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Parameterisation and impact of aerosol uptake of HO₂ on a global tropospheric model

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Abstract

HO₂ is an important atmospheric trace gas, whose sink to aerosol is poorly understood yet significant. Previous parameterisations of the rate of uptake have been limited by the lack of laboratory studies. This paper creates a parameterisation for γ_{HO_2} based on the available laboratory studies. The calculated global mean γ_{HO_2} is 0.028, significantly lower than previous work (0.2). Modelled concentrations of HO₂ show significant regional sensitivity to the value of γ_{HO_2} (up to +106 % at the surface with the parameterisation of γ_{HO_2} in this work as compared with a value of 0.2), but global sensitivity is small (+3.2 %). The modelled response in O₃ is also highly regional, being up to +27 % at the surface over China, and only +0.3 % globally (with the parameterisation of γ_{HO_2} in this work as compared with a value of 0.2). The impact of γ_{HO_2} on sulfate is more complex, with up to +16 % over China and −5 % over high latitudes, resulting in a global change of +1.2 % (with the parameterisation of γ_{HO_2} in this work as compared with a value of 0.2). Uncertainty in the reaction mechanism and hence products (previously assumed to be H₂O₂) impacts the processing of sulfur and hence aerosol loads. Further laboratory studies are desirable to constrain the rate of reaction and to elucidate the reaction mechanism and products.

1 Introduction

Oxidants are a key component of the atmospheric system as they help control the concentrations of some pollutants and greenhouse gases. The key oxidants in the troposphere are the hydroxyl radical (OH), the nitrate radical (NO₃), ozone (O₃), and hydrogen peroxide (H₂O₂) (Logan et al., 1981). Many of these oxidants are linked by the hydroperoxyl radical (HO₂). As well as participating in gas-phase reactions, HO₂ is also taken up by aerosol particles (Jacob, 2000). The uptake of HO₂ reduces HO₂ concentrations and thus reduces OH and O₃ concentrations. HO₂ uptake has received less attention in laboratory and modelling studies than the uptake of N₂O₅, but may

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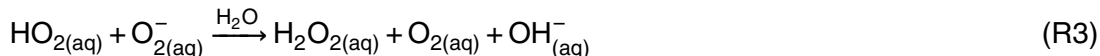


play a significant role in the atmospheric system (Tie et al., 2001; Martin et al., 2003; Liao et al., 2006).

The rates of reactions on aerosol particles (“heterogeneous reactions”) are determined by the available aerosol surface area, and an uptake coefficient γ (γ), defined as “the probability that a molecule impacting the surface of the particle undergoes irreversible reaction” (Schwartz, 1986). Determinations of the value of γ_{HO_2} from laboratory, field, and modelling studies span several orders of magnitude (<0.05 to 1.0) (Mozurkewich et al., 1987; Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996; Gershenson et al., 1999; Saathoff et al., 2001; Remorov et al., 2002; Thornton and Abbatt, 2005; Bedjanian et al., 2005; Taketani et al., 2008, 2009; Cantrell et al., 1996a,b; Plummer et al., 1996; Jaeglé et al., 2000; Loukhovitskaya et al., 2009). This paper reviews the laboratory studies of HO_2 uptake by tropospheric aerosol and constructs a parameterisation based on these studies. It then assesses the impact of this on tropospheric composition with a global model.

2 Previous studies

The uptake of HO_2 by tropospheric aerosol is thought to proceed via acid-base dissociation of HO_2 (Jacob, 2000, and references therein) followed by electron transfer to produce H_2O_2 (Reactions R1–R3):



A γ_{HO_2} value of 0.2 was recommended for use in models of tropospheric chemistry by Jacob (2000). This value 0.2 is based on a combination of limited laboratory data (yielding values of 0.05–0.2) (Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996; Gershenson et al., 1999) together with results from model-observation

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comparisons (giving higher values of 0.2–1.0) (Cantrell et al., 1996a,b; Plummer et al., 1996; Jaeglé et al., 2000). The very high values for γ_{HO_2} required by these modelling studies may in fact reflect the omission of halogen chemistry which cycles HO_2 to OH (Kanaya et al., 2002; Bloss et al., 2005) and hence decreases HO_2 concentrations.

5 A limited set of laboratory determinations of γ_{HO_2} exist for conditions relevant to the troposphere (Saathoff et al., 2001; Remorov et al., 2002; Thornton and Abbatt, 2005; Bedjanian et al., 2005; Taketani et al., 2008). Generally these studies find much lower values than the recommended value of 0.2 (Jacob, 2000). However, laboratory
10 determinations of the rate of reaction have also found that transition metals (such as Cu(II) and to a lesser extent Fe(II)) catalyse the reaction, leading to very large γ_{HO_2} values often greater than 0.5 (Mozurkewich et al., 1987; Cooper and Abbatt, 1996; Thornton and Abbatt, 2005).

A parameterisation based on aqueous-phase reaction mechanisms has been suggested by Thornton et al. (2008). On all aerosol types other than dust, an aqueous
15 phase recombination mechanism based on Reactions (R1) to (R3) is used to calculate uptake of HO_2 to aqueous aerosol. Uptake to dust is assumed to be uniform at 0.2 due to potential transition metal ion catalysis. They find γ_{HO_2} to be low (<0.05) in the lower troposphere especially in the tropics, but larger (0.1–0.3) in the upper troposphere. This trend is due to the temperature dependence of Reaction (R1). The
20 calculations assume there is enough free Cu(II) in dust aerosol (and also in the continental boundary layer) to give large γ_{HO_2} values (0.2), and thus high γ_{HO_2} values are reached at the surface near dust outflow regions (e.g. the Sahara). As acknowledged in the paper, assumptions concerning aerosol pH, Cu ion speciation, and the value of the accommodation coefficient mean the parameterisation of Thornton et al. (2008) is
25 an upper limit, in some cases leading to higher calculated γ_{HO_2} values than those found from laboratory studies.

The gas-phase self-reaction of HO_2 produces H_2O_2 (Atkinson et al., 2004). It has been assumed that this is also the product of the reaction on aerosol (Mozurkewich et al., 1987), and model studies generally represent the heterogeneous reaction as

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$\text{HO}_2 \rightarrow \frac{1}{2} \text{H}_2\text{O}_2$. However, laboratory studies tend not to monitor the composition of the products, thus the actual products of this reaction are uncertain. Many laboratory studies have observed first- rather than second-order kinetics, which suggests a mechanism other than self-reaction (Hanson et al., 1992; Gershenzon et al., 1995; Cooper and Abbatt, 1996; Remorov et al., 2002). It has also been postulated that a reaction involving sulfur compounds may occur, or that a HO_2 -water complex may form (Cooper and Abbatt, 1996; Gonzalez et al., 2010) which would not lead to H_2O_2 production. Only one laboratory study indicates that H_2O_2 is the product of the reaction (Loukhovitskaya et al., 2009). In this study H_2O_2 is observed from the reaction of HO_2 on solid (dry) sea salt particles. However, the majority of aerosol surface area in the troposphere is not dry sea salt. For other aerosol types (such a sulfate) the observed kinetics suggest other reactions may occur (Cooper and Abbatt, 1996; Gonzalez et al., 2010). Reaction with sulfur-compounds in the aerosol (forming water and sulfate) have also been suggested as alternative reaction products (Mao et al., 2010).

Thus the measured value of γ_{HO_2} varies widely (by two orders of magnitude), with the majority of laboratory studies since Jacob (2000) giving lower values than the currently accepted value of 0.2. Thornton et al. (2008) use an aqueous-phase mechanism giving a range of γ_{HO_2} values, but this is likely an upper-limit. There is some limited evidence to support H_2O_2 as the product of the reaction (Loukhovitskaya et al., 2009) but this is uncertain. Here, laboratory data is used to create a new parameterisation of uptake of HO_2 , and the impact of the reaction products is investigated.

3 A new parameterisation

A new parameterisation is built up from available laboratory data (Table 1) in a similar manner to Evans and Jacob (2005). This includes data for different particle compositions, as well as temperature and humidity as determining factors (where data is available). A significant portion of the available laboratory measurements have been made on sea salt aerosol. A temperature dependence has been determined for the uptake

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onto sea salt (Remorov et al., 2002), with colder temperatures giving larger γ_{HO_2} values. The effect of temperature on uptake to sulfate aerosol has not been measured systematically. The data points that exist (for different studies at different temperatures) fit the temperature dependence found for sea salt aerosol. Thus this relationship is applied to sulfate aerosol also. Taketani et al. (2008) measure uptake of HO_2 on $(\text{NH}_4)_2\text{SO}_4$ at a range of relative humidities, finding an increase in γ_{HO_2} with increasing relative humidity. These data are used to incorporate humidity as a determining factor in calculating uptake of HO_2 by sulfate aerosol. This dependency on humidity is only applied above 35 % RH, as there are limited data available at humidities below this value. Below 35 % RH, γ_{HO_2} is assumed to be 0.01 (Thornton and Abbatt, 2005). As the majority of laboratory studies tend to report lower limits (due to laboratory methods), and we ignore the impact of transition metal catalysation, the parameterisation presented here likely represents a lower limit to γ_{HO_2} .

We use the GEOS-Chem global chemical-transport model version v8-02-04 (<http://acmg.seas.harvard.edu/geos/>) (Bey et al., 2001), driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Global Modelling Assimilation Office (GMAO). Simulations are run at 4° latitude by 5° longitude, with 47 vertical layers. The model carries five externally-mixed aerosol types (sulfate, black carbon, organic carbon, dust, and sea-salt), with a relative-humidity-dependent size distribution based on Martin et al. (2003) and references therein. Simulations are run using γ_{HO_2} of 0.2 as recommended by Jacob (2000), and then with the parameterisation as given in Table 1. A simulation is also run with the mechanism of Thornton et al. (2008). Finally a simulation with γ_{HO_2} of zero is run to simulate no heterogeneous reaction. In order to test sensitivity to the reaction products, the simulations just outlined are repeated with H_2O_2 production shut off (i.e. $\text{HO}_2 \rightarrow$ no products, rather than $\text{HO}_2 \rightarrow \frac{1}{2} \text{H}_2\text{O}_2$).

For each grid-box, γ_{HO_2} is calculated as the mean γ over all aerosol components, weighted by the relative contribution of each component to the total aerosol surface area of that grid-box (Evans and Jacob, 2005). First-order loss rate coefficients are

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calculated using the equation of Schwartz (1986). Each simulation is run for two years. The analysis is performed on the second year of output, and the first year discarded as spin-up. The GEOS-Chem model has been extensively used and has previously been evaluated against observations for many locations (Bey et al., 2001; Martin et al., 2003; Evans and Jacob, 2005; Zhang et al., 2008; Nassar et al., 2009).

4 The value of γ_{HO_2}

Figure 1 shows the surface and zonal mean γ_{HO_2} for January and July as calculated in the model using the parameterisation in Table 1. The highest values of γ_{HO_2} (~ 0.1 in the zonal mean) are found at high latitudes, due to the temperature and humidity dependence (γ_{HO_2} increases with decreasing temperature and increasing relative humidity). High surface values are found over Antarctica in July (Figure 1). At this time temperatures are ~ 210 K, and relative humidity is $< 60\%$, giving a γ_{HO_2} on sea salt aerosol of ~ 0.1 . High wind speeds generate a higher sea salt flux to the atmosphere here compared to other regions. Dust outflow regions (such as to the west of the Sahara and off the tip of South America) also have high γ_{HO_2} values. Over dust emission areas themselves however, the uptake is low, as they are dry. The lowest values of γ_{HO_2} are found in the tropical regions and around 30°N – 50°N in the summer. Sulfate and organic aerosol dominate at this time, which combined with higher temperatures and low relative humidity, give rise to γ_{HO_2} values of ~ 0.01 . The global mass-weighted annual average γ_{HO_2} is 0.028, around an order of magnitude lower than 0.2 recommended by Jacob (2000).

The results here are in contrast to Thornton et al. (2008). Figure 2 shows the surface and zonal mean γ_{HO_2} as calculated in the model using the parameterisation of Thornton et al. (2008). The stronger dependence on temperature of Thornton et al. (2008) leads to high values in the cold upper troposphere (0.1–0.3) and low values in the lower troposphere (< 0.01). The global mass-weighted annual average γ_{HO_2} is 0.1. Figure 3 shows the ratio of γ_{HO_2} calculated using the parameterisation in Table 1

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compared to the scheme of Thornton et al. (2008). This work finds γ_{HO_2} values up to 2–5 times greater in the lower troposphere than the parameterisation in Table 1. However, in the cold upper troposphere, Thornton et al. (2008) find γ_{HO_2} an order of magnitude greater than this work. The majority of aerosol surface area above 5 km is contributed by sulfate ($\sim 2 \mu\text{m}^2 \text{cm}^{-3}$), with the next highest contribution from organic carbon ($\sim 1 \mu\text{m}^2 \text{cm}^{-3}$). The strong gradient in γ_{HO_2} with altitude seen by Thornton et al. (2008) is not simulated in this work, as the available laboratory studies suggest a weaker temperature dependence than that of Thornton et al. (2008). Laboratory studies on cold sulfuric acid measure γ_{HO_2} of around 0.05 (Hanson et al., 1992; Gershenson et al., 1995; Cooper and Abbatt, 1996). For the same conditions, the Thornton et al. (2008) mechanism predicts higher (>0.1) values. Laboratory studies have yet to confirm the strength of the temperature dependence for either parameterisation, the only study being on sea salt aerosol (Remorov et al., 2002), which has been adopted by this work. The discrepancy between these two approaches suggests our understanding of the appropriate γ_{HO_2} values is weak, and further laboratory studies are needed to resolve these issues.

5 Impact on tropospheric composition

Figure 4 shows the changes in annual mean surface concentrations of HO_2 , OH , H_2O_2 and O_3 , and zonal mean concentrations of SO_2 and SO_4^{2-} , when moving from a γ_{HO_2} of 0.2 to the parameterisation as in Table 1 (global mean γ_{HO_2} of 0.028). Regionally significant impacts are seen, notably over China, with surface concentrations of HO_2 doubling in some regions, and an increase in OH of up to 31 %. O_3 is also seen to increase by up to 27 % in regions where HO_x increases. However, globally the impact is small, with HO_2 and OH changing by +3.2 % and +1.1 % respectively. The global impact on O_3 is even smaller (+0.3 %) due to the competing effects of $\text{HO}_2 + \text{NO}$ (which leads to (NO_2) and thus O_3 production) and $\text{HO}_2 + \text{O}_3$ (which consumes O_3). Regions showing an increase in O_3 are those with high NO_x and/or VOC concentrations. A

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decrease in H_2O_2 is seen in the same regions as the HO_2 increase. Table 2 shows the impact of different parameterisations of γ_{HO_2} on global annual mass-weighted mean burdens and concentrations of various species. While the value of γ_{HO_2} has a significant impact in regions with high aerosol loading and HO_2 concentrations (Fig. 4, e.g. S. E. Asia, surface changes of +27 % to +106 %), when globally integrated the impact is reduced to only a few percent. From Table 2 it is clear that at a global scale, H_2O_2 is the most significantly impacted species. Reaction of H_2O_2 with SO_2 in cloud drops is the most significant pathway by which sulfate is formed (Seinfeld and Pandis, 2006). The reduction in H_2O_2 results in less SO_2 being consumed and thus the burden of SO_2 increases (Fig. 4). This results in a reduction in sulfate at lower altitudes. The transport of SO_2 to higher altitudes (due to its longer lifetime) results in an increase in sulfate production here (Fig. 4). Thus while the global burden change of sulfate is relatively small (Table 2), the distribution of its production is impacted.

While at global scale the impact of a lower γ_{HO_2} has only a small effect on concentrations of oxidants and sulfur species, regionally the impact is significant. Although the parameterisation presented here gives rise to similar changes in global burdens of tracers as compared to Thornton et al. (2008), the vertical distribution of the impact is different, due mainly to the differing strength of the temperature dependence in their parameterisation.

6 Reaction mechanism

As described in Sect. 2, there is mechanistic uncertainty in the heterogeneous reaction of HO_2 . In order to investigate this the simulations are repeated but with the heterogeneous reaction producing no products. Figure 5 shows the impact on oxidants and sulfur species when production of H_2O_2 is turned off (i.e. $\text{HO}_2 \rightarrow$ no products, rather than $\text{HO}_2 \rightarrow \frac{1}{2} \text{H}_2\text{O}_2$). By changing the reaction products, a reduction in H_2O_2 concentrations of up to $\sim 10\%$ is seen in the zonal mean, with surface concentrations reduced by up to 35 % in regions with high aerosol loading and HO_2 concentrations, such as

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S. E. Asia. The heterogeneous reaction therefore is a significant source of H_2O_2 in certain regions, even when the value of γ_{HO_2} is relatively small (as is the case with the new parameterisation). H_2O_2 can photolyse producing two OH radicals, thus the reduction in H_2O_2 concentrations leads to a reduction in OH concentrations. The largest decrease in OH is seen at high latitudes, where O_3 , water vapour concentrations, and solar radiation are low, leading to H_2O_2 photolysis being a more important source of OH in these regions (Mao et al., 2010) (locally OH decreases by up to 8 % at high latitudes). Changes in O_3 are very small (maximum of <0.5 % at the surface). The global annual mass-weighted changes in H_2O_2 , OH, O_3 , and HO_2 are -4.3 %, -0.4 %, -0.01 % and -0.3 % respectively, when production of H_2O_2 by the heterogeneous reaction is shut off (while keeping γ_{HO_2} as in Table 1).

As mentioned previously, reaction of H_2O_2 with SO_2 in cloud drops is the most significant contributor to sulfate formation (Seinfeld and Pandis, 2006). The decrease in H_2O_2 from turning off its production by the heterogeneous reaction compared with H_2O_2 being produced by the heterogeneous reaction (-4.3 % globally) results in slightly less sulfate, and more SO_2 (globally -0.2 % and +3.0 % respectively for the case where γ_{HO_2} is the new parameterisation as in Table 1). There is a drop in SO_4^{2-} at low altitudes, and an increase at higher altitudes (Fig. 4). The reduction in H_2O_2 increases the SO_2 lifetime, thus more SO_2 escapes to the free troposphere where it is oxidised there. The overall change in sulfate is smaller than the change in SO_2 as the production is just shifted to the upper troposphere. The penultimate column in Table 2 shows the impact of simultaneously the lower γ_{HO_2} value from the parameterisation in Table 1 and also shutting off production of H_2O_2 , as compared to using the recommendation as in Jacob (2000) (i.e. a γ_{HO_2} value of 0.2 and with H_2O_2 produced). The most significant impact is on H_2O_2 (-11.2 %), as the rate of reaction has been reduced, as well as the production of H_2O_2 being shut off. The impact on SO_2 (+3.6 %) is mainly due to shutting off H_2O_2 production (as the change is only +0.6 % if only γ_{HO_2} is changed). The overall burden of sulfate is changed by just over 1 %, but as seen in Fig. 5 the main impact is on its distribution.

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The modelled impacts due to different parameterisations of γ_{HO_2} are highly regional. For most regions the variations are small and of the order of a few percent. Thus comparisons between available observations (e.g. the TRACE-P campaign conducted off the coast of S. E. Asia, data composites from Emmons et al., 2000) does not show a systematic improvement in model performance with any of the different simulations performed here.

Many tropospheric chemistry models do not currently include uptake of HO₂. The results of this study suggest that models that do not include uptake of HO₂ will slightly over-predict sulfate formation in the lowest part of the atmosphere, and underestimate it in the upper troposphere. This implies a greater role of sulfur oxidation and sulfate aerosol formation in the free troposphere than models which do not include uptake of HO₂ suggest, with implications for global aerosol nucleation rates.

In contrast to the uptake of N₂O₅ which shows both regional and global impacts (Macintyre and Evans, 2010), the impact of uptake of HO₂ is far more significant regionally than globally. Table 3 shows the same impacts as in Table 2, but with the analysis restricted to below 5 km over China. It is clear that regionally the impacts are far more significant, with HO₂ showing ~17 % increase (compared to ~3 % globally), and H₂O₂ decreasing by around 16–28 % (compared to ~7–11 % globally).

7 Conclusions

There are clearly large uncertainties in the heterogeneous reaction of HO₂, not only in terms of the rate of reaction (as manifest by γ_{HO_2}), but also the reaction mechanism. Laboratory determinations of γ_{HO_2} suggest that the value of 0.2, recommended previously, is too large. This work uses available laboratory data to construct a new parameterisation for the uptake of HO₂, finding a global mean value of 0.028, roughly an order of magnitude lower than the 0.2 recommended by Jacob (2000). The parameterisation in this work also finds lower values than recent work by Thornton et al. (2008) (global mean γ_{HO_2} ~0.1). The recent parameterisation of Thornton et al. (2008)

yields γ_{HO_2} values higher than those suggested by laboratory studies, due to the strong temperature dependence and assumptions on aerosol pH and Cu ion speciation. Laboratory studies of the temperature and relative humidity dependence of γ_{HO_2} on various aerosol types should now be undertaken, together with an assessment of the role of transition metals.

Our study also suggests that models of tropospheric chemistry that do not currently include uptake of HO_2 will slightly over-predict sulfate formation in the lowest part of the atmosphere, and underestimate it in the upper troposphere, potentially influencing transport and distribution of sulfur in the atmosphere.

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Table 1. Uptake coefficients for HO₂.

Aerosol	Reaction probability (γ) ^a	Reference
Sulfate	$\alpha \times \beta$ where $\alpha = 5.14545 \times 10^{-4} \exp(1560/T)$ $\beta = (-26.1818 \exp(-0.078 \times RH) + 1.74545)$	Remorov et al. (2002) ^b Taketani et al. (2008) ^c
Organic carbon	0.025	Ivanov et al. (1999) ^d
Black carbon	0.01	Saathoff et al. (2001).
NaCl	$5.66 \times 10^{-5} \exp(1560/T)$ (RH < 62 %) 0.05 (RH ≥ 62 %)	Remorov et al. (2002). Taketani et al. (2007).
Dust	0.1 (RH ≥ 50 %); 0.05 (RH < 50 %)	Hänel (1976) (reported in Dentener et al., 1996)

^a T is temperature (K), RH is relative humidity (%).

^b Temperature dependent relationship as for NaCl, as it fits data from Hanson et al. (1992), Cooper and Abbatt (1996) and Thornton and Abbatt (2005).

^c Exponential fit to available data.

^d 10^{-4} to 5×10^{-2} reported at room temperature. Mid-value of the range is used.

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Table 2. Impact on global annual mean burdens and concentrations of oxidants and sulfur species of different uptake schemes expressed as a fractional change as compared to γ_{HO_2} of 0.2 (Jacob, 2000). The simulation with no H₂O₂ production is run with γ_{HO_2} as in Table 1.

$\gamma_{\text{HO}_2} =$	Mean burdens	Fractional changes			
	0.2 (Jacob, 2000)	Thornton et al. (2008)	This work	(no H ₂ O ₂ production)	0.0
HO ₂ (pptv)	5.47	+2.7 %	+3.2 %	+2.9 %	+4.0 %
OH (10 ⁶ molec cm ⁻³)	1.17	+0.8 %	+1.1 %	+0.7 %	+1.7 %
H ₂ O ₂ (ppbv)	0.85	−6.2 %	−7.3 %	−11.2 %	−9.2 %
O ₃ (Tg)	429	+0.1 %	+0.3 %	+0.3 %	+0.7 %
SO ₂ (Tg S)	3.62	+0.6 %	+0.6 %	+3.6 %	+0.9 %
SO ₄ ^{2−} (Tg S)	4.97	+1.0 %	+1.2 %	+1.4 %	+1.6 %

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**Impact of HO₂ uptake
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$\gamma_{\text{HO}_2} =$	Mean burdens	Fractional changes			
	0.2 (Jacob, 2000)	Thornton et al. (2008)	This work	(no H ₂ O ₂ production)	0.0
HO ₂ (pptv)	7.41	+17.3 %	+17.8 %	+16.7 %	+23.4 %
OH (10 ⁶ molec cm ⁻³)	1.69	+6.7 %	+7.2 %	+6.4 %	+9.3 %
H ₂ O ₂ (ppbv)	1.99	−15.7 %	−16.9 %	−27.5 %	−21.5 %
O ₃ (Tg)	2.73	+3.4 %	+3.9 %	+3.8 %	+5.1 %
SO ₂ (Tg S)	4.1 × 10 ⁻²	−0.9 %	−1.3 %	+4.2 %	−1.1 %
SO ₄ ²⁻ (Tg S)	2.4 × 10 ⁻²	+6.3 %	+7.4 %	+5.6 %	+9.4 %

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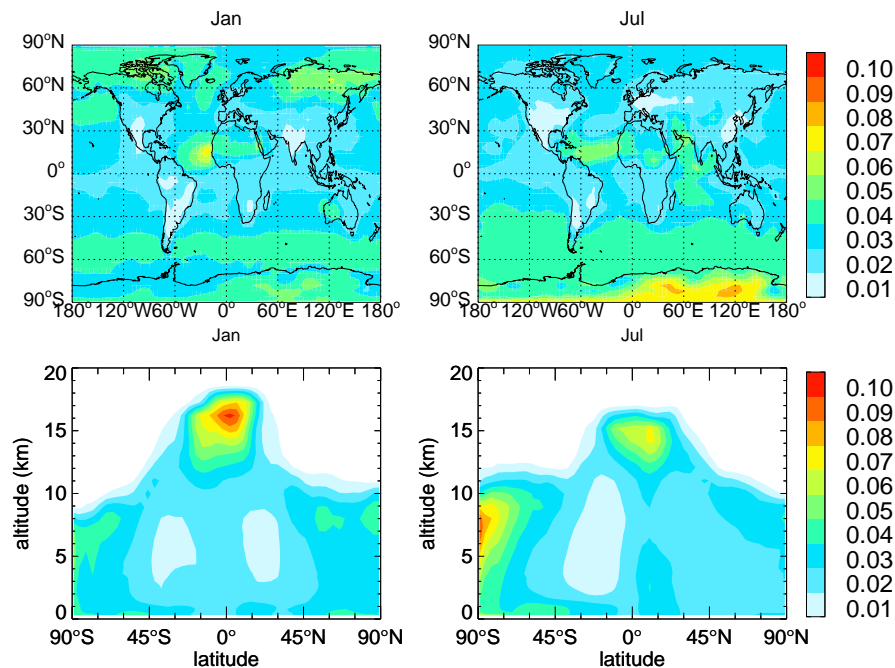
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Fig. 1. Surface and zonal mean HO₂ reaction probabilities (γ_{HO_2}) for January and July as calculated in the model using the parameterisation in Table 1.

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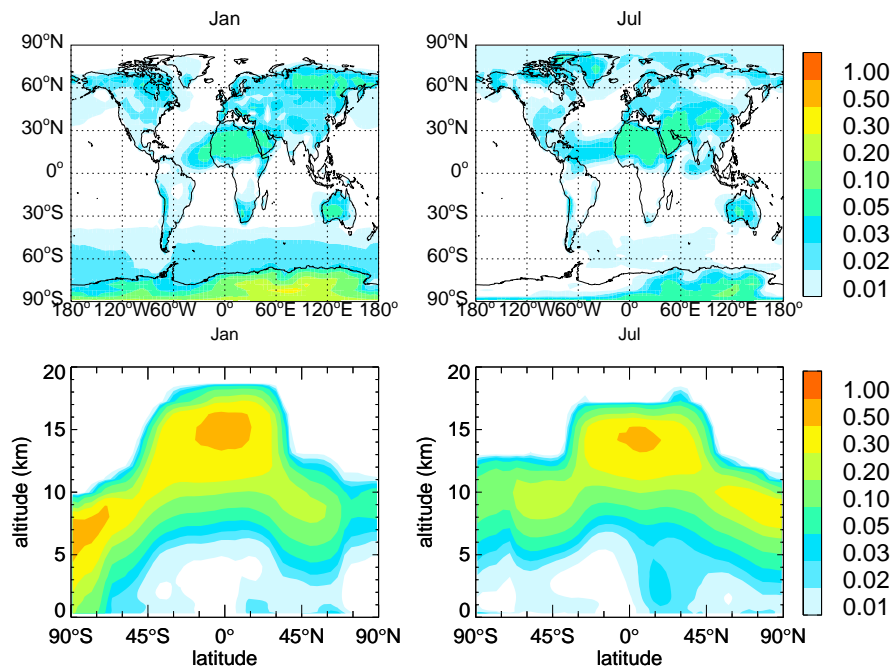
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Fig. 2. Surface and zonal mean HO₂ reaction probabilities (γ_{HO_2}) for January and July as calculated in the model using the parameterisation of Thornton et al. (2008).

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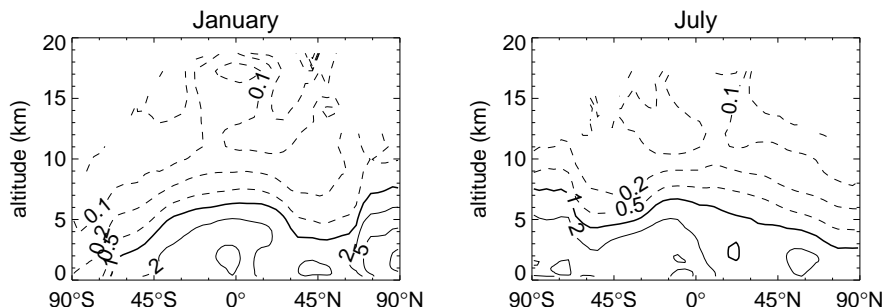


Fig. 3. Zonal mean ratio of γ_{HO_2} calculated using laboratory data (this work) compared to the parameterisation of Thornton et al. (2008). Using laboratory data (this work) yields lower values of γ_{HO_2} in the upper troposphere (dashed lines) and higher values nearer the surface (solid lines) than the parameterisation of Thornton et al. (2008).

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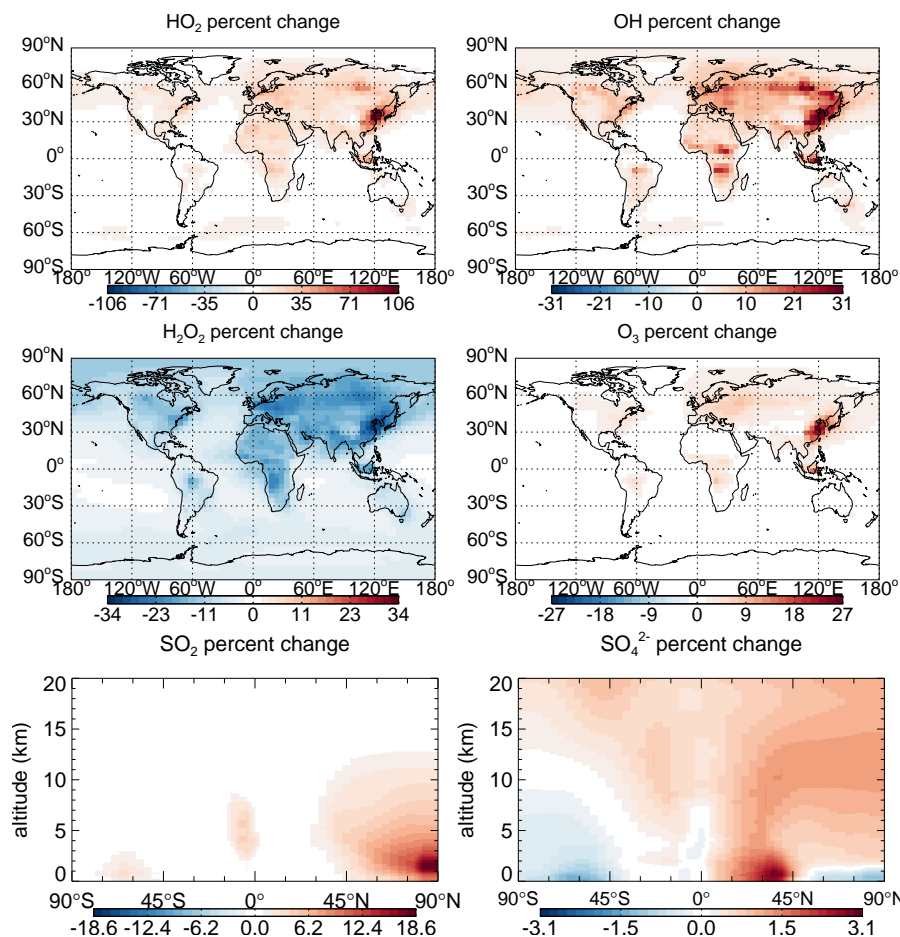


Fig. 4. Impact on annual mean concentrations of oxidants and sulfur species when moving from a γ_{HO_2} of 0.2 (Jacob, 2000) to the scheme presented in Table 1.

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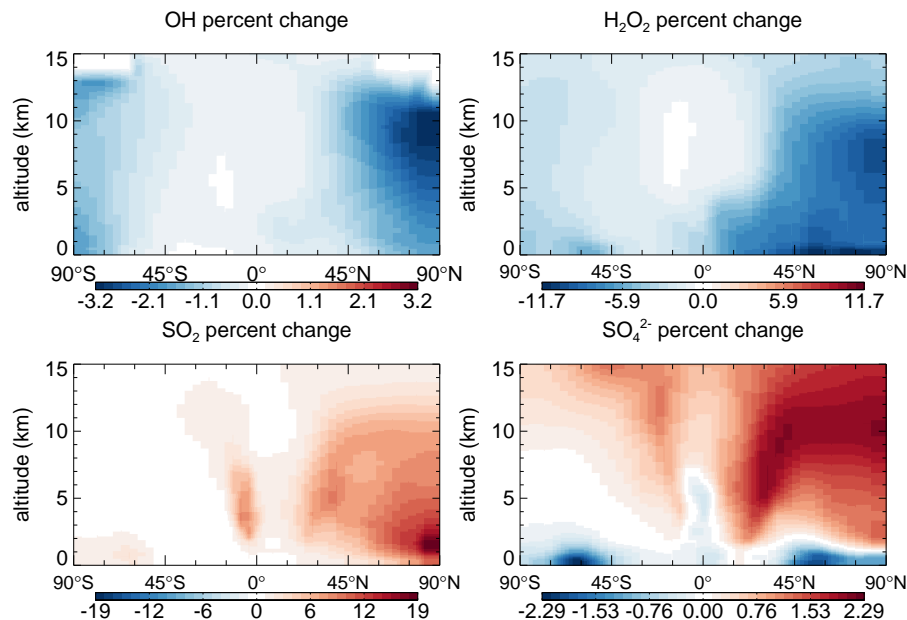


Fig. 5. Impact of not producing H₂O₂ from the heterogeneous reaction of HO₂, using γ_{HO_2} as in Table 1.

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