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Relative roles of climate and emissions changes on future tropospheric oxidant concentrations

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Abstract. A Lagrangian chemistry-transport model (STOCHEM) was driven with meteorology derived from a slab ocean general circulation model for conditions appropriate to the present-day and at double CO₂, and with emission scenarios appropriate for present day conditions and for the year 2075. The results show conclusively that the effect of including the predicted changes to future climate is to reduce the simulated tropospheric ozone concentrations. The response of global tropospheric ozone in the period 1990-2075 was an increase of 6.4 ppb when both climate and emissions changes were included, compared to an increase of 10.3 ppb when only emissions changes were considered. This difference is mainly due to water vapor and temperature increases, together with some dynamical effects. There are considerable changes to other tropospheric oxidants, with OH, HO₂, and H₂O₂ all increasing considerably in response to climate changes. In contrast, OH decreases when only the emissions are allowed to change. A replicate run of the control scenario with STOCHEM using a different year of meteorology showed considerable interannual variability in local monthly mean ozone concentrations.

1. Introduction

It is widely accepted that tropospheric ozone is one of the most important radiatively active trace gases along with carbon dioxide, methane, and nitrous oxide. However, estimates of radiative forcing due to tropospheric ozone are inherently more uncertain than those for the other trace gases for several reasons. There are no equivalent ice core records of historical concentrations for ozone which are comparable with those of other trace gases, and, owing to the shorter lifetime of ozone, the available measurements are inadequate to assess its recent changes. Consequently, ozone changes have to be estimated with atmospheric chemistry models and important questions remain about the adequacy with which chemical processes are represented in current chemistry-transport models [Prather *et al.*, 1995].

The importance of tropospheric ozone as a radiatively active trace gas through its absorption and emission of terrestrial infrared radiation in the 8-10 μm region and absorption in the visible and ultraviolet was first recognized two decades ago [Fishman *et al.*, 1979; Ramathan and Dickinson, 1979]. The extent of human influences on tropospheric ozone has been documented

with models of progressively increasing complexity from global models [Crutzen, 1974], one-dimensional (1-D) models [Thompson and Cicerone, 1986], two-dimensional (2-D) models [Fishman and Crutzen, 1978; Derwent, 1982; Hough, 1991], and more recently three-dimensional (3-D) models [Penner *et al.*, 1991; Kasibhatla *et al.*, 1991, Jacob *et al.*, 1993; Lelieveld and Crutzen, 1994].

The steps in the assessment process for radiatively active trace gases have been laid out by Albritton [1994] and are implied in the Intergovernmental Panel on Climate Change (IPCC) process [Houghton *et al.*, 1990; Prather *et al.*, 1995]. Anthropogenic emissions result in changes to atmospheric composition which lead directly or indirectly to changes in the radiative forcing of the climate system. This process leads in turn to changes in the global climate, and eventually this climate change will affect the concentrations of atmospheric trace gases.

In this study, we have used a global Lagrangian chemical-transport model (STOCHEM) to study how tropospheric ozone responds to changes in anthropogenic emissions through to the year 2075. Then we have studied the role of the climate system response on the tropospheric ozone change. The climate system response used was that from a doubling of carbon dioxide concentration and includes changes to atmospheric circulation, temperature, humidity, convection, cloud amount, and precipitation. Here we restrict the analy-

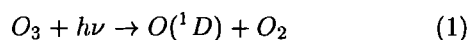
sis to changes in tropospheric ozone and other oxidants and do not consider changes to the model other than from surface emissions and climate change through the meteorological diagnostics which drive STOCHEM.

There are many potential feedbacks between tropospheric chemistry and climate change. Studies by *Thompson and Cicerone* [1986] and *Thompson et al.* [1989, 1990, 1991] established that perturbations to tropospheric oxidants were likely to occur as a result of relative changes to CH₄, CO, and NO_x emissions in different regions and that both stratospheric ozone depletion and increases to tropospheric water vapor from climate change were also important determinants of the oxidant changes. Increasing CH₄ and CO emissions were found to suppress OH and increase O₃ except in areas where NO_x emissions and O₃ growth were sufficient to increase OH. Increased levels of water vapor were found to decrease O₃ and increase OH. Despite the recognition of the importance of feedbacks from climate change, there have been few global-scale quantitative studies of their importance. Many studies of changes to tropospheric oxidants have been made with the assumption that emission changes are the only determinants [e.g., *van Dorland et al.*, 1997].

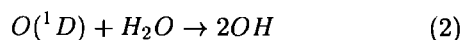
The potential role of climate change in altering natural emissions has also received some attention. The role of climate changes in altering the emissions of isoprene was considered by *Turner et al.* [1991], and *Atherton et al.* [1995] show how these changes affect ozone and OH in a global tropospheric chemistry model. There has been considerable discussion of potential climate feedbacks on the natural sources of methane [*Houghton et al.*, 1990, 1995], and natural NO_x emissions may also change with climate [*Atherton et al.*, 1995; *Toumi et al.*, 1996]; however, there are considerable uncertainties attached to these, particularly in the parameterization of the lightning NO_x source as a function of convective characteristics [*Gallardo and Rodhe*, 1997].

The chemical mechanisms used in tropospheric chemistry models are sensitive to climate changes through a variety of mechanisms. In the first place, changing temperatures and humidities can alter the production and destruction of important tropospheric constituents; second, changes in atmospheric transport can affect the distribution of species; and finally changes to clouds and precipitation can affect photolysis rates and the removal of certain trace gases from the atmosphere.

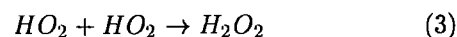
The main reactions involving the destruction of ozone and the generation of hydroxyl radicals (OH) are sensitive to water vapor:



is followed by



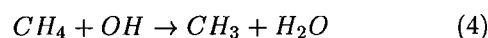
Also, the formation of hydrogen peroxide (H₂O₂) is water catalyzed:



where [*Atkinson et al.*, 1997],

$$k_3 = (2.2 \times 10^{-13} e^{(600/T)} + 1.9 \times 10^{-33} e^{(980/T)}) \times ((1 + 1.4 \times 10^{-21} e^{(2200/T)} [H_2O])$$

Many of the rate coefficients of the reactions which control the life cycles of methane and ozone are temperature sensitive, for example,



with [*Atkinson*, 1994]

$$k_4 = 7.44 \times 10^{-12} T^2 e^{(-1820/T)}$$

This reaction has a temperature sensitivity of 2.4 %/K at 288 K. Other rate coefficients which have high temperature sensitivities include the thermal decomposition of peroxyacetyl nitrate (PAN) (CH₃COO₂NO₂), N₂O₅, and other compounds, which have temperature sensitivities in excess of 10 %/K.

Predictions of temperature and humidity changes from climate change experiments are nonuniform, and it is therefore necessary to use three-dimensional global climate and chemistry models to extrapolate from the sensitivities discussed above to establish the global effects of climate change on trace gas life cycles. The experiments described below were done using a three-dimensional tropospheric chemistry model which is run using data from the Hadley Centre Climate Model. Natural emissions were assumed constant, and the effect of changes to stratospheric constituents were ignored in order to determine the role of climate changes on tropospheric chemistry.

2. Description of the Models

The results described in section 3 were obtained from simulations of tropospheric chemistry in a Lagrangian model (STOCHEM). The meteorological diagnostics required by STOCHEM (winds, temperature, humidity, cloud height and amount, surface pressure, and precipitation) were taken from simulations of the Hadley Centre Climate Model archived at a 6 hour time resolution. The atmospheric GCM used was version HADAM2b of the unified forecast and climate model [*Cullen*, 1993], with a horizontal grid spacing of 2.5° of latitude by 3.75° of longitude and 19 vertical levels. This was coupled to the 50 m mixed layer ocean model of *Cattle and Crossley* [1995]. For further details of the atmospheric model see *Johns et al.* [1997] and *Senior* [1999].

Only a brief general description of STOCHEM is included here, as a more detailed description has already been published [*Collins et al.*, 1997] and [*Stevenson et al.*, 1998] evaluates the transport characteristics of this model. Recent changes to the model are described in more detail. STOCHEM is a three-dimensional model

of the global troposphere to 100 hPa, which incorporates the chemistry of ozone and oxidant formation within a fully Lagrangian framework. The version used here has 50,000 Lagrangian cells whose motion is driven by three-dimensional winds provided from the archived diagnostics of the GCM. The cell locations are solved by Runge-Kutta integration with linear interpolation of the 6-hourly winds with respect to time and horizontal direction and with cubic interpolation in the vertical. The diurnal chemistry of 70 species is treated in the model. This chemical scheme is different to that described by *Collins et al.* [1997] in that it now includes dimethylsulfide (DMS) chemistry and aqueous-phase sulphate production, and the hydrocarbon scheme has been improved by the inclusion of organic peroxides derived from propene, butane, and isoprene and with the addition of propane and acetone chemistry. An iterative backward Euler solution is used to solve the chemical equations [*Hertel et al.*, 1993]. The following emissions were included in the model: NO_x, CO, CH₄, HCHO, H₂, NH₃, C₂H₆, CH₃CHO, n-C₄H₁₀, DMS, SO₂, C₂H₄, C₃H₆, C₃H₈, CH₃COCH₃, 1,2-dimethyl benzene (*o*-xylene), isoprene, and methyl benzene (toluene). The model provides a horizontal output resolution of 5° × 5° with nine layers between the surface and 100 hPa. A 3 hour time step for the Lagrangian advection together with a 5 min time step for the chemical integration was used in these simulations.

The HADAM2b model runs at 1 × CO₂ and 2 × CO₂ as described by *Senior* [1999] were restarted to provide the diagnostics required by STOCHEM. These restarts were taken from sections of the original run after the models had reached equilibrium. Two years diagnostics for the 1 × CO₂ experiment and 1 year of the 2 × CO₂ experiment were available. Inspection of the temperature and humidity differences between the two equilibrium experiments suggested that the amount of change in globally averaged temperature and humidity was approximately equal to those provided by the transient climate change experiment forced by greenhouse gases of *Mitchell et al.* [1995] at the year 2075. Emission estimates for 2075 were interpolated from *Leggett et al.* [1992] using the IPCC IS92a scenario. Methane concentrations appropriate for 2075 were predicted from a previous 2-D model [*Hough*, 1991] run with the IS92a scenario emissions. These were consistent with the predictions presented by *Houghton et al.* [1996] and were used to initialize STOCHEM simulations for 2075. The initial concentrations of ethane and carbon monoxide were also set appropriately.

STOCHEM was run using the four scenarios shown in Table 1. For each case the model was run for a total period of 15 months, with only the final 12 months contributing to the results analyzed here. This set of scenarios was chosen to show (1) the role of the interannual variability in the climate model on the predicted concentrations, (2) the effect of the double CO₂ climatology compared with the control, and (3) the role of

Table 1. Scenarios Used

Scenario	CON ^a	REP ^b	2MET ^c	BOTH ^d
×CO ₂ in GCM	1	1	2	2
Year of GCM run	1	2	1	1
Emissions	1990	1990	1990	2075
Initial CH ₄ (ppb)	1720	1720	1720	3224

^aControl scenario.

^bRepeat scenario.

^c2 × CO₂ climatology scenario.

^d2 × CO₂ climatology with 2075 emissions scenario.

See text for further details of each scenario.

changes to emissions compared to climate change. In all scenarios, the natural emissions were assumed to remain constant, as was the concentration of ozone above the model domain.

The first scenario (CON) was used as the control and used the first year's meteorological diagnostics from the control slab model run with 1990 emission estimates. Scenario REP was identical to CON but used the second year's meteorological diagnostics from the 1 × CO₂ run of HADAM2b in order to show the effect of the internal variability of the GCM on the results from STOCHEM. Scenario 2MET used the 2 × CO₂ model meteorology, with 1990 emissions. Scenario BOTH used the same meteorology as 2MET, with 2075 emission estimates. A separate scenario for emissions changes only was not done, as the role of emissions changes appropriate for 2 × CO₂ conditions may be identified as the difference between scenarios BOTH and 2MET. We have previously found that there are only minor differences between an emissions scenario applied with the present day meteorological diagnostics and the same emissions applied with the 2 × CO₂ diagnostics. Table 1 lists the four scenarios, together with the global mean initial concentrations of methane and carbon monoxide. These were taken from a prior 100 year run of the Meteorological Office two-dimensional model of tropospheric chemistry with time dependent IS92a trace gas emissions.

3. Results

3.1. Climate Model Properties

Table 2 shows the equilibrium globally averaged temperature and humidity changes in the troposphere of the climate model described in section 2 due to the imposed double CO₂ forcing. The fractional changes to humidity are much larger in the upper than the lower troposphere. Temperature and humidity changes are greater in the tropics and subtropics than elsewhere, with the exception of the polar regions where the temperature change is also large because of the ice feedback. Figures 1 and 2 show the annual and zonal mean changes to these properties at 1 × CO₂ and 2 × CO₂. Changes to temperature are generally greater in midtroposphere than near to the surface, with humidity changes be-

Table 2. Globally Averaged Temperature and Humidity for the $1\times\text{CO}_2$ and Their Respective Changes for the $2\times\text{CO}_2$ Equilibrium Climate Experiments

Level, hPa	$1\times\text{CO}_2$, K	$2\times\text{CO}_2$, K	$1\times\text{CO}_2$, mass ratio $\times 10^{-3}$	$2\times\text{CO}_2$, mass ratio $\times 10^{-3}$
<i>January</i>				
200	214.3	2.20	0.02	0.01
350	237.6	3.80	0.21	0.12
600	263.3	3.37	1.82	0.55
870	278.5	3.09	5.85	1.17
<i>July</i>				
200	213.6	4.01	0.02	0.01
350	239.1	4.50	0.24	0.15
600	265.3	3.72	2.06	0.60
870	281.6	3.28	6.51	1.37

ing greater nearer the surface. Senior [1999] documents the response to doubling CO_2 in the cloud amount and height in the climate model used here. A noticeable feature is the increase in the strength of the Hadley circulation, which produces more cloud in the inter-tropical convergence zone and less cloud in the subsidence regions of the subtropics. The transport characteristics of the model are also expected to change because of increases to the tropopause height and the vertical range of convection at double CO_2 .

3.2. STOCHEM Results

3.2.1. Role of natural variability of the general circulation model. The role of natural variability of the GCM on the STOCHEM results was assessed by the differences between the monthly mean results from runs CON and REP of STOCHEM where these runs were identical except that they used different meteorological diagnostics taken from consecutive years of the $1\times\text{CO}_2$ GCM experiment. Table 3 lists the to-

tal global model burdens for various species in January and July. Only minor differences between the control run (CON) and its repeat using the next years meteorology (REP) can be observed. Changes to local surface layer monthly mean ozone concentrations in January and July were generally less than 20 ppb between these scenarios, while the globally averaged changes for January and July at various model levels (Table 4) are generally less than about 1 ppb. Mean surface ozone concentrations in the control experiment (CON) were 27.0 ppb in January and 34.8 ppb in July. In the following year of the GCM (REP), these concentrations had increased slightly by about 1.2 ppb in winter and decreased by 0.7 ppb in summer. Much of the increase in winter was due to increases over the tropical Atlantic and in the Gulf of Mexico. The summer decreases were located over each of the major continental areas.

These differences are quite large locally and reflect the influence of atmospheric circulation changes on the transport of ozone from the stratosphere, from tropical biomass burning, and from human activities. They

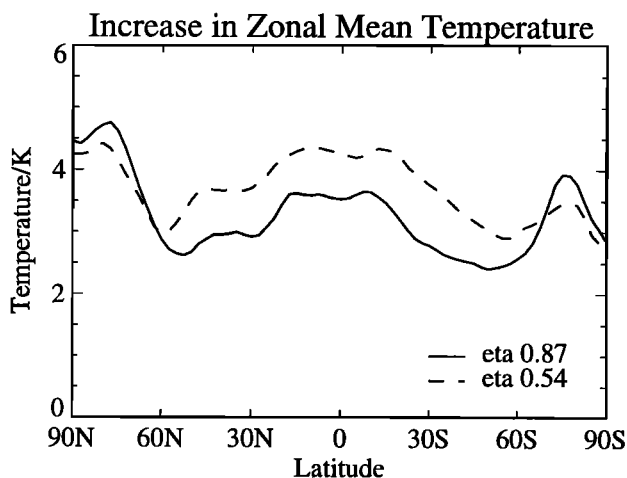


Figure 1. Change in zonal, annual mean of temperature at eta 0.87 and 0.54 between the $1\times\text{CO}_2$ and $2\times\text{CO}_2$ simulations of the slab-ocean GCM.

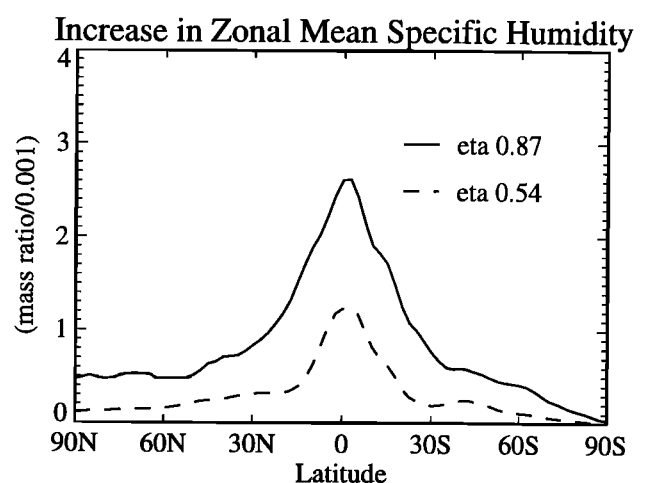


Figure 2. Change in zonal, annual mean of specific humidity at eta 0.87 and 0.54 between the $1\times\text{CO}_2$ and $2\times\text{CO}_2$ simulations of the slab-ocean GCM.

Table 3. Total Global Inventories of Selected Species for January and July

Species	Multiplier	CON	REP	2MET	BOTH
<i>January</i>					
NO _x	(×10 ³³)	6.83	6.63	6.76	30.97
HNO ₃	(×10 ³³)	4.03	3.94	4.27	7.21
PAN	(×10 ³⁴)	1.77	1.86	1.33	2.12
CO	(×10 ³⁶)	7.44	7.46	7.31	12.47
O ₃	(×10 ³⁶)	4.52	4.56	4.12	4.97
OH	(×10 ³⁰)	4.74	4.70	5.27	4.62
HO ₂	(×10 ³²)	3.26	3.19	3.66	4.39
H ₂ O ₂	(×10 ³⁴)	3.65	3.53	4.31	6.10
<i>July</i>					
NO _x	(×10 ³³)	4.10	4.17	3.90	6.30
HNO ₃	(×10 ³³)	5.12	5.18	5.42	9.98
PAN	(×10 ³⁴)	1.83	1.70	1.16	1.84
CO	(×10 ³⁶)	7.45	7.42	7.30	11.68
O ₃	(×10 ³⁶)	4.60	4.66	4.14	5.17
OH	(×10 ³⁰)	5.43	5.52	6.18	5.66
HO ₂	(×10 ³²)	3.73	3.79	4.24	5.02
H ₂ O ₂	(×10 ³⁴)	4.73	4.79	5.50	7.61

The inventories are given in molecules.

reflect a sample of the interannual variability within the GCM and provide a yardstick against which emission and other changes can be compared for likely significance. Clearly interannual variability is significant within our model and cannot be quantified reliably with one replicate year. This issue is being addressed in further work not reported here. Mean surface OH volumetric mixing ratios in the control experiment (CON) were 5.33×10^{-14} in January and 6.38×10^{-14} in July. In the following year, these values had increased slightly by 2.6% in January and 1.2% in July. In the upper troposphere, the global mean winter concentration remained unchanged, but the summer concentration decreased.

Table 5 shows the annual ozone budget for the model scenarios. There appears to have been significant changes to the input of ozone into the model from the stratosphere, with less in REP than CON; however, there is less chemical destruction, and the annual average

Table 4. Globally Averaged Ozone Concentrations for the Control Scenario (CON) and the Changes From CON at Various Model Levels for Other Scenarios

Scenario	950hPa	750hPa	550hPa	350hPa
<i>January</i>				
CON	27.0	35.0	39.4	49.7
REP-CON	1.23	0.89	0.82	-0.95
2MET-CON	-1.85	-2.80	-2.28	-3.52
BOTH-CON	5.03	6.17	7.31	7.10
BOTH-2MET	6.88	8.97	9.59	10.62
<i>July</i>				
CON	34.8	39.5	43.5	51.7
REP-CON	-0.73	-0.31	-0.60	-0.75
2MET-CON	-4.20	-5.42	-5.72	-5.03
BOTH-CON	5.36	4.74	5.10	7.50
BOTH-2MET	9.56	10.16	10.82	12.53

Concentrations are given in ppb.

Table 5. Globally Averaged Annual Budget for Ozone

Scenario	CON	REP	2MET	BOTH
Stratospheric input	730	679	777	777
NO + HO ₂	2607	2623	2693	3911
NO + CH ₃ O ₂	711	712	777	1258
NO + RO ₂	630	631	651	773
Total production	4678	4644	4899	6719
O(¹ D) + H ₂ O	1779	1765	2058	2679
O ₃ + HO ₂	1007	1000	1019	1553
O ₃ + OH	342	338	357	417
O ₃ + hydrocarbons	103	102	99	111
Dry deposition	1237	1238	1152	1512
Other processes	210	210	213	439
Total loss	4678	4653	4900	6712
Net chem. prodn	507	550	374	742
Ann. avg burden, Tg	364	368	327	404
Lifetime, days	28.4	28.8	23.2	22.0

The budget for ozone is given in units of Tg/yr.

ozone inventories are very similar. The global inventories of other oxidants (OH, HO₂, and H₂O₂) in REP remain within a few percent of the control run (Table 3). The differences between the CON and REP runs of STOCHEM serve to indicate whether the changes observed in other runs are significant.

3.2.2. Changes to oxidants with 2× CO₂ climatology. The role of changes in meteorological factors at double CO₂ was assessed by running STOCHEM using diagnostics from the 2× CO₂ meteorology (2MET) with no emission changes compared to the control. The response of the global inventory of tropospheric oxidants to these conditions (Table 3) shows that OH has increased by 11% in January and by 14% in July, while O₃ has decreased by around 10%. H₂O₂ increased by 18% in January and 16% in July. In line with the OH changes, NO_x concentrations have decreased in both months, with HNO₃ concentrations increasing. PAN concentrations decreased by 25% in January and 37% in July, and CO concentrations decreased slightly.

The decline in tropospheric ozone appears to have been mainly caused, see Table 5, by the increased fraction of the ozone photolysis that acts as a net ozone loss through equations (1) and (2) where the loss of O(¹D) is enhanced because of the increased water vapor concentration associated with the double CO₂ meteorology. Table 5 shows that this term of the ozone budget is balanced by changes to ozone production and loss, largely through dry deposition. The overall effect is to decrease the ozone lifetime, with the net chemical production some 130 Tg yr⁻¹ less than in the control scenario. This more than compensates for the increase in stratospheric ozone flux transported into the top of the model which is caused by changes to the stratospheric circulation at double CO₂. In January, the global mean ozone decrease amounts to 1.9 ppb in the surface layer and 3.5 ppb in the upper troposphere. Local changes approach +10 and -20 ppb, and there is a tendency for all model responses to be zonal in distribution and to in-

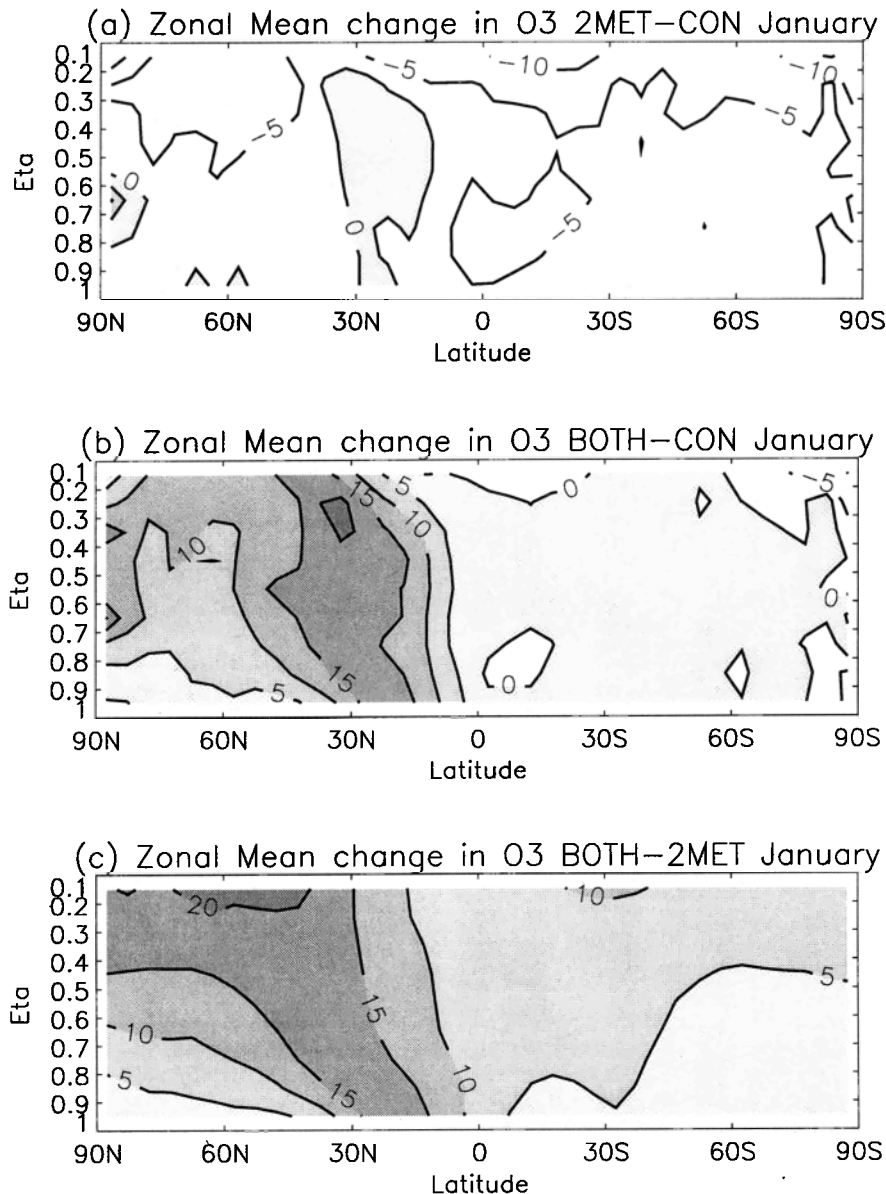


Figure 3. Zonal mean cross section of ozone differences between scenarios for January (ppb); shaded regions denote increases and unshaded regions denote decreases. (a) 2MET-CON, (b) BOTH-CON, and (c) BOTH-2MET.

crease with height in the model. The greatest decreases appear to be in the tropics. In July, global mean ozone decreases are larger than their winter values and are in the range 4.2-5.7 ppb but show less variation with height. Local ozone decreases exceed 20 ppb, are zonal in distribution, and are not obviously restricted to the tropics.

Figures 3a and 4a show that the zonal mean ozone has decreased throughout the model, with the largest changes at the top, and Table 4 shows that the global average decrease for several heights ranges from 1.8 ppb near the surface to 3.5 ppb at 350 hPa. Table 6 and Figures 5a and 6a show that the increases to the zonal mean OH concentrations are most important above 700 hPa in the tropics and the summer hemisphere. Nearer the surface, there are decreases to OH in the summer hemi-

Table 6. Globally Averaged OH Concentrations for the Control Scenario (CON) and Changes From CON at Various Model Levels for Other Scenarios

Scenario	950hPa	750hPa	550hPa	350hPa
<i>January</i>				
CON	5.33	6.60	6.03	5.61
REP-CON	0.17	0.19	0.09	-0.02
2MET-CON	0.02	0.13	0.79	0.75
BOTH-CON	-0.62	-1.01	-0.34	-0.21
BOTH-2MET	-0.64	-1.14	-1.13	-0.96
<i>July</i>				
CON	6.38	7.96	7.24	6.56
REP-CON	-0.08	-0.19	-0.22	-0.14
2MET-CON	-0.06	-0.01	0.70	0.79
BOTH-CON	-0.33	-1.07	-0.29	-0.03
BOTH-2MET	-0.27	-1.06	-0.98	-0.82

Concentrations are given in units of mixing ratio $\times 10^{-14}$.

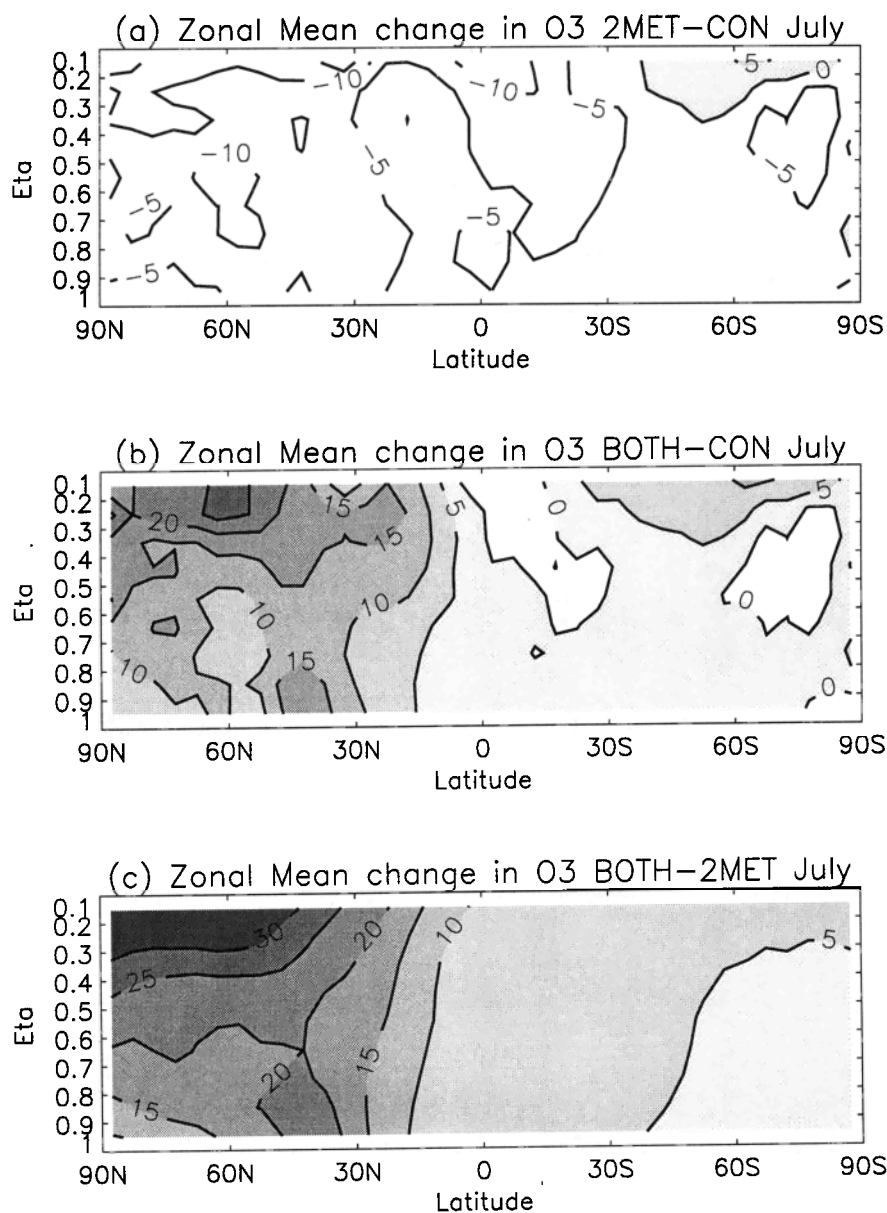


Figure 4. Zonal mean cross section of ozone differences between scenarios for July (ppb); shaded regions denote increases and unshaded regions denote decreases. (a) 2MET-CON, (b) BOTH-CON, and (c) BOTH-2MET.

sphere between 0° and 30° . The increases to OH concentrations are caused by increases to the production rate of OH through the increased water vapor (equation (2)) and occur despite the decreases to ozone. Decreases to OH in the tropics near the surface appear to be caused by increases to $\text{CH}_4 + \text{OH}$ fluxes driven by increased temperatures there.

The increase in hydrogen peroxide concentrations is mainly due to increases to HO_2 in the double CO_2 experiment, as the role of increases to water vapor concentrations on its formation rate coefficient (k_3) act in opposition to the effect of increased temperature. The combined effect of the global mean changes to temperature and humidity in January at 870 hPa (Table 2) on k_3 is to increase it by 2.5%.

The influences of global climate change on tropospheric chemistry are not restricted to the effect of increased water vapor concentrations. The global budgets of PAN and methane are significantly affected by increases in temperature. In the case of PAN increases in temperature lead to a dramatic increase in thermal decomposition rate and hence to its much reduced global inventory. For methane, the lifetime with respect to OH has reduced by 15% in the double CO_2 climatology.

3.2.3. Role of changes to emissions and climate. The role of changes to both emissions and climate compared to the control run was done using the $2\times \text{CO}_2$ meteorology together with the emissions changes appropriate to 2075 (run BOTH). Analysis of the changes to the global inventories of ozone with re-

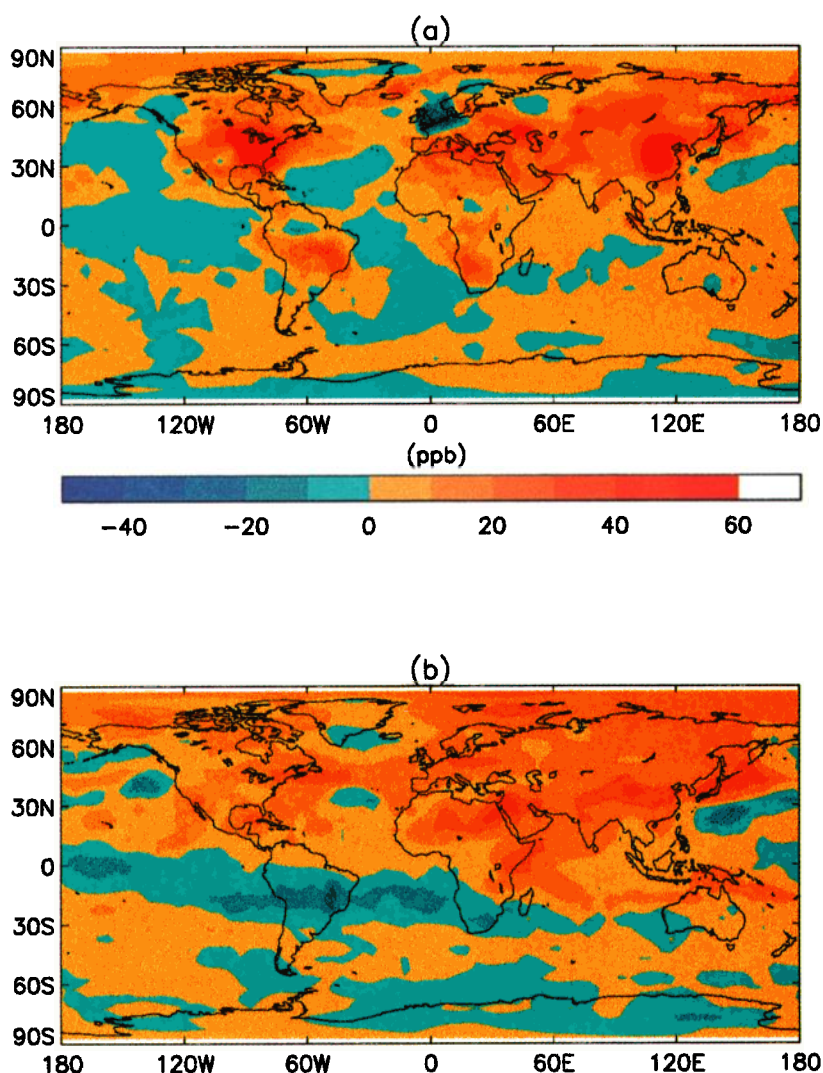


Plate 1. Difference in ozone concentrations between the run using double CO_2 meteorology and 2075 emissions (BOTH) and the control run (CON) for July. (a) 950 hPa and (b) 550 hPa.

spect to the control run shows a considerable increase, with the globally and seasonally averaged tropospheric ozone increasing by 6.4 ppb. OH inventories are only slightly different (Table 3) to the control scenario. H_2O_2 inventories have increased by around 60% compared to the control. There are large increases to NO_x inventories because of the increase in emissions.

In the model experiment with increasing emissions (BOTH), ozone concentrations increase significantly relative to the control experiment. In January, global mean ozone concentrations increase by about 5 ppb at the surface and 7 ppb in the upper troposphere (Table 4). These increases are not greatly different in July, and Figures 3b and 4b show that they are mainly in the Northern Hemisphere. Zonal mean ozone concentrations increase by 10–30 ppb concentrated in a zonal band at around 30°N during January and over much of the Northern Hemisphere in July. The zonal mean

changes mask considerable meridional variation, and Plate 1 shows the differences between scenario BOTH and the control for two heights in July. Near the surface, the response of the model is dominated by ozone increases over North America and Asia, but there are significant decreases of around 10 ppb over oceanic areas such as the North and central Pacific and the South Atlantic. In midtroposphere, ozone increases follow the surface changes in the winter but not in the summer. In July a large region of ozone decrease is apparent stretching from Indonesia across the Pacific, Atlantic, and Indian Oceans. This feature is caused by changes to the vertical transport in this region.

The zonal mean OH changes in scenario BOTH are shown in Figures 5b and 6b. These show significant decreases to OH concentrations in the lower troposphere, in contrast to the increases in scenario 2MET. This is expected owing to the increases to CH_4 and CO and

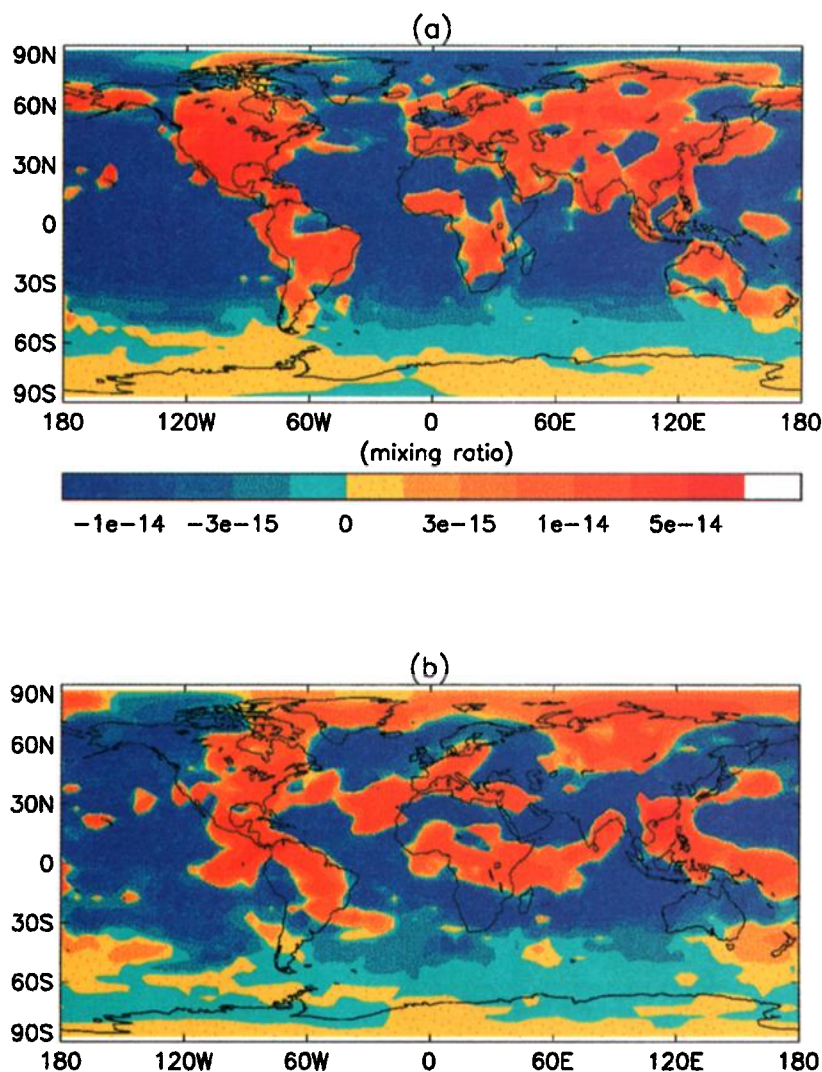


Plate 2. Difference in OH concentrations between the run using double CO₂ meteorology and 2075 emissions (BOTH) and the control run (CON) for July. (a) 950 hPa and (b) 550 hPa.

is the basis for the positive feedback between methane and its sink [Chameides *et al.*, 1976; Sze, 1977; Isakson, 1988; Prather, 1994]. As with ozone, there is considerable meridional variability, in this case evident as continental increases and oceanic decreases in the lower troposphere in July in Plate 2. This behavior is caused by increases in the rate of reaction of OH with CO and CH₄ throughout much of the model, tending to decrease OH, combined with increases in the flux of HO₂ with NO over continental areas where NO_x has increased, providing an increase in OH. NO_x has a much shorter atmospheric lifetime compared with CO and methane, so that its response to emissions changes is limited to those areas where there are significant emissions.

The present study diverges dramatically from the 2-D and 3-D model responses reviewed by Prather *et al.* [1995] which all showed an increase in methane lifetime following a step change in concentration. Here, despite an even larger methane step change, the methane

lifetime has decreased by 2.5%. OH radicals have decreased by less than the increase in methane concentrations leading to an increased flux of OH + CH₄. This increased flux has clearly been driven by the increase in water vapor concentrations and temperatures associated with the 2 × CO₂ experiment.

3.2.4. Role of changes to emissions. The role of emissions changes in STOCHEM was not assessed separately in these scenarios, but it may be obtained from the difference between runs 2MET and BOTH made with the meteorological diagnostics from the 2 × CO₂ meteorology. It is expected that the sensitivity of the model to emissions changes will depend on meteorological factors, but the results from earlier experiments showed that this effect is small, so the sensitivity of the model to emissions changes at 2075 is expected to be similar to that in 1990. An earlier series of experiments done with the chemical mechanism described by Collins

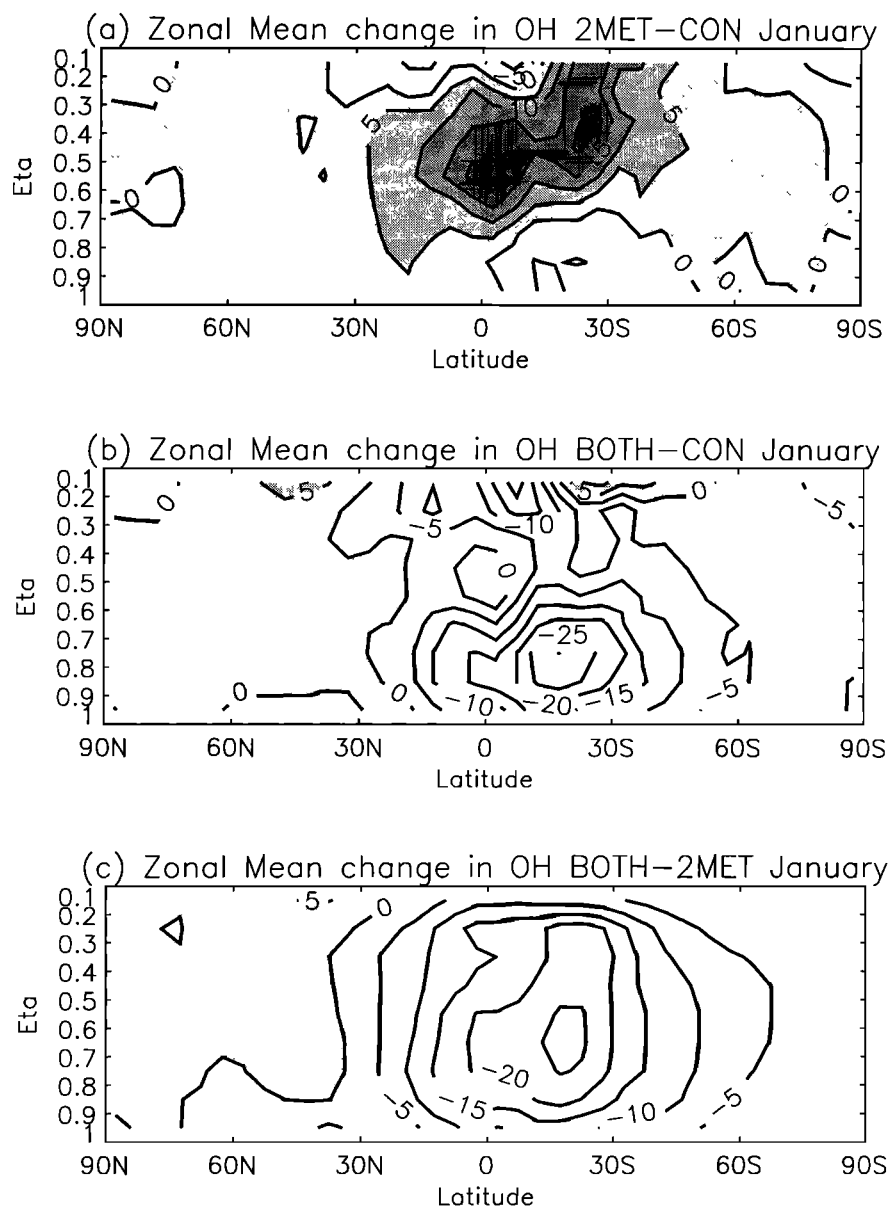


Figure 5. Zonal mean cross section of OH differences between scenarios for January (mixing ratio $\times 10^{-15}$); shaded regions denote increases and unshaded regions denote decreases. (a) 2MET-CON, (b) BOTH-CON, and (c) BOTH-2MET.

et al. [1997] showed that the response of the model to the increase in emissions between 2075 and 1990 differed only slightly when the experiment was done with a $2 \times \text{CO}_2$ climatology instead of a $1 \times \text{CO}_2$ climatology. Midtropospheric changes to OH were 16% larger using a $2 \times \text{CO}_2$ climatology compared to the present day, and the O_3 response was 8% less. These changes are somewhat less than the differences between the scenarios discussed here.

For ozone, the effect of emission-only changes lead to ozone increases in all areas of the model in contrast to the changes shown where both emissions and climate change. The changes to global-mean ozone assessed by the difference between scenarios BOTH and 2MET are therefore elevated over the differences between BOTH

and CON. The global and annual mean tropospheric ozone response to emissions changes between 2075 and 1990 was 10.3 ppb, around 60% higher than the response to emissions combined with climate change. Figures 3c and 4c show the zonal mean ozone differences generated by emission changes alone and show that there is a larger increase in ozone in the Southern Hemisphere and an elevated response of ozone in the upper part of the model in the Northern Hemisphere than generated by the same emission changes with climate change. The zonal mean OH changes shown in Figures 5c and 6c for emissions changes alone show an enhanced response compared to those for emissions and climate change with decreases extending throughout the troposphere.

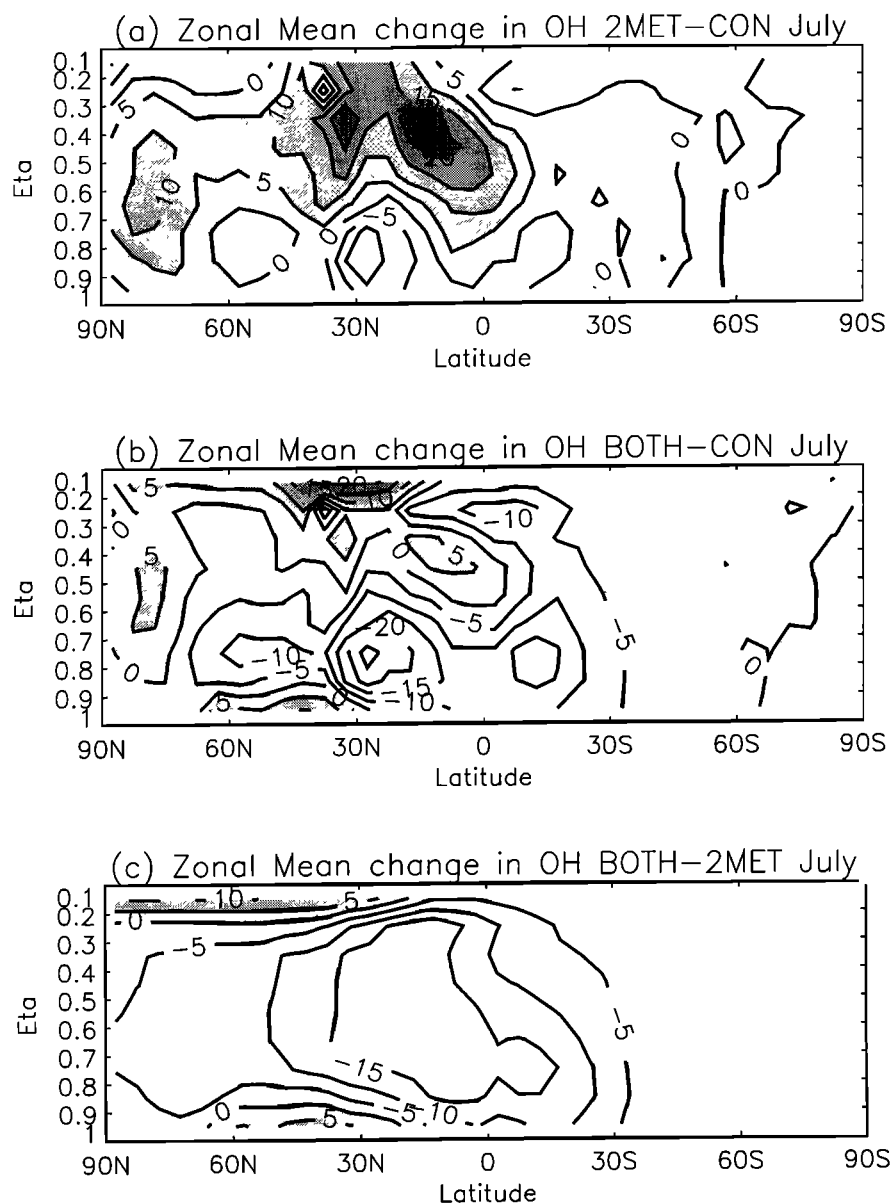


Figure 6. Zonal mean cross section of OH differences between scenarios for July (mixing ratio $\times 10^{-15}$); shaded regions denote increases and unshaded regions denote decreases. (a) 2MET-CON, (b) BOTH-CON, and (c) BOTH-2MET.

4. Discussion

Many features of the climate model can effect the behavior of the chemical model, and various features of this feedback have already been discussed [Ramanathan *et al.*, 1987]. Previous work by Hameed and Cess [1983] showed an 11% loss of ozone due to an increase in global mean surface temperature at double CO_2 of 2.9 K, though methane concentrations were also allowed to decline in this study. Thompson *et al.* [1989] has focused on the role of enhanced water vapor and temperature in simple models, but more recently Fuglestedt *et al.* [1995] report responses of tropospheric ozone and OH in a 2-D chemical model to increases in temperature and water vapor concentrations provided from a

GCM simulation, with ozone concentrations decreasing by 10% in response to increases in temperature and water vapor for a global temperature increase of 3.9 K.

The results presented above show that the predicted climatic changes from an equilibrium double CO_2 experiment with a slab ocean GCM have a significant effect on both ozone and tropospheric oxidants predicted by an off-line model. As an example, the globally averaged ozone change at around 500 hPa in July predicted in a model which used 2075 emissions and $2 \times \text{CO}_2$ meteorology was shown to be almost half that predicted from a model which ignored the meteorological changes (Table 4). For a change in climate, we report a 9.7% decrease in global mean tropospheric ozone with a midtropospheric temperature increase of 3.5 K. It is likely that these

changes are mainly caused by increases to water vapor and temperature, and in this respect the results agree with those of *Hameed and Cess* [1983], *Thompson et al.* [1989], and *Fuglestevdt et al.* [1995]. However, there is evidence that changes to the global circulation have a significant impact, for example in the comparison between scenarios BOTH and CON, there are significant decreases in ozone in the western Pacific and in an area stretching eastward from the central Pacific to Australia (Figures 3b and 4b). These areas seem to be correlated with changes to vertical motion in the GCM. The effect of additional cloudiness (reported by *Senior* [1999]) is unknown at this stage. Further analysis of the results presented here should increase our knowledge about the role of individual factors on the chemical fluxes in the model. Further experiments in which each factor is varied individually could be helpful.

Both the predictions of future climate change by GCMs and the response of the chemical model to climate change have considerable uncertainties. In the case of the GCMs, this is due to different model formulations giving a range of responses to predictions of future greenhouse gas and aerosol forcing. This is evident in both the magnitude and patterns of the model response and is treated in detail by *Kattenberg et al.* [1996]. The assumption made here is to associate the equilibrium response of a slab-ocean GCM with the magnitude of the changes in a coupled ocean-atmosphere GCM with greenhouse gas forcing in order to identify the date when these might be expected. As sulphate aerosol forcing was not considered, this date could be expected to be an underestimate. If the experiment of *Mitchell et al.* [1995], including sulphate aerosol, was used instead, the date would have been around 2100 instead of 2075. This difference is within the uncertainty range of reported GCMs.

The global average increase in tropospheric ozone over all seasons for a change of emissions between 1990

Table 7. Globally Averaged Annual Budget for OH

Scenario	CON	REP	2MET	BOTH
O(¹ D) + H ₂ O	74	74	86	112
HO ₂ + NO	54	55	56	81
HO ₂ + O ₃	21	21	21	32
H ₂ O ₂ + hν	14	14	17	24
Other processes	4	4	4	6
Total OH production	167	167	184	255
CO + OH	74	74	78	113
CH ₄ + OH	22	22	26	44
HCHO + OH	13	13	15	20
HO ₂ + OH	7	7	9	9
O ₃ + OH	7	7	7	9
H ₂ + OH	7	7	8	8
CH ₃ OOH + OH	7	7	9	12
H ₂ O ₂ + OH	6	6	7	9
C ₅ H ₈ + OH	5	5	5	5
Other processes	19	19	20	26
Total OH loss	167	167	184	255

The annual budget for OH is given in Tmole/yr.

Table 8. Globally Averaged Annual Budget for HO₂

Scenario	CON	REP	2MET	BOTH
CO + OH	74	74	78	113
HO ₂ NO ₂ + M	27	27	28	52
HCHO + hν	19	19	20	28
CH ₃ O ₂ + NO	15	15	16	26
HCHO + OH	13	13	15	20
O ₃ + OH	7	7	7	9
H ₂ O ₂ + OH	6	6	7	9
H ₂ + OH	7	7	8	8
Other processes	16	15	47	75
Total HO ₂ prodn	184	183	198	288
HO ₂ + NO	54	55	56	81
HO ₂ + HO ₂	48	48	54	72
HO ₂ + NO ₂	27	27	28	52
HO ₂ + O ₃	21	21	21	32
HO ₂ + CH ₃ O ₂	19	18	22	33
HO ₂ + OH	7	7	9	9
Other processes	8	7	8	9
Total HO ₂ loss	184	183	198	288
Total OH → HO ₂	108	108	117	161
Total HO ₂ → OH	75	76	78	114

The annual budget for HO₂ is given in Tmole/yr.

and 2075 and evaluated using the double CO₂ climatology is 10.3 ppb. Over the period 1990-2050 and evaluated using the present day climatology, the model gives an increase in globally averaged ozone of 9.2 ppb. *van Dorland et al.* [1997] report a change of 8 Dobson units (DU) for the period 1850-1990 and a change of 70% of this (5.6 DU) for the period 1990-2050 using the IS92a emission scenario. This is equivalent to a mean tropospheric increase of 8.8 ppb, very close to our result for the same period.

The behavior of tropospheric oxidants with respect to concurrent changes to climate and emissions is crucial in determining the model response in future conditions, and Tables 7 and 8 shows the globally averaged annual budget for OH and HO₂ for each scenario. Total OH production is around 10% larger in the model using double CO₂ climatology (2MET) than the control, and there is almost no difference between the control and the control repetition. The increase in OH production is mainly due to an increase in the flux of O(¹D) + H₂O, which despite the decrease in ozone concentrations, has increased owing to the rise in water vapor. This increase is balanced by a rise in the reaction fluxes of OH with CO and CH₄. In the case of the reaction with CH₄, this flux is enhanced by the temperature rise experienced. For the scenario using 2075 emissions with double CO₂ climatology, there is a dramatic increase in OH production, with O(¹D) + H₂O increasing further owing to the increase in ozone, with the increases to HO₂, NO_x, and O₃ contributing to the increase in the rate of production of OH from HO₂. This highlights a major difference between the radical budget response observed in scenario BOTH, where the percentage rises in total OH production and total HO₂ → OH fluxes in the BOTH scenario being approximately equal, and the

response of scenario 2MET, where the percentage rise in total OH production is much greater than the rise in $\text{HO}_2 \rightarrow \text{OH}$ flux driven by the change in $\text{HO}_2 + \text{NO}$ in the BOTH scenario.

The changes to tropospheric oxidants reported here are very large, with globally averaged hydrogen peroxide inventories in the BOTH scenario increasing by as much as 40% in July (Table 3) compared with the control. It is clear that changes to oxidants will have a significant effect on sulphate aerosol calculations in the future. This argument may also apply to the oxidation of DMS to sulphate aerosol, so that there may be an additional feedback between climate and DMS derived aerosol in addition to that proposed by *Charlson et al.* [1987].

5. Conclusions

A global three-dimensional Lagrangian chemistry transport model driven by meteorological diagnostics from a global climate model has been used to estimate ozone and other tropospheric oxidant concentrations appropriate to the conditions of the present day and to the year 2075. Changing the trace gas emissions from their present day values to those appropriate to 2075 without changing the meteorological diagnostics used leads to a global ozone increase which varies from about 6.9 ppb near the surface to 10.6 ppb in the upper troposphere during January, with increases of 9.6 and 12.5 ppb in the summer. These increases are consistent with those reported for other models [*van Dorland et al.*, 1997].

The role of climatic changes was assessed by running the model using meteorological diagnostics from a climate model run for double CO_2 conditions, with no change to emissions. The globally averaged changes to water vapor were around 20% near the surface, with temperature changes between 2.5 and 3.5°C. Ozone decreases at different levels in the troposphere varied between 6 and 8% in January and between 12 and 14% in July. Globally averaged OH volumetric mixing ratios increased by up to 14%.

The interaction of altered climatic conditions with increases to emissions was taken into account in a scenario (BOTH) which used meteorological diagnostics from a double CO_2 climatology together with trace gas emissions taken from the IPCC IS92a scenario for the year 2075. The ozone increases are smaller than was found for the emissions only scenario, 5.0 ppb near the surface and 7 ppb in the upper troposphere in both January and July. A global and seasonal mean tropospheric ozone change of 6.4 ppb was estimated, 38% less than where only emissions changes were considered. The OH response in this scenario was different to those from scenarios which consider only emissions changes in that much smaller decreases to OH were found. For example, the global mean OH decrease at 550 hPa in the BOTH scenario was only 30% of that estimated from emissions

changes alone. The OH changes in the BOTH scenario are noticeably heterogeneous, especially near the surface, where decreases over remote regions occur together with increases over the major continental areas. The changes to OH due to climate change produce a significant decrease in the lifetime of methane. This change is in the opposite direction to that produced by the increase in methane itself together with other emission changes. Current estimates of future methane concentrations may therefore be overestimated. The nature of the present experiment precludes calculation of the future course of methane, but it is clear that this must be estimated with an interactive climate-chemistry model. The significance of climate change to OH concentrations points to an inconsistency in the calculation of future methane concentrations in the IPCC process, where *Schimel et al.* [1996] present methane concentrations calculated without inclusion of the effects of increasing water vapor and temperature, despite the reported increases in these quantities in other sections of the report by *Houghton et al.* [1996].

Various mechanisms have been used to explain how the climate model response has influenced the ozone changes. Increased temperatures influence certain reaction rate coefficients which affect the ozone budget, notably the $\text{CH}_4 + \text{OH}$ reaction and the thermal decomposition of PAN. Water vapor concentrations have increased leading to increased formation rates of the free radicals from ozone photolysis. The increases to radical concentrations in response to the climatic change are responsible for increases in both the production and loss of ozone but lead to a decrease of 25% in the net chemical production of ozone and to an 18% decrease to the simulated lifetime of ozone. Changes to atmospheric circulation are less obvious but are noticeable in the midtroposphere to upper troposphere where increases to the Hadley circulation are apparent as decreases in areas of updraught and increases in downdraught regions.

The climate responses of temperature and water vapor increases have already been shown [*Fuglestedt et al.* 1995] in a two-dimensional model study to lead to decreased ozone concentrations by the year 2050 relative to the simulation without climate feedback. *Fuglestedt et al.* [1995] report a 10.2% decline in tropospheric ozone by 2050 due to temperature and humidity increases relative to the no feedback case. The results from our study are in excellent agreement, with an overall reduction in tropospheric ozone of 10% resulting from the use of a 2075 climatology in STOCHEM with 1990 emissions. The reduction in the increases caused by the projected emission changes from 1990–2075 to the globally averaged tropospheric ozone predicted by the model is larger, reducing by around 40% with the inclusion of the appropriate climatology.

The internal variability of the slab-ocean GCM produces significant local changes to mean monthly ozone and other oxidants in the off-line chemistry model, but there is little change to globally averaged properties. As

only two separate years were assessed in the model simulations, the range of results is not likely to encompass the expected range over a long time period.

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