

Heterogeneous chemistry in the STOCHEM model.

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Contents

1	Heterogeneous chemistry in the STOCHEM model	1
1.1	Introduction	1
1.1.1	Model setup	2
1.2	Inclusion of heterogeneous chemistry	3
1.3	Comparison with observations	4
1.4	Methane lifetime	6
1.5	Reaction pathways	7
1.6	Conclusions	7
1	Appendix	23
A	Comparison of aerosol fields with observations	23
B	Enhanced photolysis rates	24

1. Heterogeneous chemistry in the STOCHEM model

1.1 Introduction

Aerosol particles constitute a minute fraction of the total atmospheric volume, but these small liquid or solid droplets provide a surface on which chemical reactions can occur. The presence of aerosols, therefore, can affect the concentration of a wide range of atmospheric trace gases. Treatment of reactions occurring on and within aerosol particles (heterogeneous reactions), is not used in the standard version of STOCHEM, but may be important in the simulation of atmospheric chemistry for air quality assessments. For example, oxides of nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$) are important in the atmosphere as they can produce ozone (O_3) and OH, the main tropospheric oxidants (Levy 1971, Crutzen 1974). NO_x can be removed from the atmosphere by conversion to nitric acid aerosol and the subsequent deposition of the aerosol. In the presence of sunlight (when OH concentrations are high), this conversion mostly occurs through the reaction of NO_2 with OH. At night, OH concentrations are low and the conversion takes place via NO_3 by reaction on the surface of aerosols; NO_2 can combine with NO_3 to form N_2O_5 , which can be hydrolysed to HNO_3 within aerosol particles. Another important heterogeneous pathway is the reaction of NO_x taken up into the aerosol phase with water to produce HONO, which at dawn is then photolysed to produce OH and NO. These heterogeneous pathways provide additional sources and sinks for important trace gases and thus their inclusion in STOCHEM is likely to be important.

A number of works have investigated the importance of heterogeneous reactions on tropospheric composition. Dentener and Crutzen (1993) found the simulation of the heterogeneous reaction of NO_3 and N_2O_5 to decrease the annual mean NO_x burden by 50% (80% in winter and 20% in summer). For this work, Dentener and Crutzen (1993) used off-line sulphate and sea-salt

aerosol fields to calculate the particle surface area. The authors assume a reaction probability (the probability that a molecule will remain on the aerosol surface after impaction, γ) of 0.1. Jacob (2000) reviewed a range of field and laboratory studies and presented recommended values of reaction probabilities for a range of heterogeneous reactions of NO_x and HO_x . Evans and Jacob (2005) updated the $\gamma\text{N}_2\text{O}_5$ values used to account for measured dependencies on relative humidity, temperature and aerosol composition. They found that these updated reaction probabilities increased global mean NO_x , O_3 and OH concentrations by 7, 4 and 8% respectively.

To assess the importance of heterogeneous chemistry in STOCHEM, preliminary simulations were carried out in which heterogeneous reactions on sulphate aerosols were included. This simulation will underestimate the total aerosol surface area as other aerosol species (such as sea-salt, black carbon and mineral dust aerosol) can all contribute to the total aerosol surface area on which heterogeneous reactions can occur, however, the setup considered is sufficient for a first estimate of the importance of heterogeneous chemistry in STOCHEM.

1.1.1 Model setup

Four heterogeneous reactions are considered in this work, a summary of these reactions and the reaction probabilities assumed is given in Table 1.1. The N_2O_5 rates used are the same as those used by Evans and Jacob (2005).

Reaction	Reaction Probability	Reference
HO_2 to H_2O_2	0.2	Jacob (2000)
NO_2 to $\text{HONO} + \text{HNO}_3$	1.0×10^{-4}	Jacob (2000)
NO_3 to HNO_3	1.0×10^{-3}	Jacob (2000)
N_2O_5 to HNO_3	$\gamma = \alpha \times 10^\beta$ $\alpha = 2.79 \times 10^{-4} + 1.3 \times 10^{-4}$ $\times \text{RH} - 3.43 \times 10^{-6} \times \text{RH}^2 +$ $7.52 \times 10^{-8} \times \text{RH}^3$ $\beta = 4 \times 10^{-2} \times (\text{T} - 294) \text{ (T} \geq 294)$ $\beta = -0.48 \text{ (T} < 294)$	Kane et al. (2001) Hallquist et al. (2003)

Table 1.1: *Summary of the heterogeneous reactions considered and the reaction probabilities assumed.*

STOCHEM currently has a very simple treatment of the effect of cloud cover on photolysis

rates. Although a computationally cheap scheme, this simple treatment tends to underestimate photolysis rates when some cloud is present. To account for this bias in these simulations, calculated photolysis rates are artificially increased by 25%. The value of this increase was chosen as it has been shown give realistic methane lifetimes. This assumption is explored further in Appendix B. For this work, the model was run using generated winds for the years 1991 to 1992, but the emission grids used are based on data for the year 2000, thus the model simulations are representative of the year 2000.

1.2 Inclusion of heterogeneous chemistry

Global fields of NO_x , O_3 and OH calculated in the presence and absence of heterogeneous chemistry are shown in Figures 1.1 to 1.6. The species considered are all sensitive to the inclusion of heterogeneous chemistry; in the presence of heterogeneous chemistry, NO_x concentrations decrease by ≥ 100 pptv over most polluted continental regions, with decreases of ≥ 500 pptv simulated in large regions of Europe, N. America and China. These changes correspond to a percentage reduction of over 50% and are a result of the increase in the rate of loss of NO_x (due to the presence of an additional loss pathway). As NO_x can be a source of O_3 , the reduction in NO_x concentrations produces a reduction in O_3 in many regions; O_3 concentrations fall by ≥ 5 ppb throughout most of the tropics and parts of the northern hemisphere. The change in OH due to heterogeneous chemistry is complex; concentrations decrease (by > 0.01 ppt) throughout the tropics (due to the reduction in O_3). In the December - February simulations, OH concentrations increase (by > 0.05 ppt) in the polluted regions of Europe, N. America and China. In addition, a small (0.002 ppt) increase in OH concentrations is predicted in Europe in the September - November run. This is similar to the findings of Dentener and Crutzen

Case	Gas	NH		Tropics		SH		Glob
		NA	MO	NA	MO	NA	MO	
STOCHEM	NO_x	-57	-32	-19	-22	-19	-25	-29
Dentener and Crutzen (1993)	NO_x	-75	-45	-22	-15	-13	-37	-49
STOCHEM	O_3	-15	-13	-11	-13	-7	-7	-11
Dentener and Crutzen (1993)	O_3	-20	-13	-7	-6	-4	-10	-9

Table 1.2: *Comparison with Dentener and Crutzen (1993)*

(1993), who found OH concentrations to increase in polluted regions of the NH (in winter) in the presence of heterogeneous chemistry as the rate of loss of OH by reaction with NO_x is considerably reduced, however they note that this change is of little importance as the absolute change in OH is small (as OH concentrations are generally small in the winter hemisphere).

The simulated changes are compared to those found by Dentener and Crutzen (1993) in Table 1.2. The changes simulated in STOCHEM are in reasonable agreement with the findings of Dentener and Crutzen (1993), however, there are two main differences between the works, which will cause differences in the findings:

1. Unlike this work, Dentener and Crutzen (1993) also simulated sea salt aerosol. It is reasonable, therefore, that the change in the NO_x concentration predicted by STOCHEM are generally smaller than that found by Dentener and Crutzen (1993).
2. This work uses more up-to-date reaction probabilities (summarised in Table 1.1) this includes the use of a N_2O_5 reaction probability that is dependent on temperature, pressure and relative humidity (as used by Evans and Jacob 2005). Overall, the rates used are generally smaller than those used by Dentener and Crutzen (1993).

The simulation of heterogeneous chemistry reduces the NH NO_x concentration in STOCHEM by 57% in the November-April scenario, and by 32% between March and October. The global average NO_x concentration decreases by 29% and O_3 by 11%. Clearly these changes are significant, thus further consideration should be given to the simulation of heterogeneous chemistry in STOCHEM.

1.3 Comparison with observations

To assess the importance of the changes in trace gas concentrations described in Section 1.2, comparison was made with observations. The simulated concentrations of O_3 , CO and CH_4 are compared to observations in Figures 1.7 to 1.9. In general, the inclusion of heterogeneous chemistry tends to lead to a shift in the magnitude of the simulated species (up or down), rather than a change in the seasonal cycle. In the presence of heterogeneous chemistry, the correlation of STOCHEM CH_4 concentrations with observations deteriorates slightly as the

modelled CH_4 concentrations increase away from observed values. CO and O_3 concentrations show regions of improved and reduced agreement with observations; in the NH sites CO is generally underestimated in standard run but this is slightly improved when heterogeneous reactions are included. In contrast, the standard run tends to overestimate CO in the SH and the inclusion of heterogeneous chemistry elevates CO concentrations further away from the observations. O_3 concentrations are overestimated in the absence of heterogeneous chemistry in some regions (e.g. Mauna Loa and Barbados), which is improved in the presence of heterogeneous chemistry, but in other regions the correlation of the model data with observations worsens.

Simulated concentrations are compared to measurements (of O_3 , CO , HNO_3 , PAN, NO_x and H_2O_2) carried out during the PEMWEST and TRACE field campaigns in Figures 1.10 to 1.12. The changes occurring in the presence of heterogeneous chemistry are summarised below:

- O_3 concentrations decrease in all regions. In general, this decrease leads to an underestimation in the simulated O_3 concentrations.
- CO concentrations increase, leading to improved agreement in some regions, but also producing regions in which the CO concentration is overestimated.
- HNO_3 concentrations agree better with observations. When heterogeneous chemistry it is not included HNO_3 concentrations are overestimated, but in its presence HNO_3 concentrations fall to more realistic values.
- PAN concentrations decrease, which generally improves simulated values.
- A slight increase in H_2O_2 is predicted in some regions, but the overall change in H_2O_2 concentrations is small.
- NO_x concentrations fall, which improves comparison with observations at low altitudes. In both simulations STOCHEM fails to capture the increase in NO_x concentrations observed in the free troposphere in many regions.

The change in NO_x is explored further in Figure 1.13, which compares the annual mean concentration of NO_x (simulated in the presence and absence of heterogeneous chemistry) with NO_x observations from the EMEP network. Model data is for the year 2000 and EMEP data are averaged over the years 1999-2001 (data from three years were used to ensure the spatial

coverage was sufficient). The EMEP network was chosen as the European measurement sites correspond to a region where the predicted change in NO_x is large (Figure 1.1).

In the absence of heterogeneous chemistry, STOCHEM significantly overpredicts the surface NO_x concentration; much of England and central Europe is predicted to have a concentration of ≥ 2000 pptv, but the observations do not give such high values. In addition values of ≥ 500 pptv are predicted in Scandinavia but the observations do not give values of over 200 pptv for the same region. In the presence of heterogeneous chemistry, NO_x concentrations are reduced leading to a significant improvement in the comparison with observations, but even with heterogeneous chemistry the model tends to overestimate NO_x concentrations.

The presence of heterogeneous chemistry improves the seasonal cycle of NO_x ; without this chemistry NO_x concentrations build up in the northern hemisphere winter leading to a overestimation in the strength of the seasonal cycle (Figure 1.14). With heterogeneous chemistry, this effect is reduced and the season cycle is brought into line with that of other models.

1.4 Methane lifetime

The atmospheric lifetime of methane can be used as a measure of the oxidising capacity of the atmosphere. Global model simulations suggest that for 1992, the methane lifetime is in the range of 6.6 to 10.5 years (Isaksen and Jackman 1999), this is predicted to increase (to between 6.81 to 10.69 years) by the year 2015 due to changes in emissions. Figure 1.15 shows the modelled methane lifetime in the presence and absence of heterogeneous chemistry. The methane lifetime is increased in the heterogeneous simulation as the concentrations of OH is reduced (throughout most of the globe). Both model estimates of the methane lifetime are within the range of suggested values, but whereas the simulation without heterogeneous chemistry is in the middle of this range, the methane lifetime in the presence of heterogeneous chemistry is at the top end of the suggested range. In the presence of heterogeneous chemistry, but without the increase in photolysis rates, the methane lifetime simulated in STOCHEM is > 11 yrs, which is out-with the range suggested by other models.

1.5 Reaction pathways

The importance of the different reaction pathways can be seen from Figure 1.16, which shows the first order rate constants calculated in STOCHEM. The rate constant calculated in STOCHEM for the reaction of N_2O_5 is of the same magnitude as that calculated by Dentener and Crutzen (1993), but differences arise due to the different reaction probabilities assumed and the different aerosols treated. The rate of reaction of HO_2 is large at all altitudes, but the other reactions show a strong decrease in reaction coefficient with altitude.

1.6 Conclusions

The importance of including heterogeneous chemistry in STOCHEM has been examined. In line with the work of Dentener and Crutzen (1993), the inclusion of heterogeneous chemistry in STOCHEM is found to reduce the global burden of NO_x and O_3 as the heterogeneous chemistry provides an additional pathway of NO_x removal. The concentration of OH has a complex dependence on heterogeneous chemistry; in most regions the OH concentration decreases when heterogeneous reactions are included, but in winter a small increase in OH is predicted in some polluted regions. This occurs because the reduction in the NO_x concentration in this region results in a decrease in the rate of removal of OH by reaction with NO_x .

Overall, the inclusion of heterogeneous chemistry has a complex effect of the comparison of STOCHEM results to observations; the simulation of CH_4 concentrations deteriorates slightly and CO and O_3 concentrations both show regions of improved and worsened comparison with observations. The reduction in NO_x concentrations leads to a significant improvement in the comparison with observations in Europe, but even in the presence of heterogeneous chemistry the model still overestimates NO_x concentrations in this region.

The presence of heterogeneous pathways has been widely observed in the atmosphere and as they have been shown to have a non-negligible effect of the simulated chemistry, heterogeneous chemistry should be included in the standard model version. Future work should focus on other deficiencies in the model which may explain some of the deviations of model values away from the observations which occur in the presence of heterogeneous chemistry.

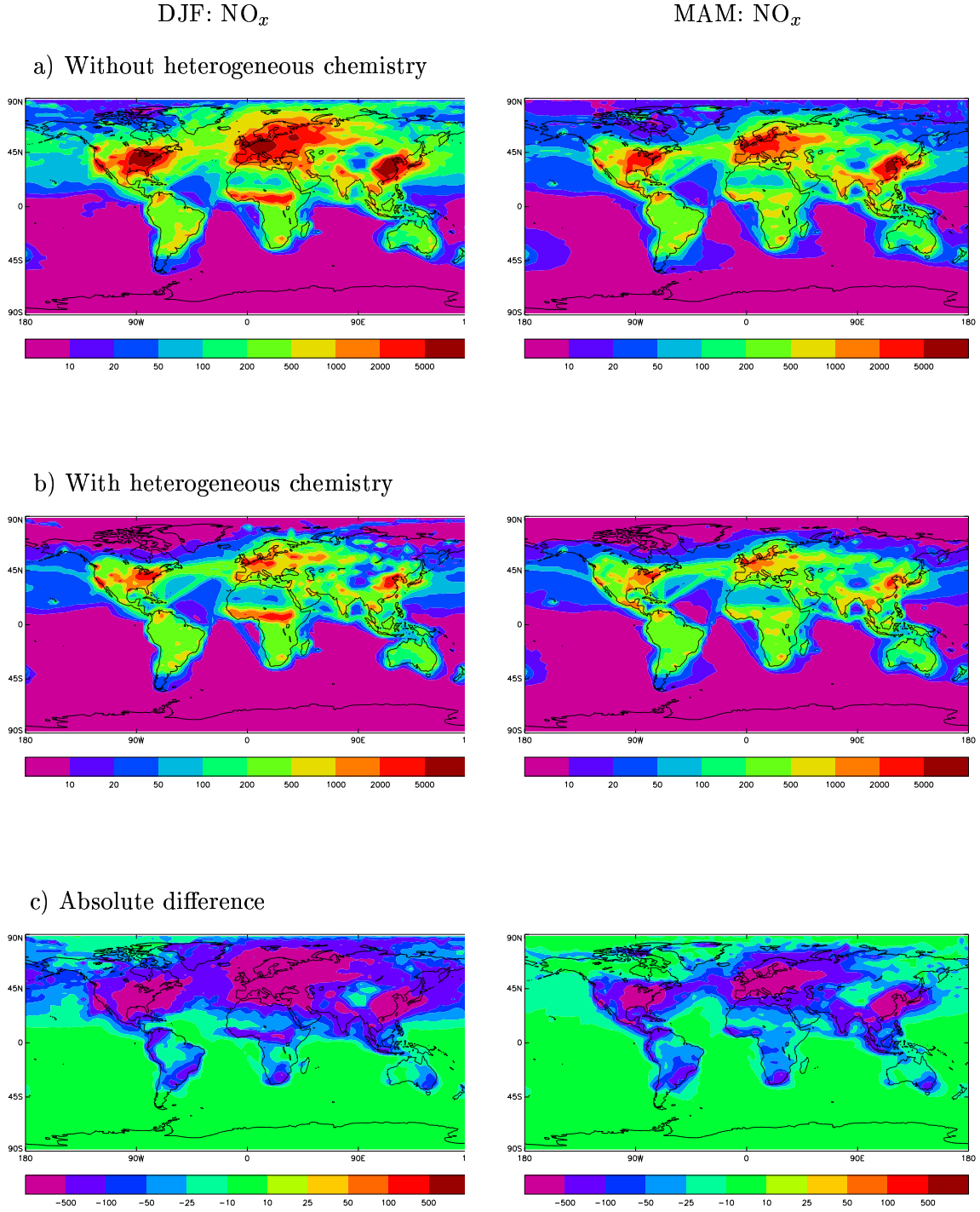


Figure 1.1: *Change in the simulated concentration of NO_x arising from the inclusion of heterogeneous chemistry on sulphate aerosol in the STOCHEM model. Panels show three month average concentrations (a) without and (b) with heterogeneous chemistry and (c) the absolute difference in concentrations (pptv). Left column shows December - February average and the right column the March - May average*

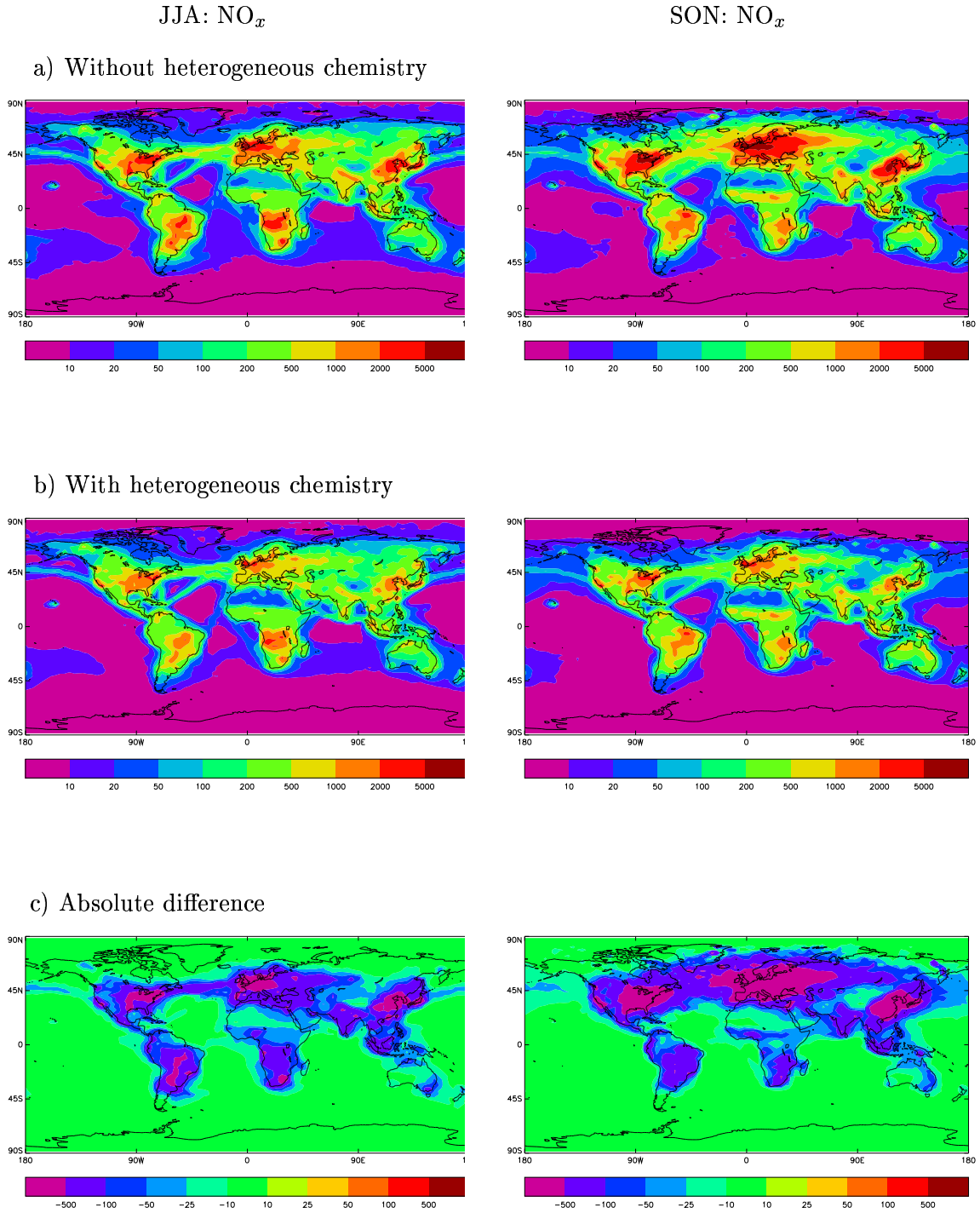


Figure 1.2: As Figure 1.1 but left column shows July - August average and right column September - October

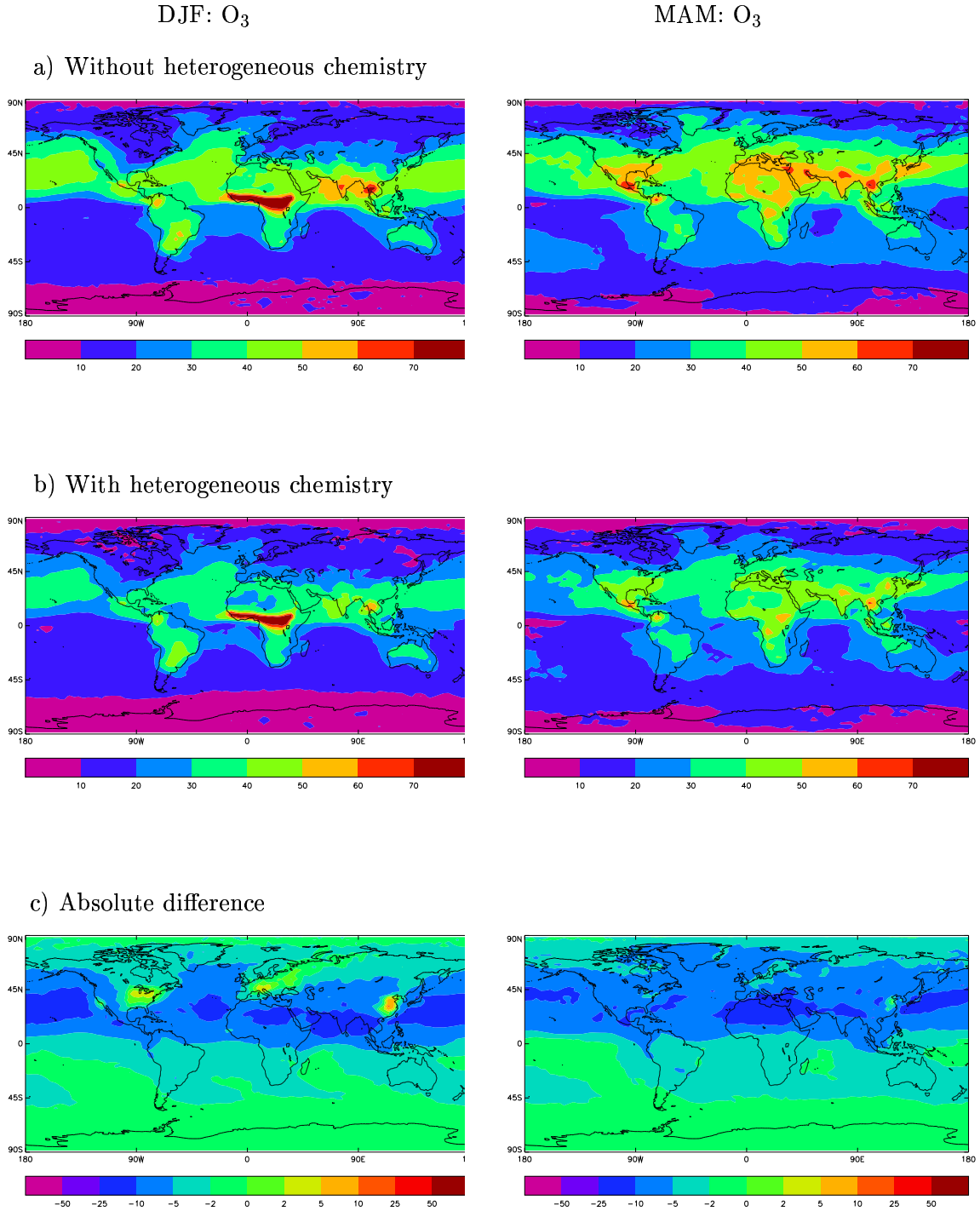


Figure 1.3: As for Figure 1.1, but for O₃ (ppbv). Left column shows December - February average and the right column the March - May average.

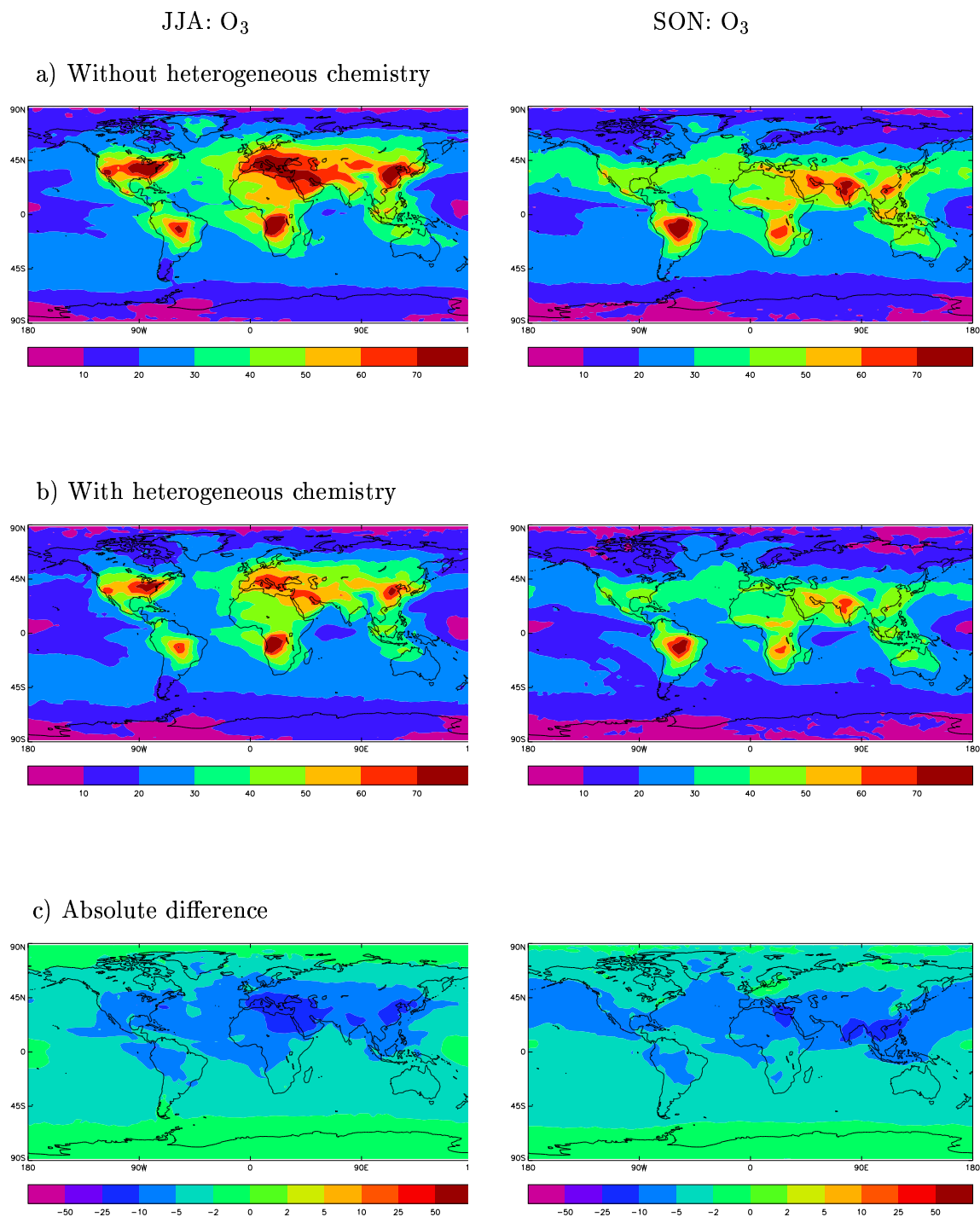


Figure 1.4: As Figure 1.3 but left column shows July - August average and right column September - October

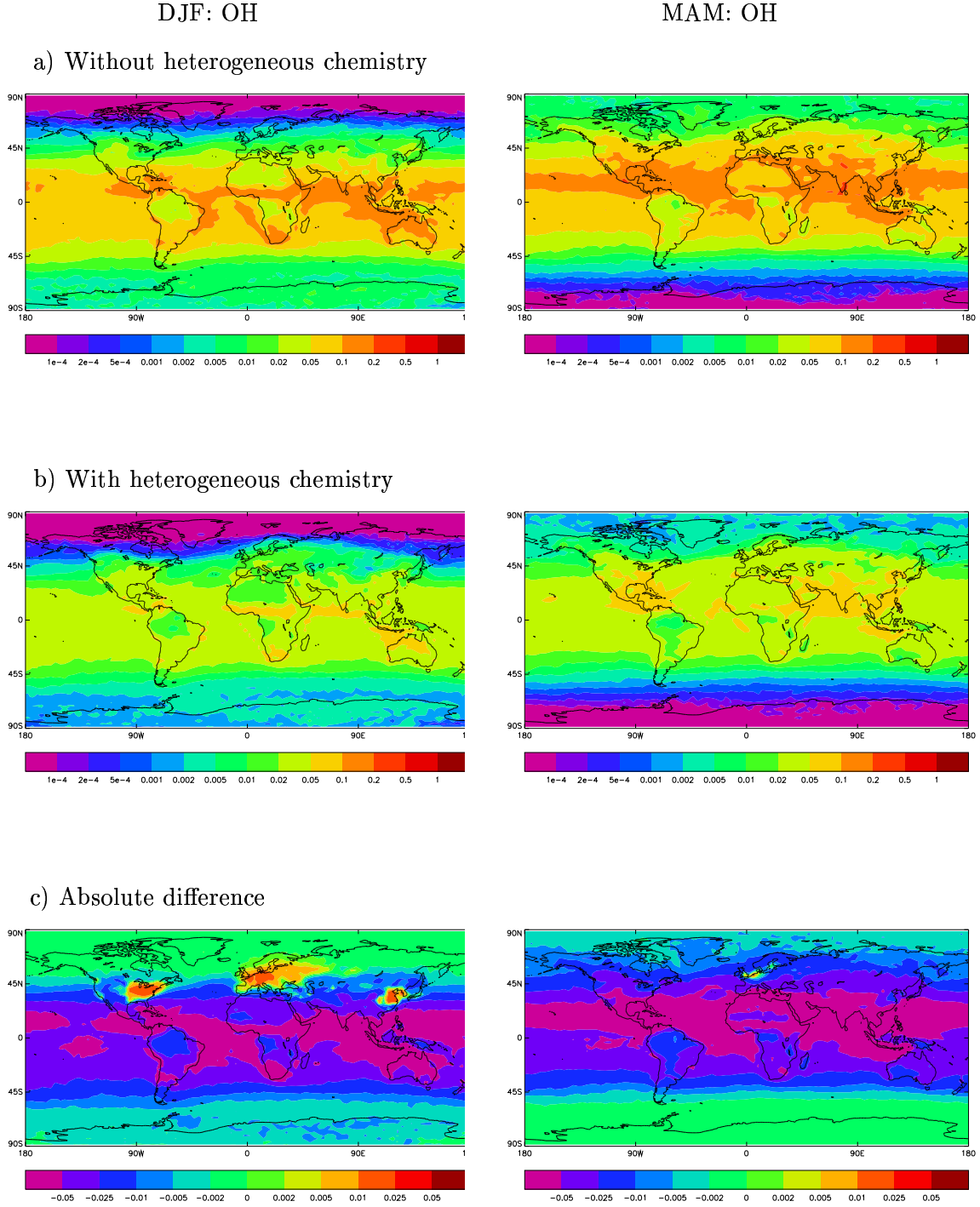


Figure 1.5: As for Figure 1.1, but for OH (pptv). Left column shows December - February average and the right column the March - May average.

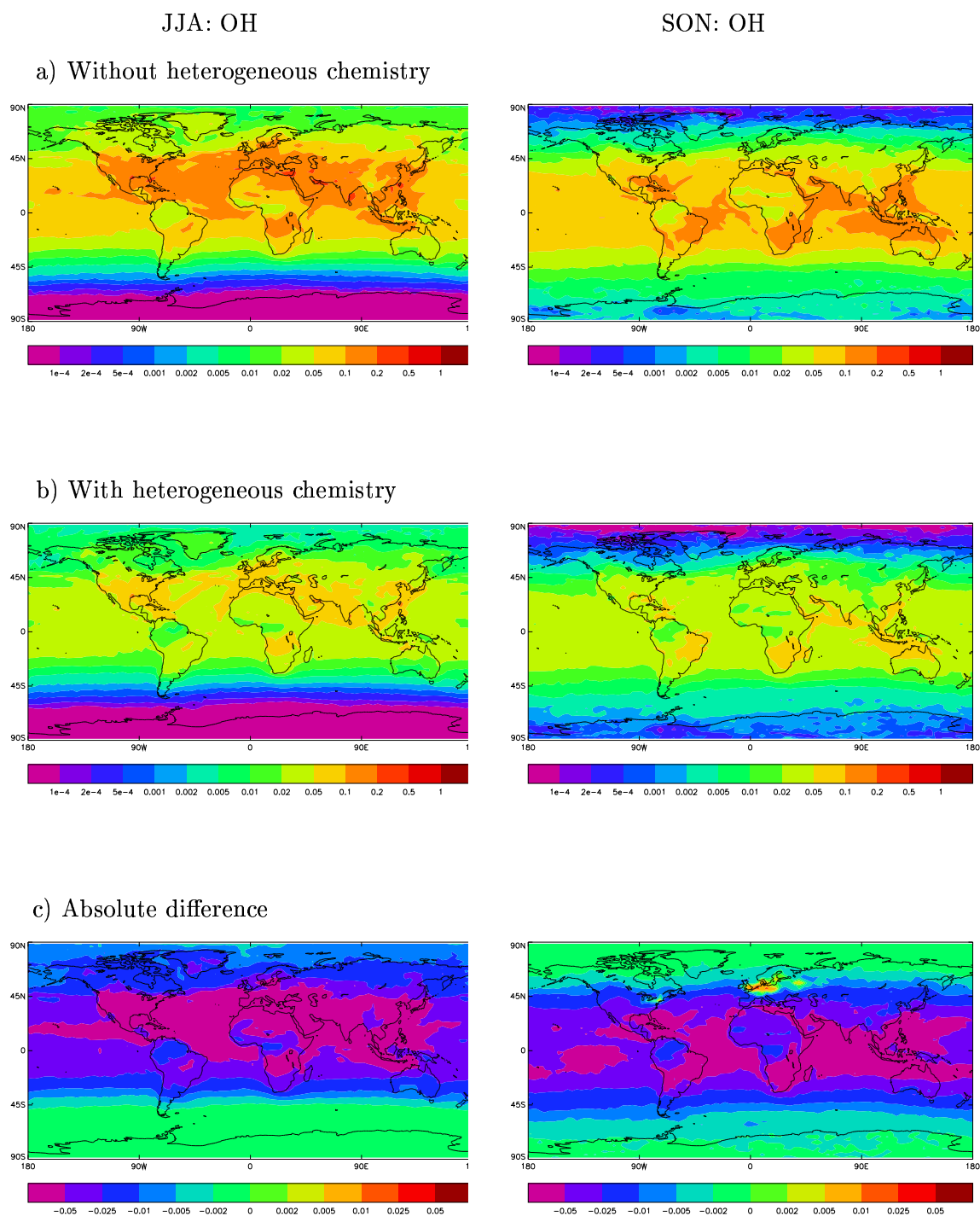


Figure 1.6: As Figure 1.5 but left column shows July - August average and right column September - October

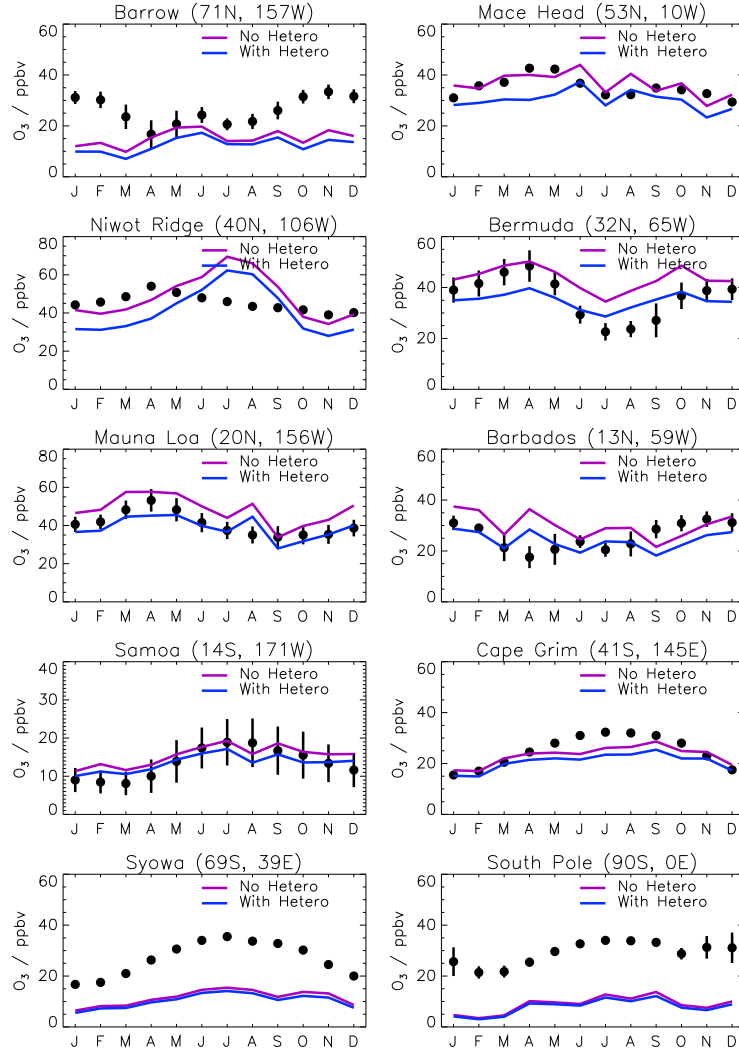


Figure 1.7: Comparison of modelled O_3 concentrations with observed data (black). Simulations including (purple) and excluding (blue) heterogeneous chemistry are shown (ppbv).

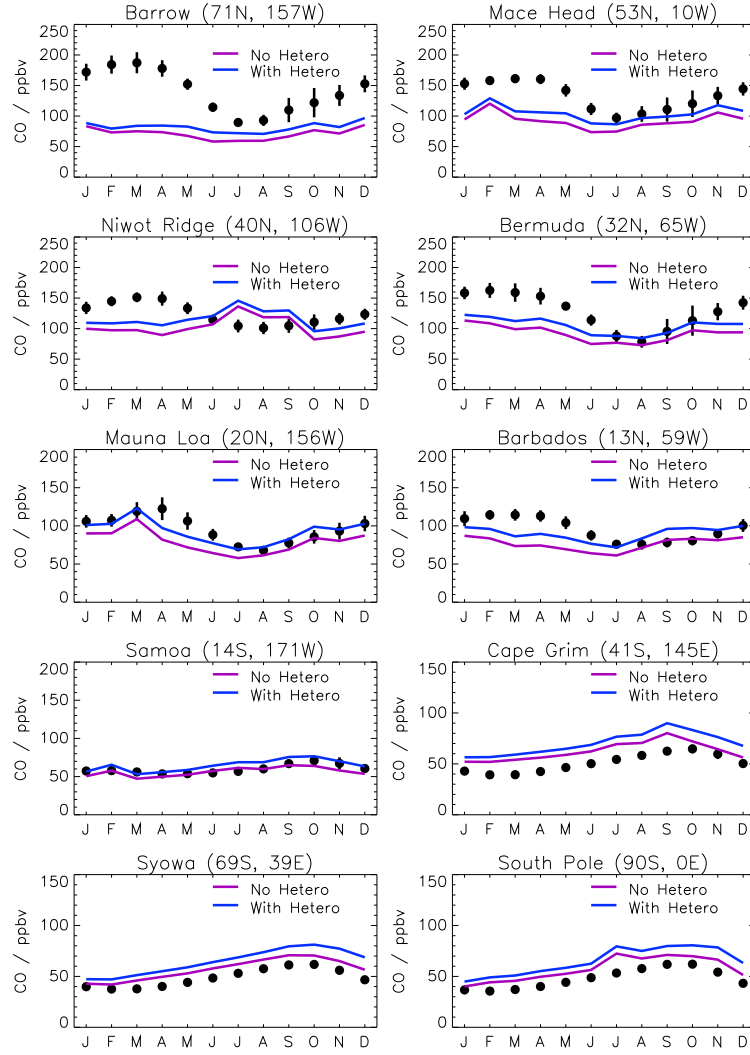


Figure 1.8: *As Figure 1.7, but for CO (ppbv).*

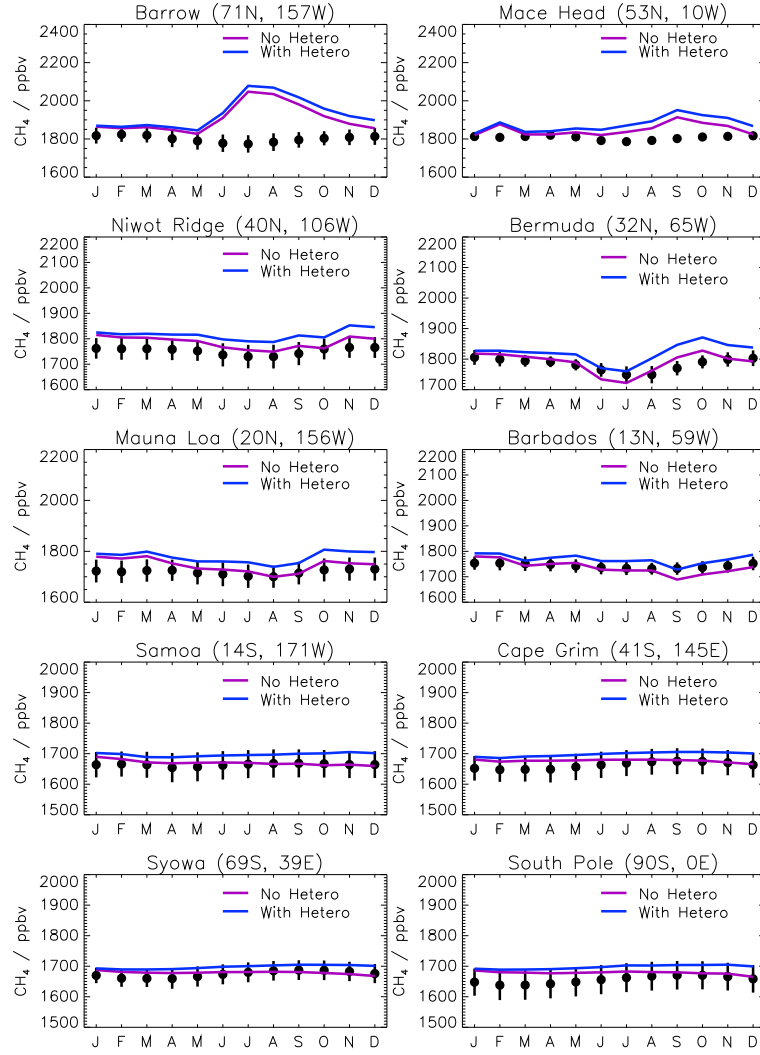


Figure 1.9: As Figure 1.7, but for CH_4 (ppbv).

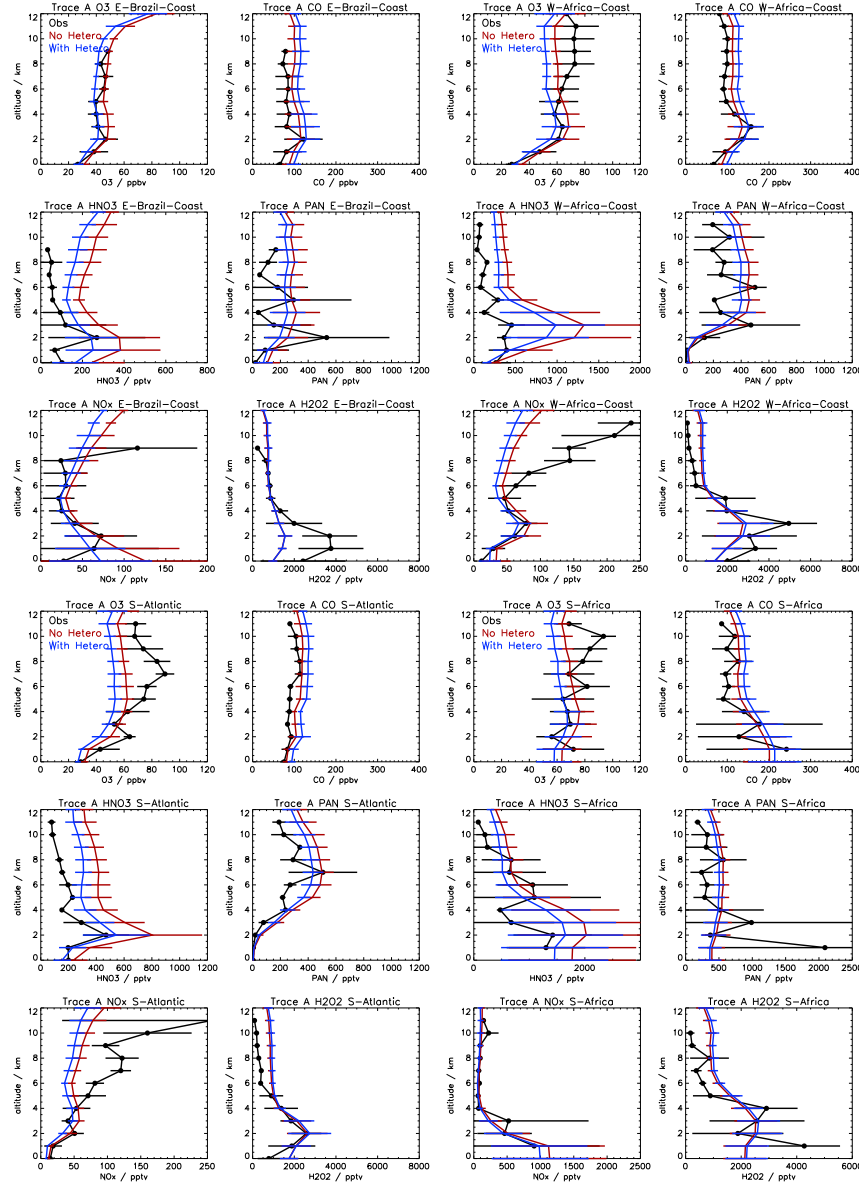


Figure 1.10: Comparison of modelled O_3 , CO , HNO_3 , PAN , NO_x and H_2O_2 concentrations simulated in STOCHEM without heterogeneous chemistry (red) and with heterogeneous chemistry (blue). Observations from the TRACE field campaign are also plotted (black).

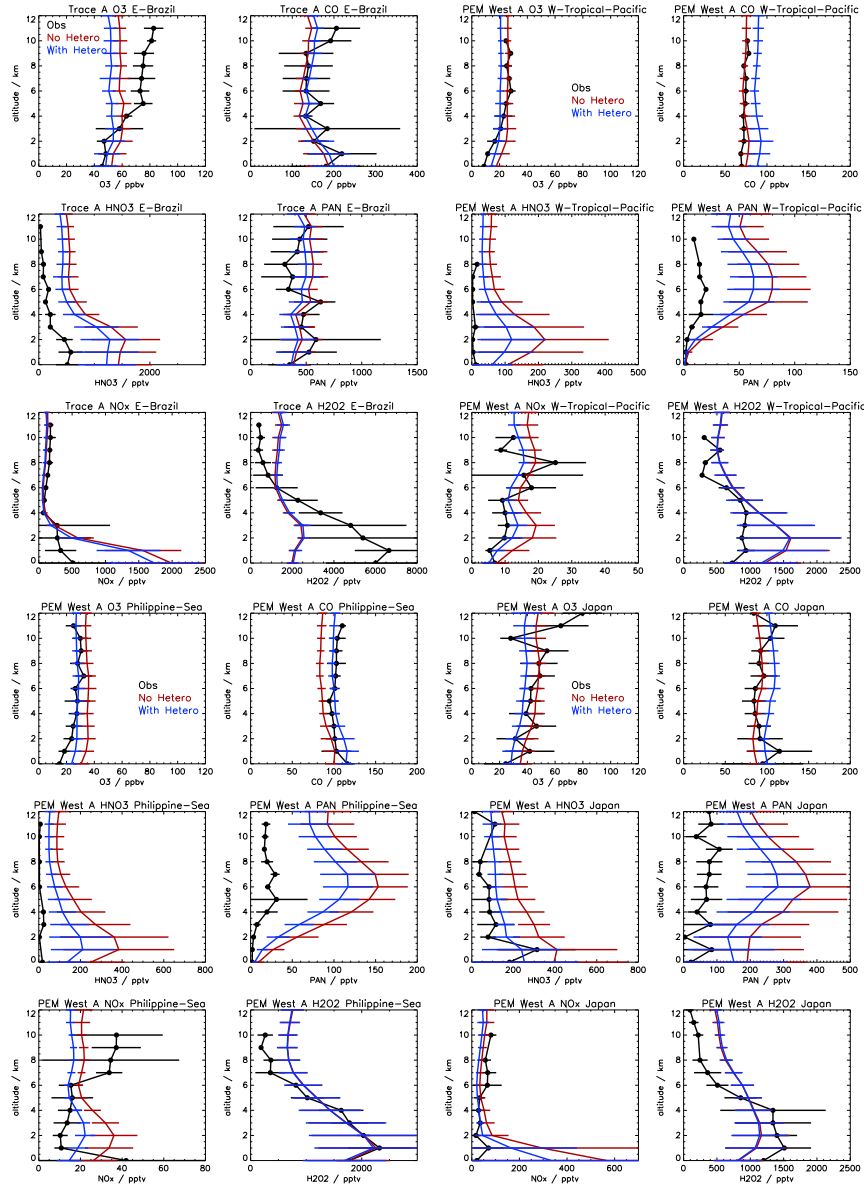


Figure 1.11: As for Figure 1.10, but the top three row show observational data from the TRACE campaign (black), and the bottom three rows show data from the PEMWEST field campaign (black).

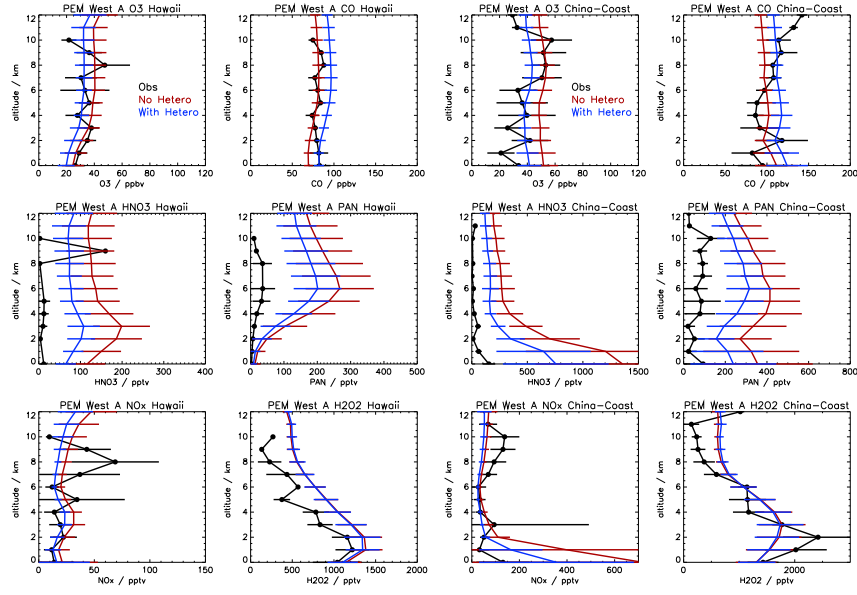
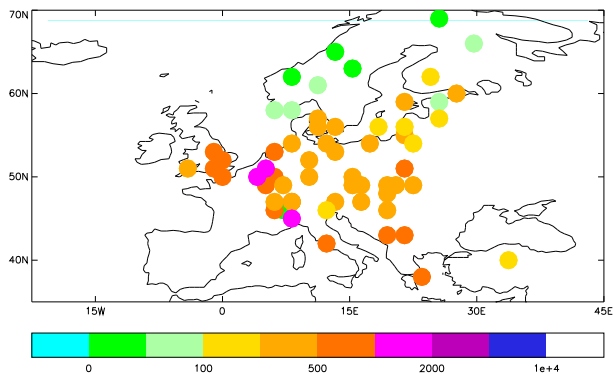
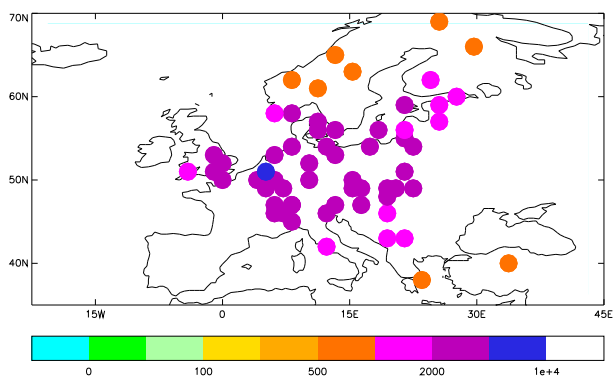


Figure 1.12: As for Figure 1.10, but observational data from the PEMWEST field campaign is presented (black).

a) EMEP (pptv)



b) Without heterogeneous chemistry



c) With heterogeneous chemistry

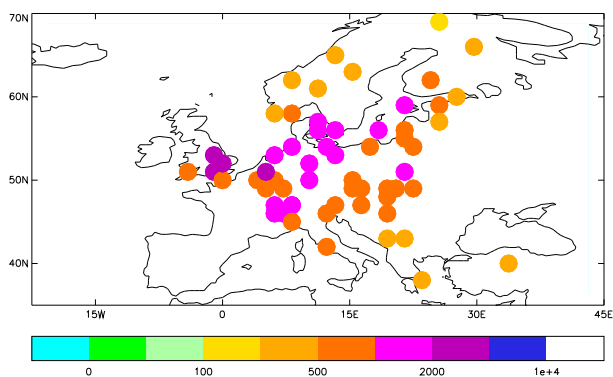


Figure 1.13: a) Surface NO_x concentration measured by the EMEP network (pptv, annual average from the years 1999-2001). Annual average NO_x predicted in STOCHEM model (b) without and (c) with heterogeneous chemistry (pptv).

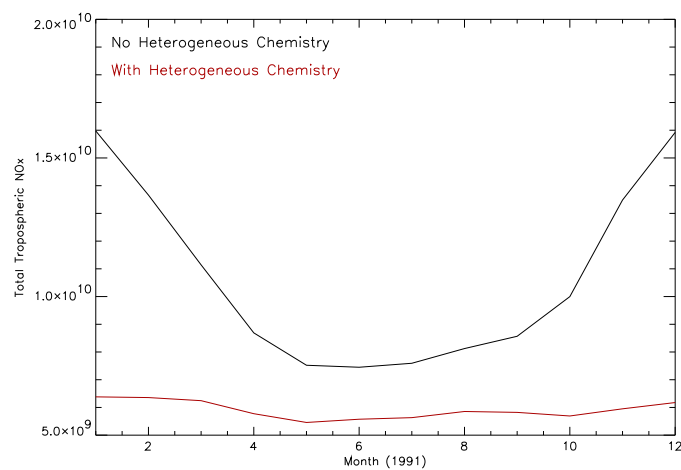


Figure 1.14: *Seasonal cycle of the total tropospheric NO_x concentration simulated without (black) and with (red) heterogeneous chemistry.*

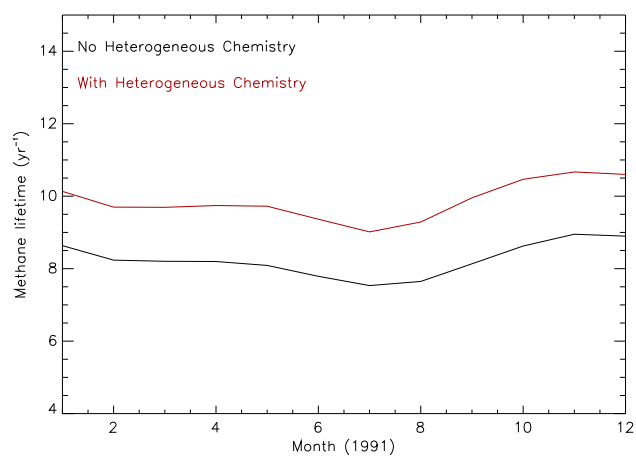


Figure 1.15: *Methane lifetime calculated for the simulations with (red) and without (black) heterogeneous chemistry.*

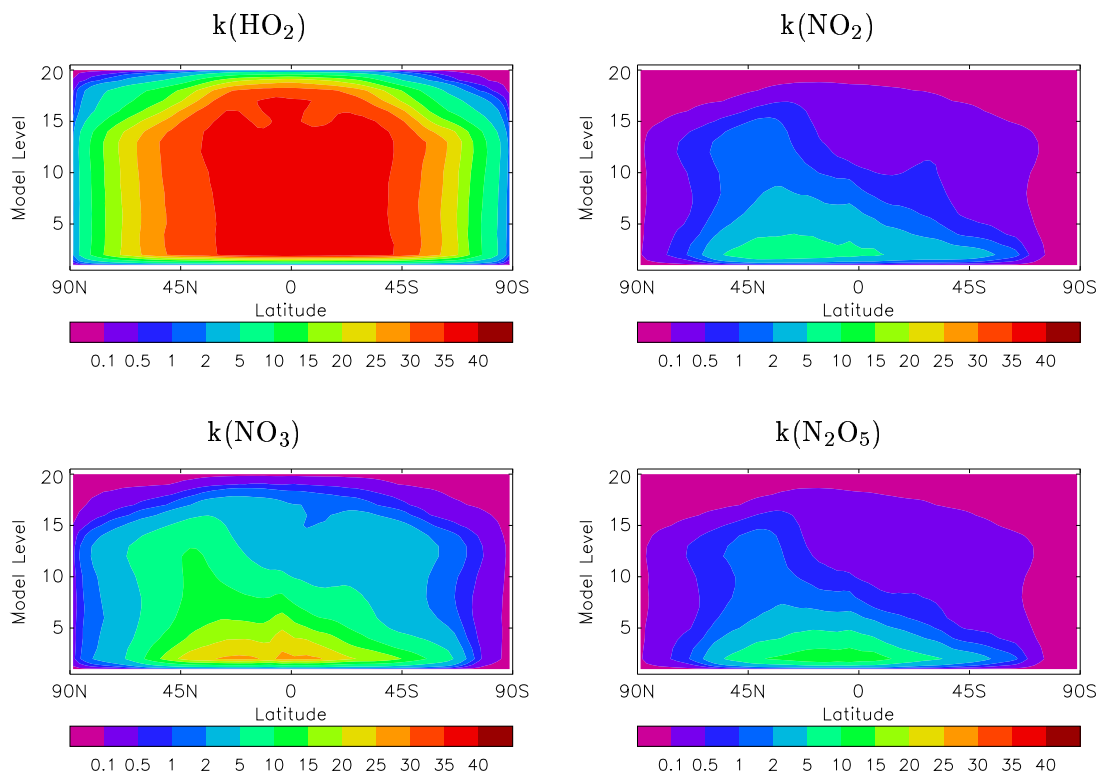


Figure 1.16: Zonal and annual mean pseudo-first order reaction coefficients for the reactions of (a) HO_2 , (b) NO_2 , (c) NO_3 and (d) N_2O_5 on sulphate aerosol ($\times 10^5 \text{ s}^{-1}$).

1. Appendix

A Comparison of aerosol fields with observations

This report examines the sensitivity of STOCHEM to heterogeneous chemistry. For this study to be useful, simulated aerosol concentrations must be realistic. The following section outlines some model validation work carried out to ensure that the accuracy of the aerosol simulated in STOCHEM is sufficient for the parameterisation of heterogeneous chemistry.

Fields of surface SO_2 and SO_4 are compared to the observations from the EMEP network in Figure B.1. STOCHEM tends to underestimate the concentration of SO_2 in Europe, although the distribution of SO_2 is similar to the observed distribution. Modelled sulphate concentrations show some overestimation and some underestimation compared to the measured values; in central Europe the model tends to overestimate sulphate concentration (more sites with concentrations $> 1 \mu\text{g m}^{-3}$ than observations), but the model underestimates concentrations in Spain and more remote areas.

The simulated mass of sulphate aerosol is compared against more observations in Figure B.2. Observations from EMEP, IMPROVE, GAW and the University of Miami datasets are all compared. In this more global comparison, there is a clear underestimation in the simulated sulphate concentrations: STOCHEM values are typically about half of the measured values. The underestimation is worst in comparison with the University of Miami dataset, which mostly consists of remote sites with low sulphate loadings.

Overall, the simulated sulphate mass concentration is found to be sufficiently accurate for the simulation of heterogeneous chemistry, but the problem is further complicated by the fact that the calculation of heterogeneous chemistry is sensitive to the aerosol surface area. In STOCHEM sulphate mass is converted to an approximate surface area by simply assuming that the aerosol

is distributed in a single lognormal mode, the standard deviation of which is fixed and the mean diameter grows according to the relative humidity. This simple treatment of the aerosol size distribution leads to complex uncertainties in the calculated aerosol surface area that are hard to remove without a detailed aerosol scheme.

B Enhanced photolysis rates

The simulations presented in this report rely on the use of photolysis rates that have been artificially increased by 25%. This increase was deemed necessary to account for deficiencies in the parameterisation of cloud cover in the model. The value of the increase was chosen to give reasonable methane lifetimes. For completeness, this section explores the importance of changing the photolysis rates.

The simulated annual cycle of CO, CH₄ and O₃ with the standard (old) and the increased (new) photolysis rates are compared in Figures B.3 to B.5. Increasing the photolysis rates significantly improves the comparison of simulated CH₄ concentrations to observations. When the standard rates are used, the model over predicts CH₄ concentrations and tends to overestimate the weak annual cycle, this is rectified if the photolysis rates are increased. The seasonal cycle of CO is captured more accurately when the photolysis rates are increased. O₃ concentrations show some improvement with the increased rates; the remote Southern Hemisphere values are under predicted to a lesser extent but there is little change in the simulated annual cycle. Overall, although the method of increasing the photolysis rates is crude and should receive attention in future works, it is considered sufficient for this work.

For completeness, an examination of the role of heterogeneous chemistry was also examined in simulations in which the photolysis rates were not increased. These results are not presented because although there are some small deviations in the absolute numbers, the overall conclusions reached are unchanged.

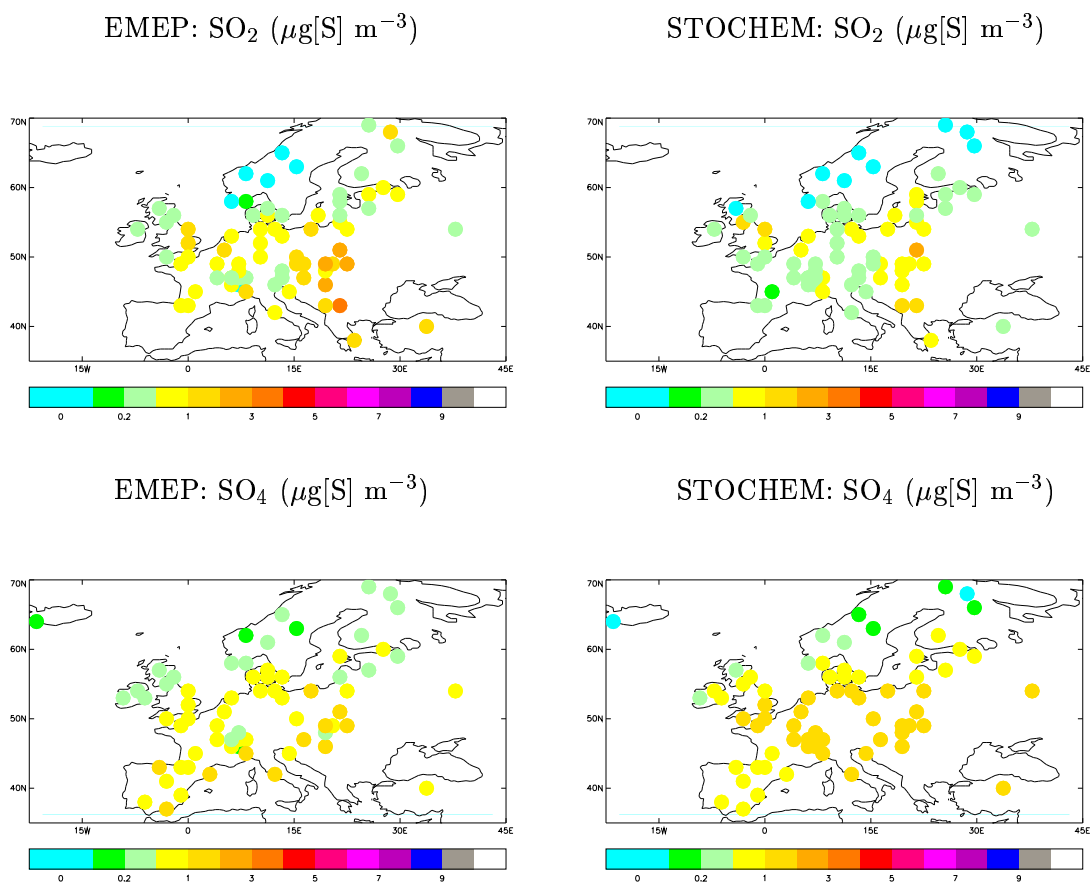


Figure B.1: Surface concentration of SO_2 (a) measured by EMEP and (b) simulated in STOCHEM. Plots (c) and (d) are the same as (a) and (b), but show sulphate mass.

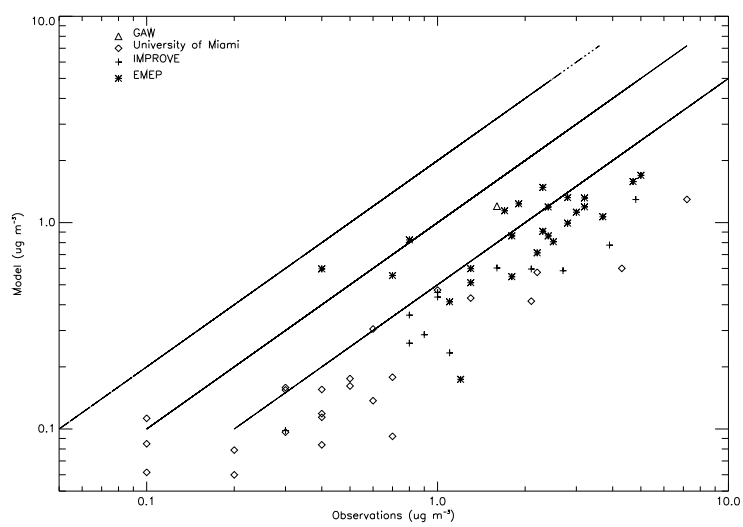


Figure B.2: *Comparison of modelled surface sulphate concentrations with observed. Annual mean model values for the year 1990 are shown.*

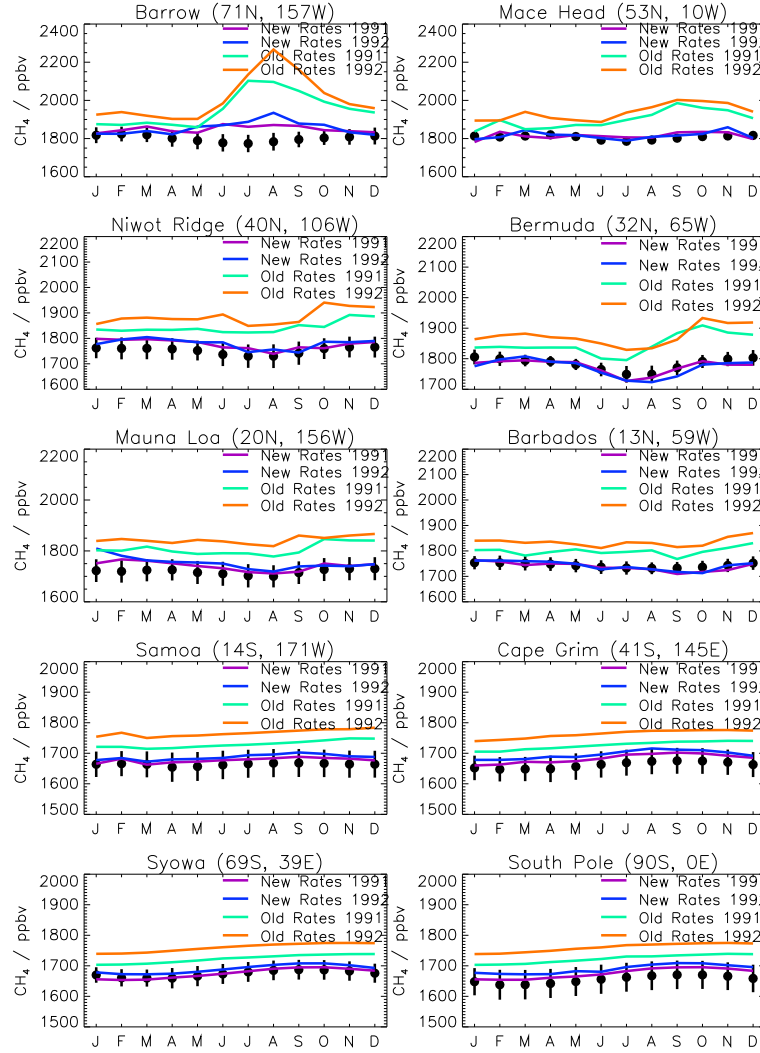


Figure B.3: Comparison of modelled CH_4 concentrations with observed data (black). Simulations including using the “old” (or standard) photolysis rates (green, 1992 = orange) are compared to simulations in which the photolysis rates have been increased by 25% (“new”, 1991 = purple, 1992 = blue). All data in ppbv.

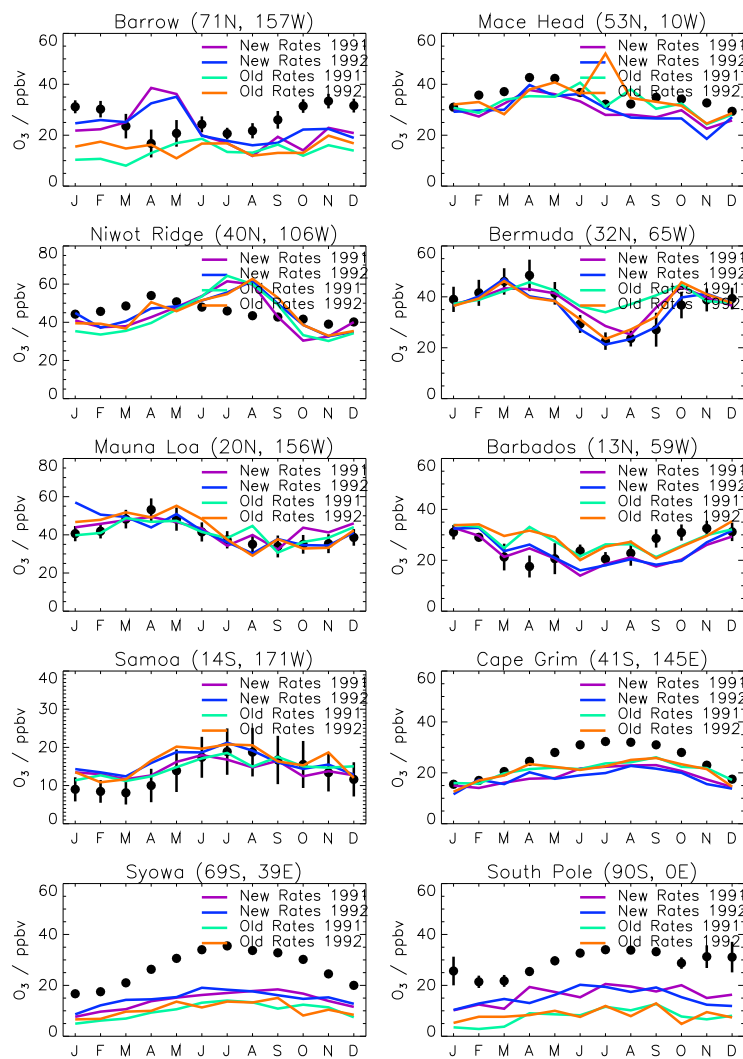


Figure B.4: Same as Figure B.3, but for O_3 .

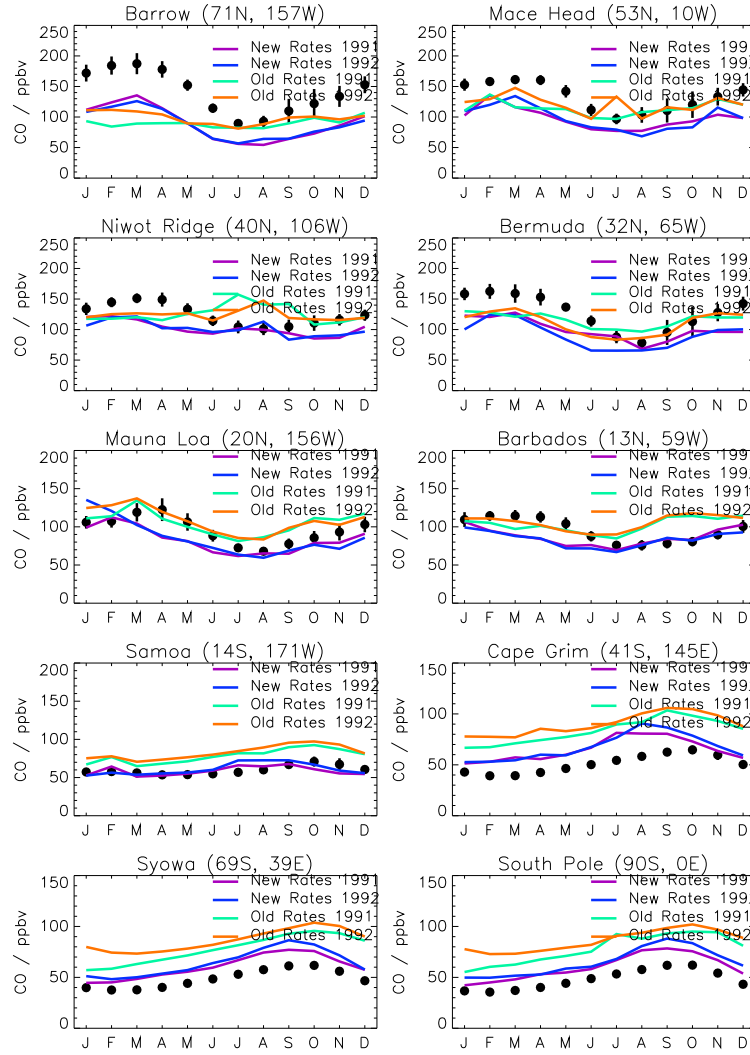


Figure B.5: Same as Figure B.3, but for CO.

References

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