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Understanding trends in stratospheric NO_y and NO_2

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Abstract. Nitrous oxide (N_2O), an important greenhouse gas, has been increasing since 1980 at a rate of about +3% per decade. Recently, a notably greater rate of increase of about +5% per decade since 1980 was reported for measurements of stratospheric nitrogen dioxide (NO_2) over Lauder, New Zealand. Since N_2O is the dominant source of odd-nitrogen compounds in the stratosphere, including NO_2, this presents an obvious conundrum. Analysis here shows that these apparently conflicting trends are generally consistent when viewed in a global-change framework, specifically, when concurrent trends in stratospheric ozone and halogens are included. Using a combination of photochemical and three-dimensional chemistry-transport models, we predict a 1980–2000 trend in the NO_2, as measured over Lauder, New Zealand, of +4.3%/decade when these concurrent trends are considered. Of this, only +2.4%/decade is attributed directly to the increase in N_2O; the remainder includes +2.5%/decade due to the ozone change and −0.6%/decade to the increased halogens' impact on odd-nitrogen partitioning. The slant column densities of NO_2, as measured from the zenith scattered sunlight during twilight, are found to (1) overestimate the trend by +0.4%/decade as compared to the true vertical column densities and (2) display a diurnally varying trend with a maximum during the night and large gradients through sunrise and sunset in good agreement with measurement. Nonetheless, measurements such as these are essential for identifying global change and provide a lesson in understanding it: careful simulation of the time, location, and geometry of measurements must be combined with concurrent trends in related chemical species and climate parameters.

1. Introduction

Global change, including trends in atmospheric chemical composition, is usually complex and fueled by many interacting and competing components. A thorough understanding of such change, as well as a correct interpretation of its ramifications, requires realistic modeling of all components. An excellent example of this is provided by a recent report of stratospheric nitrogen dioxide (NO_2) trends from Lauder, New Zealand (45°S, 170°E). On the basis of measurements of zenith scattered visible sunlight between 1981 and 1999, stratospheric NO_2 over Lauder was observed to be increasing

at a rate of ~5%/decade [*Liley et al.*, 2000]. It is difficult to obtain vertical profiles from this technique, and even the retrieval of vertical column densities (VCDs, or the vertically integrated number density profile) requires some knowledge of the profile shape [*McKenzie et al.*, 1991]. Thus the measured trend is reported in terms of slant column densities (SCDs), a quantity described as the integrated path of the sunlight, from the top of the atmosphere to the instrument, weighted at each point with the local NO_2 number density.

The primary source of stratospheric odd nitrogen, NO_y (the sum of all reactive nitrogen species, including NO_2), is nitrous oxide (N_2O). In addition to being the source of NO_y which controls the abundance of stratospheric ozone, N_2O is also an important greenhouse gas. Primarily because of anthropogenic perturbations to the global nitrogen cycle [*Mosier et al.*, 1998], N_2O has steadily increased from a preindustrial value of ~275 ppb (10^{-9} mole fraction relative to dry air) to about 300 ppb in 1980 [*Prinn and Zander*, 1999]. However, the recent rate of N_2O growth has been placed at only 2.5–3.0%/decade, barely half that of NO_2.

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Unless these differing trends are examined in global-change framework, they will remain incompatible (within our current understanding). Specifically, the concurrent change in stratospheric ozone [*Bojkov and Hudson*, 1999], increase in halogens (inorganic chlorine, Cl$_y$, and bromine, Br$_y$; *Prinn and Zander*, 1999), cooling of the stratosphere [*Chanin and Ramaswany*, 1999], and possibly changes in stratospheric sulphate abundance [*Godin and Poole*, 1999] must be considered as they will all impact stratospheric NO$_2$. In this study we attempt to reconcile these apparently conflicting growth rates by estimating the decadal trends in NO$_y$ and NO$_2$ through the use of atmospheric models and these other measured atmospheric changes. Further, we seek to quantify how each of these components contributes to the overall trend.

2. Simulating Stratospheric Trends

2.1. Atmospheric Models

Three modeling tools have been employed in this study. The first model is the University of California, Irvine (UCI) chemical transport model (CTM) [*McLinden et al.*, 2000; *Olsen et al.*, 2001] driven by meteorological fields from the Goddard Institute for Space Studies (GISS) general circulation model (GCM), version II [*Rind et al.*, 1988].

The UCI CTM employs an N$_2$O–NO$_y$ chemistry based on a set of pre-calculated coefficients [*Olsen et al.*, 2001] which describe the N$_2$O loss frequency, the yield of NO$_y$ from N$_2$O loss, the NO loss frequency, and the fraction of photolyzed NO converted back to NO$_y$. Diurnal averages of these coefficients are tabulated as a function of altitude, latitude, and month. While simple, these co-efficients produce realistic stratospheric N$_2$O and NO$_y$ profiles, gradients, correlations, and lifetimes (Olsen et al., 2001). The tabulated chemical coefficients are calculated using zonal, monthly mean ozone [*McPeters*, 1993] and temperature [*Nagatani and Rosenfield*, 1993] climatologies. An expanded version of this chemistry is also used. Linearized ozone (or Linoz) [*McLinden et al.*, 2000], a third tracer, is linked to all the N$_2$O–NO$_y$ chemistry coefficients through a series of linearizations about local and column ozone. The feedback loop is closed as Linoz is allowed to respond to NO$_y$ through an additional linearization. This allows NO$_y$ to respond to the ozone perturbation it induces [see *Prather*, 1998].

The second model is a photochemical box model [*Prather*, 1992; *McLinden et al.*, 2000] which is used to calculate the coefficients for the chemistry described above and the NO$_2$:NO$_y$ ratios required to convert NO$_y$ into NO$_2$ profiles. The third model is a radiative transfer model [*Bassford et al.*, 2001; *McLinden et al*, 2001] and is used to generate the weighting functions which enable the calculation of NO$_2$ SCDs from number density profiles.

2.2. Trends in Stratospheric NO$_y$

The trend in stratospheric NO$_y$ from 1980 to 2000 is calculated as the difference between two steady state CTM simulations: a Y1980 with 300 ppb N$_2$O prescribed lower boundary condition and a Y2000 with 318 ppb. The above values were selected to correspond with a linear trend of +3.0%/decade in the N$_2$O growth rate despite the fact that a 2000 value of 316 ppb is likely more realistic (on the basis of a 1998 reported values of 314 ppb). Model NO$_y$ decadal trends (and model NO$_2$ decadal trends in Section 2.3) are calcu-

Table 1. Y1980 and Y2000 Prescribed Atmospheres

Quantity	Y1980	Y2000
Well Quantified Trends		
N$_2$O[a]	300 ppb	318 ppb
NO$_y$	determined by CTM	determined by CTM
O$_3$	climatology[b]	climatology+ observed trend[c]
Cl$_y$[d]	2.3 ppb	3.6 ppb
Br$_y$[d]	14 ppt	20 ppt
Sensitivity-Study Trends		
Temperature	climatology[e]	climatology −0.5 K/decade
Aerosols	Y1980 levels[f]	Y1980 levels ×0.9
Held Constant		
stratospheric H$_2$O	climatology[g]	climatology

[a]Lower boundary condition in chemical transport model (CTM).
[b]*McPeters* [1993].
[c]*Bojkov and Hudson* [1999, Figure 4-32].
[d]Value at 60 km, *Prinn and Zander* [1999].
[e]*Nagatani and Rosenfield* [1993].
[f]*Thomason et al.* [1997].
[g]*McLinden et al.* [2000].

Table 2. Annual Mean Stratospheric NO$_y$ Vertical Column Density Trends[a]

Trend Driver	Global	NH	SH	VCD at 45°S
N$_2$O trend	2.3	2.3	2.4	2.3
+ NO$_y$ induced O$_3$ trend[b]	2.4	2.4	2.5	2.5
+ chlorine induced O$_3$ trend[c]	3.0	2.8	3.2	3.4
+ a −0.5 K/decade temperature trend	2.4	2.2	2.6	2.8

Model results begin with a +3%/decade linear trend in N$_2$O (without feedbacks) and are cumulative with additional imposed trends.

[a]Vertical column density (VCD) trends are in %/decade.

[b]Obtained using coupled N$_2$O–NO$_y$–O$_3$ chemistry.

[c]*Bojkov and Hudson* [1999, Figure 4-32].

lated from the difference of these two simulations: $T = (CD_{2000}/CD_{1980} - 1) \times 50\%$, where T is the trend in %/decade and CD represents either stratospheric VCD or SCD. In addition to the increase in N$_2$O, other trends that impact NO$_y$ include ozone and temperature. As only a single year of GCM meteorology is used, the impact of changes in stratospheric circulation between Y1980 and Y2000 on NO$_y$ trends cannot be assessed. The specifications of the Y1980 and Y2000 atmospheres, including the assumed trends in various constituents, are listed in Table 1. Decadal trends in the annual mean stratospheric NO$_y$ vertical column density (VCD) are summarized in Table 2. The first line gives the trend due solely to an increase in N$_2$O (i.e., without any chemical coupling to ozone), while subsequent lines introduce additional effects which alter the NO$_y$ trend. Note that these effects are cumulative.

The impact of changing N$_2$O alone was simulated in the CTM by fixing the Y2000 O$_3$ to the climatology (that of Y1980). This results in an NO$_y$ increase of +2.3%/decade, a value which varies little with latitude. At 45°S the trend as a function of altitude varies from about +1.5%/decade in the upper and lower stratosphere to a maximum of +2.5%/decade near 25-30 km.

The less-than-proportional response of NO$_y$ to N$_2$O is the result of NO$_y$ photochemical loss in the upper stratosphere and mesosphere (∼30% of the total) being driven by reaction sequence (1) and (2a):

$$NO + h\nu \longrightarrow N + O \qquad (1)$$

$$N + NO \longrightarrow N_2 + O \qquad (2a)$$

$$N + O_2 \longrightarrow NO + O. \qquad (2b)$$
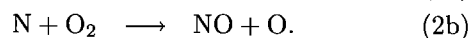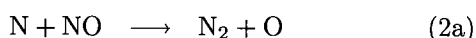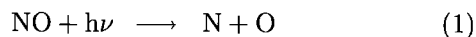
This loss rate is generally quadratic in NO$_y$ because most N reacts via (2b). Hence, if this were the only loss of NO$_y$, it would lead to an NO$_y$ increase about half that of N$_2$O. This is not the case as transport to the tropopause is the dominant (and linear) sink.

The impact of changing O$_3$ during this period was evaluated in two ways. First, through the use of the expanded N$_2$O–NO$_y$–O$_3$ chemistry in the CTM, the trend in stratospheric O$_3$ due solely to increasing N$_2$O is calculated (with feedback). The associated NO$_y$ increase induces an ozone deficit in the upper stratosphere and an excess in the lower stratosphere. The net effect of this change in the UV field and the O(^{1}D) densities is a marginal increase in the NO$_y$ VCD trend, +0.1%/decade, which is less than that predicted in a one-dimensional (1-D) model [*Prather*, 1998]. Second, the O$_3$ change over this 20-year period is taken from observations [*Bojkov and Hudson*, 1999, Figure 4-32] and now also includes the O$_3$ trend driven by increased chlorine levels and, to a lesser extent, increases in N$_2$O and CH$_4$. This modified O$_3$ (Y2000) is obtained by applying the observed ozone trends to the original Y1980 climatology (see Table 1) and using this distribution in recalculating the chemical coefficients for the N$_2$O–NO$_y$ chemistry for use in the Y2000 simulation. In this case the NO$_y$ trend increases to +3.0%/decade globally and +3.4%/decade at 45°S. It is almost seasonally invariant and ranges from −1%/decade in the upper stratosphere (from increased photolysis of NO) to a maximum of +4%/decade between 20 and 25 km (from enhanced O(^{1}D)).

Ozone and other climatic changes have led to an overall cooling of the stratosphere [*Chanin and Ramaswany*, 1999). However, it is difficult to define a pattern of temperature change that can be used in these calculations. We therefore adopt, as a sensitivity test, a cooling of the entire stratosphere by 0.5 K/decade. This assumption led to a reduction in the trends to +2.4%/decade globally and 2.8%/decade at 45°S. This is due in part to the strong temperature dependence of the reaction (2b). While likely not a realistic temperature trend, this nevertheless indicates the direction and magnitude of the NO$_y$ response.
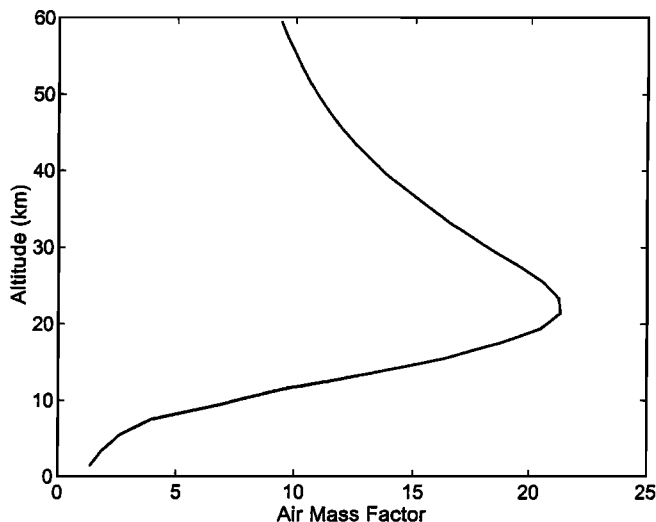
Figure 1. Sample air mass factors (or weighting factors) used to calculate slant column densities. These were calculated using a multiple scattering model for a solar zenith angle of 90°, background (Y1980) stratospheric sulphates, and a surface albedo of 0.3 at a wavelength of 442 nm.

On the basis of this analysis, the observed NO₂ trend cannot be entirely explained through the increase in NO_y alone. In fact, the model NO_y trend is only about two thirds the observed NO₂ trend, and so a shift in the partitioning of NO_y must have occurred between Y1980 and Y2000.

2.3. Trends in Stratospheric NO₂

NO_y profiles were converted into NO₂ using $NO_2{:}NO_y$ ratios calculated by the photochemical box model. Direct comparisons with the Lauder NO₂ SCD trends [*Liley et al.*, 2000] were made by integrating these NO₂ vertical profiles with the appropriate air mass factor (AMF, or weighting function) [e.g., *McKenzie et al.*, 1991]. AMFs describe the increase in absorption experienced by sunlight as it traverses a slant path. They are calculated using the multiple scattering model at a wavelength of 442 nm (the midpoint of the NO₂ SCD spectral fitting window) and for a solar zenith angle of 90°. A plot of AMF versus height, shown in Figure 1, indicates a peak enhancement near 20 km. For model results shown below, the NO₂ SCD to VCD ratio is ~17.

A comparison of measured NO₂ SCDs at Lauder, New Zealand (45°S), to those calculated by the model in Figure 2 shows very good agreement. The absolute magnitude, the annual cycle, and sunrise-sunset differences are reproduced with the model being systematically 10% below observations. For this comparison, model SCDs were calculated assuming 30 ppt of NO₂ in the troposphere. This amounts to a tropospheric SCD of ~8 × 10¹⁴ cm⁻², or ~2% of the overall SCD.

A summary of the model NO₂ SCD and VCD annually averaged trends are given in Table 3. As with the comparison of Figure 2, the SCDs were calculated as-

suming 30 ppt in the troposphere for both Y1980 and Y2000. Varying the tropospheric mixing ratio from 0 to 60 ppt had no effect on the SCD trends (to within 0.1%/decade) owing to the small fraction of the VCD in the troposphere and its reduced weighting (see Figure 1). The VCD trends are derived from stratospheric NO₂ only. In addition to N₂O, O₃, and temperature, change in halogens and aerosols are also considered (see Table 1). The N₂O trend by itself gives a NO₂ SCD trend of +2.4%/decade. In this case the trend is simply due to the NO_y trend, and there is no change in the $NO_2{:}NO_y$ ratio.

Including the observed change in ozone acts to increase the trends and introduces a diurnal variation. At a solar zenith angle of 90° the sunrise (or a.m.) value is +5.6%/decade, and the sunset (or p.m.) value is +4.2%/decade. The larger increase in the a.m. trend is due to a decrease in the rate of NO₂+O₃ and hence HNO₃ formation throughout the night. After sunrise, there is increased NO₂ (owing to reduced HNO₃), but it competes with a reduced production rate of NO₂ via NO+O₃. This explains the smaller increase in the p.m. trend. Overall, the change in trend from +2.4%/decade to (+5.6/+4.2)%/decade (a.m./p.m.), about one third of the increase is due to the O₃ change enhancing the NO_y and the other two thirds from its altering the $NO_2{:}NO_y$ ratio. Allowing for the upward trend in halogens between Y1980 and Y2000 acts to decrease these SCD trends to (+4.8/+3.7)%/decade, comparable to but less than the measured trends by ~1%/decade.
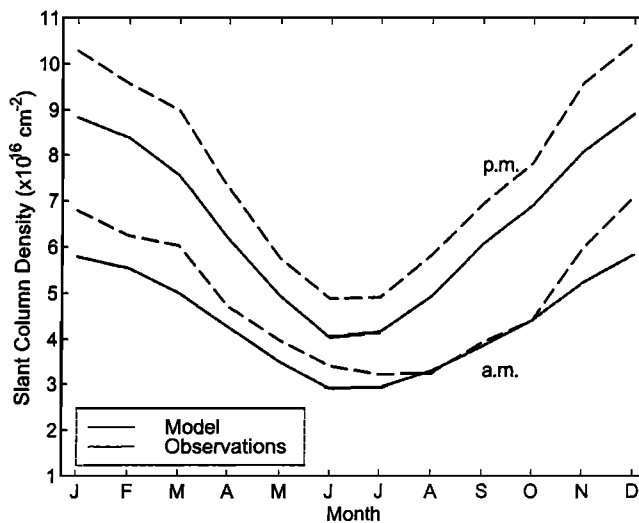

Figure 2. Comparison of modeled and measured p.m. (or sunset; top line and symbols) and a.m. (or sunrise; bottom line and symbols) twilight NO₂ slant column densities (SCDs). Model SCDs are from Y1980; measured SCDs are from 1981, the first full year of the time series [*Liley et al.*, 2000]. Model SCDs are calculated assuming 30 ppt of NO₂ in the troposphere, which amounts to a tropospheric SCD of 8 × 10¹⁴ cm⁻². The slight model-measurement mismatch (1980 versus 1981) leads to a ~0.5% underestimate of model SCDs.

Table 3. Annual Mean Stratospheric NO₂ Slant Column and Vertical Column Density Trends[a]

Trend Driver	SCD at 45°S		VCD at 45°S			VCD Global
	A.M.	P.M.	A.M.	P.M.	Diurnal Mean	Diurnal Mean
N₂O trend	2.4	2.4	2.4	2.4	2.4	2.4
+ observed O₃ trend[b,c]	5.6	4.2	5.2	3.9	4.7	4.0
+ halogen trends[d]	4.8	3.7	4.5	3.4	4.1	3.6
+ −10% aerosol surface area change	5.6	4.4	5.2	4.1	4.7	4.0
+ −0.5 K/decade temperature trend[c]	6.0	3.8	5.6	3.5	4.6	3.8
Measured trend[e]	5.9 ± 2.4	4.6 ± 1.5				

Modeled quantities were obtained by applying NO₂:NO_y ratios and air mass factors to CTM NO_y profiles. Model results begin with trends from increase in N₂O alone (without feedbacks) and are cumulative with additional imposed trends.

[a]Slant column density (SCD) and vertical column density (VCD) trends are in %/decade.
[b]*Bojkov and Hudson* [1999, Figure 4-32].
[c]Effects NO₂ through (1) NO_y and (2) NO₂:NO_y ratio.
[d]*Prinn and Zander* [1999].
[e]*Liley et al.* [2000].

This decrease is due principally to the increased rate of nitrate production during the night, which explains the larger decrease in the a.m. trend.

A possible decrease in stratospheric aerosol loading in Y2000 relative to that in Y1980 was investigated by scaling the original surface area profiles, derived from 1979–1980 SAGE II measurements [*Thomason et al.*, 1997], by 0.9. This constant scaling factor represents a sensitivity study and is not meant to quantify Y1980 versus Y2000 differences. The result was an increase in trends to (+5.6/+4.4)%/decade, values which are very near the measured trends. This is a result of a decrease in the conversion of N₂O₅ and BrONO₂ to HNO₃ via hydrolysis. This reduction in aerosols almost perfectly counteracted the increase in halogens. Finally, adding the hypothetical temperature trend of −0.5 K/decade results in values of (+6.0/+3.8)%/decade. This represents a shift of (+0.4/−0.6)%/decade in the trends from the previous scenario. It is due in part to a decrease in NO_y (this temperature trend shifted the NO_y VCD trend by −0.6%/decade; see Table 2) and in part to a repartitioning of NO_y. The a.m./p.m. difference is due to differing temperature responses of the reactions which control NO₂ during the night and day. In particular, the rates of O₃+NO and O₃+NO₂ decrease with temperature, leading to a smaller NO₂ production rate during the day (and hence smaller p.m. trends) and a smaller NO₂ loss rate during the night (and hence larger a.m. trends).

Table 3 also shows that SCD trends are generally 0.3–0.5%/decade larger than their VCD counterparts. This is a result of the AMF peak (from Figure 1) roughly coinciding with the location of the maximum increase in NO₂: the 25–30 km region of the stratosphere.

The diurnal behavior of the trend components is examined in Figure 3. The Y1980 NO₂ number density

profile is shown in Figure 3a and absolute changes in NO₂ number density due to the addition of N₂O, ozone, and halogen trends are given in Figures 3b–3d. (Note that unlike Tables 2 and 3, Figures 3b–3d do not dis-
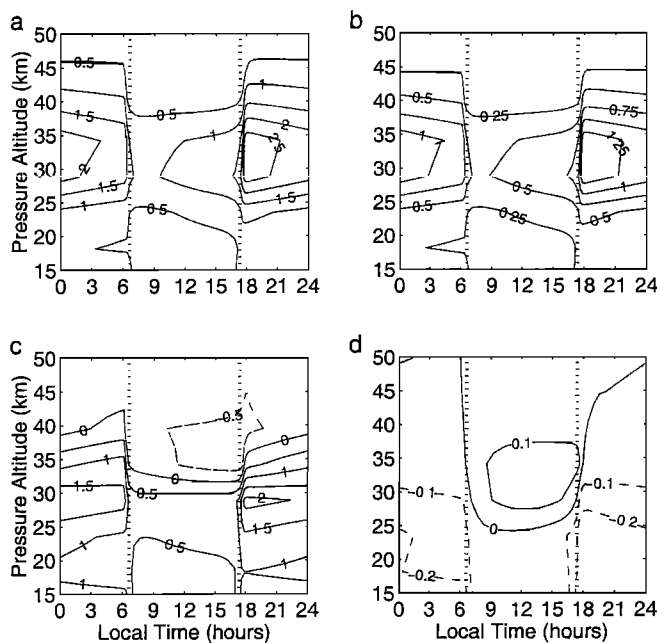

Figure 3. Diurnal variation of NO₂ and its recent trend broken into components and based on zonal mean values from the 3-D CTM for April at 45°S: (a) the Y1980 NO₂ number density (10^9 cm^{-3}) profile and the Y2000-Y1980 difference in NO₂ number density (10^8 cm^{-3}) due to (b) the increase in N₂O, (c) the decrease in ozone, and (d) the increase in halogens. Dashed contours are negative. Note that (b)–(d) show individual trend components and not are cumulative. Dotted vertical lines indicate time of sunrise and sunset at Lauder, New Zealand. Pressure altitude is defined as $16 \log_{10}(1000/P)$, where P is pressure in hPa.
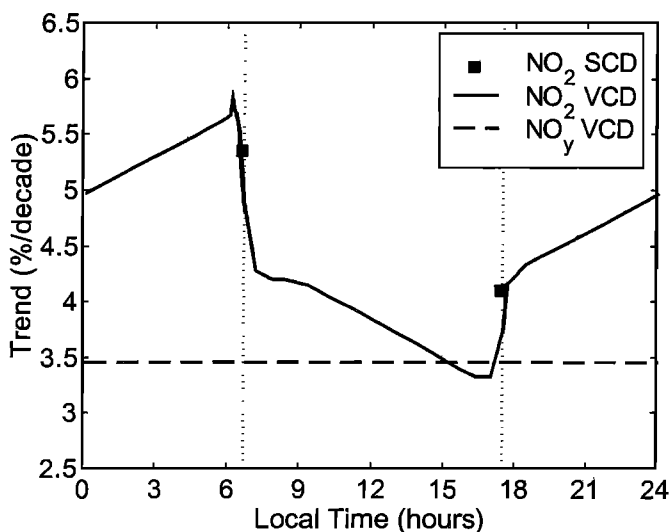
Figure 4. Modeled diurnal variation of decadal trends in the NO_y VCD, the NO_2 VCD, and the NO_2 SCD based on zonal mean values from the 3-D CTM for April at 45°S. Dotted vertical lines indicate time of sunrise and sunset at Lauder, New Zealand.

play cumulative differences.) The increase due solely to N_2O (panel b) closely resembles the NO_2 (panel a). The ozone trend led to larger increases at night with the peak at 28 km, just below that for NO_2 itself, due to a slower conversion of NO_2 to NO_3 and N_2O_5. The halogens had a smaller and mostly negative impact on NO_2 with roughly equal contributions from chlorine (middle stratosphere) and bromine (lower stratosphere).

Vertically integrated trends are shown in Figure 4 (when considering the effects of N_2O, ozone, and the halogens). Over a day the VCD trend varies by nearly a factor of 2 ($\sim$3.3–5.8%/decade) and is a maximum during the night and a minimum during the day. Also, large gradients are evident during sunrise and sunset. The measurements of *Liley et al.* [2000] are reported at a solar zenith angle of 90°. However, this is a local value at the measurement site, and the incoming sunlight will intercept portions of atmosphere where the local solar zenith angle is < 90°. Use of NO_2:NO_y ratios and AMFs at an "effective" solar zenith angle of, e.g., 88° changes the modeled SCD trends of Figure 4 by about −0.2%/decade which indicates this is not a critical assumption.

Finally, we make comparisons with another modelling study of NO_2 trends [*Fish et al.*, 2000]. Overall, the Fish et al. model trends of (+5.9/+4.3)%/decade (a.m./p.m.) are consistent with both our results and the measurements. However, there were several important differences: Fish et al. considered trends in H_2O, used local (over Lauder) temperature trends, and a 20% decrease in aerosols. They did not consider changes in halogens and assumed the trend in NO_y was equivalent to that in N_2O. The fact that these somewhat differing approaches lead to essentially the same conclusion

further underscores the importance of quantifying and considering all varying parameters and feedbacks.

3. Conclusions

Atmospheric models have been employed to estimate the decadal trends in stratospheric NO_y and NO_2. The measured NO_2 slant column density (SCD) trends over Lauder, New Zealand (45°S) of (+5.9/+4.6)%/decade (a.m./p.m.) are generally consistent with a +3%/decade increase in N_2O if the observed trends in ozone and the halogens (chlorine and bromine) are also allowed for. Roughly half the model trend of (+4.8/+3.7)%/decade is due to an increase in NO_y, and half is due to a shift in partitioning of NO_y toward more NO_2. Trends in temperature and aerosols are also potentially important. The model NO_2 trend was found to peak near 25–30 km, and owing to the increased weighting of SCDs in this region, SCD trends were 0.3–0.4%/decade larger than trends in vertical column density (VCD).

Modeled NO_2 VCD trends varied diurnally by nearly a factor of 2 with a minimum during the day, a maximum at night, and large gradients through twilight. This complex behavior implies that SCD trends derived from twilight measurements should not be understood as simply a proportionate change in assessing effects. For example, ozone destruction via the NO_x catalytic cycle (i.e., the rate-limiting step NO_2+O) would follow the daytime trend. While gradients are large through sunrise and sunset, measurements at this time are reliable and highly reproducible with a good signal-to-noise ratio. The large volume of data from a decade of measurements across the globe, especially the Network for the Detection of Stratospheric Change (NDSC) sites, is a valuable resource and represents "cornerstone" observations required for identifying global change. However, these measurements can be properly understood and interpreted only in the context of good photochemical, dynamical, and radiative models.

Finally, while NO_2 trends have been reported as annual means, model trends exhibited an annual cycle which mimics, and hence exaggerates, the annual cycle of NO_2 itself (i.e., a maximum in summer, a minimum in winter). Once sufficiently long time series are available we, expect observations to also show this and hence confirm our understanding.

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