS data over the Indian Antarctic Station Maitri have been analysed in the present study. A statistical correlation analysis of the fluctuations over different months has been performed to estimate the correlation period (To) and the effective length of the data sample (T). The rms variability in the mean ozone level during different months is given by $\sigma_T = \sigma_1 \sqrt{T_0 / T} \sqrt{\Delta t}$ where σ_1 is the rms variability in the scatter of the observed total ozone values ($\delta t = 1$ day). Values of total ozone during an "ozone hole" period show characteristic fluctuations with low values of $\sigma_1 = 15$ D.U. and large values of $\sigma_T = 6$ D.U. ($T_0 / VT = 0.4$). Atmospheric "noise" accounts for an rms uncertainty = 3 D.U. in the measured total ozone values at the "ozone hole" levels. Thus, the rms variability in the mean ozone level represents a "signal" of about 3 D.U. during the "ozone hole" period of September 1987.

The observed ozone loss during the "ozone hole" period is attributed to its catalytic destruction by chlorine and bromine in the lower stratosphere. The process of catalysis may be represented by a simple "death process" in stochastic approach to chemical kinetics. It is then possible to estimate the inherent fluctuations of statistical origin in the process of catalysis. A model set of values of depleted ozone by chlorine and bromine catalysis are taken as 87.5 % and 12.5 %, respectively. The variance (σ^2) in the scatter of total ozone values is the sum of the variances due to chlorine = 45 (D.U.)^2 and bromine = 9 (D.U.)^2, respectively, for September 1987. The rms variability in the mean ozone level due to inherent statistical fluctuations in the process of catalysis is then $\sigma_x \sqrt{T_0 / VT} = 3$ D.U.

The fluctuations in total ozone in the months of October to December show large values of $\sigma_1 = 40$ D.U. and low values of $\sigma_T = 3$ D.U. These fluctuations in the mean ozone levels could possibly be due to dynamical processes (Randel, 1988). The fluctuations in the months of January to April, and also during the "ozone hole" of August and September of 1990 and

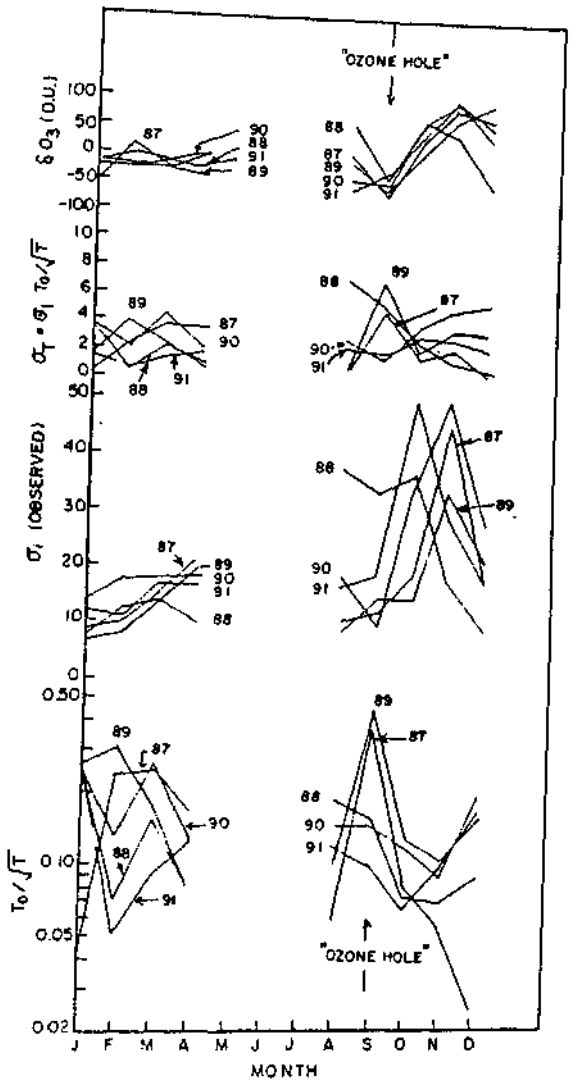

Fig. 3. Plots of th$T_0/\sqrt{T}$*, observed rm fluctuation obtained through ordinary methods* (σi)*, and the rms variation in the mean ozone level* (σ_T) *obtained through expression (2). An approximate change in the mean ozone level* (δO_3) *in different months is also presented.*

1991, show low values of both $\sigma i \approx 15$ D.U. and $\sigma_T \approx 2$ D.U. These could probably be of statistical origin through certain unimolecular reactions (as predicted in stochastic theory of chemical kinetics), The rms variability in the mean ozone level during the non-"ozone hole" months is, however, below or just at the rms uncertainty in the TOMS measurements (≈5

D.U.). An estimate of the rms variability in the mean ozone level is required to understand both chemical and dynamical processes leading to ozone depletion in the stratosphere, and for predicting future ozone trends.

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