A model study of the stratospheric budget of odd nitrogen, including effects of solar cycle variations

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ABSTRACT

A two-dimensional diabatic circulation model of the stratosphere and the troposphere is used to study the budget of total odd nitrogen (NO_y) and to simulate the response of odd oxygen and nitrogen species to the 11-year solar cycle variations. Firstly the results are discussed in terms of influence regions of the various NO_y production processes including surface sources (anthropogenic sources, soil exhalation), lightning, N_2O oxidation, galactic cosmic rays (GCRs) and high-latitude input from the thermosphere and mesosphere. Although the N_2O oxidation process is the dominant odd nitrogen source throughout the stratosphere, NO_y produced within the thermosphere and transported through the stratopause at high latitude during winter, may affect NO_y distribution, particularly during periods of large solar activity. In the lower stratosphere, the lightning contribution becomes significant (about 60% and 30% at the local tropopause in equatorial and polar regions, respectively). The GCR contribution is found to be rather weak even at the high-latitude tropopause (about 10%). Input parameters which vary with the solar cycle include ultraviolet photon fluxes, GCRs and downward flux at the high-latitude winter stratopause. The effect of the thermospheric production is confined to the high and middle polar stratosphere. We find, for instance, less than 4% variations in NO_y at 19 km in the winter hemisphere, where the main effect from solar cycle variations stems from changes in photon fluxes. Increases in photon fluxes lead to less NO_y production.

1. Introduction

Incoming solar radiation and energetic particle precipitation which change over the 11-year solar cycle can provide substantial chemical modifications (including O_3 and nitrogen oxides) in the stratosphere. Until now, observational studies have not proven the existence of a clear connection between the variability of these species concentrations and the 11-year solar cycle. Since rather weak variations are expected in ozone (a few % of the O_3 column per decade), accurate measurements over several cycles are required. Only recently are analyses of such measurement series starting to become available. Concerning the nitrogen species, it has been claimed that a correlation exists between nitrate deposition in antarctic ice and solar activity

(Parker and Zeller, 1979; Zeller and Parker, 1981; Laird et al., 1982). However, other studies (Herron, 1982; Legrand and Delmas, 1984 and 1986) do not agree with the earlier analyses.

Using a 2-D model (16 to 116 km elevation), Garcia et al. (1984) studied changes in the chemistry and the dynamics of the stratosphere and the mesosphere caused by modulation of both particle precipitation intensity and ultraviolet (UV) photon flux over the 11-year solar cycle. Although large variations in phase with solar cycle are produced in these calculations, only moderate changes are expected in the lower stratosphere. Garcia et al. (1984) therefore pointed to the difficulty in explaining the large NO_3 variations sometimes reported from analyses of antarctic ice.

A main purpose of the present study is to study

changes in the total amount of odd nitrogen. NO$_y$, accompanying the 11-year solar cycle variations. We have used a two-dimensional (2-D) diabatic circulation model of the stratosphere and the troposphere. In this work, we have separately studied the effects of solar cycle variations in three various NO$_y$ production mechanisms; the thermospheric production, the N$_2$O oxidation and the production due to galactic cosmic rays (GCRs). Before looking at these variations we investigate the contribution of each NO$_y$ source to the budget at various locations. We have then also included two significant sources which do not undertake variations on the 11-year time-scale, namely sources at the surface and in lightning. In some cases we distinguish between the total amount of odd nitrogen, NO$_y$, and the quantity NO$_x$, which we define as NO$_y$ − HNO$_3$.

2. Model description

A two-dimensional transport-chemistry model of the troposphere and the stratosphere (0–50 km) is used. The model covers latitudes from pole to pole. It employs the diabatic circulation with small eddy diffusion coefficients in the stratosphere. The model has been shown to reproduce reasonably well distributions of various trace species (N$_2$O, CH$_4$, H$_2$O, O$_3$ and chlorofluorocarbons) in the stratosphere. Model description and results are given elsewhere (Stordal et al., 1985) and we present here only the basic assumptions of the model.

Insofar the waves (eddies) are assumed to be approximately steady and conservative, the net transport of chemical species is provided by a near cancellation between the mean circulation and eddy processes (Andrews and McIntyre, 1976; Dunkerton, 1978; Holton, 1981; Garcia and Solomon, 1983). Under these conditions, the transport of species is provided by the diabatic circulation in thermally direct cells (rising motions in the tropics and sinking motions at high latitudes) as qualitatively depicted by the early "Brewer-Dobson" circulation. From observed temperature distributions and precalculated diabatic heating rates, the diabatic circulation (denoted here with the notation $\bar{v}^\star$ and $\bar{w}^\star$ which is commonly used for the residual circu-

lation) which under certain circumstances is identical to the diabatic circulation, see, e.g., Dunkerton (1978), is computed for 4 seasons (December–February, March–May, June–August, September–November) using the continuity equation and the thermodynamic equation (see Stordal et al. (1985)):

$$\delta\bar{\theta}/\delta t + \bar{v}^\star\,\delta\bar{\theta}/\delta y + \bar{w}^\star\,\delta\bar{\theta}/\delta z = \overline{Q}. \tag{1}$$

Here overbars denote zonal mean, θ is the potential temperature, $v^\star$ and $w^\star$ are the diabatic velocities in meridional (y) and vertical (z) directions.

The source term $\overline{Q}$ represents various diabatic heating processes including, in the stratosphere, heating (and cooling) by solar (and infrared) radiation, and in the troposphere also release of latent heat. As pointed out by Stordal et al. (1985), the obtained diabatic circulation is very sensitive to the adopted heating rates. In the present work, the heating rates used for the derivation of the circulation are described in Isaksen and Stordal (1986).

In the real stratosphere, since waves are not quite steady and conservative, it is necessary to include diffusion terms to simulate the non stationary eddy transport processes in the continuity equation of the species:

$$\delta\bar{\mu}/\delta t + \bar{v}^\star\,\delta\bar{\mu}/\delta y + \bar{w}^\star\,\delta\bar{\mu}/\delta z$$
$$= \overline{S} + 1/\rho\cos\varphi\,\delta/\delta y(\rho\cos\varphi\,K_{yy}\,\delta\bar{\mu}/\delta y)$$
$$+ 1/\rho\,\delta/\delta z(K_{zz}\,\delta\bar{\mu}/\delta z). \tag{2}$$

Here μ is the mixing ratio, S refers to the net chemical sources and sinks, φ is the angle of latitude and ρ is the air density.

The values used for K_{yy} and K_{zz} are the same as used by Stordal et al. (1985); 3×10^9 cm^2 s^{-1} and 10^3 cm^2 s^{-1} respectively. In the troposphere, the diffusion is dominated by non stationary processes. Therefore larger diffusion coefficients are applied (Isaksen and Rodhe, 1978; Stordal et al., 1985).

Chemical reactions involve oxygen (O, O(^{1}D), O$_3$), hydrogen (H, OH, HO$_2$, H$_2$O$_2$), carbon (CO*, CH$_4^\star$, CH$_3$, CH$_3$O, CH$_3$O$_2$, CH$_2$O, CHO, CH$_3$OOH), nitrogen (N$_2$O*, HNO$_3^\star$, N, NO, NO$_2$, NO$_3$, N$_2$O$_5$, HNO$_2$, HO$_2$NO$_2$) and chlorine (CCl$_4^\star$, CH$_3$Cl*, HCl*, Cl, ClO, HOCl, ClONO$_2$) species. Species with a star denote long-lived species which are transported individually in the model. For the other components the

family approach is taken and only the family quantities are transported. The chemical scheme is given in Stordal et al. (1985) and by Isaksen and Stordal (1986). In all the presented experiments, only a background level of 1 ppb of stratospheric chlorine is used, originating from the source gases CH_3Cl and CCl_4.

The experiments presented here are based on time dependent integrations. The model describes annual cycles due to seasonal variations in the solar declination, the temperatures and the diabatic circulation. Cyclic variations on the 11-year time-scale are also described, since three of the NO_y sources undertake variations on this time-scale. The way this is parameterized is described below. The experiments have been run until the seasonal and 11-year variations repeat themselves.

Although the primary photochemical variations during the 11-year solar cycle stem from the altered photon fluxes and photodissociation rates, important changes in the chemistry arise from the induced temperature variations, which influence the temperature dependent chemical kinetic rates. We find significant ozone changes due to the solar cycle variations. Since the major heating within the stratosphere occurs through the solar radiation absorption by O_3, changes in temperatures and dynamics can be expected. In the present calculations we have assumed that the adjustment to changes in the solar heating is purely radiative (Fels et al., 1980) through infrared relaxation:

$$\Delta T = \tau \Delta H. \tag{3}$$

ΔH is the heating rate as calculated in the present model (by O_3 and NO_2), τ is the thermal relaxation time for which we have taken values from the recent studies of Kiehl and Solomon (1986) and Gille and Lyjac (1986).

Eq. (3) is a reasonable approximation in most of the stratosphere, since the changes in the meridional gradients of the heating is moderate, and thus the meridional circulation is only moderately influenced. On the other hand, Chanin et al. (1987) have measured large temperature variations from 1979 (solar maximum) to 1985 (solar minimum), apparently induced by variability in the planetary wave activity. Their measurements only cover half a solar cycle so it is still uncertain whether the observed temperature

changes are induced by solar variability. In case they are, wave activity will influence the temperatures to a greater extent than the changes in the solar heating rates, especially during the winter.
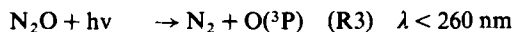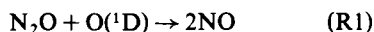
The region of the model where the temperature changes are less well described by eq. (3) is the lower stratosphere (Fels et al., 1980) where dynamical heating plays a significant role. Brasseur and Hitchman (1988) and Eckman et al. (1987) have pointed to the problems of calculating temperature changes in this region, where also the emission and absorption of infrared radiation by ozone is noticeable.

3. Specification of nitrogen oxide sources and modulations by the 11-year solar cycle

Nitrogen oxides are emitted from the Earth's surface (anthropogenic and biogenic processes) as well as produced directly within the atmosphere by various mechanisms including lightning, GCRs, N_2O oxidation, ionization and predissociation of nitrogen in the thermosphere and mesosphere. They can also be produced by thermal decomposition of N_2 and O_2 during meteor fall or nuclear tests, by ion chemistry during solar proton events or by nitrogen dissociation by enhanced X-rays or short ultraviolet (UV) light following supernovas (see Jackman et al., 1980 for review of these phenomena). In this paper we have not considered these sporadic sources, but only the sources described below.

3.1. N_2O oxidation

Nitrous oxide, continuously released from the Earth's surface by both anthropogenic and natural processes is destroyed within the stratosphere by photolysis and by reactions with $O(^1D)$:
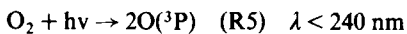
$$N_2O + O(^1D) \rightarrow 2NO \qquad (R1)$$

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \qquad (R2)$$

$$N_2O + h\nu \quad \rightarrow N_2 + O(^3P) \quad (R3) \quad \lambda < 260 \text{ nm}$$

Reaction (R1) constitutes the main source of stratospheric NO_y. In the stratosphere, the $O(^1D)$ atom is produced mainly by the O_3 photolysis in

the Hartley Band:

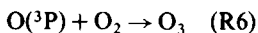$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (R4) \quad 200 < \lambda < 310 \text{ nm}$$
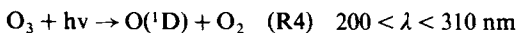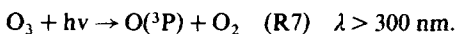
O_3 is also affected by the photolysis of O_2 in the Hertzberg continuum $(200 < \lambda < 240 \text{ nm})$ and Schumann-Runge bands $(\lambda < 200 \text{ nm})$:

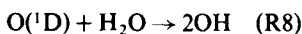$$O_2 + h\nu \rightarrow 2O(^3P) \quad (R5) \quad \lambda < 240 \text{ nm}$$

followed by:

$$O(^3P) + O_2 \rightarrow O_3 \quad (R6)$$

and by the photolysis of O_3 in the Huggins band:

$$O_3 + h\nu \rightarrow O(^3P) + O_2 \quad (R7) \quad \lambda > 300 \text{ nm}.$$

$O(^1D)$ plays a significant role in the stratosphere by initiation of photochemical activity through the reaction with water vapour:

$$O(^1D) + H_2O \rightarrow 2OH \quad (R8)$$

Any photon flux change should provide modification of the $O(^1D)$ production and therefore on production of NO_y (R1) and on stratospheric chemistry in general through reaction R8. A direct influence of NO_y change on ozone will come from the pair of reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R9)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (R10)$$

It is clear that NO_y changes are largely controlled by photon flux variations and the changes in the chemistry induced by ozone changes. The response in NO_y is therefore a result of a complex stratospheric chemistry.

A major uncertainty in estimates of solar cycle impacts on stratospheric chemistry is due to a lack of accurate measurement of UV light $(\lambda < 310 \text{ nm})$ over the 11-year solar cycle. The early proposed large increase (80% at 200 nm, 35% at 250 nm: Heath and Thekaekara, 1977) has not been confirmed by more recent measurements. Garcia et al. (1984) used more moderate variations, based on results obtained with the model of Lean et al. (1982), namely 20% at 185–200 nm, 11% at 210–240 nm, 5% at 260 nm and 0% above 300 nm. In a recent review on solar cycle variations (Lean, 1987) these values were regarded as an upper limit. The numbers used in this study are still lower, and are based on SBUV data and the analyses of Heath and Schlesinger (1984; 1986). The following perturbations are

used: 12% at 175–190 nm, 10% at 190–210 nm, 4% at 210–240 nm, 3% at 240–260 nm and 1% at 260–300 nm. Even these changes are now considered to be an upper limit (WMO, 1986), since the SME data show smaller changes (Rottman and London, 1984; Rottman, 1985). The present calculations ignore the observed asymmetry of the solar cycle since a simple sine variation of the solar fluxes is assumed.

3.2. Thermospheric and mesospheric sources

Large production of NO occurs in the thermosphere via the nitrogen dissociation provided by photolysis and especially in auroral zones by the action of relativistic electron precipitation (e*):

$$N_2 + h\nu \rightarrow 2N \quad (R11) \quad \lambda < 100 \text{ nm}$$

$$e^* + N_2 \rightarrow 2N + e \quad (R12)$$

$$N + O_2 \rightarrow NO + O \quad (R13)$$

In these upper layers, NO molecules are efficiently destroyed:

$$NO + h\nu \rightarrow N + O \quad (R14) \quad \lambda < 190 \text{ nm}$$

$$NO + N \rightarrow N_2 + O \quad (R15).$$
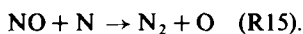
Using a 2-D model with coupled chemistry and dynamics, Garcia et al. (1984) showed that during the polar winter, downward transport from the thermosphere supplies the upper stratosphere at high latitudes with NO_y. During summer, this source is considerably reduced because firstly NO is rapidly photolyzed (R14), secondly the large scale transport opposes downward diffusion. One interesting feature of this source of NO_y in the upper stratosphere is that there is believed to be a strong modulation due to solar cycle variations. Satellite measurements showed high nighttime NO_2 abundance near the winter stratopause during a year of high solar activity (1979), lending support to the above considerations (Russel et al., 1984). In order to simulate the impact of the thermospheric source on the stratospheric budget of NO, we have applied the following boundary conditions in our calculations: a downward flux $(\Phi\downarrow)$ of NO at the stratopause for latitudes higher than 50° in the winter hemispheres. We have modulated the flux in accordance with solar activity: maximum flux $(\Phi_m\downarrow)$ during the years of solar maximum, reduced to zero at the years of

minimum solar activity. Jackman et al. (1980) estimated the downward flux at the winter mesopause to be in the range 2.3 to 5.6×10^7 NO molecules $cm^{-2} s^{-1}$. In this work, calculations are performed by adopting two different values of $\Phi_m \downarrow$ at the stratopause: 2×10^7 and 6×10^7 molecules $cm^{-2} s^{-1}$.

It should be noted that large uncertainties are connected with the understanding of the thermospheric and mesospheric source of NO_y. In a recent paper Baker et al. (1987) suggest that the energies of relativistic electrons are greater than assumed earlier. They have even measured a solar cycle variation in the electron precipitation which is out of phase with the 11-year solar cycle.

3.3. Galactic cosmic rays

Galactic cosmic rays (very energetic proton precipitation) deposit their energy in the lower stratosphere and in the troposphere, producing NO molecules via dissociative ionization and dissociation of nitrogen. Nicolet (1975) estimated this ion production to have a maximum between 12 and 13 km elevation. This source is more efficient at high latitudes. During periods of high solar activity, intense solar wind occurs, partly deflecting the GCR from the Earth's magnetic field. Thereby NO production varies in opposite phase to the 11-year solar cycle. We have used Nicolet's (1975) spatial and temporal ion production rates and have assumed that in an average 1.25 molecule of NO is produced per ionization event (see Jackman et al., 1980).

3.4. Lightning

As proposed by Noxon (1976), the fixation of nitrogen by lightning via a thermal decomposition of O_2 and N_2 is a potential main source of nitrogen oxides in the free troposphere. Although there are large uncertainties in the global strength of this source (1 to 40 MT per year have been proposed), it appears now to be a growing consensus among workers that the global production ranges between 1 and 8 MT per year (Borucki and Chameides, 1984). The latitudinal distribution adopted in this work assumes a production largely confined to tropical areas (30°N to 30°S) with a maximum near 10°N in accordance with satellite data (Orville and Spencer, 1979). Due to the very effective scavenging of nitric acid near the ground, the global impact of this source

highly depends on its height distribution. Although the height distribution of instantaneous production rates is not well established, the role of cloud-to-cloud and in-cloud discharges (less energetic but more frequent than cloud to ground discharges, Ogawa, 1982) should be important. Here we have adopted production rates which decrease slightly from the ground up to 15 km elevation, with a relative maximum at 10 km elevation. The global strength used in the model (2.8 MT per year) is taken from Borucki and Chameides (1984).

3.5. Surface sources

In this work, anthropogenic and biogenic productions are distributed latitudinally according to the industrial and biological activity (94% and 55% respectively of the global releases are in the Northern Hemisphere (Isaksen, 1979)).

4. Influence regions for the various NO_y sources

The global NO_y production from N_2O oxidation is estimated to 0.7 MT per year in our model. This result agrees well with previous estimates (0.56 MT from Nicolet and Vergison, 1971; 1.0 MT from Johnston et al., 1979; 1.1 MT from Jackman et al., 1980) and with a recent estimation by Crutzen and Schmailzl (1983) (0.4–0.7 MT per year) which is deduced from the N_2O distribution provided by satellite data. The altitudinal and latitudinal distribution of the production rates resulting from the present experiments is depicted in Fig. 1. In the winter hemisphere NO_y production drops off at high latitudes (>60°), the peak production (about 250 NO molecules $cm^{-3} s^{-1}$) occurs at 30 km elevation near the tropics. During spring and fall the peak production is located near the Equator and the production remains significant at high latitudes. This feature points clearly to the role of $O(^1D)$ and the expected effect of insolation.

As pointed out in Table 1, surface sources are larger by one order of magnitude than atmospheric sources (except perhaps lightning). However due to an efficient dry and wet deposition at the surface and in the troposphere, the contribution from the surface sources on the odd nitrogen budget of the stratosphere is thereby

strongly reduced. This phenomenon is clearly shown in the NO_y distribution in Fig. 2. Indeed, the asymmetry of the NO_y concentrations (annual values) between the hemispheres is very important in the boundary layer as a result of the larger anthropogenic emissions in the Northern Hemisphere (see Table 1). This difference disappears near 19 km elevation indicating a weak contribution of surface sources at this level.
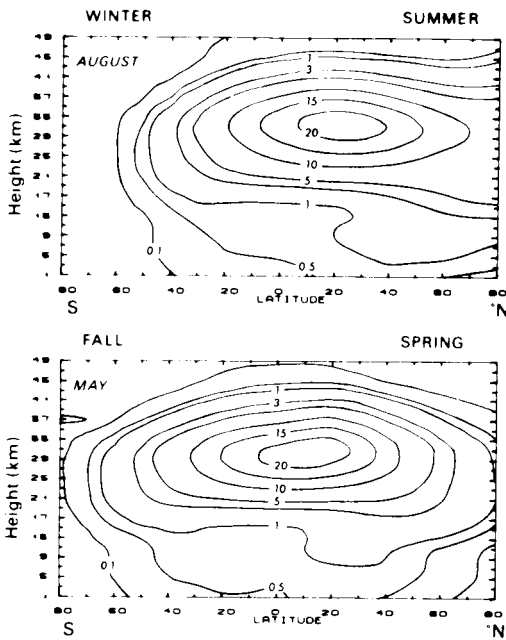
The latitudinal and height distribution of odd nitrogen produced by lightning has recently been evaluated by Ko et al. (1986). Their 2-D model study points to a large contribution from this source at the equatorial tropopause. Using the above described lightning source our model confirms this result. To determine the impact of the lightning source, a control experiment was performed, in which this source was omitted. Fig. 3 shows the increase in NO_x due to inclusion of the lightning source. Large increases are found in tropical areas, where the lightning is seen to be the dominating source of the NO_x concentrations in the upper troposphere. Furthermore the increase remains significant at high latitudes (10% at 17 km, 40% at the polar tropopause in spring, Fig. 3). This large latitudinal expansion of the
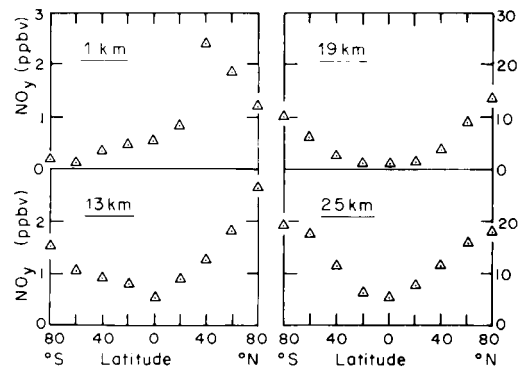

Fig. 1. NO_y production rates provided by N_2O oxidation (10 molecules cm^{-3} s^{-1}).

Fig. 2. Calculated latitudinal distribution of NO_y in ppbv (provided by all the sources) at various elevations. The anthropogenic source is given for the year 1986.

Table 1. *Listing of NO_y sources used in the model and their respective region of influence (see discussion in Section 4)*

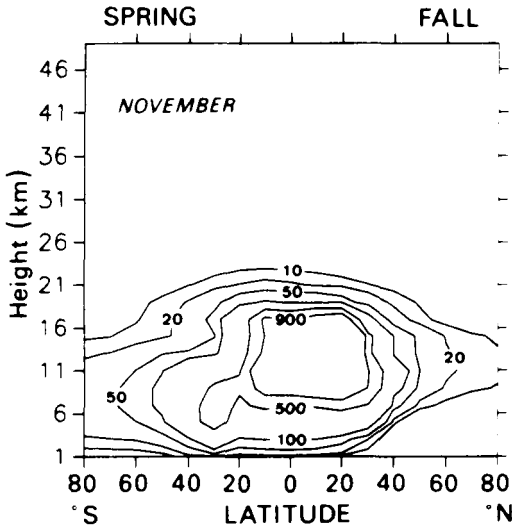| Source	Location	Altitude region of influence	Strength (MT N yr^{-1})
anthropogenic source	surface (94% NH)	troposphere	14.4
soil exhalation	surface (55% NH)	troposphere	10.8
lightning	troposphere (0–15 km)	troposphere + lower stratosphere	2.8
N_2O oxidation	stratosphere (20–50 km)	stratosphere	0.7 (calculated, see text)
galactic cosmic rays	stratosphere + troposphere (5–30 km)	stratosphere + troposphere	solar maximum 0.06, solar minimum 0.086 (Nicolet, 1975; Jackman et al., 1980)
input from the mesosphere	thermosphere >85 km	mesosphere + auroral winter stratosphere	solar maximum 0.003–0.01, solar minimum ~0 (see text)

Fig. 3. Percentage increase in NO_x when lightning source is considered.
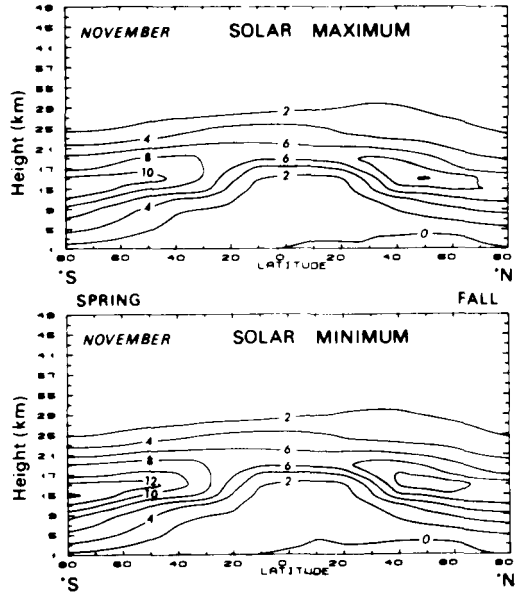

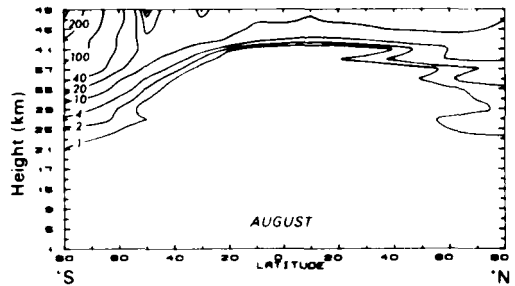Fig. 4. Increase (in %) of NO_x when GCRs are considered, during solar maximum and solar minimum.

Fig. 5. Percentage change in NO_y from solar minimum to solar maximum for near solstice conditions, when a maximum downward flux ($\Phi_m\downarrow$) equal to 6×10^7 molecules cm^{-2} s^{-1} is considered.

lightning production reflects partly the effect of the diabatic circulation: due to the rising motion in tropical areas, the lower stratosphere is supplied by an important part of the NO_y produced by lightning within the troposphere.

The instantaneous NO production from GCRs exhibits a maximum between 12 and 13 km elevation at all latitudes (Nicolet, 1975). When this source is added to the other sources, NO_x concentrations increase by 6% at solar maximum (see Fig. 4) at 21 km elevation in tropical areas. This GCR contribution is twice as high in polar regions (12% at 13 km elevation at solar maximum).

The contribution from thermospheric NO_y can be examined from Fig. 5 which shows the percentage increase in NO_y from solar minimum ($\Phi\downarrow = 0$) to solar maximum ($\Phi_m\downarrow = 6 \times 10^7$ NO molecules cm^{-2} s^{-1}) in an experiment in which solar cycle variations in the other sources (N_2O oxidation and GCRs) has been omitted. As expected, the contribution from the thermosphere appears to be very large at the winter stratopause at high latitudes but is strongly reduced at low latitudes. During the summer the contribution is very small. Calculating the height variation and comparing with previous estimates of Garcia et al. (1984) it is concluded that $\Phi_m\downarrow$ is likely to range between 2 and 6×10^7 NO molecules cm^{-2}

s^{-1}. As rather high values of K_{zz} were applied by Garcia et al. (1984) (3×10^5 cm^2 s^{-1} at 50 km elevation, see Garcia and Solomon, 1983) compared to our values (10^3 cm^2 s^{-1}), they obtain a more pronounced effect at low altitudes (Fig. 6). However, in later versions of their model, they have significantly reduced the K_{zz} values (Solomon and Garcia, 1984; Solomon et al., 1985).
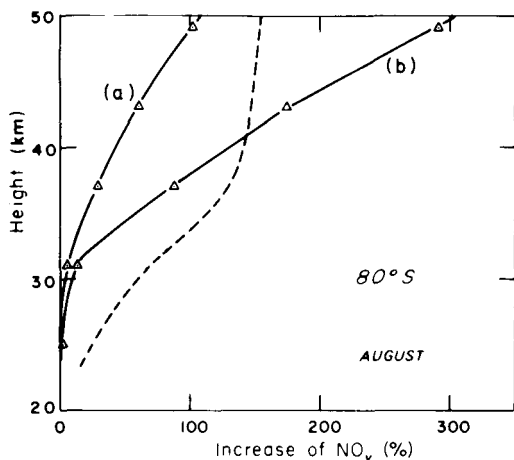
Fig. 6. Increase (in %) of NO_y from solar minimum to solar maximum conditions, provided by the thermospheric source, as a function of the elevation during winter. Solid lines and triangles refer to this work: (a) and (b) using $\Phi_m\downarrow$ values equal to 2 and 6×10^7 molecules cm^{-2} s^{-1} respectively. The dashed line represents the results from Garcia et al. (1984).

From the above considerations, relative contribution of surface sources, lightning, GCRs, N_2O oxidation and thermospheric source on the local NO_y budget can be examined (see Table 2). In the middle stratosphere, at least at low latitudes, NO_y is exclusively provided by the oxidation of N_2O. In the high stratosphere, where N_2O oxidation still is preponderant, the thermospheric production can be significant at high latitudes (especially at solar maximum in the darkness). At lower layers, the contribution of lightning and GCRs become significant. Indeed, at the equatorial tropopause we find that almost half of NO_x is provided by lightning and more than a quarter (3 times higher than by GCRs) at the polar tropopause.

5. Response to 11-year solar cycle variations

5.1. Mesospheric and thermospheric production

As previously discussed, in the upper stratosphere, thermospheric NO_y production induces large variations at high latitudes in winter in phase with the solar cycle; 100% and 300% increase in NO_y from solar minimum to solar maximum for $\Phi_m\downarrow$ equal to 2×10^7 and 6×10^7 molecules cm^{-2} s^{-1} respectively (see Figs. 5 and 6). Fig. 5 shows very weak variations in the lower stratosphere even when the highest value of $\Phi_m\downarrow$ is considered (1% increase at 21 km, 10% at 30 km). In the lower stratosphere the modulation of NO_y occurs with a pronounced delay compared to the modulation in the flux from the mesosphere. Fig. 7 shows that the delay at the 19 km level at 80°S is about 2 years. At the 30 km level the delay is about 1 year (not shown). These delays are considerably longer than the vertical transport times from the stratopause to the respective locations. Further investigations reveal that this is due to a recirculation of the excess NO_y in the stratosphere. NO_y is diffused horizontally from high towards low latitudes where it is transported to higher levels again with the diabatic circulation (Stordal, 1988).

5.2. Solar photon fluxes and N_2O oxidation

We have examined the photochemical response of stratospheric odd nitrogen to the previously specified changes in photon fluxes during the solar cycle. Since the NO_y production is caused by oxidation of N_2O by $O(^1D)$, a detailed calculation of the ozone chemistry is involved. Although the present investigation is based on complete ozone chemistry, the discussion here will be directed strictly towards the NO_y variations. Fig. 8a depicts percentage

Table 2. *Relative contribution (in %) of the various NO_x; sources at different locations of the lower stratosphere*

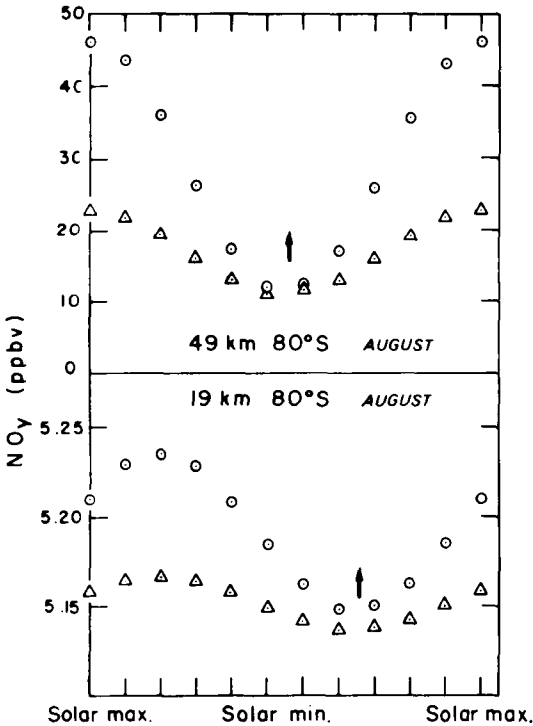| Sources	Equatorial tropopause	Equator 25 km elevation	Polar tropopause	80°S 19 km elevation
surface sources	insignificant	insignificant	} 64%	insignificant
N_2O oxidation	31%	86%		83%
lightning	63%	10%	27%	6%
GCRs	6%	4%	9%	12%
thermosphere	insignificant	insignificant	insignificant	<1%

Fig. 7. NO$_y$ modulation (ppbv) at 80°S in winter in the upper (49 km) and lower (19 km) stratosphere due to an 11-year variation in a thermospheric/mesospheric source. Triangles and circles refer to the case with a $\Phi_m\downarrow$ equal to 2×10^7 and 6×10^7 molecules cm^{-2} s^{-1}, respectively. Arrows show the delay between high and low-layer modulation.

changes in NO$_y$ from solar minimum to solar maximum as well as some other components.

The main loss mechanism for N$_2$O is photodissociation in the stratosphere (R3). N$_2$O (Fig. 8b) therefore decreases from solar minimum to solar maximum. The decrease is most pronounced at high altitudes, where the dissociation is strongest. At the stratopause level N$_2$O decreases by more than 15% at all latitudes. In the entire stratosphere the variations in O(^{1}D) (Fig. 8c) are smaller in magnitude than the N$_2$O variations, so that N$_2$O will dominate the variations in the NO$_y$ production.

O(^{1}D) (Fig. 8c) increases in the upper part and decreases in the lower part of the stratosphere. In the sunlit part of the stratosphere the variations range from -2.5 to $+3.5$%. O(^{1}D) is therefore partly counteracting and partly strengthening the

variations in NO$_y$ production caused by N$_2$O. The variation in O(^{1}D) is strongly connected to the variations in ozone. Fig. 8d shows that O$_3$ increases with the solar fluxes in the upper and middle stratosphere. This is due both to the increased production of O$_3$ initiated by the dissociation of O$_2$ (R5), and a less efficient ozone loss by nitrogen oxides (R9 and R10), as schematized in Fig. 9. The latter of these effects contributes only modestly near the stratopause, but becomes increasingly important lower down in the stratosphere where NO$_y$ induced loss makes a large fraction (50% at 35 km, see Stordal and Isaksen, 1987) of the total ozone loss. The largest changes in the temperatures resulting from the ozone changes occur at the stratopause level, where the temperature varies 1.3 K at low latitudes during one solar cycle.

Although N$_2$O and O(^{1}D) concentrations vary in opposite directions at some altitudes the larger N$_2$O change provides a net decrease in odd nitrogen species (R1) from solar minimum to solar maximum conditions. In the upper stratosphere, increased dissociation of NO (R14) during solar maximum conditions also contributes to NO$_y$ decrease.

The response in NO$_y$ due to 11-year solar cycle variations has been simulated in other models: 4% increase of NO$_x$ was proposed by Penner and Chang (1980), whereas Brasseur and Simon (1981) computed 5% decrease from solar minimum to solar maximum. These studies both used larger variations in the UV fluxes. Besides, Penner and Chang (1980) based their computations on a one-dimensional model which will not represent the transport of all the species involved properly.

The hydroxyl radical OH (Fig. 8e), which is involved in many important chemical cycles, also varies with the solar cycle. Its variation is very much like the one of O(^{1}D), since OH is formed when O(^{1}D) reacts with water vapour. The OH variation is shown here because of the variation it causes in the partitioning between HNO$_3$ (Fig. 8f) and the other odd nitrogen species, NO$_x$ (given in Fig. 8g). In most of the stratosphere the balance is shifted in the disfavour of HNO$_3$ during solar maximum conditions. Only in the lower stratosphere this can be explained by the reduction in OH there which suppresses the formation of HNO$_3$ from NO$_2$. In the upper
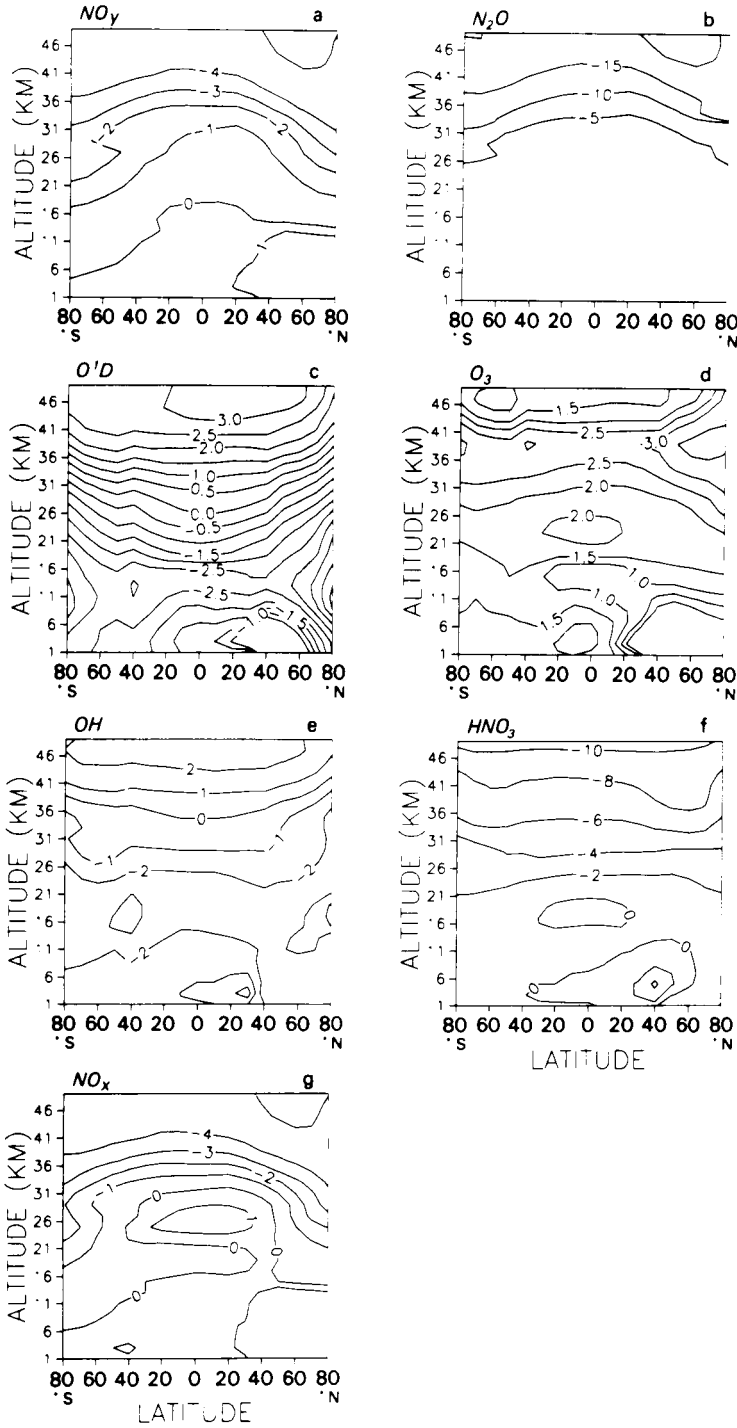
Fig. 8. Percentage change in the concentrations of various species due to modulation of the solar fluxes, from solar minimum to solar maximum conditions (given as (max–min)/min × 100%). The results represent March conditions.
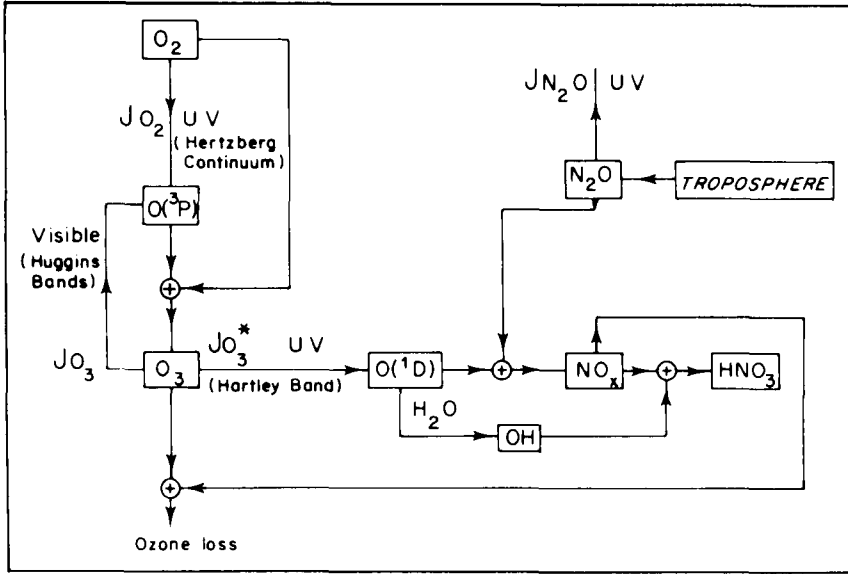
Fig. 9. Principal reactions occurring within the stratosphere between O_x and NO_x species, and HNO_3 and N_2O.

stratosphere HNO_3 is also reduced compared to NO_x, in which case it is due to a stronger dissociation of HNO_3 during solar maximum.

HNO_3 undergoes relatively large variations in the upper stratosphere; 10% near the stratopause, almost as pronounced as N_2O. In the lower stratosphere, however, the variations are considerably smaller for HNO_3 as well as NO_x. In the same way as discussed in Section 5.1 the variations in NO_x and HNO_3 are delayed in the lower stratosphere. Fig. 10 shows the time variation of NO_x and HNO_3 at 19 and 37 km near the South Pole during the course of a solar cycle. The figure demonstrates that near the region of maximum production of odd nitrogen (the 37 km level) the variations are in phase with the solar intensity. Down to 19 km there is a pronounced delay, about 2 years. This points to the fact that the numbers given in Fig. 8, depicting changes from solar minimum to solar maximum conditions, will be smaller than the range of the variations in the lower stratosphere; e.g., at the 19 km near the South Pole, the peak to peak variation of HNO_3 and NO_x is 2.6% and 3.0%, respectively.

5.3. Galactic cosmic rays

As discussed above, the region where the GCRs have the largest impact on the odd nitro-

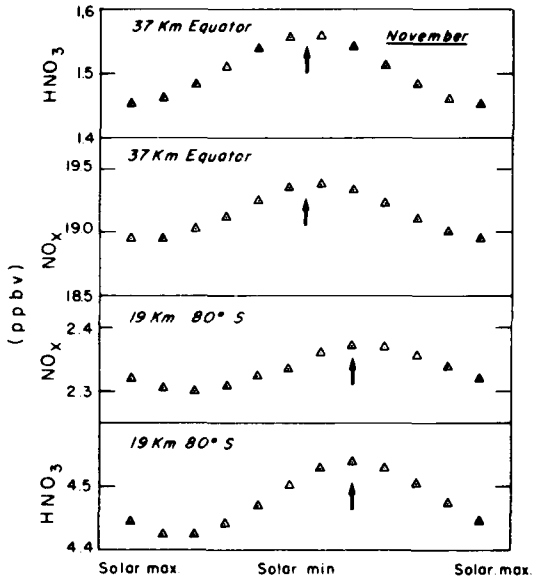Fig. 10. Calculated concentrations of NO_x and HNO_3 (in ppbv) during one solar cycle (November) at 80°S (19 km elevation) and at the equator (37 km elevation) in the experiment where solar cycle variations in the solar fluxes are included.

gen budget is the lower stratosphere. The variation during the sunspot cycle is relatively weak. A comparison between panels (a) and (b) in Fig. 4 shows maximum NO_x variation of 1% at low

and 2% at high latitude in the lower stratosphere as a consequence of the 11-year variation in the GCR source. Note that this variation has a phase which is opposite to the solar variation. In contrast to the variations discussed in the two previous sections there is no delay in the response, because the GCRs act as a local source in the lower stratosphere.

6. Geochemical implications

Our study of the NO_y response to the 11-year solar cycle allows us to conclude that in the lower stratosphere maximum variations of about 4% of NO_x as well as HNO_3 are produced and it is in almost opposite phase with the 11-year solar cycle (it could be up to 2 years delayed compared to the exact opposite phase). Parker and Zeller (1979), Zeller and Parker (1981) and Laird et al. (1982) claimed to have observed strong variations (in phase with solar activity) of nitrate deposition in antarctic snow. Assuming that nitrate present in antarctic precipitation is provided exclusively from the stratospheric reservoir the increase of nitrate observed by these authors is in the order of 100% between solar maximum and solar minimum. These previous results were not confirmed by other studies performed in Greenland (Herron, 1982) and also in Antarctica (Legrand and Delmas, 1984; 1986). A new set of measurements performed recently by Zeller et al. (1986) gave increase of nitrate fluxes in relation with sporadic solar events such as the 1972 solar proton event, but no convincing evidence of modulation over a solar cycle was seen. Therefore despite results reported in earlier studies, the connection between solar activity and nitrate deposition at high latitudes remains an open question. A possible role of ice particles present in the stratosphere at high latitudes has been alluded to provide greater NO_x and HNO_3 variations within the troposphere than those calculated by models at the tropopause level (Garcia et al., 1984). However, the fact that these ice particles are mainly formed during winter disagrees with the observation of maximum HNO_3 content in antarctic snow during summer (Legrand and Delmas, 1984). Sudden very strong downward air motions which occurs sporadically at these high latitudes can possibly enhance the

transport of NO_x and HNO_3 further down. This is however not supported by observations made by Herron (1982) and by Legrand and Delmas (1986) of nitrate antarctic profiles which exhibit rather smooth variations.

7. Conclusions

We have used a two-dimensional model to study: (a) the impact of various NO_y productions (surface sources, lightning, N_2O oxidation, galactic cosmic rays, input from the thermosphere) in general, and (b) the response of the stratospheric NO_y to the 11-year solar cycle in particular.

Although the N_2O oxidation is the dominant NO_y production process throughout the stratosphere, other sources contribute to the NO_y budget in certain regions. Firstly at the tropopause, in equatorial (70% of NO_x) and polar (30% of NO_x) regions, NO_y is produced by both lightning and galactic cosmic rays. Secondly, near the high latitude stratopause, the downward transport of NO_y from the thermosphere can play a dominant role in winter especially during time periods of high solar activity.

The response of the stratospheric NO_y to the 11-year solar variations is simulated by modulating GCR production, NO_y downward flux from the thermosphere and UV fluxes between solar maximum and solar minimum. The main response is likely to come from the N_2O oxidation (modulated by UV light), although, as discussed above the variation of the solar fluxes are still not very accurately known. The UV modulation provides NO_y changes in opposite phase with solar activity. Even strengthened by the GCR effect (especially in the lower stratosphere), the resulting effect remains modest (3 and 7% changes at 35 km elevation for NO_x and HNO_3, respectively, and about 4% at 19 km elevation). The crude approximation of temperature changes in the lower stratosphere and the lack of dynamical feedback in the model will most significantly influence the calculated NO_y variations in the lower stratosphere. However, accurate treatment of all feedback mechanisms is not believed to alter the conclusion that the changes in NO_y in the lower stratosphere, due to the 11-year variations in the processes considered, are moderate.

In addition to the variations in the lower

stratosphere, which are almost in opposite phase with solar cycle, there is a modulation of the thermospheric and mesospheric sources which appears significant only near the polar winter stratopause. In the model simulations, this modulation has been assumed to be in phase with solar cycle. A recent work of Baker et al. (1987) raises the possibility that the modulation could be stronger than assumed, and even in opposite phase with the solar cycle.

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