Stratospheric ozone depletion at northern mid latitudes in the 21st century: The importance of future concentrations of greenhouse gases nitrous oxide and methane

L. K. Randeniya, P. F. Vohralik, and I. C. Plumb

CSIRO Telecommunications and Industrial Physics, PO Box 218, Lindfield, NSW 2070, Australia

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[1] There is evidence that the halogen loading of the atmosphere has peaked and stratospheric ozone levels are expected to recover to pre-1980 levels this century. However, N_2O concentrations in the atmosphere are increasing, resulting in increasing levels of NOx in the stratosphere. In addition, the growth rate in the atmospheric methane burden has declined in recent years, leading to the suggestion that methane emissions have stabilized. A 2-D chemical transport model is used to calculate stratospheric ozone from 2000 to 2100 for a range of IPCC scenarios. The model predicts that mid-latitude stratospheric ozone will recover only partially towards pre-1980 levels over the next 50 years, but will then decline, largely due to increases in stratospheric NOx. If greenhouse gas mitigation strategies result in lower future methane levels, mid-latitude stratospheric ozone levels in 2100 are predicted to be lower than current values, particularly in late summer and autumn. *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 1610 Global Change: Atmosphere (0315, 0325); 6615 Public Issues: Legislation and regulation

1. Introduction

[2] In the 1998 WMO study [*WMO*, 1999], ten 2-D models calculated global ozone trends over the period 1979–2050 in response to a range of prescribed boundary conditions for halogen compounds, CH_4 and N_2O. In all cases, the models showed partial recovery of ozone during the 21st century, although the calculated rates of recovery varied widely and in no case had ozone returned to 1979 levels by 2050. Since the time of the WMO study, there have been new laboratory measurements for several key reactions involving oxides of nitrogen which have been shown to affect calculated ozone trends [*Portmann et al.*, 1999]. In addition, the WMO study considered only cases where future methane concentrations continue to increase or remain constant through till 2050.

[3] In the present work, we use the CSIRO 2-D chemical transport model to study future ozone trends to 2100, using the updated rate coefficients for NOx [*Portmann et al.*, 1999] and lower boundary conditions for CH_4 and N_2O [*Ehhalt and Prather*, 2001] which are based on the IPCC Special Report on Emissions Scenarios (SRES) [*Nakicenovic et al.*, 2000]. The present study does not consider effects of greenhouse gas-induced temperature changes, changes in H_2O or changes in aerosols explicitly, although the effects of each of these on future ozone trends are discussed briefly. Because 2-D models are not capable of predicting future trends in tropospheric ozone accurately, we focus on changes in stratospheric ozone. Results from the IPCC Third Assessment Report are used to estimate future tropospheric ozone trends which, when combined with the 2-D model results for the stratosphere, give estimates for future total ozone columns.

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2. Method

[4] The CSIRO model [*Randeniya et al.*, 1997; *Vohralik et al.*, 1998], which was included in the WMO study, has been upgraded to include low temperature aerosol chemistry. In addition, the model residual circulation is now based on radiative heating rates calculated using the CCM3 Column Radiation Model Version crm-2.1–ccm-3.6 [*Kiehl et al.*, 1996], rather than the archived heating rates of Rosenfield used previously [*Randeniya et al.*, 1997, and references therein]. The heating rate calculations use average NCEP temperatures for the period 1979–1998, the MMII ozone climatology of *Logan and McPeters* [1999] and mean cloud parameters for the period 1983–1993 [*Rossow and Shiffer*, 1991]. Zonal temperature variations based on NCEP reanalyses [*Kalnay et al.*, 1996] are included both in the calculation of aerosol properties [*Carslaw et al.*, 1995] and in the calculation of rate coefficients. These changes are described in detail in a forthcoming publication (P.F. Vohralik, et al., manuscript in preparation, 2001).

[5] Boundary conditions for halocarbons are based on the A/A3 scenario given in Table 11-3 of the WMO report [*WMO*, 1999]. The A3 scenario represents the case where maximum production is allowed for all halocarbons subject to the Montreal Protocol and its amendments, including approved essential uses but no illegal production. Figures 1a and 1b show the organic chlorine and bromine mixing ratios at the ground for the period 1980–2100. Ozone depletion began to be observable around 1980. According to this scenario, organic chlorine and organic bromine concentrations at the ground return to 1979 levels in around 2045 and 2065, respectively. However, Cly and Bry concentrations in the stratosphere lag values at the ground by approximately 5 years [*Anderson et al.*, 2000]. Thus estimates of the time when stratospheric Cly (Bry) would be expected to return to its 1979 level should be based on the 1974 tropospheric value of 1.67 nmol mol^{-1} (9.42 pmol mol^{-1}), instead of the 1979 value of 2.23 nmol mol^{-1} (10.15 pmol mol^{-1}). Because concentrations will fall much more slowly in the second half of the 21st century than they were rising in the late 1970s, stratospheric Cly and Bry will not return to pre-depletion values until around 2075 and 2090, respectively.

[6] For N_2O (Figure 1c) and CH_4 (Figure 1d), boundary conditions based on IPCC SRES emission scenarios A1FI and B1 were used. The A1FI scenario describes a future world with rapid economic growth, a reduction in regional differences in per capita income, low population growth and the rapid introduction of new and more efficient technologies, with energy needs supplied largely by fossil fuels. The B1 scenario describes a world with the same population growth and improving equity, but with an emphasis on environmental sustainability. These two emission scenarios give concentrations of N_2O and CH_4 which are close to the maximum and minimum values for all of the SRES scenarios.

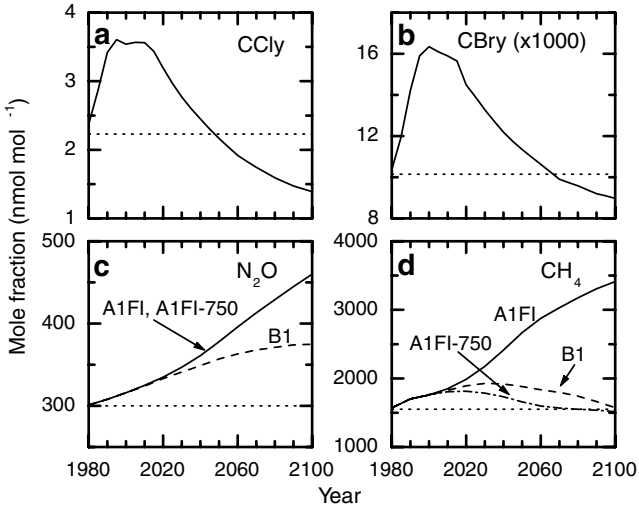

Figure 1. Volume mixing ratios at the ground used in the present work as functions of time. (a) Total organic chlorine (CCly), (b) total organic bromine (CBry), (c) N_2O and (d) CH_4. For the scenarios considered, see text. The dotted horizontal lines represent 1979 levels.

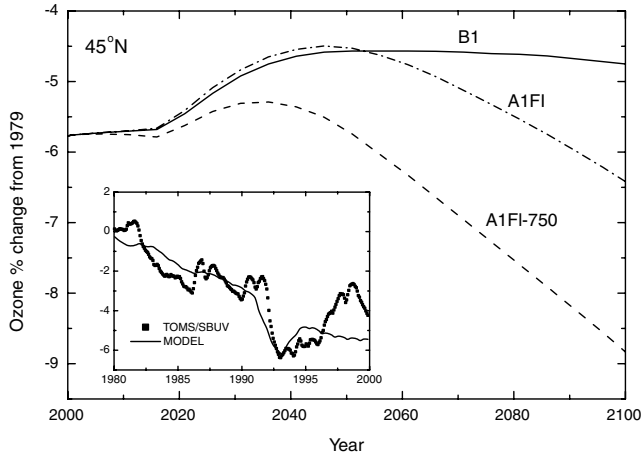

Figure 2. Percent change in annual average stratospheric ozone at 45°N from 1979 levels for the period 2000–2100, for the A1FI, B1 and A1FI-750 scenarios described in the text. The inset shows the total ozone changes calculated by our model at 45°N for the period 1980–2000, together with NASA/GSFC merged results from TOMS and SBUV satellite measurements for the same latitude. A 25-month boxcar filter was used to smooth the results after removing the annual cycle.

[7] None of the SRES scenarios include greenhouse gas mitigation strategies. We have constructed a third scenario, based on the A1FI case, where, following the approach of *Kheshgi et al.* [1999], CH_4 emissions are reduced at the same rate as fossil CO_2 emissions in order to stabilize CO_2 at 750 μmol mol^{-1} (while CO and NOx follow the A1FI scenario). This scenario, which has the same N_2O boundary conditions as A1FI, is referred to as A1FI-750. CH_4 emissions for A1FI-750 in 2100 are approximately 60% lower than for A1FI and result in CH_4 concentrations in 2100 which are close to those for B1 (see Figure 1d).

3. Results and Discussion

[8] Figure 2 shows the calculated changes in annual average stratospheric ozone at 45°N relative to 1979 values as functions of time during the 21st century for the three scenarios. In the early part of the century, the differences in trend are due to moderation of chlorine catalytic cycles by methane (methane levels are highest for A1FI during this period) and to changes in N_2O. The calculated recovery in ozone continues until around the middle of the century. In the second half of the century, stratospheric ozone columns decrease, even though halogen levels continue to decline. The decline in ozone in the second half of the century is sensitive to both N_2O and CH_4 levels. Increasing N_2O and reducing CH_4 both result in reduced ozone amounts. In 2100, the stratospheric ozone column is approximately 2.4% lower for A1FI-750 than for A1FI and this difference is entirely due to a reduction in CH_4 of approximately 60% in A1FI-750. The stratospheric ozone column for A1FI-750 is approximately 4% lower than for B1 in 2100 and this is due mainly to a 23% higher N_2O for A1FI-750.

[9] The calculated stratospheric ozone column change at 45°N relative to 1979 is shown as a function of time of year in Figure 3, both for current (2000) conditions and for the 3 scenarios in 2100. The ozone reduction for current conditions is greatest in spring, in agreement with trends for the total column derived from satellite observations [*WMO*, 1999], although the seasonal cycle is somewhat weaker than observed trends. For both A1FI and B1 in 2100, most of the predicted recovery relative to 2000 occurs between late winter and early summer, while in late summer and autumn, stratospheric ozone columns in 2100 are comparable to or lower than those in 2000. Lowering methane (A1FI-750) results in almost season-independent reductions in ozone relative to A1FI in 2100. The significance of these findings is that most of the recovery in northern mid-latitude stratospheric ozone over the next 100 years is predicted to occur in spring, a time when UV levels at the surface of the Earth are comparatively low. In late summer, when UV levels at the ground are high, stratospheric ozone columns in 2100 are predicted to be comparable to or lower than their current depleted values and may be even lower if methane levels decline.

[10] Figure 4a shows changes to the vertical profile of ozone between 2000 and 2100 for the A1FI scenario for the four seasons of the year. The changes are plotted in concentration units, so that the areas under the curves give the contributions to ozone column changes. Increases in ozone below approximately 22 km and above about 34 km are due mainly to reductions in the halogen content of

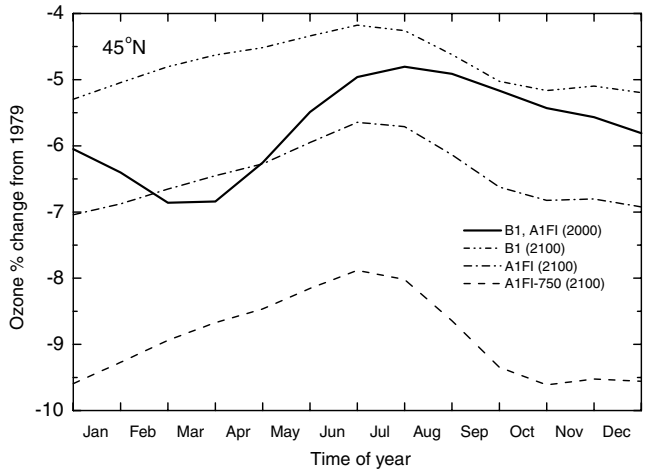

Figure 3. Percent change in stratospheric ozone at 45°N from 1979 levels as a function of time of year, for the A1FI case in 2000 (current conditions) and in 2100 for the A1FI, B1 and A1FI-750 scenarios described in the text.

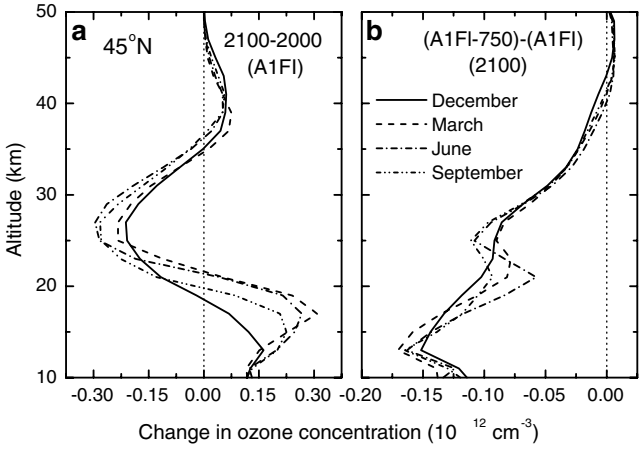

Figure 4. Change in ozone concentration as a function of altitude and season at 45°N (a) between 2000 and 2100 for the A1FI case and (b) between A1FI and A1FI-750 in 2100. The areas under the curves give the contributions to the column changes.

the atmosphere over this period. Halogens have their largest impact on ozone in these altitude ranges [*Nevison et al.*, 1999; *Portmann et al.*, 1999; *Solomon*, 1999] and their contribution to ozone loss in the lower stratosphere peaks in late winter/early spring. There is also a component in the lower stratosphere due to the increase in CH_4 over the period, as discussed further below. The decrease in ozone between 22 km and 34 km altitude is due to the increase in NOx resulting from the approximately 45% rise in atmospheric N_2O levels over the century. In contrast to the halogen catalytic cycles in the lower stratosphere, NOx chemistry is most effective in summer and autumn [*Nevison et al.*, 1999] when conversion of NOx to HNO_3 by heterogeneous chemistry is slower. In the lower stratosphere, the increase in NOx cycles is offset by reductions in HOx and halogen cycles [*Wennberg et al.*, 1994], whereas in the middle stratosphere, NOx cycles are dominant and are less affected by competing cycles [*Nevison et al.*, 1999; *Portmann et al.*, 1999]. It should be noted, however, that the maximum fractional decrease in ozone at 27 km is only approximately 7%, far smaller than the fractional increase in N_2O (45%) and NOy (33%) over the 100 year period. Increased ultraviolet transmission leading to increased production (self-healing of ozone), reductions in the NO_2/NO ratio due to lower O_3, ClO and HO_2, reductions in contributions to ozone loss from halogen cycles and transport processes all limit ozone reductions due to increased NOx.

[11] The effect of different levels of methane in the atmosphere on vertical profiles of ozone is illustrated in Figure 4b, which shows differences in ozone between scenarios A1FI and A1FI-750 in 2100. The largest ozone changes are in the lower stratosphere, where reductions in ozone are due to reductions in the rate of photo-oxidation of methane, which is a major ozone production process at these altitudes. Decreases in methane also result in reductions of HOx radicals which dominate ozone loss at these altitudes, but the changes in production rate outweigh the changes in loss rate, particularly in summer. Decreases in ozone above 20 km are due mainly to increases in NO_2 caused by reductions in OH from smaller CH_4 and H_2O, leading to slower conversion to HNO_3.

[12] *Dvortsov and Solomon* [2001] have shown that recent observed increases in stratospheric humidity may produce additional depletion of midlatitude ozone of approximately 0.3% per decade, although smaller effects on ozone are expected in the future as halogen levels decline. Similarly, *Solomon et al.* [1996] and *Tie and Brasseur* [1995] have shown that variations in aerosols are likely to have a large effect on ozone recovery while halogens are elevated, but towards the end of the century, the effect of aerosols will be smaller. Cooling of the stratosphere due to increases in greenhouse gases is expected to moderate ozone loss via NOx reactions [*Rosenfield and Douglass*, 1998], to enhance polar ozone loss [*Shindell et al.*, 1998], and may also result in changes to stratospheric H_2O and to atmospheric transport, all of which could affect ozone trends. We have performed additional calculations in which reaction rates were determined using temperature changes due to greenhouse gases from the GISS GCM [*Shindell et al.*, 1998] (D. Shindell, personal communication). These temperature changes result in an increase in calculated ozone columns at northern mid latitudes in 2100 of approximately 1%.

[13] Tropospheric ozone is expected to increase over the period 2000–2100 for most of the SRES emission scenarios [*Ehhalt and Prather*, 2001], due to changes in emissions of CH_4, CO, NOx and volatile organic compounds (VOCs) and these increases may offset to some extent decreases in stratospheric ozone. 2-D models are not capable of predicting tropospheric ozone trends accurately, due to the strong spatial variations in emissions of the short-lived precursor compounds NOx and VOCs, together with non-linearities in the chemistry. An estimate of the change in tropospheric ozone (in DU) relative to 2000 can be obtained from the expression [*Ehhalt and Prather*, 2001]

$$\delta(\mathrm{trop\,O_3}) = 6.7 \times \delta \ln(\mathrm{CH_4}) + 0.17 \times \delta(\text{e-NOx}) + 0.0014 \times \delta(\text{e-CO}) + 0.0042 \times \delta(\text{e-VOC}) \quad (1)$$

where changes in mixing ratio of CH_4 and in emission rates of NOx (e-NOx, Tg(N) yr^{-1}), CO (e-CO) and VOCs (e-VOC) (both in Tg yr^{-1}) are relative to 2000 values. Equation (1) applies to annual and global average tropospheric ozone changes, but should give a rough estimate of the mid-latitude northern hemisphere changes (although mid-latitude southern hemisphere changes would be expected to be smaller). At northern mid latitudes for scenario A1FI, the increases in tropospheric ozone over the century more than offset the decreases in stratospheric ozone and total ozone in 2100 is predicted to be slightly greater than the 1979 value. For scenario B1, a small decrease in tropospheric ozone is obtained, so that by the end of the century, total column ozone is predicted to be lower than current values.

4. Conclusions

[14] The principal findings of the present study are that northern mid-latitude stratospheric ozone levels are not predicted to recover to pre-1980 levels this century due to increasing levels of N_2O, and that the ozone levels at the end of the century will depend strongly on future methane trends. This highlights important links between climate change and UV levels which have implications for emission control policies. Methane and nitrous oxide rank second and third in importance for anthropogenic climate forcing. Reducing N_2O emissions would be beneficial both for climate change and for ozone recovery. Current anthropogenic N_2O emissions are approximately 7 Mt(N) yr^{-1}, with the largest component from cultivated soils and significant contributions from industrial processes and biomass burning [*Prather et al.*, 1995; *Nevison and Holland*, 1997; *Nakicenovic et al.*, 2000]. The SRES scenarios [*Nakicenovic et al.*, 2000] predict a range of N_2O emissions in 2100 from 4.8 to 20.2 Mt(N) yr^{-1} due largely to differences in agricultural emissions. Together with its long atmospheric lifetime ($\approx$ 120 years [*Prather*, 1998]), this means that N_2O will continue to increase for the rest of the century. In contrast to N_2O, the atmospheric adjustment time of CH_4 (taking account of chemical feedbacks) is approximately 12 years [*Prather et al.*, 1995; *Ehhalt and Prather*, 2001], so the response time of atmospheric concentrations to changes in CH_4 emissions is relatively rapid. Current anthropogenic emissions of CH_4 are approximately 310 Mt yr^{-1} [*Nakicenovic et al.*, 2000],

with large components from fossil fuel usage (68–94 Mt yr^{-1}), landfills and domestic waste (51–62 Mt yr^{-1}) and agriculture (109–158 Mt yr^{-1}). These may be targeted for substantial reductions in the future as part of greenhouse gas mitigation strategies [*US Environmental Protection Agency*, 1999]. While such reductions would be desirable from the perspective of climate change, the consequences for ultraviolet radiation levels also need to be considered carefully.

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L. K. Randeniya, P. F. Vohralik, and I. C. Plumb, CSIRO Telecommunications and Industrial Physics, PO Box 218, Lindfield, NSW 2070, Australia. (Ian.Plumb@csiro.au)