

Impacts of chemistry-aerosol coupling on tropospheric ozone and sulfate simulations in a general circulation model

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[1] We have implemented fully interactive tropospheric gas-phase chemistry and sulfate aerosol modules into the new generation state-of-the-art Goddard Institute for Space Studies (GISS) modelE general circulation model (GCM). The code has been developed with a unique flexibility to perform simulations in coupled or off-line (decoupled) mode. Both modes use identical chemical calculations, but the decoupled simulation relies on previously saved off-line oxidant and aerosol concentration fields whereas the coupled simulation is fully interactive. Here we describe the application of the model to isolate the impacts of the two-way chemistry-aerosol coupling on the predictions of sulfate aerosol and ozone pollution and to provide insights into the mechanisms that drive the different predictions between coupled and off-line models. On annual and global scales, the differences between the coupled and off-line simulations are small, but larger deviations do occur on regional and seasonal scales. The chemistry-aerosol coupling leads to $\sim 20\%$ increases in surface sulfate over SO_2 source regions in the northern hemisphere summer due to higher H_2O_2 levels and aqueous-phase oxidation rates in the coupled model. Compensating sulfate decreases occur in downwind regions and in the upper troposphere due to depleted SO_2 . At middle to high tropospheric altitudes in the northern hemisphere, ozone and OH are increased in the coupled model relative to the off-line model by $\sim 10\%$ due to reductions in sulfate loading and subsequent suppression of N_2O_5 heterogeneous hydrolysis. The use of off-line versus coupled models has implications for the simulation of the intercontinental transport of pollutants and their precursors.

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1. Introduction

[2] Tropospheric levels of sulfate aerosol and ozone have both increased significantly over the past 200 years due to human activities and industrialization especially in the northern hemisphere. Sulfate aerosol and ozone represent major components of air pollution on local, regional and global scales. Both species have contributed to climate forcing, with similar estimated magnitude but in opposite ways. The direct radiative forcing of sulfate aerosol may be -0.2 to -0.9 Wm^{-2} [Penner *et al.*, 2001], the indirect effects (the impact of sulfate aerosols on cloud cover and lifetime) are highly uncertain but likely to be negative in sign. The direct radiative forcing of ozone is estimated to be $0.35 \pm 0.15 \text{ Wm}^{-2}$ [Ramaswamy *et al.*, 2001] but may be several tenths of a Wm^{-2} larger [Shindell *et al.*, 2003]. Conversely, the distributions of sulfate aerosol and ozone are strongly influenced by processes affected by climate such as the hydrological cycle, temperature, natural emissions and winds, and will therefore respond to climate change. In addition to influencing and being influenced by the Earth's climate, the chemical processes leading to

sulfate aerosol and ozone production are also intimately linked with one another. Sulfate aerosol production depends on the levels of hydroxyl radical (OH) and hydrogen peroxide (H_2O_2) available to oxidize emissions of gaseous precursors, biogenic dimethyl sulfide (DMS) and anthropogenic emissions of sulfur dioxide (SO_2) from industrial activity and fossil fuels. At the same time, the amount of ozone (O_3), the source gas for OH, is limited by the heterogeneous hydrolysis of N_2O_5 into HNO_3 on the surface of sulfate aerosol. Modeling studies suggest that in the present day troposphere, this process leads to a reduction of O_3 in the northern hemisphere by about 6–9% [Dentener and Crutzen, 1993; Tie *et al.*, 2003]. Regional sensitivity may be much greater, with O_3 concentrations depleted by 25% at northern subtropical and mid-latitudes [Dentener and Crutzen, 1993]. Sulfate aerosol is expected to have little impact on the O_3 budget in the southern hemisphere due to the much lower sulfate aerosol loading compared to the northern hemisphere.

[3] Sulfate aerosols can also affect O_3 chemistry through scattering ultraviolet radiation and thereby modifying photolysis rates. However, the global effect of aerosols on O_3 has been shown to be small, even negligible [Liao *et al.*, 2003].

[4] It is indeed challenging to develop global atmospheric models that embrace the complexity of such chemistry-

aerosol-climate interactions and yet are practical to run with the computing resources presently available. Global models are needed not only to quantify the global radiative impacts of sulfate aerosol and ozone, but also because sulfate aerosol and ozone pollution can be transported across intercontinental scales, redefining international and domestic emissions control [e.g., *Jaffe et al.*, 1999; *Jacob et al.*, 1999; *Li et al.*, 2002; *Holloway et al.*, 2003].

[5] Previously, our approach to global tropospheric chemistry-climate modeling has been to consider gas-phase chemistry and sulfate aerosol separately such that off-line sulfate aerosol fields are used for the tropospheric chemistry simulations and off-line oxidant fields are used for the sulfate aerosol simulations [*Koch et al.*, 1999; *Shindell et al.*, 2001]. In order to limit computer processing time and electronic data storage space, the off-line fields typically comprise monthly-averaged values with imposed diurnal cycle, which is problematic not least because the chemistry-aerosol coupling processes occur on much shorter time scales (seconds to hours). Moreover, the off-line or decoupled approach does not allow for two-way interactions between gas phase and aerosol systems, which would be essential when considering feedbacks from future climate changes.

[6] To avoid such inadequacies, some groups have developed interactive models, with either one-way [*Roelofs et al.*, 1998] or two-way [*Tie et al.*, 2001; *Liao et al.*, 2003] coupling between the chemistry and aerosols. The coupled chemistry-aerosol approach provides consistent oxidant fields for the aerosol formation and consistent sulfate aerosol mass for heterogeneous reactions. The coupled approach is more physically realistic but also considerably more computationally intensive. The previous two-way chemistry-aerosol coupling model studies presented the coupled ozone and aerosol simulations but due to the limitations of the model set-up were unable to isolate the effects of the coupling itself on the sulfate and ozone composition. *Roelofs et al.* [1998] attempted to examine the effects of coupled versus decoupled oxidants on sulfate modeling only, but they used off-line oxidant fields that did not include the influence of the sulfur oxidation cycle and were therefore inconsistent with the coupled model version. They found the differences between coupled and decoupled models were dominated by the use of monthly-mean H_2O_2 in the off-line model, and the study was therefore limited in its ability to provide insights into the role of the chemistry-aerosol coupling. Thus at present it is not known under what circumstances the extra resources required for a fully coupled simulation are warranted as the magnitude of the chemistry-aerosol feedbacks are not well characterized.

[7] Heterogeneous chemical reactions on other major aerosol types such as mineral dust and carbonaceous aerosol have been shown to be important for global and regional oxidant chemistry [*Bauer et al.*, 2004; *Martin et al.*, 2003]. Simulation of this type of interaction using coupled versus off-line aerosol fields may certainly lead to differences in the oxidants. Conversely, the use of coupled versus off-line oxidants may impact the simulation of secondary organic aerosol formation. Here, we choose to focus specifically on the interactions between the sulfur cycle and photochemistry because of the intimacy of

interconnectedness between the cycles and because the chemical impact of each system on the other is known to be of global significance.

2. Model Description

[8] We have implemented fully interactive tropospheric gas-phase chemistry and sulfate aerosol modules into the new generation state-of-the-art GISS GCM, 'modelE' [*Schmidt et al.*, 2005]. The code has been designed with a flexible interface between the tropospheric gas-phase chemistry and sulfate aerosol modules allowing us to perform simulations in either coupled or off-line mode. Here we describe the application of that model to isolate the impacts of the two-way chemistry-aerosol coupling and to quantify the effects of running in coupled versus using off-line mode on the predictions of sulfate aerosol and ozone pollution. The coupled model has recently been used in a novel emissions-based approach to quantifying climate forcing by reactive greenhouse gases since the preindustrial era [*Shindell et al.*, 2005].

[9] ModelE includes several critical advances compared to previous versions and this entirely restructured model produces better climate simulations than any prior GISS GCM based on comparison with a wide suite of observations. The new model version incorporates physical processes within a single standardized structure, which is more complicated to create, but facilitates easy interaction between the model components and leads to a much higher degree of physical consistency between the representations of climate and composition than in most models. For example, the new modelE structure has facilitated coupling of the soluble trace gas and aerosol species to the GCM's hydrological cycle, including development of a dissolved species budget. Such a dissolved sulfate budget was included in a pre-modelE GISS study [*Koch et al.*, 2003]. Many other chemistry and aerosol models do not save dissolved species but instead return the dissolved (unscavenged) species to the model grid box at the end of each model time-step. In our model, we have created a dissolved species budget and this has important implications for tracer distributions. The use of the dissolved species budget dramatically decreases sulfate production from clouds since most of the sulfate is ultimately rained out instead of released back to the grid box [*Koch et al.*, 2003] and reduces the abundance of soluble O_3 precursors, such as nitric acid (HNO_3), which were systematically overestimated in previous models. The resistance-in-series dry deposition module within modelE is physically consistent with the other surface fluxes, water and heat, in the planetary boundary layer scheme of the GCM, which was not the case in earlier models (or indeed in most chemistry-climate models). ModelE offers flexible vertical and horizontal resolution options. In the present study, we use 23 vertical layers (model top in the mesosphere) and $4^\circ \times 5^\circ$ degree horizontal resolution. Prescribed decadal average monthly-varying sea surface temperature and sea ice from 1990–1999 provide the lower boundary conditions for the GCM [*Rayner et al.*, 2003]. The GCM's internally generated meteorology drives the tropospheric chemistry, the simulations are not "nudged" to observations and neither do they use off-line meteorological fields.

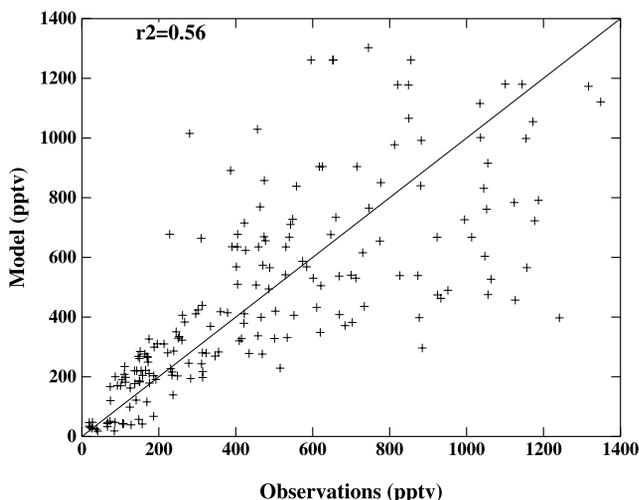


Figure 1. Comparison of simulated (off-line model) and observed annual mean surface sulfate (pptv) for an ensemble of observations including data from the IMPROVE network (<http://vista.cira.colostate.edu/improve>), the EMEP network (<http://www.emep.int>), and J. M. Prospero and D. L. Savoie (unpublished data, 1999).

2.1. Sulfate Aerosol Module

[10] The updated modelE sulfate aerosol module is described by D. Koch et al. (Sulfur, sea salt, and radionuclide aerosols in GISS modelE, submitted to *Journal of Geophysical Research*, 2005) (hereinafter referred to as Koch et al., submitted manuscript, 2005), including an extensive evaluation. The GISS model does include other major aerosol types (mineral dust, sea salt, and carbonaceous aerosols), which were all switched off in the present study (Koch et al., submitted manuscript, 2005) (S. E. Bauer and D. Koch, Impact of heterogeneous sulfate formation at mineral dust aerosol surfaces on aerosol loads and radiative forcing in the GISS GCM, submitted to *Journal of Geophysical Research*, 2005) (hereinafter referred to as Bauer and Koch, submitted manuscript, 2005). The sulfate aerosol module is based on the earlier work of Koch et al. [1999] and Koch [2001] and includes prognostic simulations of the mass distributions of DMS, MSA, SO₂ and sulfate and in decoupled mode, includes a semi-prognostic simulation of H₂O₂, full details of which can be found in the work of Koch et al. [1999]. Briefly, the H₂O₂ production rate is calculated using off-line fields of hydroperoxy radical (HO₂) concentration and H₂O₂ is destroyed photochemically and by reaction with OH using off-line fields of H₂O₂ photolysis rate and OH concentration. Physical loss by dry and wet deposition is included using the identical formulations as in the off-line chemistry model. Direct anthropogenic SO₂ emissions include those from industrial activity, fossil fuel and biomass burning. Natural SO₂ sources include a non-eruptive volcanic emission and a biogenic source from the tropospheric oxidation of oceanic DMS. In the present study, we use SO₂ emissions from fossil fuels and industrial activity compiled by the Emissions Database for Global Atmospheric Research (EDGAR3.2) representative of the year 1990 [Olivier et al., 1990]. It is evident that this source database

leads to a model overestimate of present-day sulfate levels over Europe. This weakness appears resolved with use of the IIASA (International Institute for Applied Systems Analysis) emissions used by the AEROCOM global aerosol model intercomparison (F. Dentener, manuscript in preparation, 2005), but does not significantly affect our study of chemistry-aerosol coupling. DMS emissions are parameterized as a function of the surface wind speed generated internally by the climate model (Koch et al., submitted manuscript, 2005). Processes include gas-phase chemistry, aqueous-phase chemistry, and wet and dry deposition (including settling). Aqueous chemistry and wet deposition are tightly coupled to the model cloud processes.

[11] The sulfate simulation in this study has been evaluated using a compilation of sulfate aerosol observations from the IMPROVE network over the United States (<http://vista.cira.colostate.edu/improve>), the EMEP network over Europe (<http://www.emep.int>) and a global assembly of remote sites provided by J. M. Prospero and D. L. Savoie (unpublished data, 1999). Most of the data from the total 191 sites is in the northern hemisphere, with only 17 sites in the southern hemisphere. There is a lack of data over Asia. Simulated and observed annual mean surface sulfate are correlated with $r^2 = 0.56$ (Figure 1).

2.2. Tropospheric Gas-Phase Chemistry Module

[12] The gas-phase chemistry module has been described in detail elsewhere [Shindell et al., 2003]. The model includes background HO_x-NO_x-O_x-CO-CH₄ chemistry as well as hydrocarbon families and peroxyacetylnitrates. The model contains a complete representation of sources and sinks for its 32 gases, including for methane. Full details and comparison with observations were presented for the previous version of the GCM [Shindell et al., 2003]. The current version is fairly similar, though there have been some substantial improvements going to the new GCM. In this study, we use trace gas emissions representative of present day conditions (typically 1990s). The ozone simulation has been evaluated against a compilation of ozone-sonde data from 40 stations, 16 of the stations include data at various altitudes throughout the tropospheric column, whilst the remaining 24 stations include surface observations only [Logan, 1999]. Simulated and observed annual mean ozone are correlated with $r^2 = 0.96$ (Figure 2). For the surface data only, the model captures 45% of the seasonal (monthly) and spatial variability in surface O₃ observations. The average difference between the simulated and observed annual cycle of ozone at five vertical levels (200, 300, 500, 800 and 950 mbar) for the 16 aforementioned sites is only 17% with largest discrepancies (23%) in the mid-troposphere.

2.3. Coupled and Off-Line (Decoupled) Modes

[13] The chemistry-sulfate aerosol coupling mechanism is shown schematically in Figure 3. The off-line aerosol model uses imported monthly mean fields of the radical species OH and NO₃ for reactions (1)–(3) and for the semi-prognostic simulation of H₂O₂ for aqueous reaction (4) uses monthly mean fields of HO₂ and H₂O₂ photolysis rate. The off-line fields of OH, HO₂, NO₃ and the H₂O₂ photolysis rate are scaled by daylight (based on the cosine of the zenith

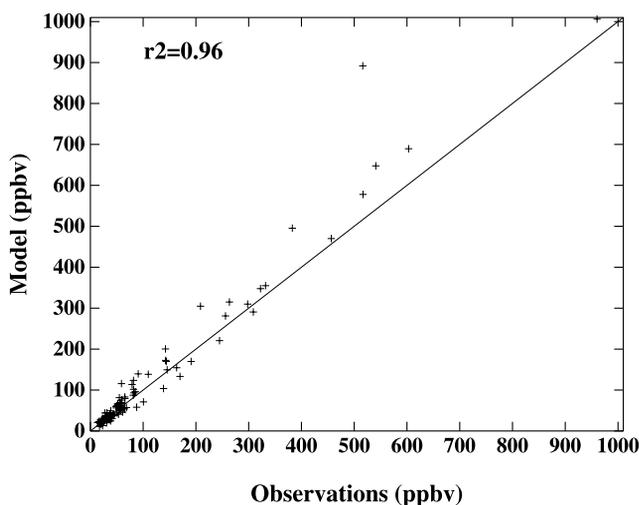


Figure 2. Comparison of simulated (off-line model) and observed annual mean ozone (ppbv) for an ozonesonde compilation of 40 stations [Logan, 1999]. Sixteen of the sites have data at 5 altitudes (200, 300, 500, 800, and 950 mbar), while the remaining 24 sites comprise surface data only.

angle) to give a diurnal cycle. DMS oxidation is highly simplified in the model. Reaction (1) has 2 pathways, the first forms SO_2 only and the second gives both SO_2 and MSA. The off-line chemistry model uses imported monthly mean fields of DMS, SO_2 and SO_4 for reactions (1)–(3) and the heterogeneous process (5). The off-line chemistry model does not include reaction (4), aqueous oxidation of SO_2 by H_2O_2 . The pseudo first order rate coefficient for reaction (5) is determined using the reaction probability formulation described by Dentener and Crutzen [1993] under which it is directly proportional to the mass of sulfate aerosol. In the present study, we use a reaction probability of 0.1 for N_2O_5 heterogeneous hydrolysis. The rates and mechanisms of heterogeneous reactions on aerosols are generally uncertain, for example, the uncertainty range in the reaction probability for N_2O_5 uptake spans 2 orders of magnitude (0.01–1) [Jacob, 2000]. We do not include any other heterogeneous mechanism for conversion of N_2O_5 to HNO_3 (for example on cloud drops, other aerosols, or on haze) and as such this study may overestimate the feedback effects of sulfate aerosol on oxidant chemistry. However, neither do we include reactive uptake of other gaseous species (e.g. HO_2 , NO_3 or NO_2), which suggests a potential underestimation of sulfate aerosol feedbacks on oxidant chemistry.

[14] In the coupled model version, the chemistry and sulfate modules are explicitly linked such that the chemical evolution of the chemistry-aerosol reaction system is determined interactively with a 30-minute time step. In effect, instantaneous concentrations of OH, NO_3 and H_2O_2 are available to the sulfate module and instantaneous concentrations of SO_4 , SO_2 and DMS are available to the chemistry module. The off-line models assume that reactions (1)–(5) are first-order (linear). However, in the coupled model, the reactions are second-order thereby introducing the potential for nonlinear interactions between the modules. For example, in the coupled model, the sulfate aerosol concentration plays a role in determining the sulfate aerosol production

rate via its influence on oxidant levels. In polluted regions, high levels of sulfate aerosol will tend to reduce oxidant concentrations via reaction (5) and therefore slow down at least the gas-phase production rate of sulfate aerosol.

[15] The rates of the photolysis reactions are computed using the FAST-J code of Wild *et al.* [2000]. In the present study, the effects of different aerosols (sulfate, carbonaceous and mineral dust) on photolysis rates are included in the radiation code, however, we use the same climatological aerosol fields in the coupled and off-line simulations. A sensitivity study of the radiative effects of aerosols on photolysis rates, which was based on complete removal of all aerosols, led to very small (negligible) differences in O_3 [Liao *et al.*, 2003]. In the light of this result, we assume the effects of using coupled versus off-line sulfate fields on photolysis rates to be tiny, and much less than the chemical effects, on which we choose to focus our attention.

[16] In order to assess accurately the impact of the coupled versus the off-line models on sulfate and ozone, we generated our off-line fields using an iterative procedure due to the additional inclusion of gas-phase DMS and SO_2 oxidation in the modelE off-line chemistry. First, off-line sulfate, DMS and SO_2 fields from a pre-modelE sulfate simulation were used to drive an initial-round off-line modelE chemistry run. Off-line oxidant fields extracted from that preliminary chemistry simulation (which included the influence of the gas-phase sulfur oxidation cycle on the oxidants in addition to the impact of sulfate aerosol itself) were then employed to drive the modelE off-line sulfate simulation for comparison with the coupled model. In a final round, the off-line chemistry model was run again, this

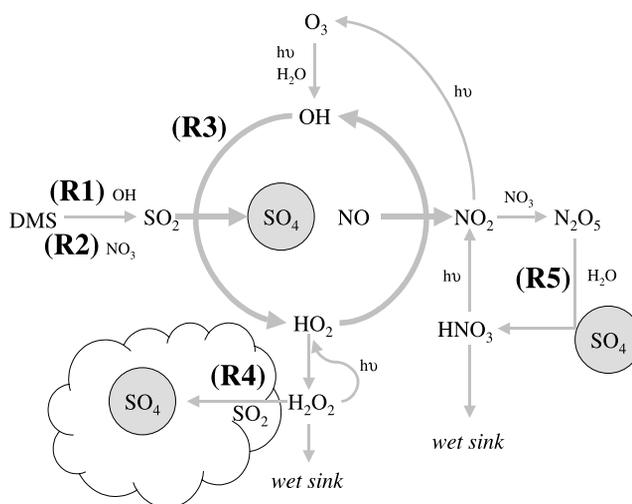


Figure 3. Schematic of sulfate-chemistry coupling in the troposphere. DMS is oxidized by OH and NO_3 radicals to form SO_2 (R1, R2, respectively). In the gas-phase, SO_2 reacts with OH radicals to form SO_4 aerosol and HO_2 radicals (R3). In low NO_x conditions, HO_2 undergoes self-reaction to form H_2O_2 . Both H_2O_2 and SO_2 dissolve in cloud droplets and react in aqueous phase to form SO_4 aerosol (R4). In high NO_x conditions, HO_2 radicals oxidize NO to NO_2 and regenerate OH. NO_2 is either photolysed to produce O_3 , the source gas for OH radicals, or reacts with NO_3 radicals to form the N_2O_5 adduct, which is hydrolysed on the surface of SO_4 aerosol to produce HNO_3 (R5).

Table 1. Sulfate and Ozone Budgets^a

	Coupled	Off-Line
Sulfate		
Sources (Tg S yr ⁻¹)		
Gas-phase SO ₂ oxidation	7.7	7.8
In-cloud SO ₂ oxidation	23.4	23.0
Sinks (Tg S yr ⁻¹)		
Dry deposition	-3.8	-3.9
Wet deposition	-29.4	-29.1
Burden (Tg S)	0.5	0.5
Lifetime (days)	5.5	5.5
Ozone		
Chemistry (Tg yr ⁻¹)	777.6	769.9
Dry deposition (Tg yr ⁻¹)	-1219.6	-1215.1
Stratosphere (Tg yr ⁻¹)	440.5	446.2
Burden (Tg O ₃)	432.4	431.4

^aThe model includes a direct source of sulfate from fossil fuel burning and industrial activity of 2.0 Tg yr⁻¹.

time constrained with off-line sulfate, DMS and SO₂ from the last sulfate simulation. We assumed convergence at this stage since the global difference between the oxidant concentrations (O₃, OH, NO₃) in the first and second off-line chemistry runs was significantly less than 1%.

[17] A previous study of the effects of coupled versus uncoupled oxidants on sulfate used off-line oxidants from a model version that did not include sulfur chemistry and also the coupled model itself [Roelofs *et al.*, 1998]. Use of the carefully constructed, fully consistent off-line fields in the present study, provides faithful insights into the effects of the chemistry-aerosol intrinsic feedbacks. In this sense, our results constitute a lower limit to the differences caused by the use of off-line fields versus using a coupled model, especially since off-line fields in other studies are usually taken from independent models.

[18] The model was run in each mode (coupled chemistry-sulfate, and off-line chemistry and sulfate) for 12 years with the same emissions each year, but with GCM meteorological interannual variability. The last 10 years of each simulation were analysed (2 years spin-up). In all cases we present the differences in X (where X = species mixing ratio or reaction rate) as $\Delta(X) = \text{coupled model}(X) - \text{off-line model}(X)$ using 10-year averages. For percentage changes in X, the difference between coupled and off-line model is shown relative to the off-line simulation, (i.e. $\Delta(X)/\text{off-line model}(X)$).

3. Results

[19] Differences between coupled and off-line models are driven via 2 possible mechanisms. Firstly, the coupled model allows feedbacks between chemistry and aerosols that are fundamental properties of the reaction system and not represented in the off-line model. Secondly, the use of monthly-mean off-line fields in the decoupled models results in time-scale discrepancies when compared to the coupled model, for example, due to physical inconsistencies between the current composition and meteorological state and the implicit assumption that the off-line concentration field is regenerated in the next time-step.

3.1. Global Budgets

[20] Table 1 shows the annual global model sulfate and ozone budgets for coupled and off-line simulations. The

differences are minimal. The coupled model appears to be more oxidizing with slightly larger rates of both ozone and aqueous phase sulfate production. The global burdens of sulfate and ozone are not significantly different for coupled and off-line modes. Despite the similarities in coupled and off-line model simulations on global and annual scales, significant differences in oxidation rates and species concentrations do occur on regional and seasonal scales, presented in the following section.

3.2. Effect of Coupled Versus Off-Line Mode on Sulfate

[21] Total column annual mean gas-phase and aqueous production rates of sulfate calculated by the off-line model are shown in Figure 4. Both production rates maximize over the anthropogenic SO₂ source regions although more sulfate is generated through the aqueous pathway on regional and global scales. However, the lifetime of the sulfate generated in the aqueous-phase is shorter than in the gas-phase [Koch *et al.*, 2003], since the sulfate near or within a cloud is prone to scavenging if the cloud precipitates. The spatial distribution of the sulfate mixing ratio itself is broadly similar to that of the gas-phase and aqueous production rates. In the June–July–August (JJA) season, highest sulfate mixing ratios are found in the northern hemisphere reflecting the high summer-time gas and aqueous phase oxidation rates of SO₂ (Figure 5). Zonal mean sulfate mixing ratios reach about 500 pptv, whilst maximum local surface sulfate values

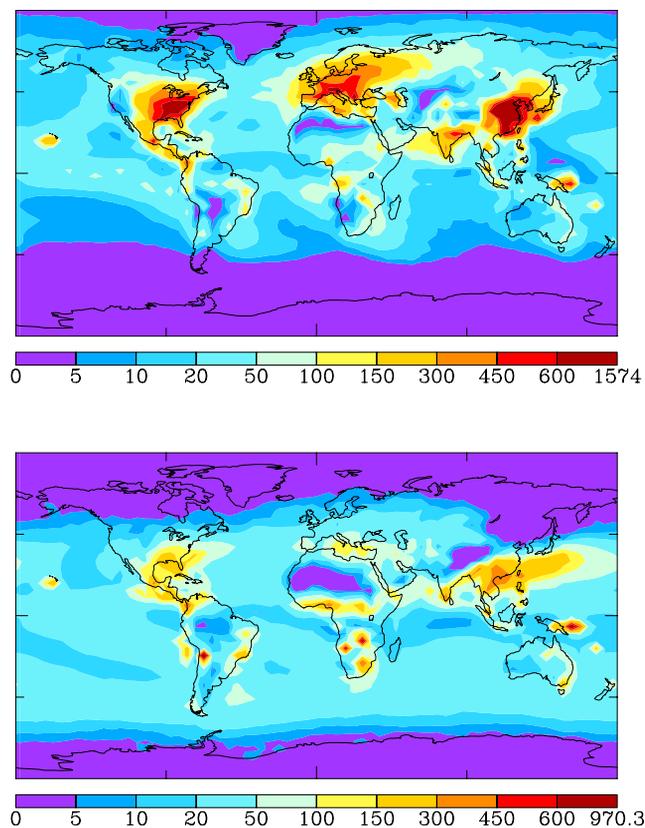


Figure 4. Total column annual mean production rates of sulfate ($10^{-13} \text{ kg}(\text{SO}_4) \text{ m}^{-2} \text{ s}^{-1}$) calculated with the off-line model. The top panel shows the aqueous-phase production pathway, and the bottom panel shows the gas-phase production pathway.

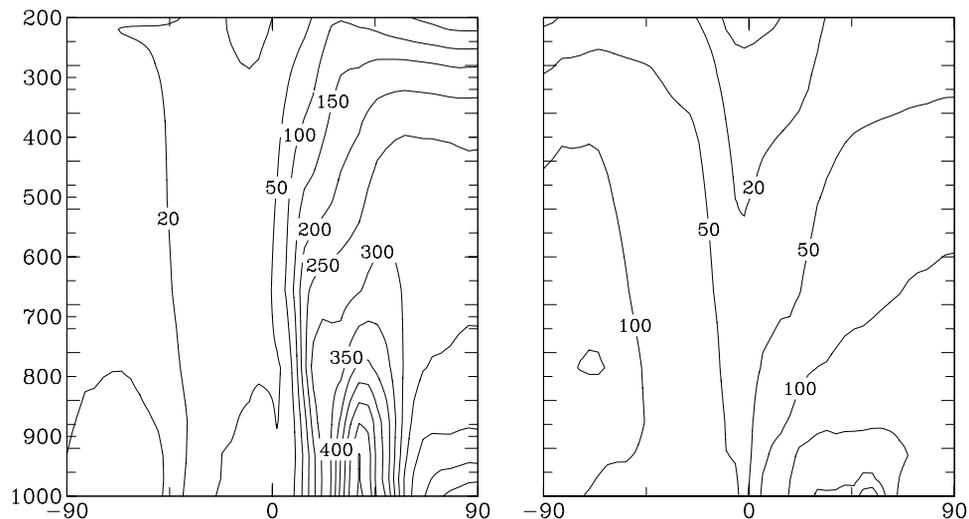


Figure 5. Simulated zonal mean sulfate mixing ratio (off-line model) in pptv for JJA season (left) and DJF (right).

reach about 2000 pptv across the polluted continental 40–45°N latitude belt. In the December–January–February (DJF) season, significant sulfate mixing ratios accumulate in the southern hemisphere (about 100 pptv on zonal average) due to oxidation of biogenic DMS emissions in austral summer.

[22] The differences in total column sulfate production rates (aqueous-phase and gas-phase) between coupled and off-line models for the JJA and DJF seasons are shown in Figure 6. In JJA, the coupled model has increased gas-phase and aqueous-phase sulfate production over eastern areas of the United States and Europe, but decreased production

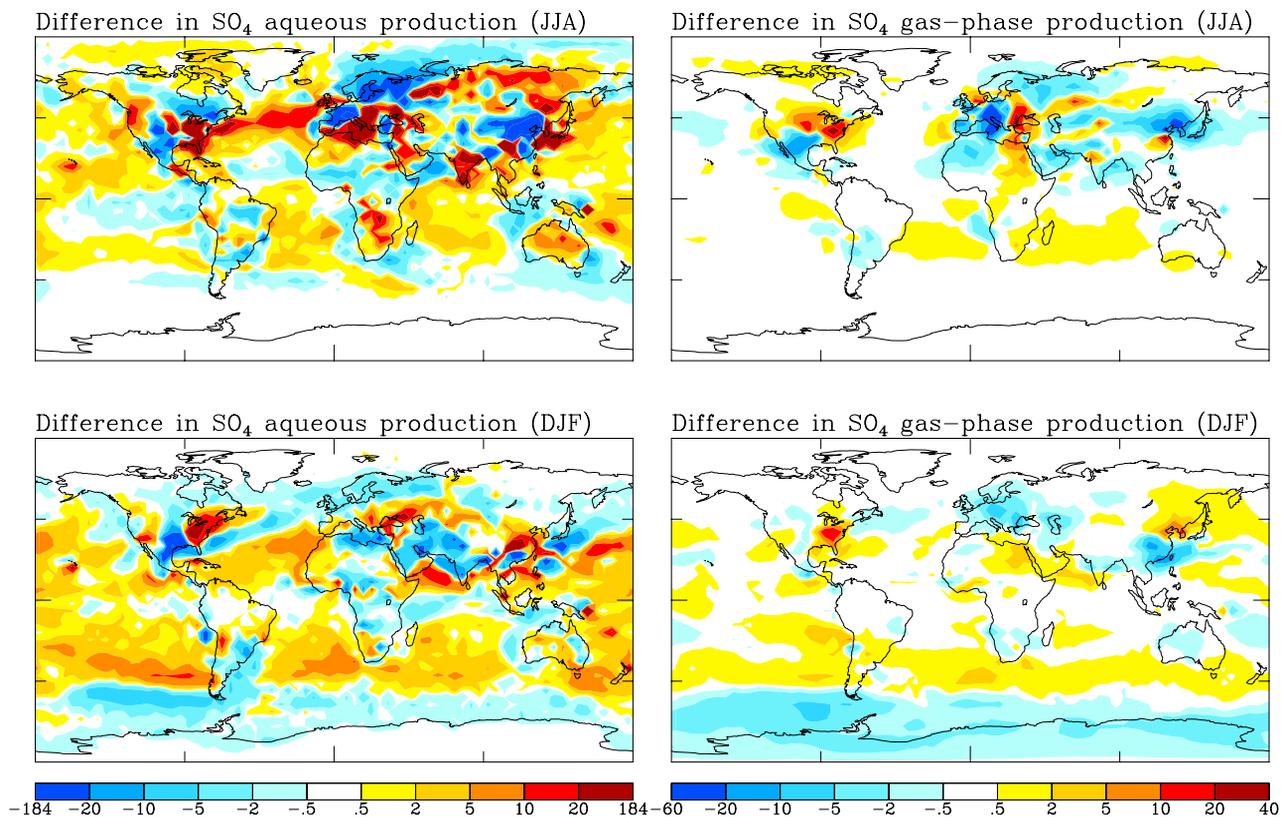


Figure 6. Differences in total column aqueous formation rate of sulfate (left) and total column gas-phase formation rate of sulfate (right) between coupled and off-line simulations for the JJA season (top) and DJF season (bottom) in units of $10^{-13} \text{ kg}(\text{SO}_4) \text{ m}^{-2} \text{ s}^{-1}$.

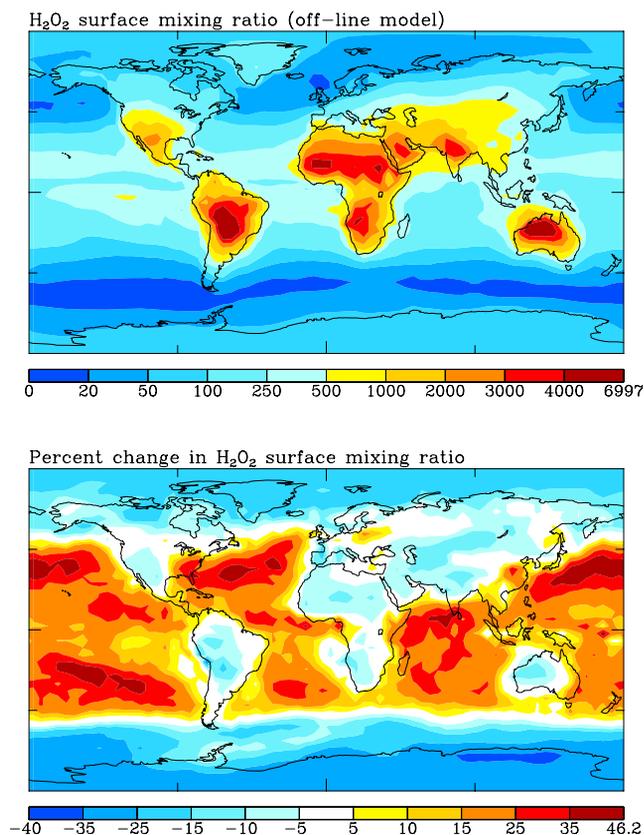


Figure 7. Annual mean H_2O_2 surface mixing ratio simulated using the off-line sulfate model in pptv (top) and the percentage change (%) between the coupled model and off-line model H_2O_2 surface mixing ratios (bottom).

over the western areas of those continents. The coupled model changes in south-east Asia are more complex. In summer, gas-phase sulfate production is increased in southern China and reduced in northern China. The reverse bias occurs in the winter season. In JJA aqueous-phase sulfate production is reduced over large areas of Asia. The changes in gas-phase production are up to $\pm 30\%$ and the changes in aqueous production are up to $\pm 100\%$.

[23] Exposure to different oxidant (H_2O_2 and OH) levels drives the differences in oxidation rates between coupled and off-line models. Figure 7 shows the semi-prognostic simulation of surface H_2O_2 mixing ratio in the off-line sulfate model and the percentage change in surface H_2O_2 between the coupled and the off-line simulations. Relative to the off-line simulation, the coupled model has decreased H_2O_2 levels over the western and central areas of continents and polar and high latitude regions, and increased H_2O_2 levels over the oceans and the eastern edges of continents. The divergence in H_2O_2 is a direct reflection of the different H_2O_2 formation rates calculated using coupled instantaneous HO_2 versus monthly-mean HO_2 (with diurnal cycle imposed). H_2O_2 levels are particularly sensitive to changes in HO_2 since the rate of formation of H_2O_2 is proportional to the square of the concentration of HO_2 radicals. A major cause of the H_2O_2 differences is that the off-line HO_2 fields used to simulate the semi-prognostic H_2O_2 are from an off-line chemistry model run that included gas-phase sulfur

oxidation but did not include H_2O_2 depletion by SO_2 . For example, over western and central continental regions where H_2O_2 levels are highest (due to oxidation of biogenic hydrocarbon emissions), H_2O_2 may act as a source of HO_x ($\text{HO}_x = \text{OH} + \text{HO}_2$) radicals, a process which has been overestimated in the off-line OH and HO_2 fields and therefore manifests as an overestimation in the H_2O_2 formation rate in the off-line sulfate simulation. Other factors contribute to the changes in the oxidant fields, which are discussed in section 3.3, for example, the impact of using coupled versus off-line sulfate fields, the correct time-scale co-evolution between the sulfur and photochemical cycles and feedbacks between the cycles.

[24] In addition to differences caused by using monthly-mean versus instantaneous radical concentrations and photolysis rates, differences in oxidation rates between the coupled and off-line model arise due to the consistent relationship between the oxidants (OH , H_2O_2) and clouds/meteorology in the coupled model. Clouds influence the levels of oxidants through changes in photolysis rates and the wet removal of soluble gases such as H_2O_2 (oxidant) and HNO_3 (precursor for oxidant formation). For example, in the coupled model, OH production will be inhibited underneath clouds, whereas use of the monthly-mean OH fields in the decoupled model will cause excessive generation of sulfate underneath clouds, which will then be

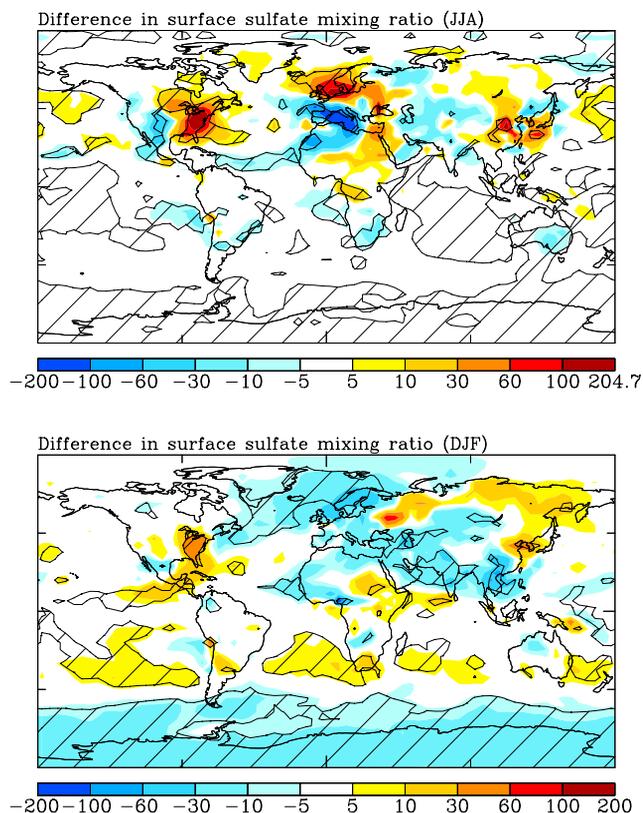


Figure 8. Difference in surface sulfate mixing ratio in pptv between coupled and off-line simulations for the JJA season (top) and the DJF season (bottom). Hatched regions indicate areas where the difference is significant at the 95% confidence level.

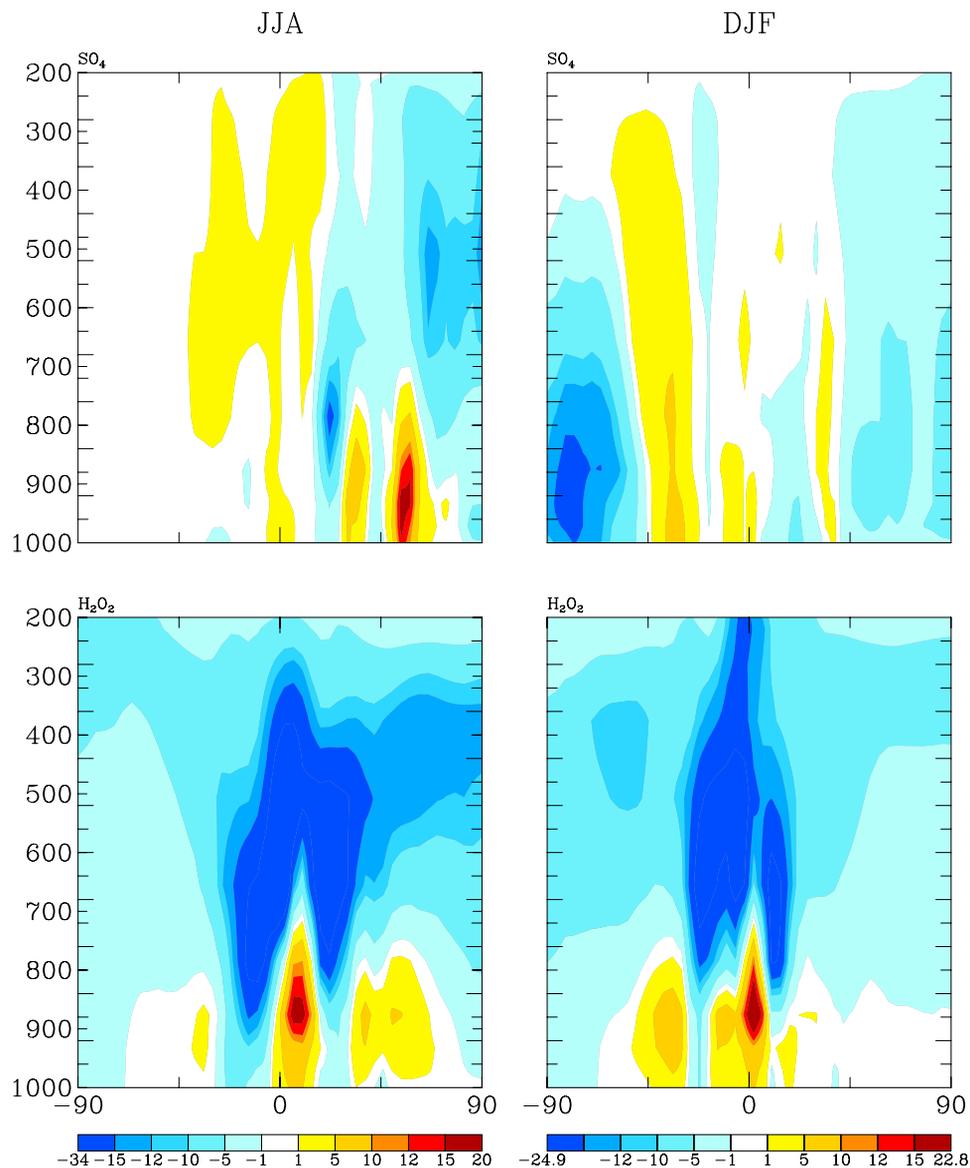


Figure 9. Difference in zonal mean sulfate (top) and zonal mean H_2O_2 (bottom) between coupled and off-line simulations for the JJA season (left) and the DJF season (right). The sulfate changes are in units of pptv and the H_2O_2 changes are in units of 10^{-1} pptv. The difference is significant at the 95% confidence level for colored regions.

washed out. The effect of consistency between clouds and H_2O_2 in the coupled model is more complex since it involves production and destruction of H_2O_2 , both photolytic processes, and physical loss of H_2O_2 through wet deposition. It is likely that physical consistency between clouds and H_2O_2 concentrations contributes to the coupled model increases in H_2O_2 over the oceans and decreases in H_2O_2 over the continents. Since the GCM meteorology is chaotic, there is always an inherent discrepancy in the decoupled model between the off-line oxidant fields and the wet removal and photolysis rates, regardless of the temporal resolution of the off-line fields.

[25] A previous study comparing coupled and off-line oxidants on sulfate in the northern hemisphere found ubiquitous decreases in aqueous production via H_2O_2 oxidation in the coupled model, up to 200% in winter [Roelofs

et al., 1998]. These reductions were attributed to oxidant limitation in the coupled model and exaggerated by the use of monthly-mean rather than semi-prognostic H_2O_2 in the off-line model.

[26] The spatial changes in gas and aqueous SO_2 oxidation rates between coupled and off-line models lead to a regional re-distribution in sulfate loading. The sulfate lifetime is dependent on the oxidation pathway; gas-phase produced sulfate typically has a longer lifetime and makes a larger contribution to the sulfate mixing ratio [Koch *et al.*, 2003]. As discussed above, clouds and OH beneath clouds are anti-correlated in the coupled model unlike the off-line model, which may lead to more sulfate being made in clear conditions where it is not subject to rain-out. Consequently, gas-phase produced sulfate should live longer in the coupled model than in the off-line model.

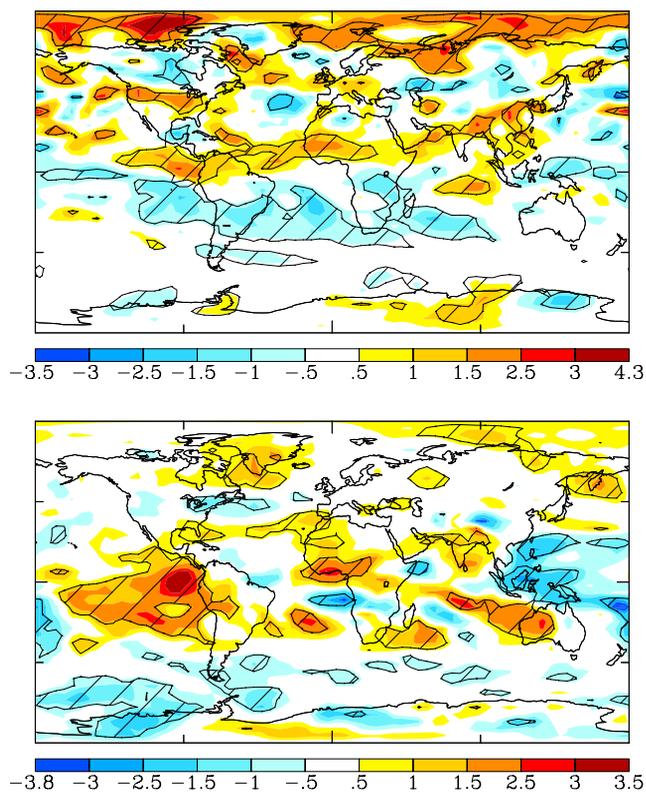


Figure 10. Difference in ozone between coupled and off-line simulations for the JJA season (top) and the DJF season (bottom) in ppbv for model level 7 (nominal pressure centered at about 500 mb). The differences are calculated from an average of 10 model years for each simulation. Hatched regions indicate areas where the difference is significant at the 95% confidence level.

[27] Surface mixing ratios are relevant for air quality considerations. Figure 8 shows the difference in surface sulfate distribution between coupled and off-line simulations, relative to the off-line simulation, for the JJA and DJF seasons. In the coupled model, the JJA surface sulfate mixing ratios are increased by up to +200 pptv or 20% relative to the off-line model over northern hemisphere continental industrial regions including north-eastern United States, northern Europe and East Asia, the regions suffering the highest levels of air pollution in today's atmosphere. Overall, the spatial pattern of differences between coupled and off-line models generally resembles that for gas-phase and aqueous production rates changes, although gas-phase changes tend to dominate in changing the surface sulfate (Figures 7 and 8). In DJF, surface level sulfate decreases in Antarctica (−10–20 pptv, −30%) and increases over the southern subtropics and mid-latitudes (20 pptv, 20%). According to Penner *et al.* [2001], models predict consistently lower aerosol optical thickness (AOT) than suggested by satellite-derived measurements between 10 and 30S. They speculate that the deficiency may be due to missing sea salt, a problematic conjecture since wind speed is low in this region. Our results indicate that coupled oxidants increase sulfate in that region and therefore improve model AOT, although the magnitude is not large enough to resolve the discrepancy fully.

[28] Differences in zonal average sulfate and H_2O_2 between coupled and off-line model are shown in Figure 9. The coupled model predicts increased sulfate mixing ratios at lower tropospheric northern mid-latitudes in JJA (+10 pptv, 5–10%) and southern mid-latitudes throughout the tropospheric column in DJF (+5 pptv, 10%), which are co-located with the differences in H_2O_2 , emphasising the determining role of changes in aqueous-phase oxidation rates. Sulfate mixing ratios are reduced downwind of source regions, for example, the lower and mid-troposphere northern subtropics in JJA (−15 pptv, −5%) and Antarctica in DJF (−15pptv, −20%) where the upwind increases in sulfate production have depleted SO_2 . The decrease in sulfate in the mid to upper troposphere is an improvement in the sulfur model, which generally over-predicts concentrations at high altitudes [Koch *et al.*, 1999].

[29] We compared the coupled and off-line sulfate simulations with the IMPROVE database. Both models consistently over-predict observed sulfate concentrations in the western United States and under-predict in the more polluted eastern United States (not shown). The coupled simulation does improve the comparison in both regions, reducing model sulfate in the western United States and increasing in the eastern United States. The largest improvements occur during the summertime. However, the differences between coupled and off-line simulations are small compared to the difference between model and observations. For the western U.S. sites, the coupled and off-line simulations are correlated with the observations with $r^2 = 0.6$. For the eastern sites the coupled model improves the correlation coefficient from $r^2 = 0.17$ to $r^2 = 0.25$. Inclusion of additional heterogeneous processes, in particular the interaction of sulfate aerosols and mineral dust particles improves the comparison with observations significantly (Bauer and Koch, submitted manuscript, 2005).

3.3. Effect of Coupled Versus Off-Line Mode on Oxidants

[30] The difference in surface ozone between coupled and off-line simulations is generally small in both solstice seasons, although significant increases in ozone (1–2 ppbv, 5%) in the coupled model occur in outflow plumes from north-eastern United States to the Atlantic, from central America to the Pacific, and over far east Asia (not shown). More significant differences in ozone occur at higher altitudes (Figure 10). At around 500 mb, ozone is significantly increased (2–3 ppbv, 10%) in the coupled simulation, relative to the off-line simulation over large parts of the northern hemisphere in JJA, including equatorial continental regions, mid-latitude polluted regions and the Arctic. Similarly, in the DJF season, ozone is increased in the coupled simulation over the southern hemisphere (2–3 ppbv, 10%), especially the eastern Pacific, central Africa and the Indian Ocean.

[31] At lower altitudes, the effect of the re-distribution in sulfate loading in the coupled model on ozone is limited due to the instability of N_2O_5 at the warmer surface temperatures, thereby inhibiting heterogeneous hydrolysis. In the middle and upper troposphere in the northern hemisphere where N_2O_5 is stable due to the lower temperatures and there is a sufficient supply of NO_x from lightning and convective transport, the heterogeneous hydrolysis of

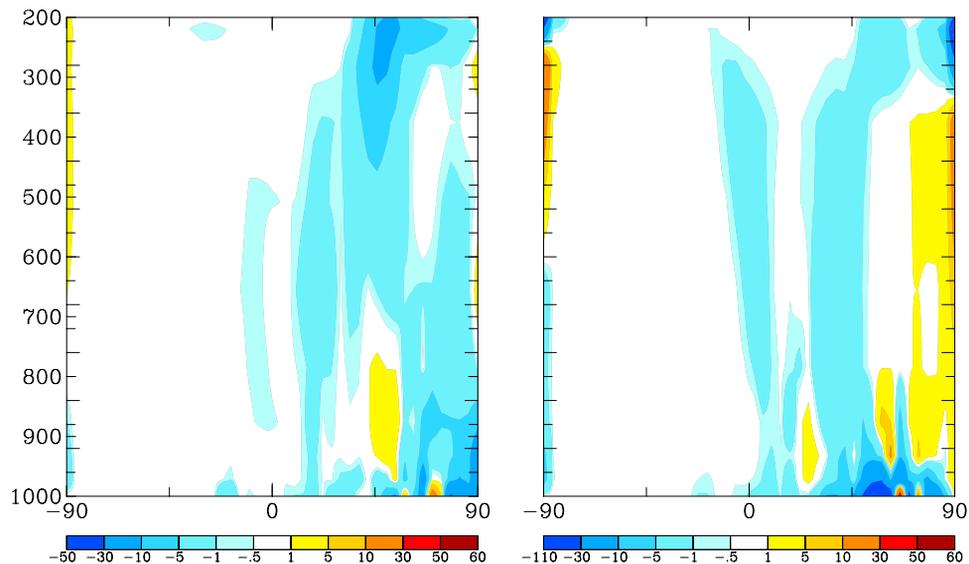


Figure 11. Difference in zonal mean N_2O_5 hydrolysis rate on the surface of sulfate aerosols between coupled and off-line simulations for the JJA season (left) and the DJF season (right) in 10^{-1} ppbv hr^{-1} . The difference is significant at the 95% confidence level for colored regions.

N_2O_5 can exert a significant impact on the photochemistry. In those higher altitude regions above clouds, where SO_2 is depleted due to increased oxidation underneath, the reduced sulfate levels in the coupled model decrease the rate of conversion of reactive nitrogen to HNO_3 via reaction (5) leading to enhanced levels of ozone and OH relative to the decoupled simulation. Indeed the rate of heterogeneous hydrolysis of N_2O_5 is reduced throughout the troposphere in the coupled model by around -10% , especially at subtropical high altitudes in JJA and mid and low subtropical latitudes in DJF (Figure 11). Zonal mean OH concentrations are increased in the coupled model throughout the tropospheric column in both seasons and all year around,

especially at higher altitudes where the difference is $+10\%$ (Figure 12).

[32] In addition to changes in the sulfate aerosol loading, coupled model changes in the SO_2 oxidation rates also affect the OH and ozone levels, both as a result of a change in the availability of SO_2 and because the off-line chemistry model does not include H_2O_2 depletion by reaction with SO_2 . The influence of the changes in SO_2 oxidation rates on ozone tends to be more important at higher altitudes, where the competition for OH reaction is reduced due to the lower abundance of CO and hydrocarbons.

[33] We compared coupled and off-line ozone simulations to the database of 40 sites used in Figure 2 (discussed

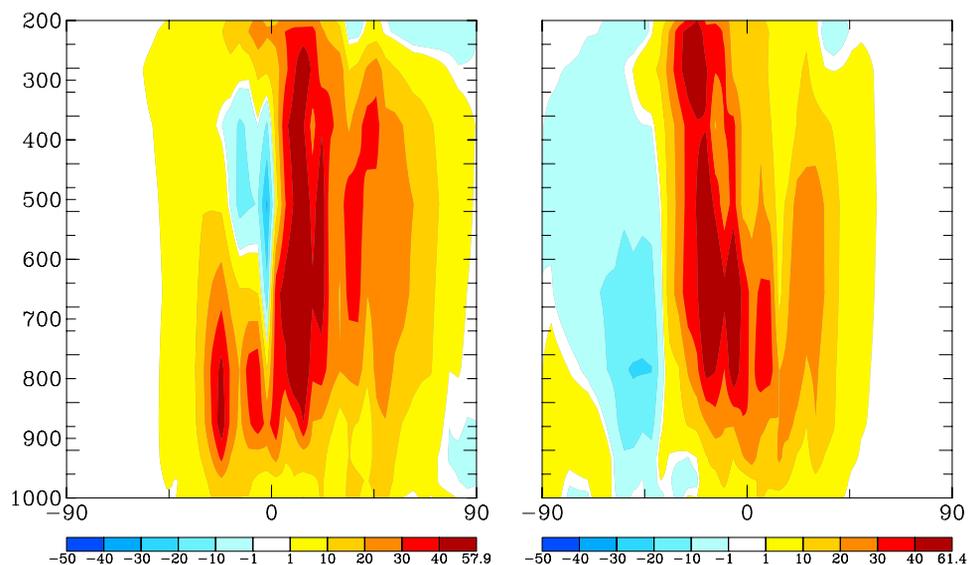


Figure 12. Difference in zonal mean OH concentration between coupled and off-line simulations for the JJA season (left) and the DJF season (right) in 10^3 molecule cm^{-3} . The difference is significant at the 95% confidence level for colored regions.

in section 2.2) and the tropospheric database compiled by *Emmons et al.* [2000] and found negligible differences between coupled and off-line predictions. The similarity between model predictions is comforting since the off-line model agreement is so impressive, however there is a dearth of observations in regions and seasons where the coupled and off-line ozone predictions differ the most, such as the tropical eastern Pacific and Far East Asia in DJF.

4. Summary and Conclusions

[34] We have implemented fully interactive tropospheric chemistry and sulfate aerosol modules within the GISS modelE climate model. The code has been designed with a flexible architecture allowing us to isolate the effects of coupled versus off-line modes on the ozone and sulfate simulations.

[35] We conclude that use of the more efficient off-line models are adequate for global and annual mean scale simulations of sulfate and ozone, since the differences between coupled and off-line simulations are small, especially relative to other uncertainties. Off-line sulfate models that use monthly-mean off-line H_2O_2 rather than a semi-prognostic H_2O_2 face the challenge of potentially much larger discrepancies. The impact of semi-prognostic versus monthly mean H_2O_2 on sulfate has been discussed in the work of *Koch et al.* [1999].

[36] Significant deviations between coupled and off-line simulations of sulfate and ozone do occur on regional and seasonal scales. We find that the coupled model predicts higher surface sulfate ($\sim 20\%$) in regions plagued by air pollution and concomitant decreases in other locations. Quantifying the impacts of intercontinental transport of pollutants and their precursors necessitates the use of global tropospheric models [*Fiore et al.*, 2003; *Park et al.*, 2004]. Our results suggest caution must be exercised when using off-line global models to simulate sulfate and ozone regional pollution and transport of pollutants and precursors across continents. Surface levels of sulfate in summer-time polluted regions are most likely to be underestimated in models that use off-line fields. The differences in the present study represent a lower limit due to the unique model set-up and consistency between coupled and off-line fields. Experiments dependent on the use of off-line fields from other models are likely to experience larger discrepancies.

[37] The current model does not include aqueous oxidation of SO_2 by ozone or the effects of variable pH on the in-cloud processing. *Rasch et al.* [2000] found O_3 oxidation to be important only over European regions in winter where SO_2 is very high and H_2O_2 levels are depleted within clouds. It appears that O_3 oxidation is typically not important for sulfate production, relative to oxidation via OH and H_2O_2 , especially when photochemical activity is high. Since the time-scale for ozone oxidation is significantly longer than H_2O_2 oxidation, the use of monthly-mean O_3 fields would not compromise the simulation to the same degree. From the perspective of the chemistry model, in-cloud oxidation of SO_2 by O_3 does not represent a significant loss of O_3 due to the very low solubility. Therefore, we believe that inclusion of in-cloud O_3 oxida-

tion would not significantly affect the results presented in this experiment.

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