

**Reply to reviewers of ACPD paper: “Impact of uncertainties in inorganic chemical rate constants on tropospheric composition and ozone radiative forcing” by Ben Newsome and Mat Evans**

We thank the reviewers for their constructive comments. We address the comments below and identify changes we would make to the paper considering their comments. Where indicated we have already run the appropriate new simulations.

**Review by R Saunders.**

**Major comments:**

**My only major concern is that apparently in all sensitivity studies the rate coefficients were *increased* but never *decreased*. Unless a certain reaction is the rate-limiting step inside a reaction cycle, making it faster has only a small effect on the overall rate of the cycle. However, making it slower could make this particular reaction rate-limiting and then the effect becomes large. Why was it never tested what effect a *decrease* of  $k$  by  $1\sigma$  has?**

We had tested this previously and found that the differences were small but didn't include this in the original paper. We would suggest that we include these results in the text and show a comparison between the results of increasing and decreasing the top ten reactions to show that although there are some differences between the conclusions from increasing vs decreasing the rates the impact is small compared to the overall conclusions of the paper.

**Minor issues and technical comments**

**Abstract: “Expert panels synthesise laboratory measurements. ”Chemicals are “synthesised” but not laboratory measurements. I think it would be better to say: “Expert panels evaluate laboratory measurements”.**

We have updated the text to reflect this suggestion.

**In the introduction you describe both the JPL and the IUPAC evaluation and then you provide Eq. (1) to describe the uncertainty. It should be noted, however, that IUPAC does not use this definition. Instead, IUPAC defines uncertainties via  $\Delta \log k$  and  $\Delta E/R$ . I think it would be helpful for the reader if you show how to convert between these different ways to express uncertainties.**

We have included a discussion of both methodologies in the text.

**In your manuscript you refer to the JPL evaluation from 2011. Have you checked if the uncertainties are still the same in the more recent JPL Evaluation Number 18 from 2015?**

We have updated our simulations to reflect the JPL18 evaluation and refer to that in the text. There were some minor changes which have marginally changed the order of the uncertainties of the reactions.

**Page 2, line 20: Change “larger uncertainties than quoted here” to “larger uncertainties than quoted here”.**

We have corrected the text.

**Page 3, line 2: Change “www.goes-chem.org” to “www.geos-chem.org”. C2**

We have corrected the text.

#### **Anonymous Referee #1**

**The authors have used an out of date version of the NASA/JPL data recommendations in their analysis. There does not seem to be any reasonable explanation for this oversight given in the present version of the manuscript. Although, the conclusions from the present work are likely to remain unchanged the authors should highlight any differences with the 2015 NASA/JPL data recommendations in their paper in Table 1.**

We have updated our simulations to reflect the changes made between versions 17 and 18 of the evaluation. This has made small changes to the absolute value of a couple of reactions but there is no overall change to the conclusions.

**The treatment of the uncertainty in the atmospheric parameters, or lack of, is unsatisfying. A thorough treatment of photolysis uncertainty may be beyond the scope of the present work, but making an across the board percentage uncertainty assumption is surely not correct. It may have been better to not include photolysis uncertainty in the present analysis.**

We agree that our analysis of the photolysis rates is simplistic but we believe it provides a useful context for understanding the relative role of photolysis uncertainty compared to reaction rate constant uncertainty. We think that leaving these simulations in the discussion make a useful contribution and helps to motivate future work in this area. We would update the text when we are discussion this to identify the need for future improved assessments of photolysis rate uncertainties.

These dates will be inserted by Copernicus Publications during the typesetting process.

# Impact of uncertainties in inorganic chemical rate constants on tropospheric composition and ozone radiative forcing

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**Abstract.** Chemical rate constants determine the composition of the atmosphere and how this composition has changed over time. They are central to our understanding of climate change and air quality degradation. Atmospheric chemistry models, whether online or offline, box, regional or global use these rate constants. Expert panels evaluate laboratory measurements, making recommendations for the rate constants that should be used. This results in very similar or identical rate constants being used by all models. The inherent uncertainties in these recommendations are, in general, therefore ignored. We explore the impact of these uncertainties on the composition of the troposphere using the GEOS-Chem chemistry transport model. Based on the JPL and IUPAC evaluations we assess the influence of 50 mainly inorganic rate constants and 10 photolysis rates, through simulations where we increase the rate of the reactions to the 1- $\sigma$  upper value recommended by the expert panels on tropospheric composition through the use of the GEOS-Chem chemistry Transport model.

We assess the impact on 4 standard metrics: annual mean tropospheric ozone burden, surface ozone and tropospheric OH concentrations, and tropospheric methane lifetime. Uncertainty in the rate constants for  $\text{NO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HNO}_3$ ,  ~~$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$~~ , and  $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$  are the ~~three~~ two largest source of uncertainty in these metrics. With the absolute magnitude of uncertainties being similar if rate constants are increased or decreased by their  $\sigma$  values. We investigate two methods of assessing these uncertainties, addition in quadrature and a Monte Carlo approach, and conclude they give similar outcomes. Combining the uncertainties across the 60 reactions, gives overall uncertainties on the annual mean tropospheric ozone burden, surface ozone and tropospheric OH concentrations, and tropospheric methane lifetime of 10, 11, 16 and 16% respectively. These are larger than the spread between models in recent model inter-comparisons. Remote regions such as the tropics, poles, and upper troposphere are most uncertain. This chemical uncertainty is sufficiently large to suggest that rate constant uncertainty should be considered alongside other processes when model results disagree with measurement.

Calculations for the pre-industrial allow a tropospheric ozone radiative forcing to be calculated of  $0.412 \pm 0.056$   ~~$0.062$~~   $\text{Wm}^{-2}$ . This uncertainty (~~14~~ 13 %) is comparable to the inter-model spread in ozone radiative forcing found in previous model-model inter-comparison studies where the rate constants used in the models are all identical or very similar. Thus the uncertainty of tropospheric ozone radiative forcing should be expanded to include this additional source of uncertainty. These rate constant uncertainties are significant and suggest that refinement of supposedly well known chemical rate constants should be considered alongside other improvements to enhance our understanding of atmospheric processes.

## 1 Introduction

The concentration of gases and aerosols in the atmosphere have changed over the last century due to human activity. This has resulted in a change in climate (?) and a degradation in air quality (?) with tropospheric ozone (O<sub>3</sub>) and methane (CH<sub>4</sub>) playing a central role. The response of these compounds to the changing emissions is complex and non-linear (?). The hydroxyl radical (OH) plays a central role in this chemistry as it initiates the destruction of many pollutants (notably CH<sub>4</sub>) and so determines their lifetime in the atmosphere. The dominant source of OH is the photolysis of O<sub>3</sub> in the presence of water vapour. The oxidation of compounds such as CH<sub>4</sub>, carbon monoxide (CO) and other hydrocarbons can lead to the production of O<sub>3</sub> if sufficient oxides of nitrogen (NO<sub>x</sub>) are present. Changes in the emissions of O<sub>3</sub> precursors between the pre-industrial (~1850) and the present day have increased O<sub>3</sub> concentrations and this has produced a radiative forcing estimated to be 410 ± 65 mWm<sup>-2</sup> (?).

The rate constants of the reactions occurring in the atmosphere have been determined by a number of laboratory studies which are ~~compiled~~ synthesised by groups such as the IUPAC (?) and JPL (?) panels. These provide recommendations for both rate constants and their associated uncertainties. These reactions are typically expressed in an Arrhenius form to represent the temperature dependence. More complicated representations are needed for three-body reactions. ~~The expressions used to represent IUPAC and JPL provide similar but different representations of the uncertainty in rate constants differs between IUPAC and JPL. For JPL, the 1σ a rate constant. For IUPAC (Eqn. 2) the uncertainty in a rate constant is described as the uncertainty in the log<sub>10</sub> of the rate constant (Δ log<sub>10</sub> k<sub>T</sub>) at a temperature (T) is expressed as an uncertainty at, with the panel giving values for the log<sub>10</sub> uncertainty at 298K (Δ log<sub>10</sub> k<sub>298K</sub>) and the rate of increase in uncertainty away from 298K described by a ΔE /R term. For JPL (Eqn. 2) the relative uncertainty in a rate constant (f(T) is described as the relative uncertainty at temperature of 298K (f (298)) together with a term (g) that expresses how quickly the uncertainty increases away from 298K (Equation 1), leading to temperature dependences which increase away from room temperature (Figure 1). Whereas, for IUPAC (Equation 2) the uncertainty in the log<sub>10</sub> of the rate constant, is described in terms of the uncertainty in the log<sub>10</sub> of the rate constant at 298K together with the uncertainty in the activation energy of the reaction (ΔE)-~~

$$f(T) = f(298K) \exp \left| g \left( \frac{1}{T} - \frac{1}{298K} \right) \right|$$

$$\Delta \log_{10} k(T) \log_{10} k_T = \Delta \log_{10} k(298K) \log_{10} k_{298K} + 0.4343 \frac{\Delta E}{R} \left( \frac{1}{T} - \frac{1}{298K} \right) \quad (1)$$

$$f(T) = f(298K) \exp \left| g \left( \frac{1}{T} - \frac{1}{298K} \right) \right| \quad (2)$$

For the reactions studied, the uncertainty at 298K typically ranges from 5% for well understood reactions to 30% for those which have significant uncertainties. Other reactions can have larger uncertainties than quoted here. The increase in uncertainty at temperatures away from 298K can range from 0% to over 40%, giving some reactions a total uncertainty of over 50% in the cold upper troposphere.



Models of atmospheric composition (whether online or offline, single box or transport etc.) use these recommended rate constants, together with estimates of the meteorology, emissions, deposition, photolysis, etc. of compounds to calculate the concentration of species in the atmosphere. These models are a central tool for our understanding of atmospheric processes and for making policy choices to minimise climate change and air pollution.

Although these models have been developed significantly over the last decades, they have, in general, all used the same basic chemical rate constants as evaluated by the IUPAC or JPL panels. Little emphasis has been placed on understanding the uncertainty in predicted atmospheric composition caused by the uncertainty in these rate constants. ~~A recent notable exception being ?.~~ The focus has been to investigate the impacts of novel chemical reactions ~~;~~ or understanding emissions etc. (e.g. ~~(??)(??)~~). Here though, we investigate the impact of this uncertainty on ~~our understanding of~~ the composition of the troposphere. We base our assessment on the uncertainties in rate constants described by the JPL and IUPAC panels ~~(??)~~ using the GEOS-Chem model and evaluate a range of model diagnostics for both the present day and the pre-industrial.

## 2 Model simulations

GEOS-Chem ~~(?)~~ ([www.geos-chem.org](http://www.geos-chem.org)) is an offline chemistry transport model. We use version v9-2. For computational expediency we use a horizontal resolution of  $4^\circ$  latitude by  $5^\circ$  longitude with 47 vertical hybrid pressure-sigma levels from the surface to 0.01 hPa. The chemistry is solved within the troposphere with the SMV-Gear solver ~~(?)~~. We use a mass based scheme for aerosol ~~(?)~~ and so can not investigate the impact of the rate constant uncertainty on aerosol number or size distribution. Stratospheric chemistry is unchanged in all simulations and uses a linearised approach to the chemistry ~~(??)~~. Global anthropogenic emissions were taken from the Emission Database for Global Atmospheric Research (EDGAR) v3 for  $\text{NO}_x$ , CO, VOCs and  $\text{SO}_x$ . Regional or source specific inventories replaced EDGAR where appropriate (EMEP, BRAVO, Streets, CAC, NEI05, RETRO, AEIC see the GEOS-Chem wiki for more details). Biogenic emissions (Isoprene, Monoterpenes, Methyl Butenol) are taken from the MEGAN v2.1 emission inventory ~~(?)~~. Biomass burning emissions were used from the GFED3 monthly emission inventory~~(?)~~.  $\text{NO}_x$  sources from lightning ~~(?)~~ and soils ~~(?)~~ were also included. As in previous studies ~~(??)~~ pre-industrial emissions are calculated by switching off anthropogenic emissions, reducing biomass burning emissions to 10% of their modern day values, and by setting  $\text{CH}_4$  concentrations to a constant 700 ppbv ~~(?)~~.

For both present-day and the pre-industrial simulations we run the model from the 1st of July 2005 to the 1st of July 2007 with GEOS-5 meteorology. We used the first year to spin up the composition of the troposphere. Metrics are derived from the second year of simulation.

We follow the methodology of JPL ~~(?)~~ for the representation of uncertainties in rate constants [converting IUPAC representation where necessary](#). For two body reactions the uncertainty is given by two parameters.  $f$  (298K) describes the relative uncertainty at 298K, and  $g$  describes how the uncertainty increases as temperature diverges from 298K, as shown in equation (1).

### 3 Reactions Studied

We limit our study to the inorganic ( $O_x$ ,  $HO_x$ ,  $NO_x$ , CO,  $CH_4$ ) reactions together with some key organic and sulfur reactions. Mechanistic uncertainties in the organic chemistry of the atmosphere makes a systematic assessment of these uncertainties difficult (?). Table 1 shows a list of reactions that are perturbed and the uncertainties assumed. We use the uncertainty recommendations from the JPL panel if provided and the IUPAC panel otherwise. We investigate the impact of 50 inorganic chemical reactions and 10 photolysis reactions (Table 1). Uncertainties in photolysis rate constants are harder to define than for the other reactions. We consider the appropriate chemical uncertainty here as the uncertainty in the absorption cross section and the quantum yield rather than the uncertainty in the photon flux which we attribute to the radiative transfer calculation. A full calculation of the chemical uncertainty in a photolysis rate is complex as it it depends upon the uncertainties at different wavelengths, the independence of the cross section and quantum yield parameters and the transfer of this information through the spectral bins used for the laboratory studies and the photolysis calculations. In order to simplify this calculation we apply a 10% uncertainty to all photolysis rates. ~~Future efforts should more systematically explore the impact of the uncertainties in cross-sections and quantum yields on atmospheric composition. Although this is not ideal it does allow us to place an uncertainty in the photolysis rates into a context of other uncertainties. An improved presentation of the photolysis uncertainty should be included in future work.~~

### 4 Single Reaction Perturbations

From each of these 60 reactions we increase the reaction rate by the  $1\sigma$  temperature dependent uncertainty given in Table 1. To allow the model to spin up we run the model for 2 years and take the 2nd year of simulation ~~and calculate for the calculation of~~ four metrics: tropospheric  $O_3$  burden, mean surface  $O_3$  mixing ratio, tropospheric mass weighted mean OH number density, and tropospheric mean  $CH_4$  lifetime. We subtract the values of these metrics from the base value of the metric (unchanged rate constants) and then take the absolute value to remove cases where the value decreases on an increase in the rate constant. Figure 2 shows the changes for all four metrics with Table 1 giving the values for the change in tropospheric  $O_3$  burden. We express these values as a percentage of the base case value.

It is evident that a relatively small number of reactions produce large uncertainties in the values of these metrics. The one that offers the most uncertainty is the reaction between  $NO_2$  and OH to product nitric acid which leads to uncertainties in the range of 6–11% in the metrics investigated here. This reaction is both highly uncertain ( $f(298K)=30\%$ ) and acts as a large global sink for  $NO_x$  and  $HO_x$ . The ~~next most significant reactions are between NO and  $O_3$  to produce  $NO_2$  and  $O_2$ , and between NO and  $HO_2$ .  $O_3 + NO$  reaction to produce  $NO_2$  and OH. These are not especially uncertainty ( $f(298K)=10\%$  and  $15\%$  respectively) but represent processes~~ is central to the partitioning of  $NO_{x,x}$  in the atmosphere, ~~in the cycling of  $HO_x$  and in the generation of  $O_3$ . Relatively small uncertainties in the large chemical fluxes of these reactions lead to a significant uncertainty building up-. Thus increasing its rate constant reduces NO concentrations in the atmosphere (leading to lower  $O_3$  concentrations) and increasing the concentration of  $NO_2$  (which favours  $NO_2$  removal) which again reduces  $O_3$  concentrations.~~ Another significant reaction is that between  $CH_4$  and OH to produce  $CH_3O_2$  radicals. The model assumes a constant  $CH_4$  concentration so an

increase in the rate constant between CH<sub>4</sub> and OH leads to an increased source of radicals but doesn't lead to a commensurate drop in the CH<sub>4</sub> concentration. Thus an increase in this rate constant in the model is effectively the same as an increase in the emission of CH<sub>4</sub> which results in a wide range of impacts such as increased CO concentrations etc. Reactions after the tenth most significant reaction for all the metrics generates an uncertainty of less than 1%.

5 The relative importance of the different reactions does not change much with the metric being investigated (see Figure 2). The rate constants of these top ten reactions are not particularly uncertain (other than for NO<sub>2</sub>+OH) compared to other reactions but they link important chemical cycles and have a very large chemical flux flowing through them. Thus relatively small changes in their uncertainties will lead to large changes in concentration. ~~After the top ten reactions, uncertainties in the other reactions lead to smaller uncertainties of less than 1%.~~

10 It ~~would be~~ is just as easy to decrease the rate constant as it is to increase them. Figure 3 shows the absolute uncertainties in tropospheric O<sub>3</sub> burden and OH global mean concentrations varies for the top ten reactions ~~if the rate constant is decreased rather than increased, compared to the values from increasing for both increasing and decreasing~~ the rate constant. Although there are some differences between the impact of increasing or decreasing the rate constant, there is a degree of consistency between the two and so for simplicity reasons we only consider further the impact of increasing the rate constants. ~~The Monte Carlo analysis discussed in the next sections inherently takes this difference into account.~~

15 Given the uncertainties for the individual reactions calculated here, the next question is as to how these uncertainties can be combined together to generate a single uncertainty from rate constants uncertainty on the composition of the atmosphere.

## 5 Addition of uncertainties

If these perturbations are independent (uncertainties in one rate constant are not related to uncertainties in another) and the model approximately linear, the total rate constant uncertainty can be found by finding the root of the sum of the individual uncertainties squared (addition in quadrature) as shown in equation (3).

$$\sigma_{total}^2 = \Sigma \sigma_{reaction}^2 \quad (3)$$

It is hard to assess the independence of the rate constants. Given the nature of the laboratory experiments used to determine them, it is likely that there is some overlap in assumptions. It would be extremely difficult to diagnose this for all 60 reactions and so we ignore this in further work.

25 Atmospheric chemistry is though non-linear (?). A doubling of a change to the model, does not necessarily lead to a doubling of the model response. Thus, is it not obvious how uncertainties from the individual rate-constant perturbations should be combined. To investigate this we perform a Monte Carlo analysis of the model. We take ten of the most significant reactions determined earlier (shown by the \* in Table 1) and generate 10 normally distributed random numbers ( $\mu = 0$ ,  $\sigma=1$ ), one for each reaction. For each of the ten rate constants we add on the calculated  $1\sigma$  uncertainty multiplied by the random number and run the model. We repeat this 50 times to produce a Monte-Carlo ensemble from which we can calculate the four metrics described earlier.

If the model is linear, the metrics calculated from each member of the Monte Carlo ensemble should be (to some level) the same as the linear addition of the individual rate-constant perturbations weighted by the Monte Carlo random numbers. Figure 4 shows the perturbation in the value of the metric calculated for each ensemble member against the calculated value of the metric using the single reaction values. The model shows a strong linear relationship between the metrics examined (intercepts of  $0.21 \pm 0.9\%$  and gradients of  $0.80 \pm 0.04$ ) thus if the errors are uncorrelated we can, at least to a first approximation, add the individual  $1\sigma$  perturbations together in quadrature using Equation 3 to calculate the overall uncertainty in the model metrics. From these simulations we estimate the quadrature approach leads to an over-estimate of the  $1\sigma$  uncertainty on the order of 10%.

We thus conclude that the adding together of the individual perturbations in quadrature gives a good approximation to the uncertainty calculated by the Monte Carlo method for significantly less computational burden.

## 6 Impacts on the present day atmosphere metrics

We show on Figure 2 the absolute percentage change in global annual mean  $O_3$  burden, surface  $O_3$ , tropospheric average OH and  $CH_4$  tropospheric lifetime from increasing each of the reaction rate constants in Table 1 in turn by their  $1\sigma$  value. They are ordered by the magnitude of the perturbation and for clarity we only show the top 20, combining the remaining 40 in quadrature into the ‘Other’ category. The fractional change in tropospheric  $O_3$  burden for all of the perturbations is given in Table 1. We show the results of combining all of these reactions in quadrature (‘Total (sum)’), the result of combining the top 10 in quadrature (‘Top 10’) and the standard deviation from the 50 Monte-Carlo simulations (‘Monte Carlo Top 10’). The relative closeness ( $\sim 10\%$ ) of the value calculated from the ‘Top 10’ and the ‘Monte Carlo Top 10’ shows that the addition in quadrature approach provides a useful approximation to the Monte Carlo methodology with significantly less computational burden.

The top ten reactions contribute over 90% of the uncertainty for all metrics, with the overall uncertainty for the annual mean tropospheric ozone burden, surface ozone and tropospheric OH concentrations, and tropospheric methane lifetime of calculated to be 10, 11, 16 and 16% respectively. These uncertainties can be compared to the inter-model spreads found from model inter-comparison exercises. The multi-model standard deviation in the ozone burden, tropospheric OH concentration and troposphere methane lifetime were found to be 7%, 10% and 10% in the ACCMIP studies (??). Thus we find that the chemical rate constant uncertainty is larger than the multi-model standard deviation spread which is usually used to give some sense of our uncertainty in our understanding of a quantity. As the models used in these inter-comparisons typically use the same rate constants, this rate constant uncertainty is not included in the inter-model spread. The and so the inter-model spread should be therefore be considered a lower estimate for model uncertainty.

## 7 Spatial distribution of uncertainty

Figure 5 shows the spatial distribution of the total uncertainty in the annual mean  $O_3$ , OH and CO concentration, for the tropospheric column, the zonal mean, and at the surface from the 60 reactions. Similar plots for a large number of other model species are shown in Figures 6–11. There is a significant degree of in-homogeneity in these uncertainties which respond to a range of factors. The uncertainties in the rate constants are largest in the upper troposphere where the temperatures are coldest and thus furthest from the 298K base temperature used to calculate the uncertainties. However, these uncertainty can only manifest if chemistry is the large source or sink for a species in that region.  $O_3$  uncertainties are relatively low in the upper troposphere as it has a large stratospheric source in this region which we have not perturbed (see Section 2). OH uncertainties on the other hand are high ( 30%) ~~there,~~ in the upper troposphere due to the low temperatures. Over continental regions the concentration of CO is not particularly uncertain as the emissions and transport control the concentration. However, over the ocean where emissions are small, the chemistry becomes more important and so uncertainty increases. Uncertainties in the CO are largest in the southern hemisphere where direct emission is ~~low~~ lower and chemical production from  $CH_4$  and other hydrocarbons is significant. In general uncertainties are largest over remote regions far from recent emissions, especially if they are particularly cold or hot compared to room temperature. Thus surface OH values are more uncertain in the cold remote southern ocean than they are in the tropics. Surface  $O_3$  values are uncertain in the warm tropics where intense sunlight and high water vapour concentrations leads to a large chemical flux through  $O_3$ .

Across the full set of simulated compounds (Figures 6–11) there are even larger uncertainties. For primary emitted hydrocarbons, large uncertainties occur in remote, photochemically active locations such as the topics where shorter lived hydrocarbons may be many OH lifetimes away from sources. Uncertainties in the OH concentrations thus multiply in these regions, leading to uncertainties of up to 60% for  $\geq C_4$  alkanes for example. Secondary products such as  $H_2O_2$ ,  $CH_3OOH$  also show significant uncertainties of up to 56% in some locations.

$NO_x$  concentrations close to emission sources are dominated by the emission and transport and so are not very sensitive to chemical uncertainty (Figure 8). However, away from these emissions uncertainties can build up. Uncertainty in the  $NO_x$  concentrations at the poles are up to a factor of 40%. Uncertainties in PAN concentrations ~~(Figure 9)~~ 9 are in general high (>20%) in most locations ( $\sim 50\%$  over the remote ocean) reflecting the complexity of the chemistry involving uncertainties in both  $RO_x$  and  $NO_x$  concentrations. Uncertainties in nitric acid (the dominant  $NO_x$  sink) concentrations are smaller however ( $\sim 5\%$ ) reflecting the mass balance constraint of emissions of  $NO_x$  having to balance  $NO_y$  sinks. Large variability in nitric acid concentrations in the southern ocean reflects non-linearities in aerosol thermodynamics of  $HNO_3$  /  $NO_3^-$  partitioning.

$SO_2$  concentrations show the largest uncertainties in the tropical upper troposphere where OH is also highly uncertain. However,  $SO_4^{2-}$  shows much smaller uncertainty, again reflecting mass conservation constraints.  $NH_4^+$  concentrations show little sensitivity to the rate constants analysed. Overall this suggests that aerosol mass is not particularly sensitive to the gas phase chemistry examined here.

Overall, we see a complex pattern of uncertainty with geographically highly variable uncertainty.

## 8 Implications for model-measurement comparisons

Comparisons between the predictions made by models and observations underpin the assessment of model fidelity. Deviations between model and measurements are often used to diagnose model failings. Attributing these differences to uncertainties in the emissions is particularly popular (see for example ??). Figure 12 shows observed monthly mean and standard deviations for CO, O<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> and NO<sub>2</sub> from the World Meteorological Organisation’s Global Atmosphere Watch Cape Verde Atmospheric Observatory (?), overlaid with the base model simulation and the chemical uncertainty (1 $\sigma$ ) calculated from the addition in quadrature of the 60 1 $\sigma$  simulations. We chose this location as it is far from recent emissions and so should show large uncertainties for primary emitted species.

Consistent with Figures 6–11 the uncertainty in the model calculation ranges from 5–30% depending upon the species. For some of the species (CO, O<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub>) much of the difference between the model and the measurements lie within the model 1 $\sigma$  uncertainty. For others such as C<sub>3</sub>H<sub>8</sub> or NO<sub>2</sub> the differences are harder to explain and other processes (emissions, transport, unknown chemistry etc.) would need to be explored.

Figures 6–11 show significant ~~vertical~~ changes in uncertainty with changes in the vertical due to increasing uncertainty with reducing temperature. Figure 14 shows a selection of ozonesonde observations from the World Ozone and Ultraviolet Data Centre (?) compared to equivalent modelled concentrations and uncertainties. Observations are derived from the surface into the middle troposphere as the temperature drops. The uncertainty thus maximises at around 10km. Above this much of the ozone in the model is produced in the stratosphere which is unperturbed in these simulations. Above this height the uncertainty in the ozone due to tropospheric chemistry uncertainty reduces.

These comparisons with observations highlight the complexity of attributing model failure to a particular cause. For some locations and for some species the chemical uncertainty can be large. For the same species, in a different location, the uncertainties may be much smaller. Inversion studies which attempt to attribute model failure to a single cause (for example uncertainties in emissions) need to have a detailed understanding of the magnitude and geographical distribution of the other model errors. We show here that they vary between different species, can be large and highly spatially varying. This should be considered when model inversion studies are undertaken.

## 9 Ozone radiative forcing

We repeat the 60 1 $\sigma$  simulations described above with pre-industrial (notionally the year 1850) emissions (see Section 2) to allow us to calculate an uncertainty in the radiative forcing of O<sub>3</sub>. For each reaction we calculate the difference in the annual mean tropospheric column O<sub>3</sub> (Dobson Units) between the present day and pre-industrial with the rate constant increased to its 1 $\sigma$  value. Then using a linear relationship between change in O<sub>3</sub> column and radiative forcing (??) of 42mW m<sup>-2</sup> DU<sup>-1</sup>, we calculate a radiative forcing associated with the uncertainty associated with each reaction. We estimate an overall uncertainty in the tropospheric O<sub>3</sub> radiative forcing in the same way as the other metrics, by adding them together in quadrature. In our base simulations we calculated the tropospheric O<sub>3</sub> radiative forcing to be 412 mWm<sup>-2</sup> consistent with previous studies (410 $\pm$ 65mWm<sup>-2</sup>) (?). Our estimate of the uncertainty in the O<sub>3</sub> radiative forcing from rate constant uncertainty is 56 mWm<sup>-2</sup>

(~~14~~15%) with reaction specific detail shown in Figure 15. Again the same set of reactions contribute the largest share to the uncertainty in the radiative forcing as in the uncertainty in present day O<sub>3</sub> burden.

This uncertainty estimate of ~~14~~15% can be compared to the 17% spread in the O<sub>3</sub> radiative forcing calculated between climate models in the recent ACCMIP (?) inter-comparison (shown in Figure 15). This spread is usually used as the uncertainty in our understanding of O<sub>3</sub> radiative forcing. However, as all of these models use the same JPL or IUPAC recommended rate constants the inter-model spread does not include the rate constant uncertainty explored here. Given that the rate constant uncertainty is comparable to the inter-model spread, it should be included in future assessment of the uncertainty in O<sub>3</sub> radiative forcing. A naive addition in quadrature approach would suggest that the uncertainty on tropospheric O<sub>3</sub> radiative forcing should be increased by roughly 30% to account for this.

## 10 10 Conclusions

We have shown that the uncertainty in the inorganic rate constants leads to significant (>10%) uncertainties in the concentration of policy relevant metrics of troposphere composition (O<sub>3</sub> burden, surface O<sub>3</sub>, global mean OH, tropospheric CH<sub>4</sub> lifetime, O<sub>3</sub> radiative forcing) with significantly higher uncertainty in other compounds. This uncertainty may have implications for climate policy through an underestimate of the uncertainty on O<sub>3</sub> radiative forcing or significant uncertainties on the CH<sub>4</sub> lifetime. This also has implication for how model-measurement disagreements are interpreted. Similar conclusions have been found for regional air quality focussed models (?).

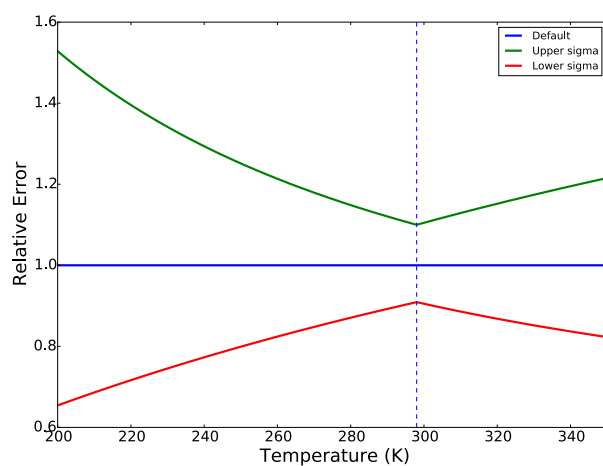
The simulation performed here likely provide a lower limit to the chemical uncertainty. We do not explore the impact in uncertainties in organic chemistry (beyond that from the initiation of hydrocarbon oxidation) or in organic mechanisms; we do not included tropospheric bromine, iodine, chlorine chemistry in our analysis or heterogeneous parameters. We have neither investigated the impact of rate constant uncertainty on the composition of the stratosphere or mesosphere, or how this may propagate through to the troposphere. There are also uncertainties in the Henry's Law constants used for wet and dry parameterisations etc. It seems likely therefore that the true chemical uncertainty in the composition of the atmosphere is significantly higher than that found here.

Although it may be challenging, reducing these uncertainties would provide significant benefits. Targeting the top 10 reactions identified here (Figure 2 (a)) would significantly reduce the overall chemical uncertainties. Despite the fact that the rate-constants for these reactions may appear 'decided', they provide the basis for determining the composition of the atmosphere. Given the difficulties in reducing the uncertainties in other areas of the climate system (we will never know the pre-industrial emissions well etc.) a redoubled effort to reduce rate constant uncertainty appears to be a relatively straightforward methodology to improve our understanding of atmospheric composition.

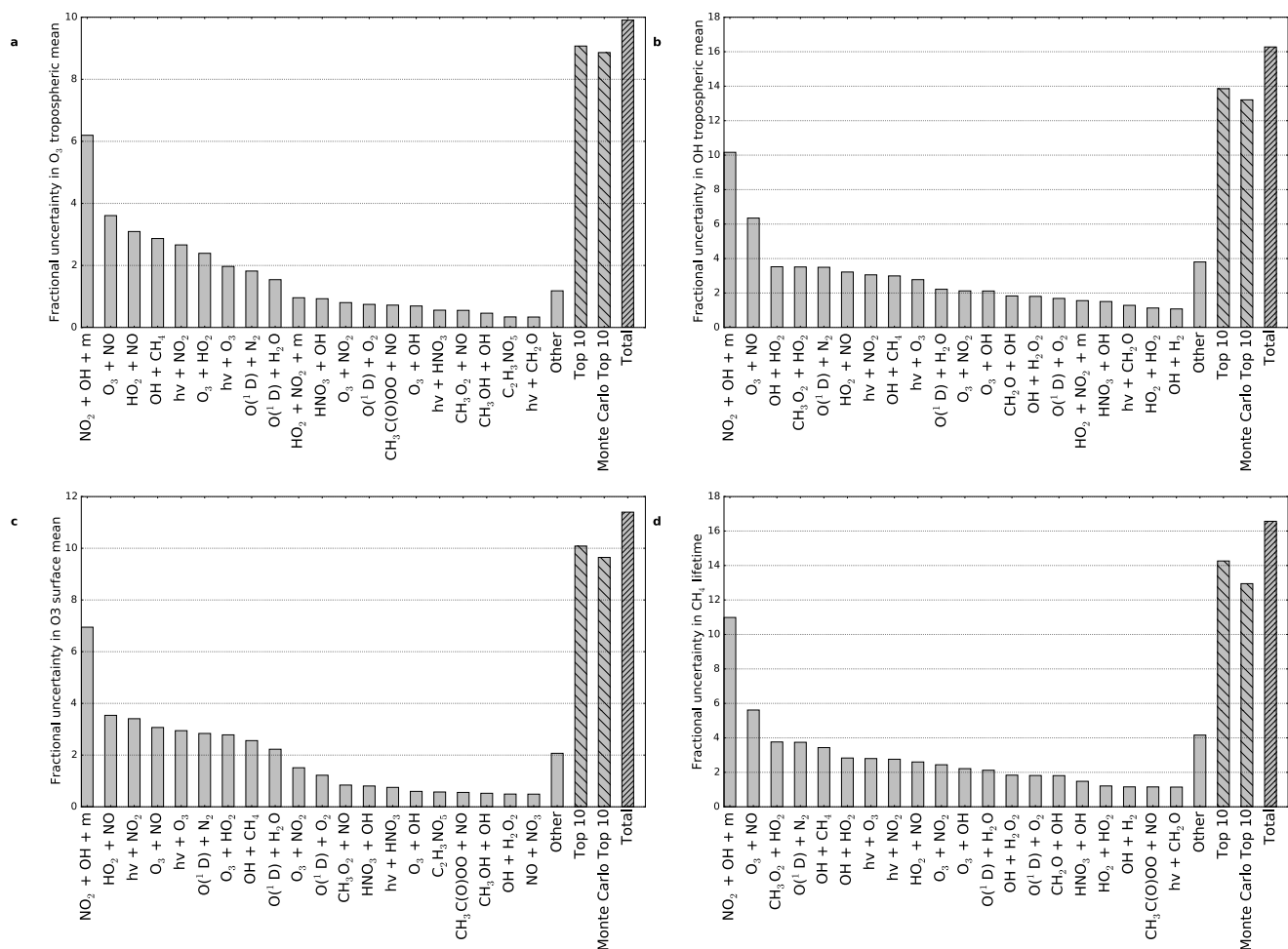
*Acknowledgements.* Ben Newsome was supported by a NERC Studentship (NE/L501761/1). This work was supported by the NERC funded BACCHUS project (NE/L01291X/1). The Cape Verde Atmospheric Observatory is supported by the NERC funded ORC3 project (NE/K004980/1) and by the National Centre for Atmospheric Science. GEOS-Chem ([www.geos-chem.org](http://www.geos-chem.org)) is a community effort and we

wish to thank all involved in the development of the model. We would also thank all the JPL and IUPAC panels for their efforts in compiling atmospheric rate constants.

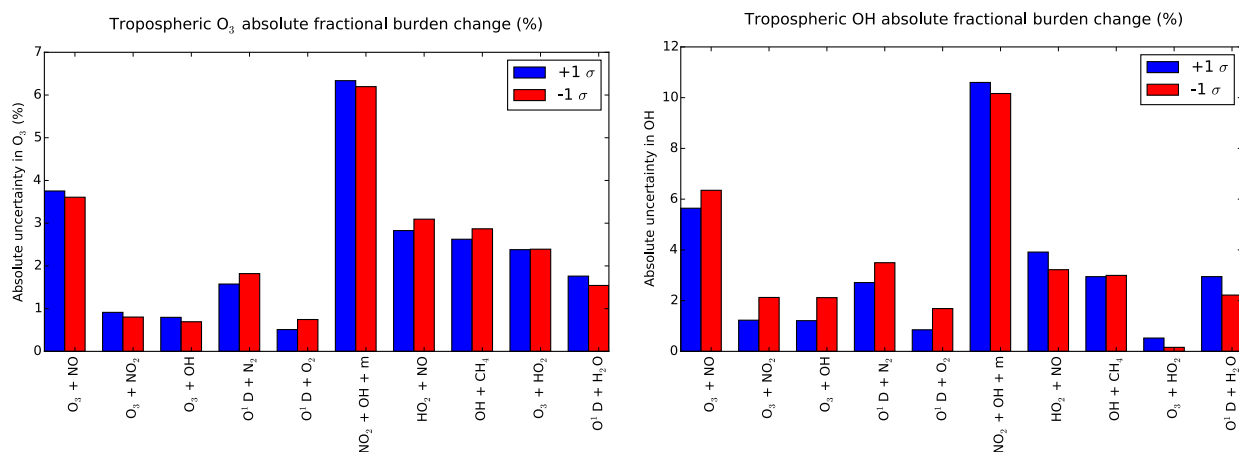




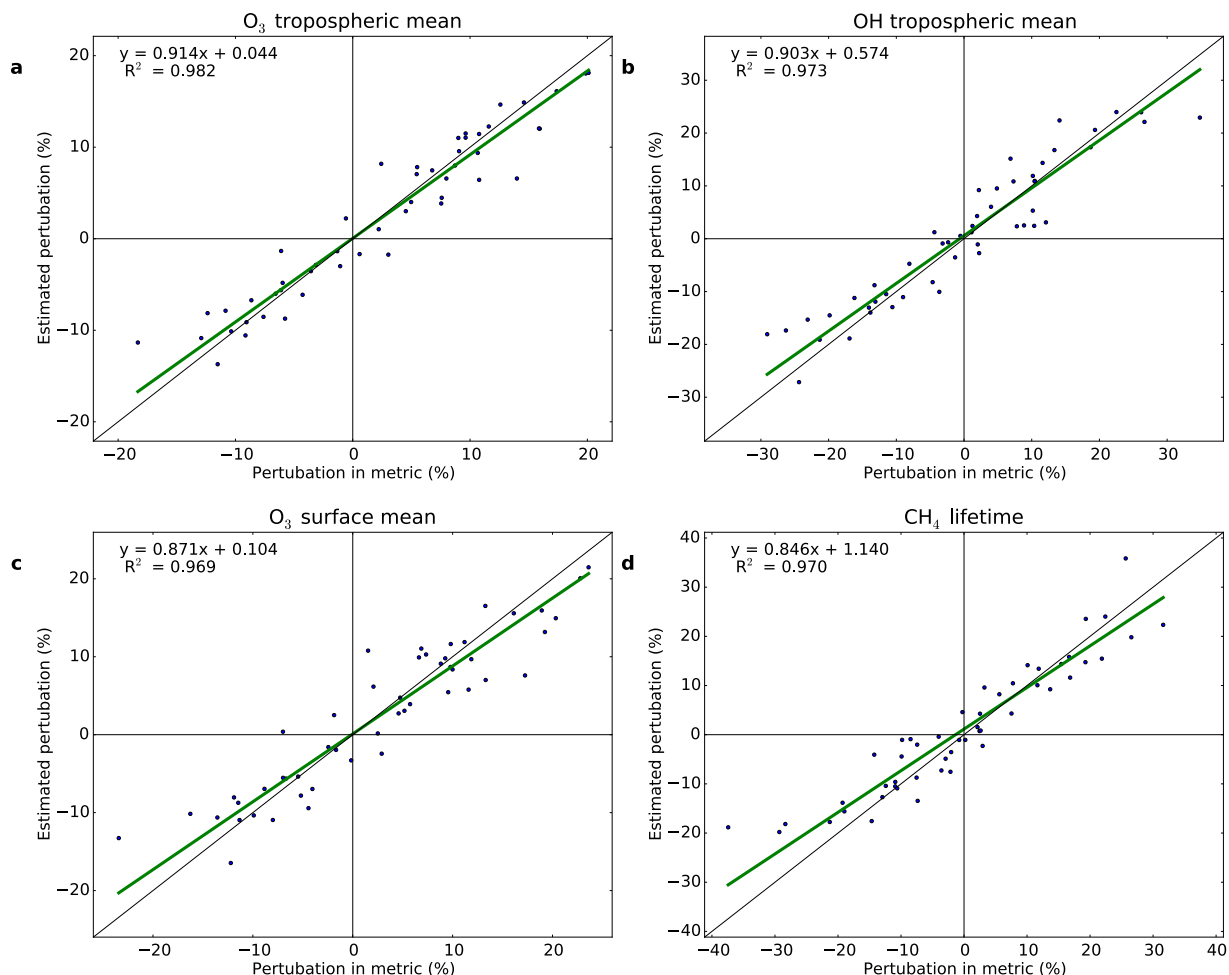
**Figure 1. Example of the uncertainty on a reaction rate constant.** The relative uncertainty of the reaction  $\text{O}_3 + \text{NO}$  is plotted as a function of temperature ~~based on the JPL methodology~~. The lowest uncertainty is at room temperature (298K) with exponentially increasing uncertainties occurring as we diverge to higher and lower temperatures.



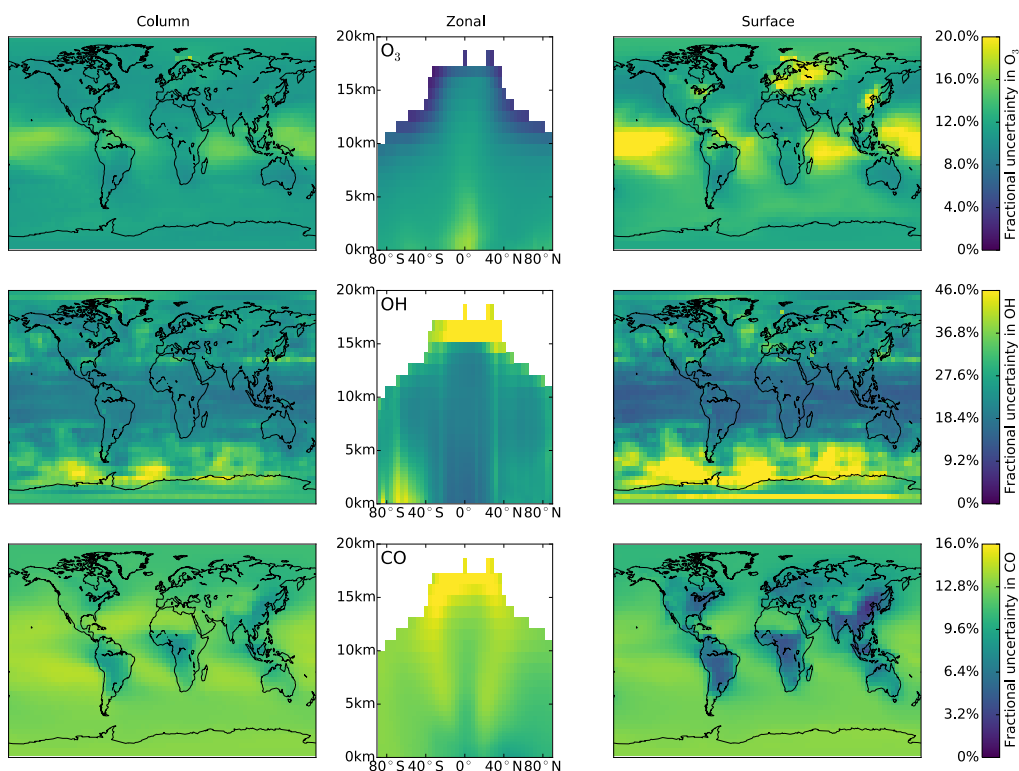
**Figure 2. Uncertainties in all metrics.** Fractional uncertainties of **a** O<sub>3</sub> tropospheric burden, **b** OH tropospheric burden, **c** O<sub>3</sub> surface concentration and **d** CH<sub>4</sub> lifetime. Each bar labelled with a reaction represents a run with a 1 $\sigma$  increase in the rate constant. ‘Other’ represents the addition in quadrature of the reactions that were not the top 20 most influential. ‘Total (Top 10)’ represents the addition in quadrature of the 10 most important reactions, and ‘Monte Carlo Top 10’ represents the standard deviation of the Monte Carlo ensemble. ‘Total’ represents the addition in quadrature of all the simulations.



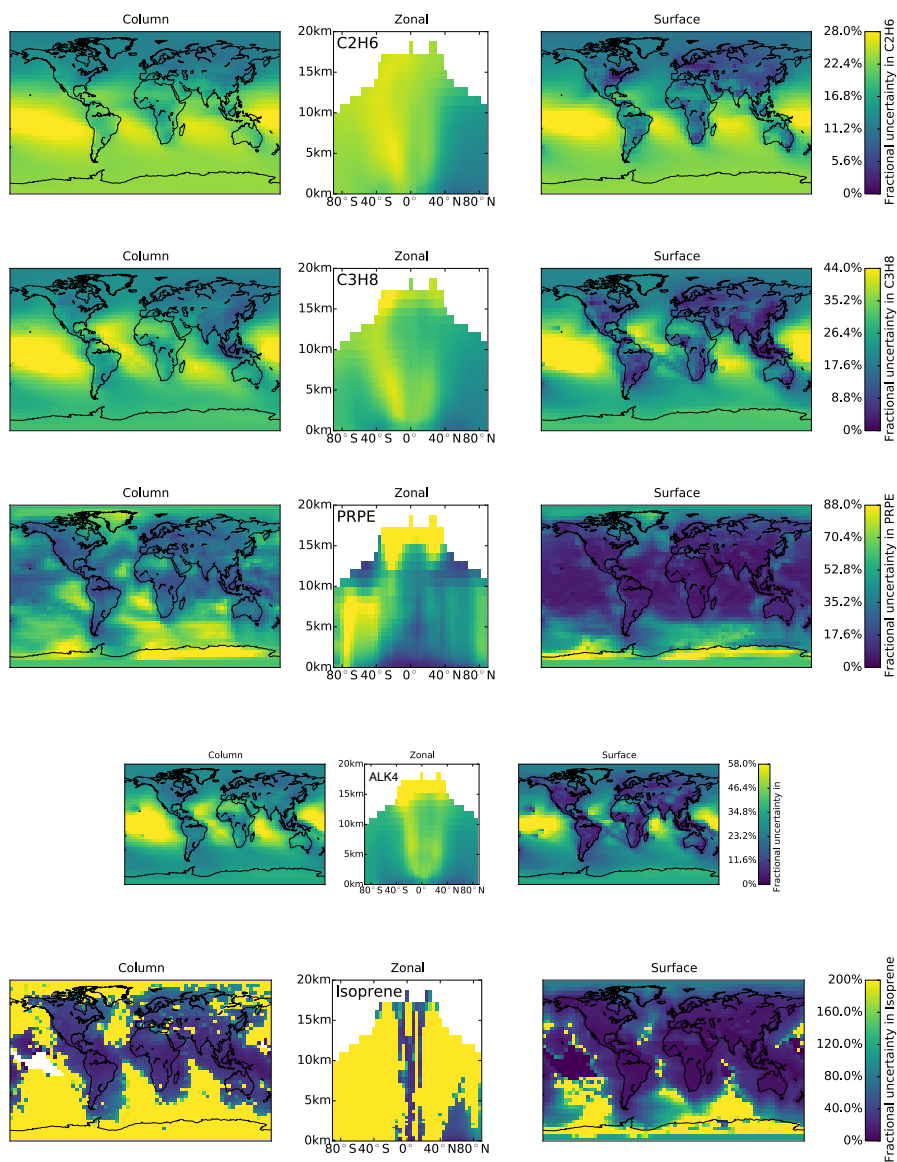
**Figure 3. Uncertainty linearity.** A comparison of absolute uncertainties in O<sub>3</sub> and OH tropospheric burdens for ~~increases~~both positive and decreases in negative changes to the rate constants~~based on the uncertainties~~. These ~~ten~~ reactions show a similar magnitude of tropospheric species concentration change if the rate is set to its lower or higher sigma level of uncertainty.



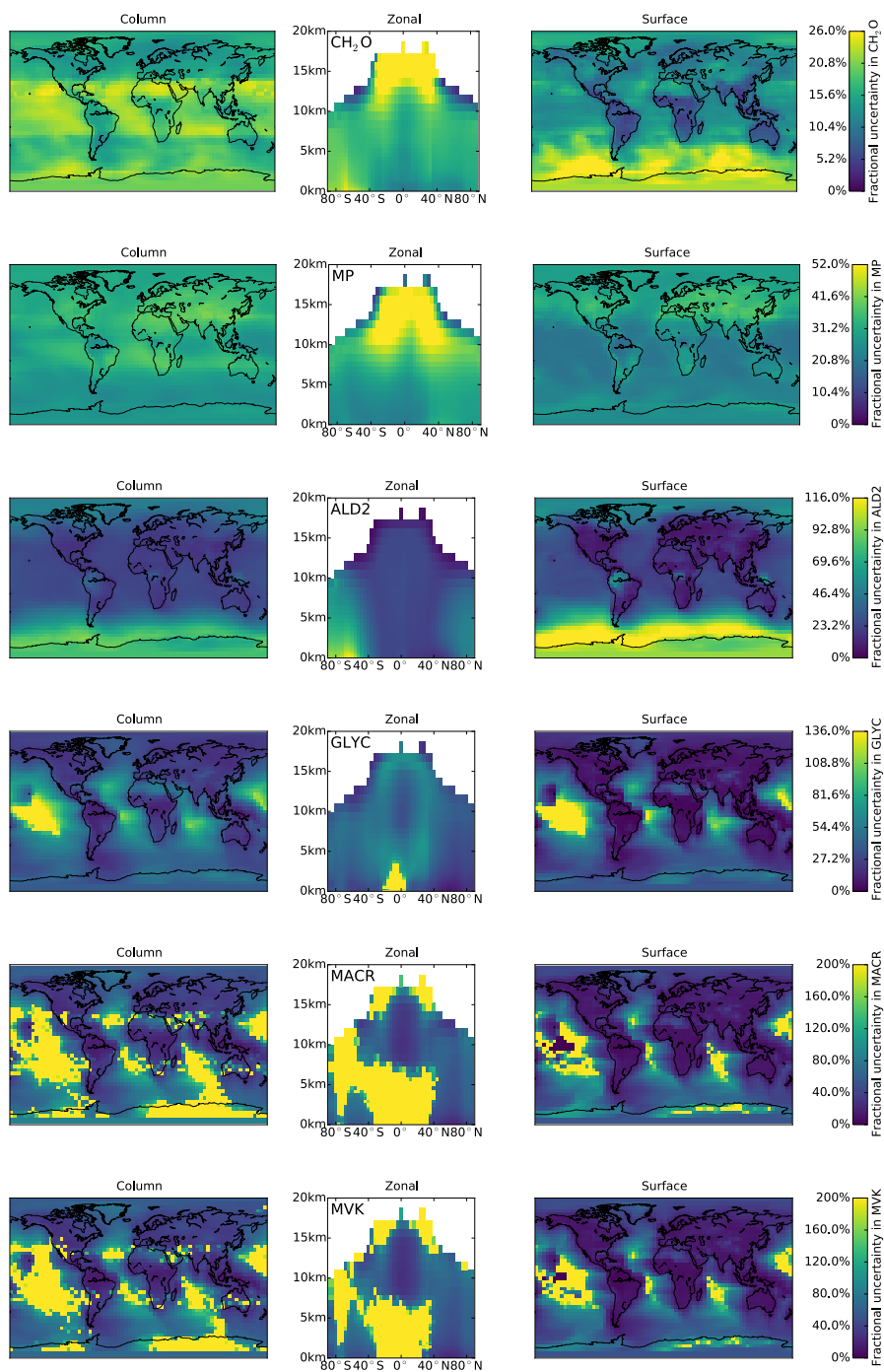
**Figure 4.** ~~Monte Carlo simulations to understand model linearity.~~ Monte Carlo simulations to understand the models linearity. The X axis values shows the percentage change in the metric value of an ensemble member compared to the simulation with no perturbations. The Y axis values show the expected percentage change of the metric based on a linear addition of the individual 1 sigma perturbation experiments weighted by the Monte Carlo perturbation values. Metrics investigated are **a** O<sub>3</sub> tropospheric burden, **b** O<sub>3</sub> mean surface concentration, **c** OH tropospheric burden and **d** CH<sub>4</sub> lifetime. We show the result of 50 Monte Carlo simulations. Each simulation perturbs 10 of the most important reactions (\* reactions in SI-Table 1) 1 $\sigma$  by normally distributed random numbers. ~~Black line is the 1 to 1 line, and the green line~~ the orthogonal regression fit.



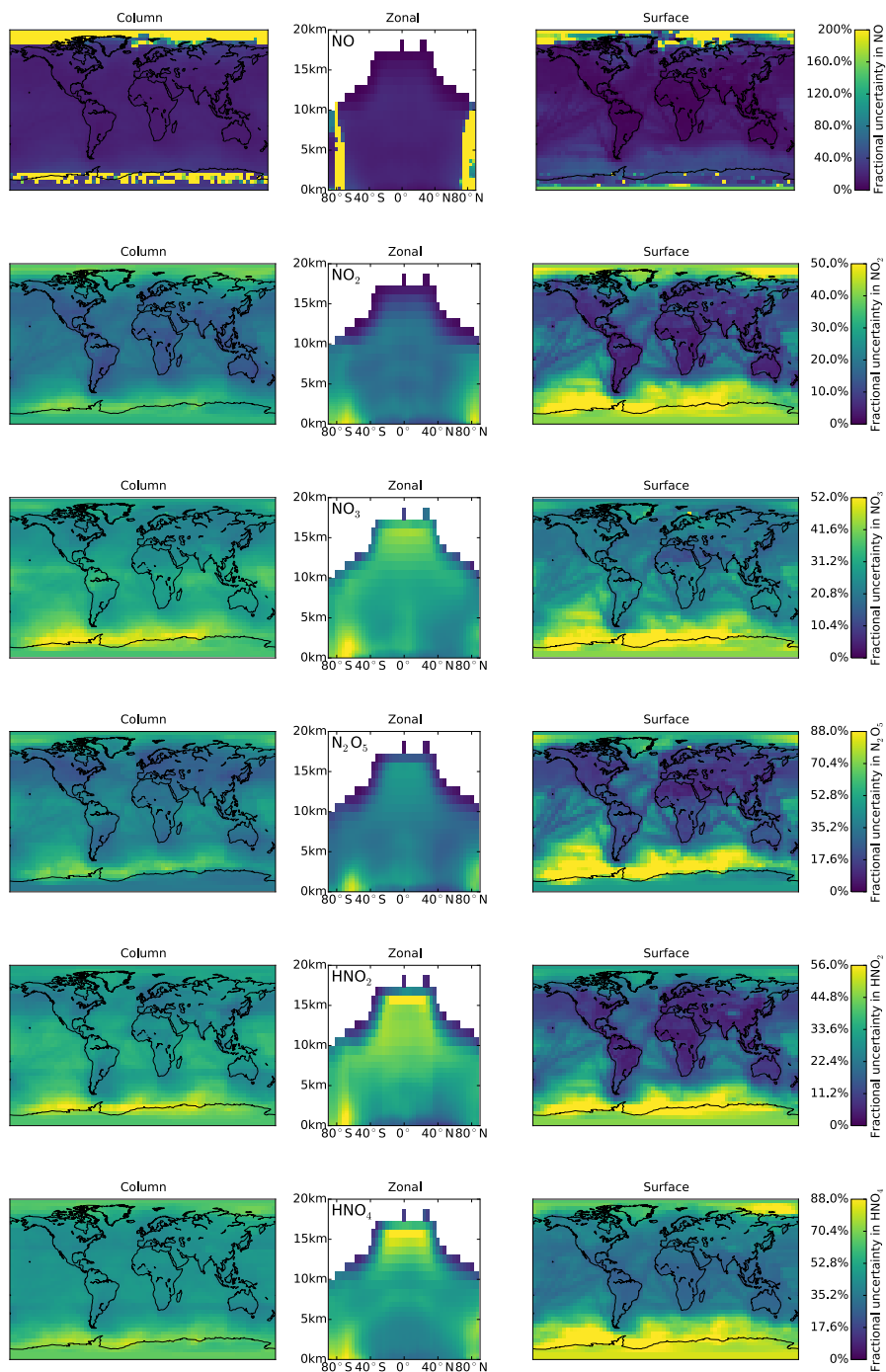
**Figure 5. Spatial distribution of uncertainties.** Fractional uncertainties calculated for  $O_3$ , OH and CO concentrations for the tropospheric column (left), the zonal mean (centre) and the surface (right) from adding together the individual reaction uncertainties from the 60 reactions studied in quadrature



**Figure 6. Primary VOCs.** Total  $1\sigma$  uncertainty in the concentrations of  $C_2H_6$ ,  $C_3H_8$ , PRPE ( $\geq C_3$  Alkenes), ALK4 ( $\geq C_4$  Alkanes) and ISOP (Isoprene) from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.

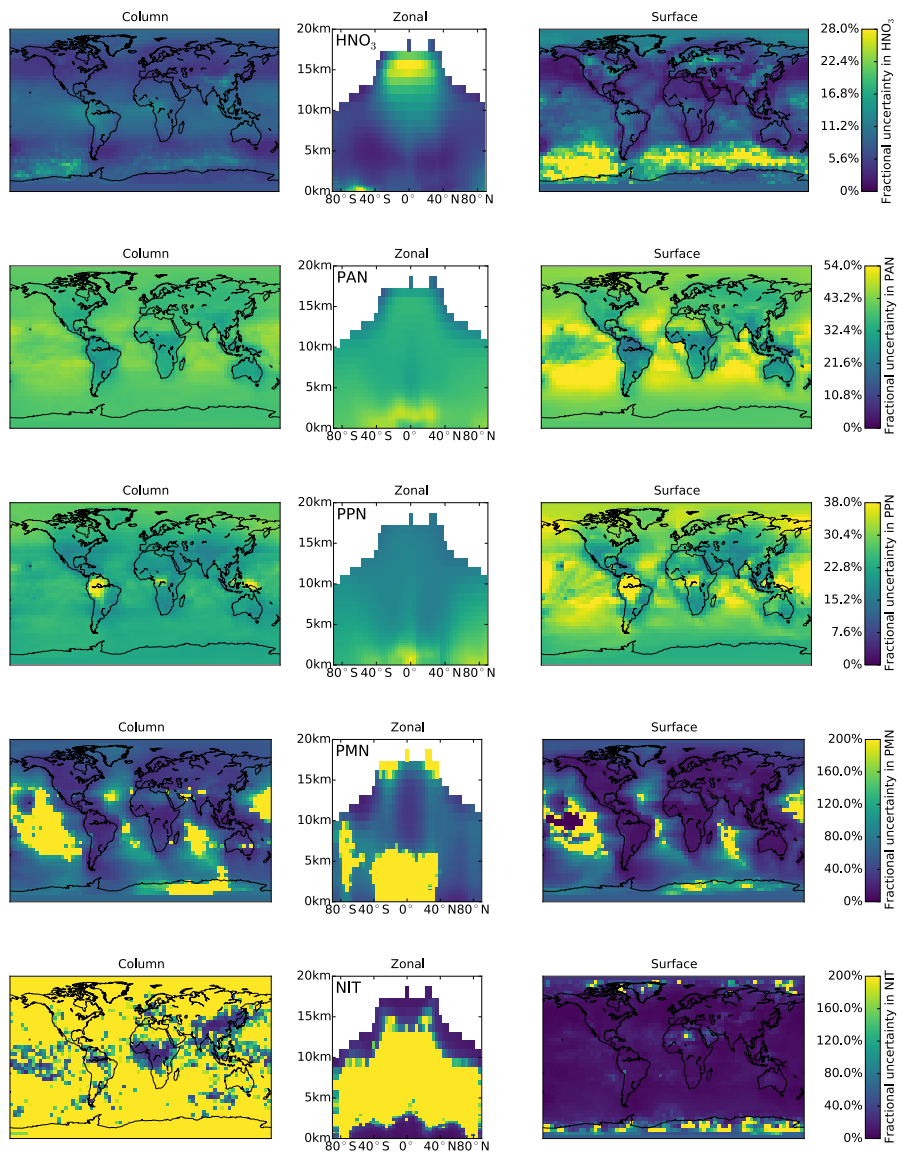


**Figure 7. Other Organics.** Total  $1\sigma$  uncertainty in the concentrations of  $\text{CH}_2\text{O}$ , MP (Methyl Hydro Peroxide), ALD2 (Acetaldehyde), GLYC (Glycoaldehyde), MACR (Methacrolein) and MKV (Methyl Vinyl Ketone) from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.

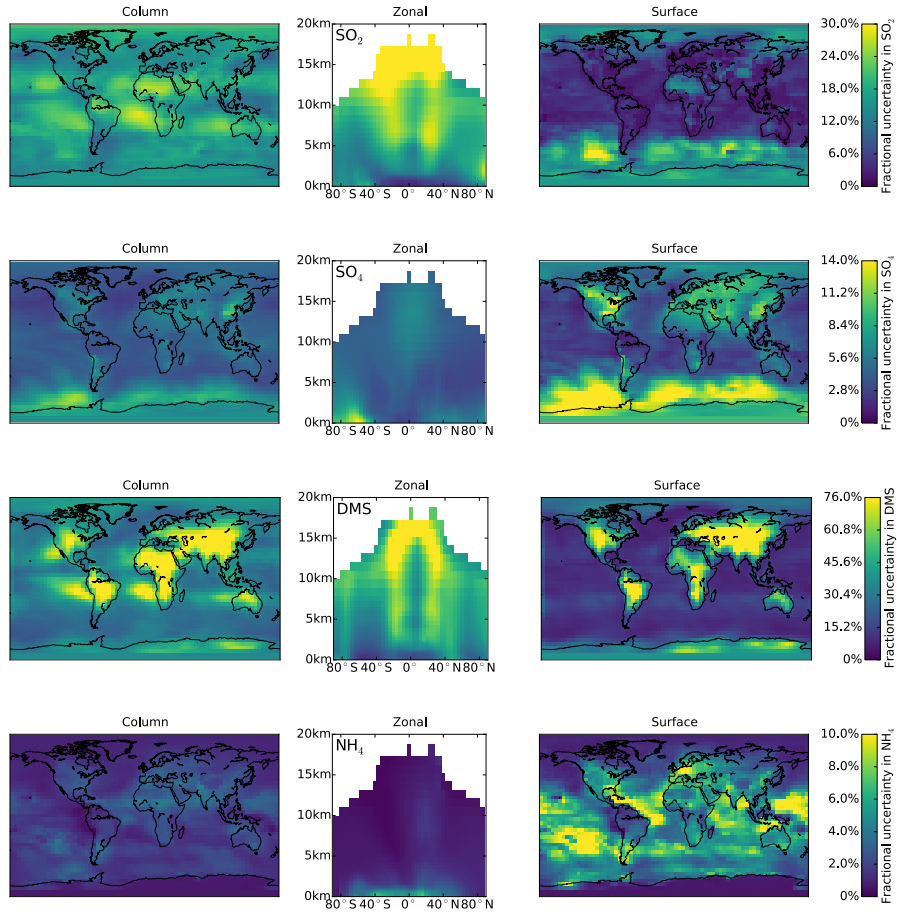


**Figure 8.**  $\text{NO}_x$ . Total  $1\sigma$  uncertainty in the concentrations of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_2$  and  $\text{HNO}_4$  from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.

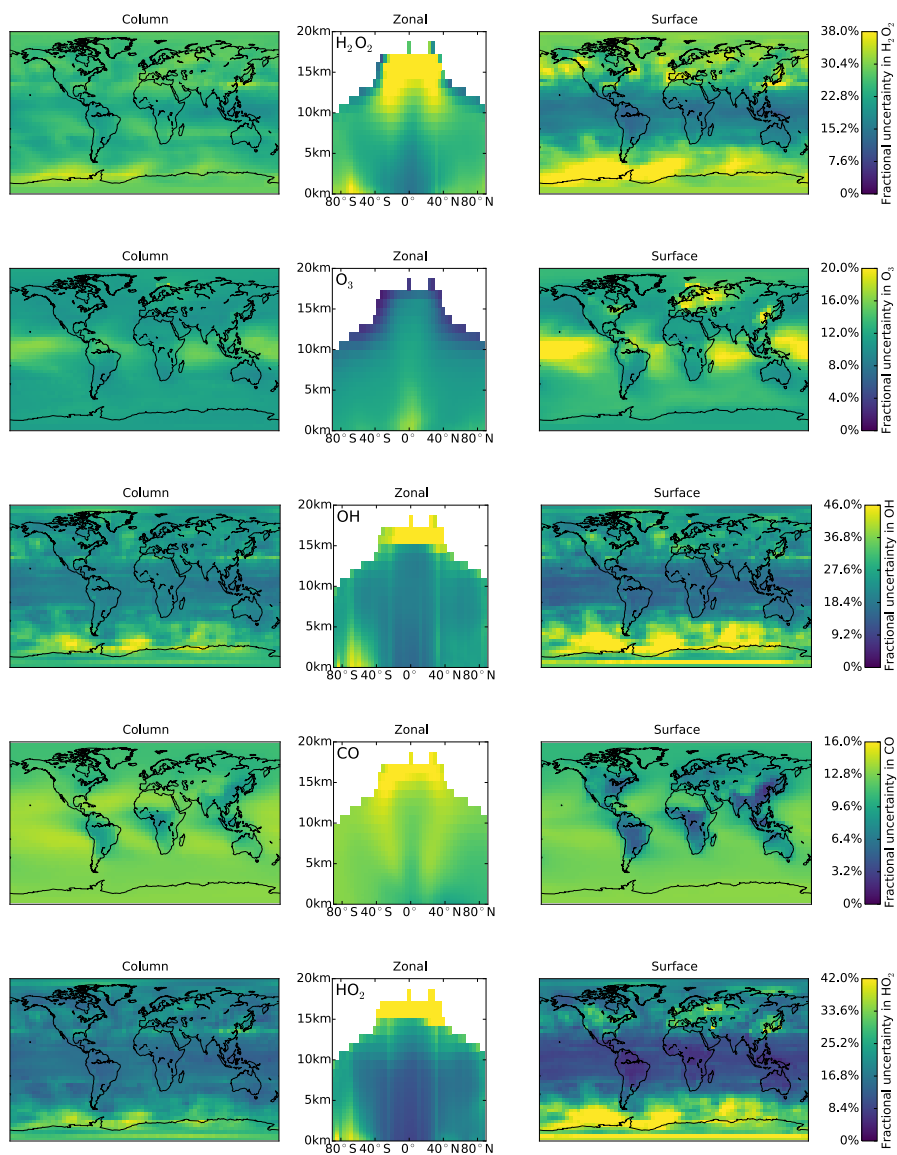




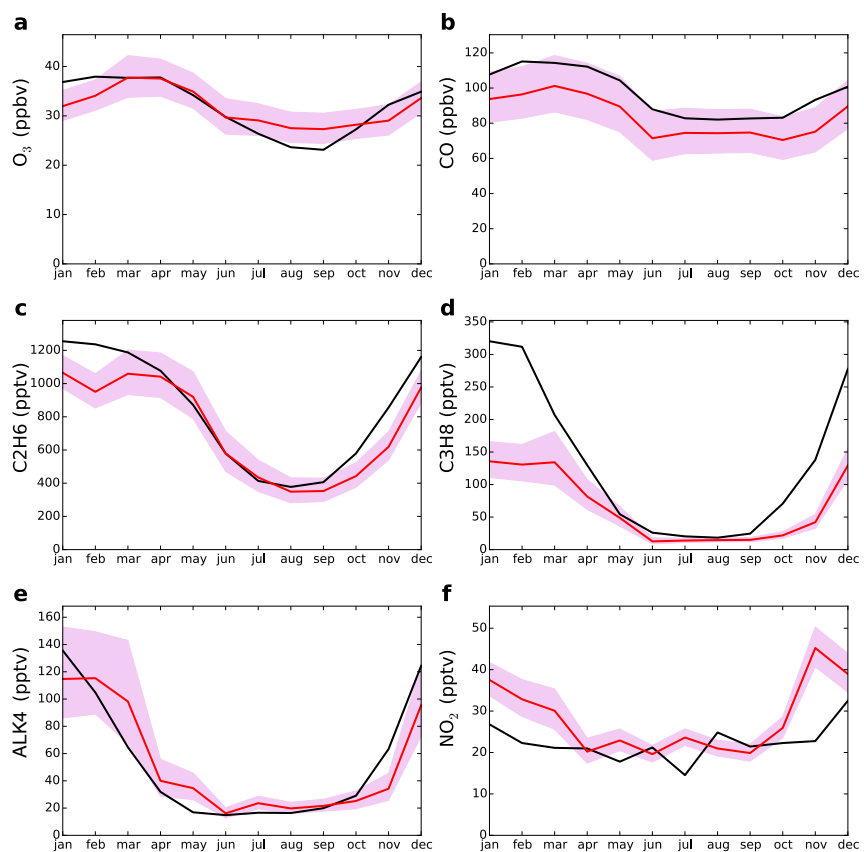
**Figure 9.**  $\text{NO}_y$ . Total  $1\sigma$  uncertainty in the concentrations of  $\text{HNO}_3$ , PAN (Peroxyacetyl Nitrate), PPN (PeroxypropionylPeroxymethacroyl Nitrate), PMN (Peroxymethacroyl Nitrate) and NIT (Inorganic aerosol nitrates) from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.



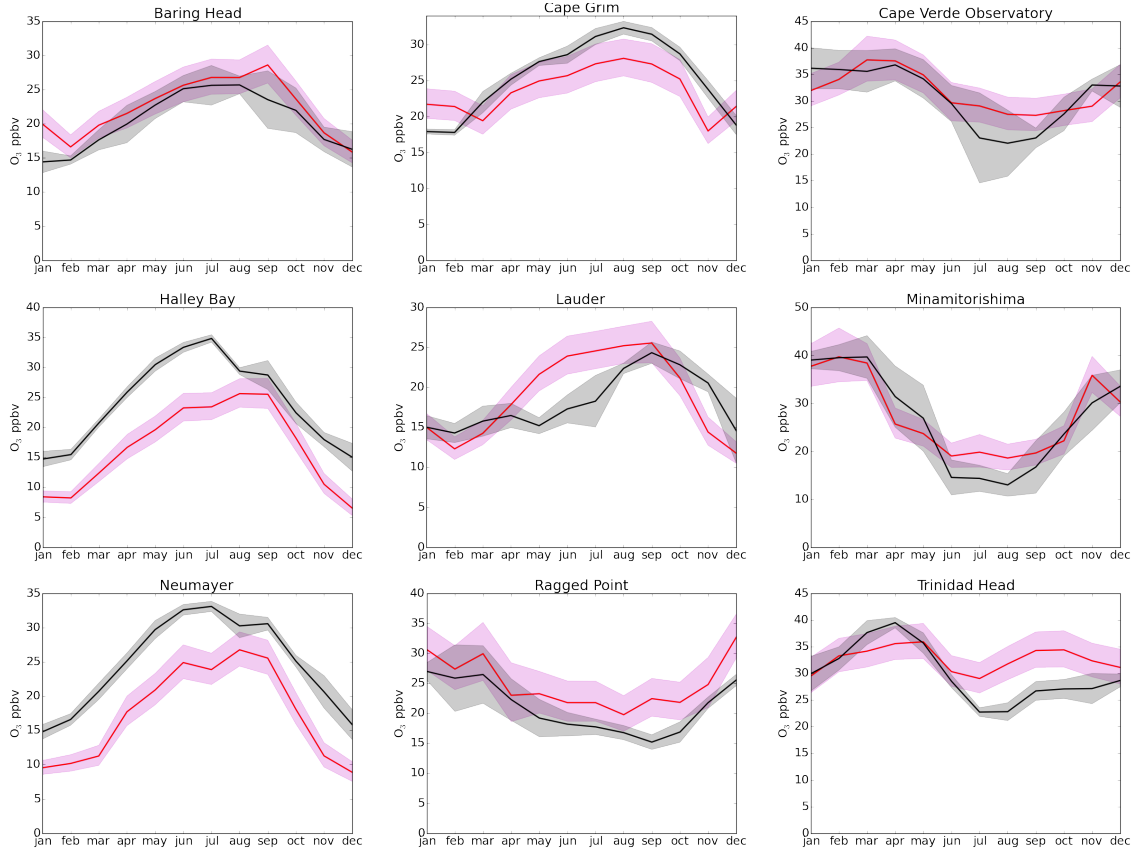
**Figure 10. Sulfur and Aerosols.** Total  $1\sigma$  uncertainty in the concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ , DMS (Dimethyl Sulfide) and  $\text{NH}_4^+$  from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.



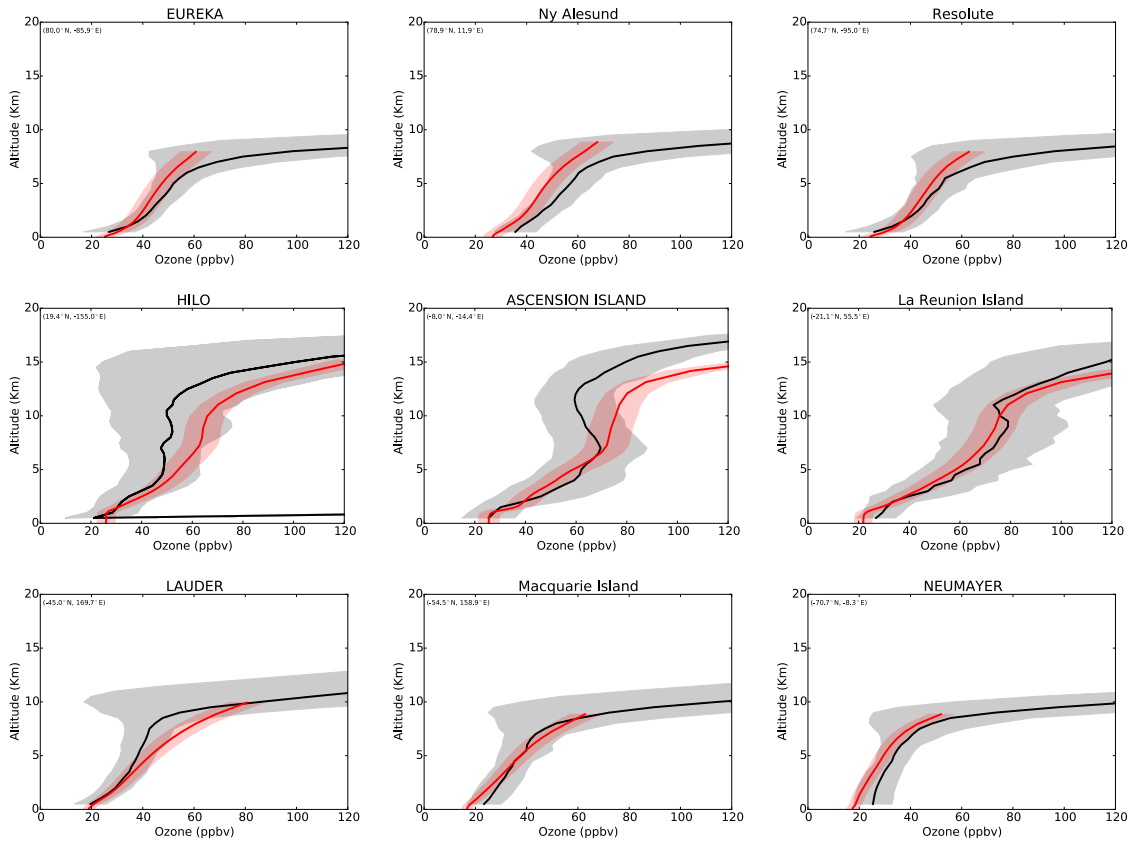
**Figure 11. Inorganics.** Total  $1\sigma$  uncertainty in the concentrations of  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{OH}$ ,  $\text{CO}$  and  $\text{HO}_2$  from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.



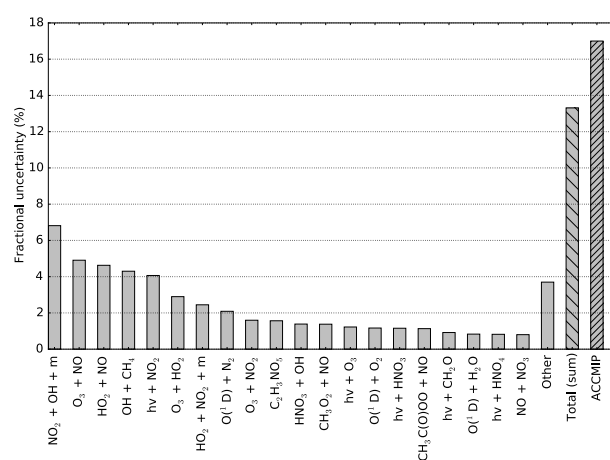
**Figure 12. Impact on model / measurement comparisons.** Modelled (red) and measured (black) annual cycle in monthly mean  $\text{O}_3$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{ALK4}$  ( $\geq \text{C}_4$  Alkanes) and  $\text{NO}_2$  mixing ratios at Cape Verde (?). Shaded area represents the  $1\sigma$  uncertainty from the 60 reactions added together in quadrature.



**Figure 13. Ozone site comparison** Modelled (red) and measured (black) concentrations of ozone at a range of sites. The pink shaded area shows the  $1\sigma$  uncertainty from the chemical kinetics. The error bars represent the  $1\sigma$  variability uncertainty of these observations. Monthly mean observational data obtained from [\(Sofen and Evans, 2015\)](#), using multiple years between 2004 and 2010 to create more complete datasets.



**Figure 14. Ozonesonde Comparisons** between the variability of annual ozonesonde measurements and model data with uncertainties. The black line shows the annual mean observation data and the shaded gray shows the  $\pm 1\sigma$  range of data. The red line shows the model data and the pink shaded line shows the chemical  $\pm 1\sigma$  uncertainty. Observations are obtained from [WOUDC \(2014\)](#).



**Figure 15. Uncertainties in  $\text{O}_3$  radiative forcing.** Absolute fractional uncertainty in tropospheric  $\text{O}_3$  radiative forcing between the preindustrial and present day, due to rate constant uncertainty. Shown on the left are the 20 most important reactions. ‘Other’ shows the addition in quadrature of the remaining 40 reactions. ‘Total (sum)’ indicates the total fractional uncertainty calculated by adding together the individual uncertainties in quadrature. ‘ACCMIP’ indicates the inter-model spread found from the ACCMIP (?) study.

**Table 1. Table of reactions studied.** f (298) indicates the JPL or IUPAC panel uncertainty estimate at 298K and g gives the rate at which this uncertainty increases away from 298K (see previous section). Reactions with 0 for the temperature dependence indicates there is zero temperature dependency or not enough information to provide a temperature varying uncertainty. The final column gives the fractional increase in the ozone burden by increasing the rate constant to its  $1\sigma$  value. Reactions with a \* are the 10 reactions used in the Monte Carlo study.

Number	Reaction	f(298)	g (K)	$1\sigma$ O <sub>3</sub> burden change (%)
1*	$\text{NO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HNO}_3$	1.3	100	-6.20
2*	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	1.1	200	-3.61
3*	$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$	1.15	20	3.09
4*	$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	1.1	100	<del>2.79</del> <u>2.89</u>
5*	$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	1.15	80	-2.39
6*	$\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$	1.1	20	1.82
7*	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	1.08	20	-1.54
8	$\text{HO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{HNO}_4$	1.06	400	-0.959
9	$\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3$	1.2	0	0.928
10*	$\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$	1.15	150	-0.803
11*	$\text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O} + \text{O}_2$	1.1	10	0.745
12	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2 + \text{CO}_2$	1.5	0	0.721
13*	$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	1.1	50	-0.693
14	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2$	1.15	100	0.553
15	$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{HO}_2 + \text{CH}_2\text{O}$	1.1	60	0.462
16	$\text{CH}_3\text{C}(\text{O})\text{OONO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OO} + \text{NO}_2$	1.2	200	0.341
17	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_3\text{C}(\text{O})\text{OONO}$	1.2	50	-0.289
18	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	1.05	100	0.282
29	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	1.15	45	0.265
20	$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	1.3	100	0.249
21	$\text{HO}_2 + \text{NO}_3 \rightarrow \text{OH} + \text{NO}_2$	1.5	0	0.248
22	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	1.4	150	-0.243
23	$\text{CH}_3\text{SCH}_3 + \text{OH} \rightarrow \text{SO}_2 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$	1.1	100	0.231
24	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	1.15	50	-0.215
25	$\text{CH}_3\text{CH}_2\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{NO}_2 + \text{HO}_2$	1.2	150	0.211
26	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OO} + \text{H}_2\text{O}$	1.07	50	0.201
27	$\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	1.15	50	0.198
28	$\text{HCOOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{HO}_2$	1.2	100	0.196
29	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_3$	1.25	50	0.195
30	$\text{CH}_3\text{CHO} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{CH}_3\text{C}(\text{O})\text{OO}$	1.3	300	0.193

continued on next page



continued from previous page				
31	$\text{HNO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	1.5	200	0.178
32	$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OO} + \text{CH}_2\text{O} + \text{CO} + \text{HO}_2$	1.05	20	0.174
33	$\text{CH}_3\text{SCH}_3 + \text{NO}_3 \rightarrow \text{SO}_2 + \text{HNO}_3 + \text{CH}_3\text{OO} + \text{CH}_2\text{O}$	1.1	150	0.172
34	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{O} + \text{O}_2$	1.2	100	0.170
35	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	1.15	100	0.166
36	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CO} + \text{HO}_2 + \text{H}_2\text{O}$	1.15	50	0.156
37	$\text{NO} + \text{OH} \xrightarrow{\text{M}} \text{HNO}_2$	1.2	50	-0.151
38	$\text{SO}_2 + \text{OH} \xrightarrow{\text{M}} \text{SO}_4 + \text{HO}_2$	1.1	100	0.151
39	$\text{NO}_2 + \text{NO}_3 \xrightarrow{\text{M}} \text{N}_2\text{O}_5$	1.2	100	-0.151
40	$\text{HNO}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$	1.3	500	0.149
41	$\text{OH} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$	1.5	100	-0.146
42	$\text{CO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2$	1.1	100	-0.144
43	$\text{NO}_3 + \text{NO}_3 \rightarrow 2\text{NO}_2 + \text{O}_2$	1.5	500	-0.144
44	$\text{OH} + \text{NO}_3 \rightarrow \text{HO}_2 + \text{NO}_2$	1.5	0	-0.143
45	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	1.1	100	-0.134
46	$\text{HNO}_4 \rightarrow \text{HO}_2 + \text{NO}_2$	1.3	270	0.104
47	$\text{CH}_3\text{O}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	1.3	150	0.0350
48	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2 + \text{OH} \rightarrow \text{HOCH}_2\text{C}(\text{OO})(\text{CH}_3)\text{CH}=\text{CH}_2$	1.07	100	-0.0323
49	$\text{NO}_3 + \text{CH}_2\text{O} \rightarrow \text{HNO}_3 + \text{HO}_2 + \text{CO}$	1.3	0	-0.0145
50	$\text{C}_4\text{H}_{10} + \text{OH} \rightarrow 2\text{H}_2\text{O} + \text{C}_4\text{H}_9$	1.06	100	0.0132
51	$\text{h}\nu + \text{NO}_2 \rightarrow \text{NO} + \text{O}(^3\text{P})$	1.1	0	2.66
52	$\text{h}\nu + \text{O}_3 \rightarrow \text{O}_2 + \text{O}(^1\text{D})$	1.1	0	-1.97
53	$\text{h}\nu + \text{HNO}_3 \rightarrow \text{OH} + \text{NO}_2$	1.1	0	0.559
54	$\text{h}\nu + \text{CH}_2\text{O} \rightarrow \text{CO} + \text{HO}_2 + \text{HO}_2$	1.1	0	0.338
55	$\text{h}\nu + \text{HNO}_4 \rightarrow \text{HO}_2 + \text{NO}_2$	1.1	0	0.262
56	$\text{h}\nu + \text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$	1.1	0	0.223
57	$\text{h}\nu + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}(^3\text{P})$	1.1	0	0.222
58	$\text{h}\nu + \text{HNO}_4 \rightarrow \text{OH} + \text{NO}_3$	1.1	0	0.200
59	$\text{h}\nu + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{OO} + \text{HO}_2 + \text{CO}$	1.1	0	0.199
60	$\text{h}\nu + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$	1.1	0	0.196

**Reply to reviewers of ACPD paper: “Impact of uncertainties in inorganic chemical rate constants on tropospheric composition and ozone radiative forcing” by Ben Newsome and Mat Evans**

We thank the reviewers for their constructive comments. We address the comments below and identify changes we would make to the paper considering their comments. Where indicated we have already run the appropriate new simulations.

**Review by R Saunders.**

**Major comments:**

**My only major concern is that apparently in all sensitivity studies the rate coefficients were *increased* but never *decreased*. Unless a certain reaction is the rate-limiting step inside a reaction cycle, making it faster has only a small effect on the overall rate of the cycle. However, making it slower could make this particular reaction rate-limiting and then the effect becomes large. Why was it never tested what effect a *decrease* of  $k$  by  $1\sigma$  has?**

We had tested this previously and found that the differences were small but didn't include this in the original paper. We would suggest that we include these results in the text and show a comparison between the results of increasing and decreasing the top ten reactions to show that although there are some differences between the conclusions from increasing vs decreasing the rates the impact is small compared to the overall conclusions of the paper.

**Minor issues and technical comments**

**Abstract: “Expert panels synthesise laboratory measurements. ”Chemicals are “synthesised” but not laboratory measurements. I think it would be better to say: “Expert panels evaluate laboratory measurements”.**

We have updated the text to reflect this suggestion.

**In the introduction you describe both the JPL and the IUPAC evaluation and then you provide Eq. (1) to describe the uncertainty. It should be noted, however, that IUPAC does not use this definition. Instead, IUPAC defines uncertainties via  $\Delta \log k$  and  $\Delta E/R$ . I think it would be helpful for the reader if you show how to convert between these different ways to express uncertainties.**

We have included a discussion of both methodologies in the text.

**In your manuscript you refer to the JPL evaluation from 2011. Have you checked if the uncertainties are still the same in the more recent JPL Evaluation Number 18 from 2015?**

We have updated our simulations to reflect the JPL18 evaluation and refer to that in the text. There were some minor changes which have marginally changed the order of the uncertainties of the reactions.

**Page 2, line 20: Change “larger uncertainties than quoted here” to “larger uncertainties than quoted here”.**

We have corrected the text.

**Page 3, line 2: Change “www.goes-chem.org” to “www.geos-chem.org”. C2**

We have corrected the text.

#### **Anonymous Referee #1**

**The authors have used an out of date version of the NASA/JPL data recommendations in their analysis. There does not seem to be any reasonable explanation for this oversight given in the present version of the manuscript. Although, the conclusions from the present work are likely to remain unchanged the authors should highlight any differences with the 2015 NASA/JPL data recommendations in their paper in Table 1.**

We have updated our simulations to reflect the changes made between versions 17 and 18 of the evaluation. This has made small changes to the absolute value of a couple of reactions but there is no overall change to the conclusions.

**The treatment of the uncertainty in the atmospheric parameters, or lack of, is unsatisfying. A thorough treatment of photolysis uncertainty may be beyond the scope of the present work, but making an across the board percentage uncertainty assumption is surely not correct. It may have been better to not include photolysis uncertainty in the present analysis.**

We agree that our analysis of the photolysis rates is simplistic but we believe it provides a useful context for understanding the relative role of photolysis uncertainty compared to reaction rate constant uncertainty. We think that leaving these simulations in the discussion make a useful contribution and helps to motivate future work in this area. We would update the text when we are discussion this to identify the need for future improved assessments of photolysis rate uncertainties.

# Impact of uncertainties in inorganic chemical rate constants on tropospheric composition and ozone radiative forcing

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<sup>2</sup>National Centre for Atmospheric Science, Department of Chemistry, University of York, York, YO10 5DD, UK.

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**Abstract.** Chemical rate constants determine the composition of the atmosphere and how this composition has changed over time. They are central to our understanding of climate change and air quality degradation. Atmospheric chemistry models, whether online or offline, box, regional or global use these rate constants. Expert panels evaluate laboratory measurements, making recommendations for the rate constants that should be used. This results in very similar or identical rate constants being used by all models. The inherent uncertainties in these recommendations are, in general, therefore ignored. We explore the impact of these uncertainties on the composition of the troposphere using the GEOS-Chem chemistry transport model. Based on the JPL and IUPAC evaluations we assess [the influence of 50 mainly inorganic rate constants and 10 photolysis rates, through simulations where we increase the rate of the reactions to the 1- \$\sigma\$  upper value recommended by the expert panels on tropospheric composition through the use of the GEOS-Chem chemistry Transport model.](#)

We assess the impact on 4 standard metrics: annual mean tropospheric ozone burden, surface ozone and tropospheric OH concentrations, and tropospheric methane lifetime. Uncertainty in the rate constants for  $\text{NO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HNO}_3$ ,  ~~$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$~~ , and  $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$  are the ~~three~~ [two](#) largest source of uncertainty in these metrics. [With the absolute magnitude of uncertainties being similar if rate constants are increased or decreased by their  \$\sigma\$  values.](#) We investigate two methods of assessing these uncertainties, addition in quadrature and a Monte Carlo approach, and conclude they give similar outcomes. Combining the uncertainties across the 60 reactions, gives overall uncertainties on the annual mean tropospheric ozone burden, surface ozone and tropospheric OH concentrations, and tropospheric methane lifetime of 10, 11, 16 and 16% respectively. These are larger than the spread between models in recent model inter-comparisons. Remote regions such as the tropics, poles, and upper troposphere are most uncertain. This chemical uncertainty is sufficiently large to suggest that rate constant uncertainty should be considered [alongside other processes](#) when model results disagree with measurement.

Calculations for the pre-industrial allow a tropospheric ozone radiative forcing to be calculated of  $0.412 \pm 0.056$   ~~$0.062$~~   $\text{Wm}^{-2}$ . This uncertainty (~~14~~ [13](#) %) is comparable to the inter-model spread in ozone radiative forcing found in previous model-model inter-comparison studies where the rate constants used in the models are all identical or very similar. Thus the uncertainty of tropospheric ozone radiative forcing should be expanded to include this additional source of uncertainty. These rate constant uncertainties are significant and suggest that refinement of supposedly well known chemical rate constants should be considered alongside other improvements to enhance our understanding of atmospheric processes.

## 1 Introduction

The concentration of gases and aerosols in the atmosphere have changed over the last century due to human activity. This has resulted in a change in climate (?) and a degradation in air quality (?) with tropospheric ozone (O<sub>3</sub>) and methane (CH<sub>4</sub>) playing a central role. The response of these compounds to the changing emissions is complex and non-linear (?). The hydroxyl radical (OH) plays a central role in this chemistry as it initiates the destruction of many pollutants (notably CH<sub>4</sub>) and so determines their lifetime in the atmosphere. The dominant source of OH is the photolysis of O<sub>3</sub> in the presence of water vapour. The oxidation of compounds such as CH<sub>4</sub>, carbon monoxide (CO) and other hydrocarbons can lead to the production of O<sub>3</sub> if sufficient oxides of nitrogen (NO<sub>x</sub>) are present. Changes in the emissions of O<sub>3</sub> precursors between the pre-industrial (~1850) and the present day have increased O<sub>3</sub> concentrations and this has produced a radiative forcing estimated to be 410 ± 65 mWm<sup>-2</sup> (?).

The rate constants of the reactions occurring in the atmosphere have been determined by a number of laboratory studies which are ~~compiled~~ synthesised by groups such as the IUPAC (?) and JPL (?) panels. These provide recommendations for both rate constants and their associated uncertainties. These reactions are typically expressed in an Arrhenius form to represent the temperature dependence. More complicated representations are needed for three-body reactions. ~~The expressions used to represent IUPAC and JPL provide similar but different representations of the uncertainty in rate constants differs between IUPAC and JPL. For JPL, the 1σ a rate constant. For IUPAC (Eqn. 2) the uncertainty in a rate constant is described as the uncertainty in the log<sub>10</sub> of the rate constant (Δ log<sub>10</sub> k<sub>T</sub>) at a temperature (T) is expressed as an uncertainty at, with the panel giving values for the log<sub>10</sub> uncertainty at 298K (Δ log<sub>10</sub> k<sub>298K</sub>) and the rate of increase in uncertainty away from 298K described by a ΔE /R term. For JPL (Eqn. 2) the relative uncertainty in a rate constant (f(T) is described as the relative uncertainty at temperature of 298K (f (298)) together with a term (g) that expresses how quickly the uncertainty increases away from 298K (Equation 1), leading to temperature dependences which increase away from room temperature (Figure 1). Whereas, for IUPAC (Equation 2) the uncertainty in the log<sub>10</sub> of the rate constant, is described in terms of the uncertainty in the log<sub>10</sub> of the rate constant at 298K together with the uncertainty in the activation energy of the reaction (ΔE)-~~

$$f(T) = f(298K) \exp \left| g \left( \frac{1}{T} - \frac{1}{298K} \right) \right|$$

$$\Delta \log_{10} k(T) \log_{10} k_T = \Delta \log_{10} k(298K) \log_{10} k_{298K} + 0.4343 \frac{\Delta E}{R} \left( \frac{1}{T} \frac{1}{T} - \frac{1}{298} \frac{1}{298K} \right) \quad (1)$$

$$f(T) = f(298K) \exp \left| g \left( \frac{1}{T} - \frac{1}{298K} \right) \right| \quad (2)$$

For the reactions studied, the uncertainty at 298K typically ranges from 5% for well understood reactions to 30% for those which have significant uncertainties. Other reactions can have larger uncertainties than quoted here. The increase in uncertainty at temperatures away from 298K can range from 0% to over 40%, giving some reactions a total uncertainty of over 50% in the cold upper troposphere.

Models of atmospheric composition (whether online or offline, single box or transport etc.) use these recommended rate constants, together with estimates of the meteorology, emissions, deposition, photolysis, etc. of compounds to calculate the concentration of species in the atmosphere. These models are a central tool for our understanding of atmospheric processes and for making policy choices to minimise climate change and air pollution.

Although these models have been developed significantly over the last decades, they have, in general, all used the same basic chemical rate constants as evaluated by the IUPAC or JPL panels. Little emphasis has been placed on understanding the uncertainty in predicted atmospheric composition caused by the uncertainty in these rate constants. ~~A recent notable exception being?~~ The focus has been to investigate the impacts of novel chemical reactions ~~or~~ understanding emissions etc. (e.g. ~~(???)~~). Here though, we investigate the impact of this uncertainty on ~~our understanding of~~ the composition of the troposphere. We base our assessment on the uncertainties in rate constants described by the JPL and IUPAC panels ~~(??)~~ using the GEOS-Chem model and evaluate a range of model diagnostics for both the present day and the pre-industrial.

## 2 Model simulations

GEOS-Chem (?) ([www.geos-chem.org](http://www.geos-chem.org)) is an offline chemistry transport model. We use version v9-2. For computational expediency we use a horizontal resolution of  $4^\circ$  latitude by  $5^\circ$  longitude with 47 vertical hybrid pressure-sigma levels from the surface to 0.01 hPa. The chemistry is solved within the troposphere with the SMV-Gear solver (?). We use a mass based scheme for aerosol (?) and so can not investigate the impact of the rate constant uncertainty on aerosol number or size distribution. Stratospheric chemistry is unchanged in all simulations and uses a linearised approach to the chemistry ~~(??)~~. Global anthropogenic emissions were taken from the Emission Database for Global Atmospheric Research (EDGAR) v3 for  $\text{NO}_x$ , CO, VOCs and  $\text{SO}_x$ . Regional or source specific inventories replaced EDGAR where appropriate (EMEP, BRAVO, Streets, CAC, NEI05, RETRO, AEIC see the GEOS-Chem wiki for more details). Biogenic emissions (Isoprene, Monoterpenes, Methyl Butenol) are taken from the MEGAN v2.1 emission inventory (?). Biomass burning emissions were used from the GFED3 monthly emission inventory(?).  $\text{NO}_x$  sources from lightning (?) and soils (?) were also included. As in previous studies ~~(??)~~ pre-industrial emissions are calculated by switching off anthropogenic emissions, reducing biomass burning emissions to 10% of their modern day values, and by setting  $\text{CH}_4$  concentrations to a constant 700 ppbv (?).

For both present-day and the pre-industrial simulations we run the model from the 1st of July 2005 to the 1st of July 2007 with GEOS-5 meteorology. We used the first year to spin up the composition of the troposphere. Metrics are derived from the second year of simulation.

We follow the methodology of JPL (?) for the representation of uncertainties in rate constants converting IUPAC representation where necessary. For two body reactions the uncertainty is given by two parameters.  $f$  (298K) describes the relative uncertainty at 298K, and  $g$  describes how the uncertainty increases as temperature diverges from 298K, as shown in equation (1).

### 3 Reactions Studied

We limit our study to the inorganic ( $O_x$ ,  $HO_x$ ,  $NO_x$ ,  $CO$ ,  $CH_4$ ) reactions together with some key organic and sulfur reactions. Mechanistic uncertainties in the organic chemistry of the atmosphere makes a systematic assessment of these uncertainties difficult (?). Table 1 shows a list of reactions that are perturbed and the uncertainties assumed. We use the uncertainty recommendations from the JPL panel if provided and the IUPAC panel otherwise. We investigate the impact of 50 inorganic chemical reactions and 10 photolysis reactions (Table 1). Uncertainties in photolysis rate constants are harder to define than for the other reactions. We consider the appropriate chemical uncertainty here as the uncertainty in the absorption cross section and the quantum yield rather than the uncertainty in the photon flux which we attribute to the radiative transfer calculation. A full calculation of the chemical uncertainty in a photolysis rate is complex as it it depends upon the uncertainties at different wavelengths, the independence of the cross section and quantum yield parameters and the transfer of this information through the spectral bins used for the laboratory studies and the photolysis calculations. In order to simplify this calculation we apply a 10% uncertainty to all photolysis rates. ~~Future efforts should more systematically explore the impact of the uncertainties in cross-sections and quantum yields on atmospheric composition. Although this is not ideal it does allow us to place an uncertainty in the photolysis rates into a context of other uncertainties. An improved presentation of the photolysis uncertainty should be included in future work.~~

### 4 Single Reaction Perturbations

From each of these 60 reactions we increase the reaction rate by the  $1\sigma$  temperature dependent uncertainty given in Table 1. To allow the model to spin up we run the model for 2 years and take the 2nd year of simulation ~~and calculate for the calculation of~~ four metrics: tropospheric  $O_3$  burden, mean surface  $O_3$  mixing ratio, tropospheric mass weighted mean OH number density, and tropospheric mean  $CH_4$  lifetime. We subtract the values of these metrics from the base value of the metric (unchanged rate constants) and then take the absolute value to remove cases where the value decreases on an increase in the rate constant. Figure 2 shows the changes for all four metrics with Table 1 giving the values for the change in tropospheric  $O_3$  burden. We express these values as a percentage of the base case value.

It is evident that a relatively small number of reactions produce large uncertainties in the values of these metrics. The one that offers the most uncertainty is the reaction between  $NO_2$  and OH to produce nitric acid which leads to uncertainties in the range of 6–11% in the metrics investigated here. This reaction is both highly uncertain ( $f(298K)=30\%$ ) and acts as a large global sink for  $NO_x$  and  $HO_x$ . ~~The next most significant reactions are between NO and  $O_3$  to produce  $NO_2$  and  $O_2$ , and between NO and  $HO_2$   $O_3$  + NO reaction to produce  $NO_2$  and OH. These are not especially uncertainty ( $f(298K)=10\%$  and  $15\%$  respectively) but represent processes 2 is central to the partitioning of  $NO_{x,x}$  in the atmosphere, in the cycling of  $HO_x$  and in the generation of  $O_3$ . Relatively small uncertainties in the large chemical fluxes of these reactions lead to a significant uncertainty building up. Thus increasing its rate constant reduces NO concentrations in the atmosphere (leading to lower  $O_3$  concentrations) and increasing the concentration of  $NO_2$  (which favours  $NO_2$  removal) which again reduces  $O_3$  concentrations. Another significant reaction is that between  $CH_4$  and OH to produce  $CH_3O_2$  radicals. The model assumes a constant  $CH_4$  concentration so an~~

increase in the rate constant between CH<sub>4</sub> and OH leads to an increased source of radicals but doesn't lead to a commensurate drop in the CH<sub>4</sub> concentration. Thus an increase in this rate constant in the model is effectively the same as an increase in the emission of CH<sub>4</sub> which results in a wide range of impacts such as increased CO concentrations etc. Reactions after the tenth most significant reaction for all the metrics generates an uncertainty of less than 1%.

- 5 The relative importance of the different reactions does not change much with the metric being investigated (see Figure 2). The rate constants of these top ten reactions are not particularly uncertain (other than for NO<sub>2</sub>+OH) compared to other reactions but they link important chemical cycles and have a very large chemical flux flowing through them. Thus relatively small changes in their uncertainties will lead to large changes in concentration. ~~After the top ten reactions, uncertainties in the other reactions lead to smaller uncertainties of less than 1%.~~
- 10 It ~~would be~~ is just as easy to decrease the rate constant as it is to increase them. Figure 3 shows the absolute uncertainties in tropospheric O<sub>3</sub> burden and OH global mean concentrations varies for the top ten reactions ~~if the rate constant is decreased rather than increased, compared to the values from increasing for both increasing and decreasing~~ the rate constant. Although there are some differences between the impact of increasing or decreasing the rate constant, there is a degree of consistency between the two and so for simplicity reasons we only consider further the impact of increasing the rate constants. ~~The Monte Carlo analysis discussed in the next sections inherently takes this difference into account.~~
- 15

Given the uncertainties for the individual reactions calculated here, the next question is as to how these uncertainties can be combined together to generate a single uncertainty from rate constants uncertainty on the composition of the atmosphere.

## 5 Addition of uncertainties

- If these perturbations are independent (uncertainties in one rate constant are not related to uncertainties in another) and the model approximately linear, the total rate constant uncertainty can be found by finding the root of the sum of the individual uncertainties squared (addition in quadrature) as shown in equation (3).
- 20

$$\sigma_{total}^2 = \Sigma \sigma_{reaction}^2 \quad (3)$$

- It is hard to assess the independence of the rate constants. Given the nature of the laboratory experiments used to determine them, it is likely that there is some overlap in assumptions. It would be extremely difficult to diagnose this for all 60 reactions and so we ignore this in further work.
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- Atmospheric chemistry is though non-linear (?). A doubling of a change to the model, does not necessarily lead to a doubling of the model response. Thus, is it not obvious how uncertainties from the individual rate-constant perturbations should be combined. To investigate this we perform a Monte Carlo analysis of the model. We take ten of the most significant reactions determined earlier (shown by the \* in Table 1) and generate 10 normally distributed random numbers ( $\mu = 0$ ,  $\sigma=1$ ), one for each reaction. For each of the ten rate constants we add on the calculated  $1\sigma$  uncertainty multiplied by the random number and run the model. We repeat this 50 times to produce a Monte-Carlo ensemble from which we can calculate the four metrics described earlier.
- 30



If the model is linear, the metrics calculated from each member of the Monte Carlo ensemble should be (to some level) the same as the linear addition of the individual rate-constant perturbations weighted by the Monte Carlo random numbers. Figure 4 shows the perturbation in the value of the metric calculated for each ensemble member against the calculated value of the metric using the single reaction values. The model shows a strong linear relationship between the metrics examined (intercepts of  $0.21 \pm 0.9\%$  and gradients of  $0.80 \pm 0.04$ ) thus if the errors are uncorrelated we can, at least to a first approximation, add the individual  $1\sigma$  perturbations together in quadrature using Equation 3 to calculate the overall uncertainty in the model metrics. From these simulations we estimate the quadrature approach leads to an over-estimate of the  $1\sigma$  uncertainty on the order of 10%.

We thus conclude that the adding together of the individual perturbations in quadrature gives a good approximation to the uncertainty calculated by the Monte Carlo method for significantly less computational burden.

## 6 Impacts on the present day atmosphere metrics

We show on Figure 2 the absolute percentage change in global annual mean  $O_3$  burden, surface  $O_3$ , tropospheric average OH and  $CH_4$  tropospheric lifetime from increasing each of the reaction rate constants in Table 1 in turn by their  $1\sigma$  value. They are ordered by the magnitude of the perturbation and for clarity we only show the top 20, combining the remaining 40 in quadrature into the ‘Other’ category. The fractional change in tropospheric  $O_3$  burden for all of the perturbations is given in Table 1. We show the results of combining all of these reactions in quadrature (‘Total (sum)’), the result of combining the top 10 in quadrature (‘Top 10’) and the standard deviation from the 50 Monte-Carlo simulations (‘Monte Carlo Top 10’). The relative closeness ( $\sim 10\%$ ) of the value calculated from the ‘Top 10’ and the ‘Monte Carlo Top 10’ shows that the addition in quadrature approach provides a useful approximation to the Monte Carlo methodology with significantly less computational burden.

The top ten reactions contribute over 90% of the uncertainty for all metrics, with the overall uncertainty for the annual mean tropospheric ozone burden, surface ozone and tropospheric OH concentrations, and tropospheric methane lifetime of calculated to be 10, 11, 16 and 16% respectively. These uncertainties can be compared to the inter-model spreads found from model inter-comparison exercises. The multi-model standard deviation in the ozone burden, tropospheric OH concentration and troposphere methane lifetime were found to be 7%, 10% and 10% in the ACCMIP studies (??). Thus we find that the chemical rate constant uncertainty is larger than the multi-model ~~standard deviation~~ spread which is usually used to give some sense of our uncertainty in our understanding of a quantity. As the models used in these inter-comparisons typically use the same rate constants, this rate constant uncertainty is not included in the inter-model spread. ~~The~~ and so the inter-model spread should be ~~therefore be~~ considered a lower estimate ~~for model uncertainty~~.

## 7 Spatial distribution of uncertainty

Figure 5 shows the spatial distribution of the total uncertainty in the annual mean  $O_3$ , OH and CO concentration, for the tropospheric column, the zonal mean, and at the surface from the 60 reactions. Similar plots for a large number of other model species are shown in Figures 6–11. There is a significant degree of in-homogeneity in these uncertainties which respond to a range of factors. The uncertainties in the rate constants are largest in the upper troposphere where the temperatures are coldest and thus furthest from the 298K base temperature used to calculate the uncertainties. However, these uncertainty can only manifest if chemistry is the large source or sink for a species in that region.  $O_3$  uncertainties are relatively low in the upper troposphere as it has a large stratospheric source in this region which we have not perturbed (see Section 2). OH uncertainties on the other hand are high ( 30%) ~~there,~~ in the upper troposphere due to the low temperatures. Over continental regions the concentration of CO is not particularly uncertain as the emissions and transport control the concentration. However, over the ocean where emissions are small, the chemistry becomes more important and so uncertainty increases. Uncertainties in the CO are largest in the southern hemisphere where direct emission is ~~low~~ lower and chemical production from  $CH_4$  and other hydrocarbons is significant. In general uncertainties are largest over remote regions far from recent emissions, especially if they are particularly cold or hot compared to room temperature. Thus surface OH values are more uncertain in the cold remote southern ocean than they are in the tropics. Surface  $O_3$  values are uncertain in the warm tropics where intense sunlight and high water vapour concentrations leads to a large chemical flux through  $O_3$ .

Across the full set of simulated compounds (Figures 6–11) there are even larger uncertainties. For primary emitted hydrocarbons, large uncertainties occur in remote, photochemically active locations such as the topics where shorter lived hydrocarbons may be many OH lifetimes away from sources. Uncertainties in the OH concentrations thus multiply in these regions, leading to uncertainties of up to 60% for  $\geq C_4$  alkanes for example. Secondary products such as  $H_2O_2$ ,  $CH_3OOH$  also show significant uncertainties of up to 56% in some locations.

$NO_x$  concentrations close to emission sources are dominated by the emission and transport and so are not very sensitive to chemical uncertainty (Figure 8). However, away from these emissions uncertainties can build up. Uncertainty in the  $NO_x$  concentrations at the poles are up to a factor of 40%. Uncertainties in PAN concentrations ~~(Figure 9)~~ 9 are in general high (>20%) in most locations ( $\sim 50\%$  over the remote ocean) reflecting the complexity of the chemistry involving uncertainties in both  $RO_x$  and  $NO_x$  concentrations. Uncertainties in nitric acid (the dominant  $NO_x$  sink) concentrations are smaller however ( $\sim 5\%$ ) reflecting the mass balance constraint of emissions of  $NO_x$  having to balance  $NO_y$  sinks. Large variability in nitric acid concentrations in the southern ocean reflects non-linearities in aerosol thermodynamics of  $HNO_3$  /  $NO_3^-$  partitioning.

$SO_2$  concentrations show the largest uncertainties in the tropical upper troposphere where OH is also highly uncertain. However,  $SO_4^{2-}$  shows much smaller uncertainty, again reflecting mass conservation constraints.  $NH_4^+$  concentrations show little sensitivity to the rate constants analysed. Overall this suggests that aerosol mass is not particularly sensitive to the gas phase chemistry examined here.

Overall, we see a complex pattern of uncertainty with geographically highly variable uncertainty.

## 8 Implications for model-measurement comparisons

Comparisons between the predictions made by models and observations underpin the assessment of model fidelity. Deviations between model and measurements are often used to diagnose model failings. Attributing these differences to uncertainties in the emissions is particularly popular (see for example ??). Figure 12 shows observed monthly mean and standard deviations for CO, O<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> and NO<sub>2</sub> from the World Meteorological Organisation's Global Atmosphere Watch Cape Verde Atmospheric Observatory (?), overlaid with the base model simulation and the chemical uncertainty (1 $\sigma$ ) calculated from the addition in quadrature of the 60 1 $\sigma$  simulations. We chose this location as it is far from recent emissions and so should show large uncertainties for primary emitted species.

Consistent with Figures 6–11 the uncertainty in the model calculation ranges from 5–30% depending upon the species. For some of the species (CO, O<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub>) much of the difference between the model and the measurements lie within the model 1 $\sigma$  uncertainty. For others such as C<sub>3</sub>H<sub>8</sub> or NO<sub>2</sub> the differences are harder to explain and other processes (emissions, transport, unknown chemistry etc.) would need to be explored.

Figures 6–11 show significant ~~vertical~~ changes in uncertainty with changes in the vertical due to increasing uncertainty with reducing temperature. Figure 14 shows a selection of ozonesonde observations from the World Ozone and Ultraviolet Data Centre (?) compared to equivalent modelled concentrations and uncertainties. Observations are derived from the surface into the middle troposphere as the temperature drops. The uncertainty thus maximises at around 10km. Above this much of the ozone in the model is produced in the stratosphere which is unperturbed in these simulations. Above this height the uncertainty in the ozone due to tropospheric chemistry uncertainty reduces.

These comparisons with observations highlight the complexity of attributing model failure to a particular cause. For some locations and for some species the chemical uncertainty can be large. For the same species, in a different location, the uncertainties may be much smaller. Inversion studies which attempt to attribute model failure to a single cause (for example uncertainties in emissions) need to have a detailed understanding of the magnitude and geographical distribution of the other model errors. We show here that they vary between different species, can be large and highly spatially varying. This should be considered when model inversion studies are undertaken.

## 9 Ozone radiative forcing

We repeat the 60 1 $\sigma$  simulations described above with pre-industrial (notionally the year 1850) emissions (see Section 2) to allow us to calculate an uncertainty in the radiative forcing of O<sub>3</sub>. For each reaction we calculate the difference in the annual mean tropospheric column O<sub>3</sub> (Dobson Units) between the present day and pre-industrial with the rate constant increased to its 1 $\sigma$  value. Then using a linear relationship between change in O<sub>3</sub> column and radiative forcing (??) of 42mW m<sup>-2</sup> DU<sup>-1</sup>, we calculate a radiative forcing associated with the uncertainty associated with each reaction. We estimate an overall uncertainty in the tropospheric O<sub>3</sub> radiative forcing in the same way as the other metrics, by adding them together in quadrature. In our base simulations we calculated the tropospheric O<sub>3</sub> radiative forcing to be 412 mWm<sup>-2</sup> consistent with previous studies (410±65mWm<sup>-2</sup>) (?). Our estimate of the uncertainty in the O<sub>3</sub> radiative forcing from rate constant uncertainty is 56 mWm<sup>-2</sup>

(+15%) with reaction specific detail shown in Figure 15. Again the same set of reactions contribute the largest share to the uncertainty in the radiative forcing as in the uncertainty in present day O<sub>3</sub> burden.

This uncertainty estimate of +15% can be compared to the 17% spread in the O<sub>3</sub> radiative forcing calculated between climate models in the recent ACCMIP (?) inter-comparison (shown in Figure 15). This spread is usually used as the uncertainty in our understanding of O<sub>3</sub> radiative forcing. However, as all of these models use the same JPL or IUPAC recommended rate constants the inter-model spread does not include the rate constant uncertainty explored here. Given that the rate constant uncertainty is comparable to the inter-model spread, it should be included in future assessment of the uncertainty in O<sub>3</sub> radiative forcing. A naive addition in quadrature approach would suggest that the uncertainty on tropospheric O<sub>3</sub> radiative forcing should be increased by roughly 30% to account for this.

## 10 10 Conclusions

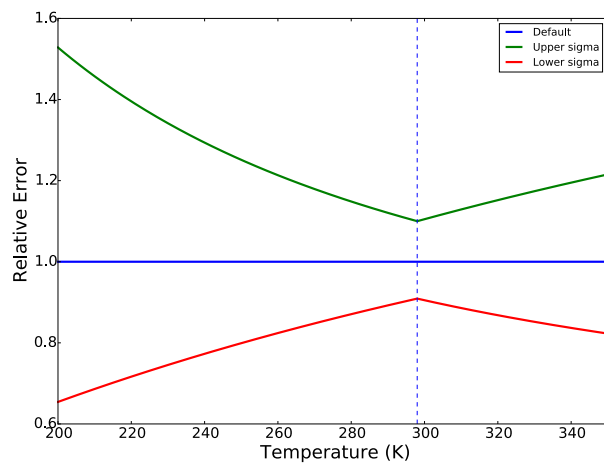
We have shown that the uncertainty in the inorganic rate constants leads to significant (>10%) uncertainties in the concentration of policy relevant metrics of troposphere composition (O<sub>3</sub> burden, surface O<sub>3</sub>, global mean OH, tropospheric CH<sub>4</sub> lifetime, O<sub>3</sub> radiative forcing) with significantly higher uncertainty in other compounds. This uncertainty may have implications for climate policy through an underestimate of the uncertainty on O<sub>3</sub> radiative forcing or significant uncertainties on the CH<sub>4</sub> lifetime. This also has implication for how model-measurement disagreements are interpreted. Similar conclusions have been found for regional air quality focussed models (?).

The simulation performed here likely provide a lower limit to the chemical uncertainty. We do not explore the impact in uncertainties in organic chemistry (beyond that from the initiation of hydrocarbon oxidation) or in organic mechanisms; we do not included tropospheric bromine, iodine, chlorine chemistry in our analysis or heterogeneous parameters. We have neither investigated the impact of rate constant uncertainty on the composition of the stratosphere or mesosphere, or how this may propagate through to the troposphere. There are also uncertainties in the Henry's Law constants used for wet and dry parameterisations etc. It seems likely therefore that the true chemical uncertainty in the composition of the atmosphere is significantly higher than that found here.

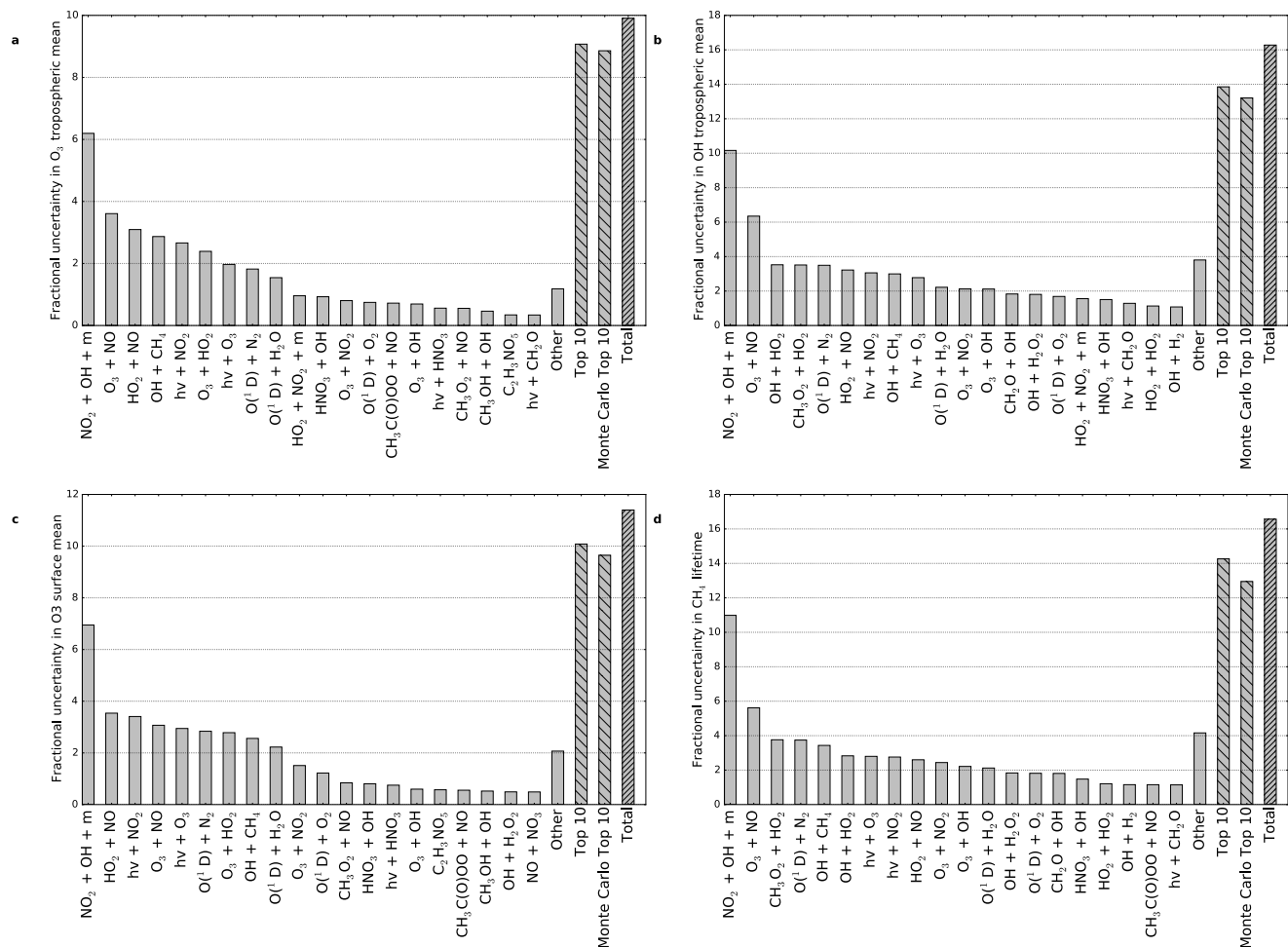
Although it may be challenging, reducing these uncertainties would provide significant benefits. Targeting the top 10 reactions identified here (Figure 2 (a)) would significantly reduce the overall chemical uncertainties. Despite the fact that the rate-constants for these reactions may appear 'decided', they provide the basis for determining the composition of the atmosphere. Given the difficulties in reducing the uncertainties in other areas of the climate system (we will never know the pre-industrial emissions well etc.) a redoubled effort to reduce rate constant uncertainty appears to be a relatively straightforward methodology to improve our understanding of atmospheric composition.

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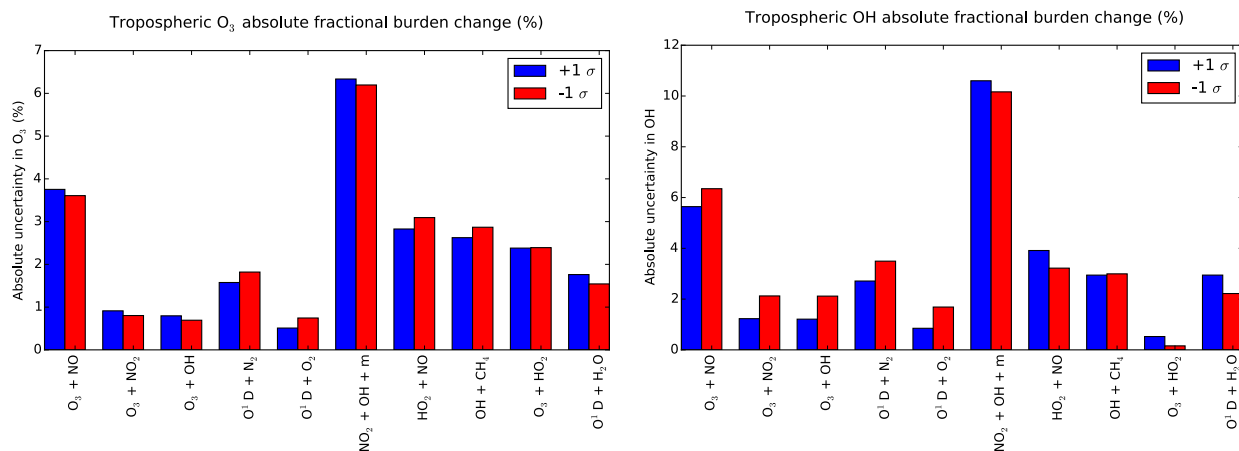
wish to thank all involved in the development of the model. We would also thank all the JPL and IUPAC panels for their efforts in compiling atmospheric rate constants.



**Figure 1. Example of the uncertainty on a reaction rate constant.** The relative uncertainty of the reaction  $\text{O}_3 + \text{NO}$  is plotted as a function of temperature ~~based on the JPL methodology~~. The lowest uncertainty is at room temperature (298K) with exponentially increasing uncertainties occurring as we diverge to higher and lower temperatures.

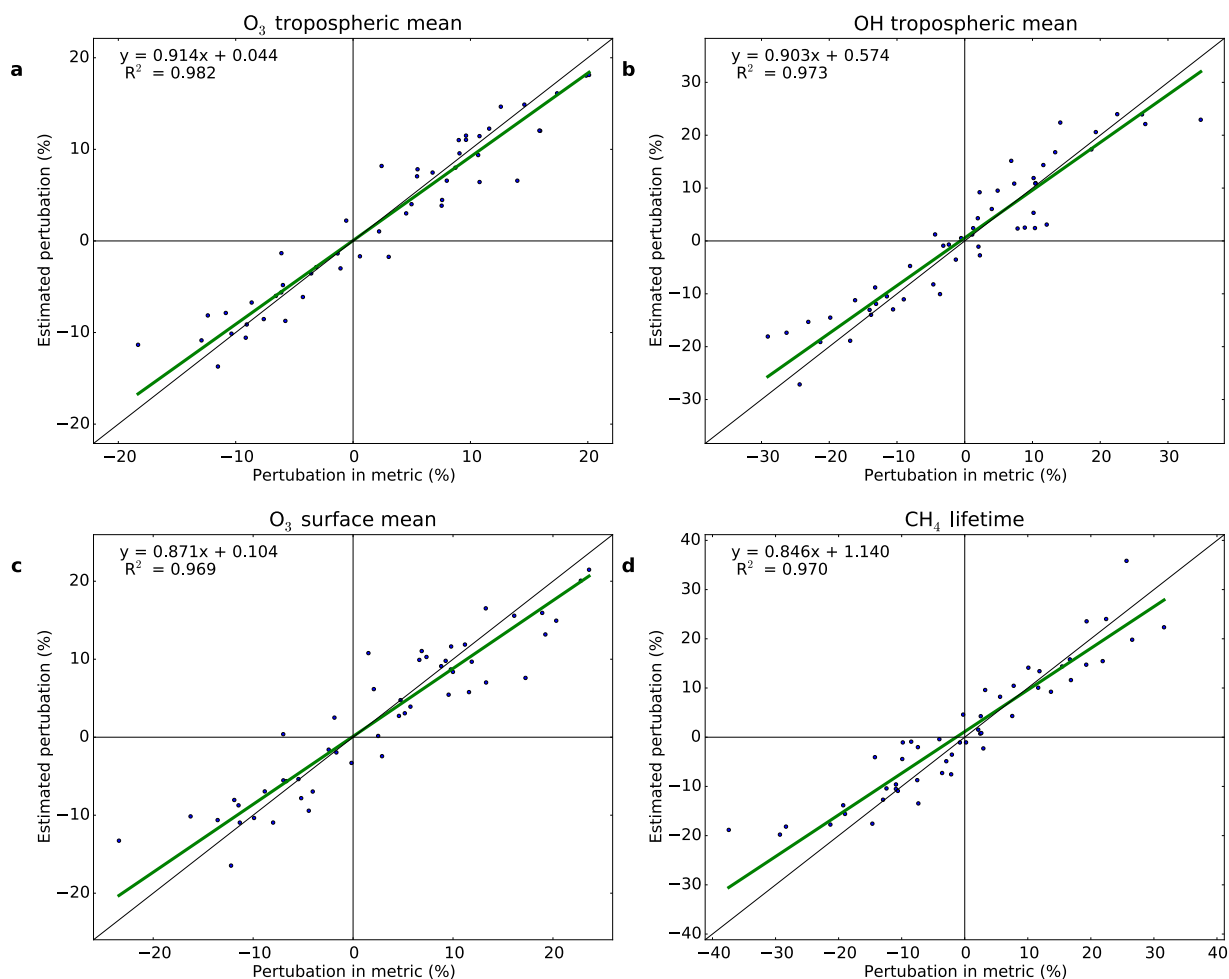


**Figure 2. Uncertainties in all metrics.** Fractional uncertainties of **a** O<sub>3</sub> tropospheric burden, **b** OH tropospheric burden, **c** O<sub>3</sub> surface concentration and **d** CH<sub>4</sub> lifetime. Each bar labelled with a reaction represents a run with a 1σ increase in the rate constant. ‘Other’ represents the addition in quadrature of the reactions that were not the top 20 most influential. ‘Total (Top 10)’ represents the addition in quadrature of the 10 most important reactions, and ‘Monte Carlo Top 10’ represents the standard deviation of the Monte Carlo ensemble. ‘Total’ represents the addition in quadrature of all the simulations.

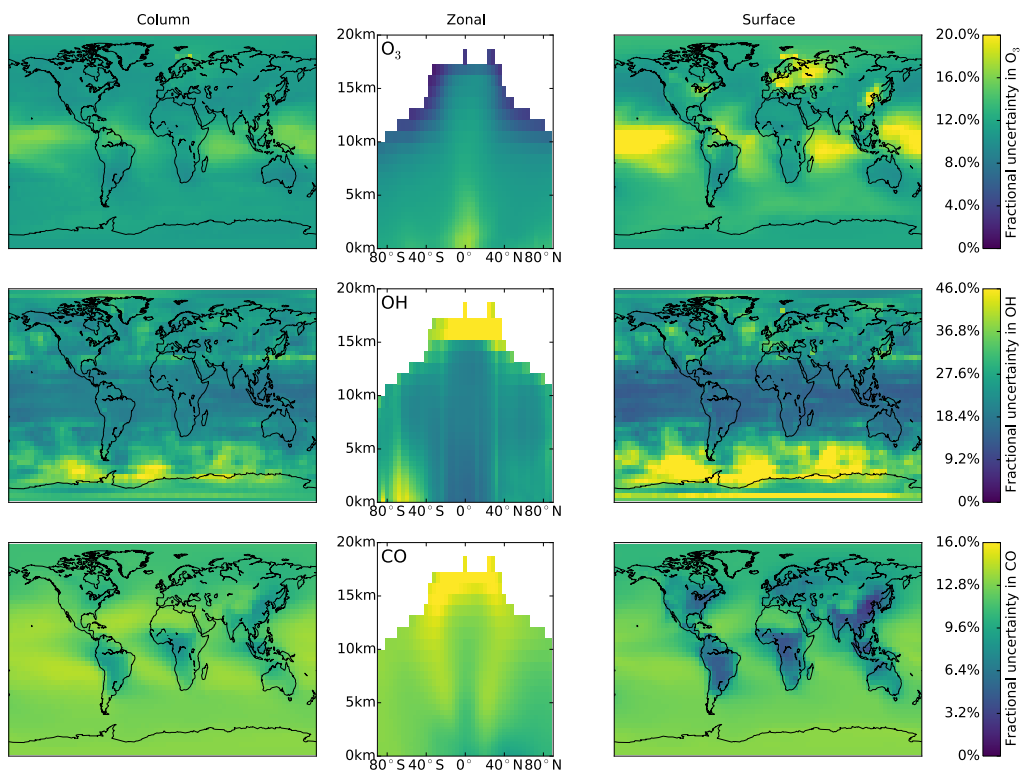


**Figure 3. Uncertainty linearity.** A comparison of absolute uncertainties in O<sub>3</sub> and OH tropospheric burdens for ~~increases~~ both positive and decreases in negative changes to the rate constants ~~based on the uncertainties~~. These ~~ten~~ reactions show a similar magnitude of tropospheric species concentration change if the rate is set to its lower or higher sigma level of uncertainty.

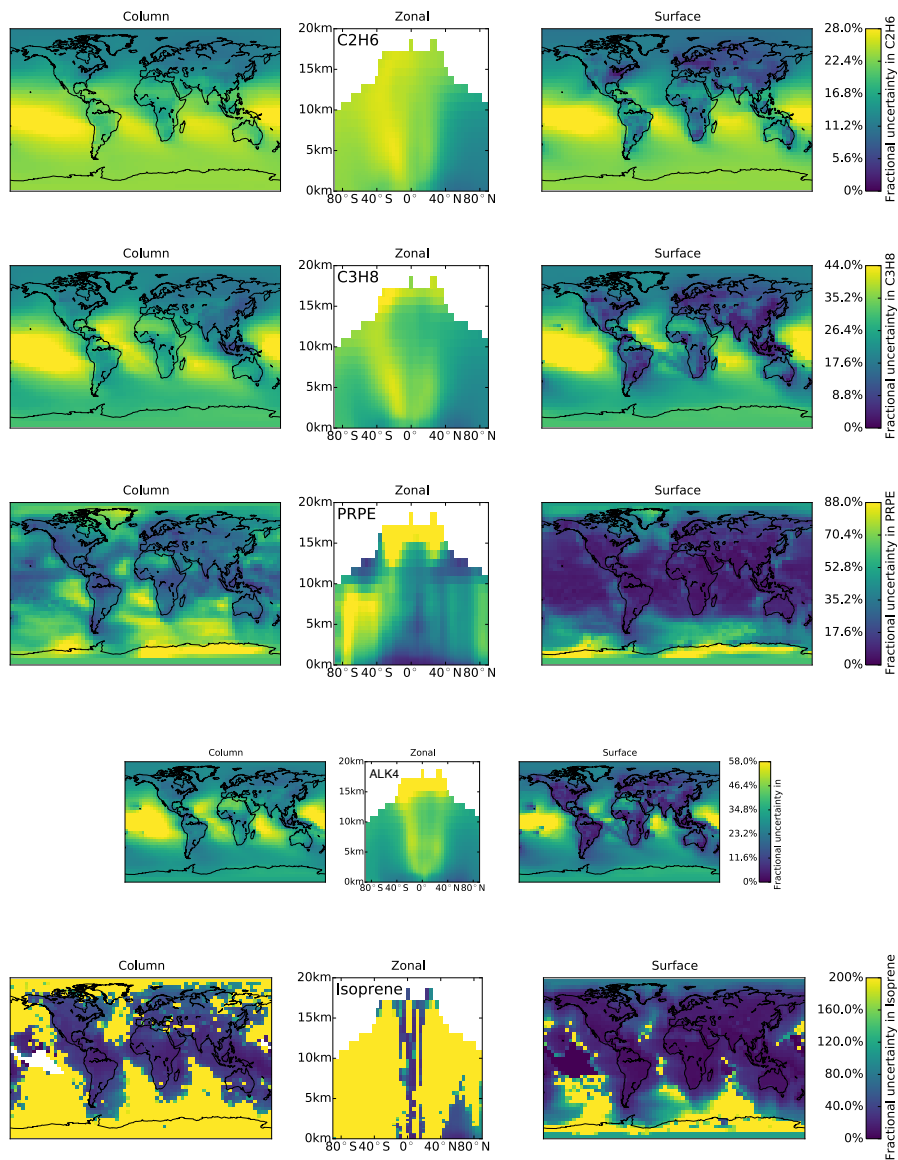




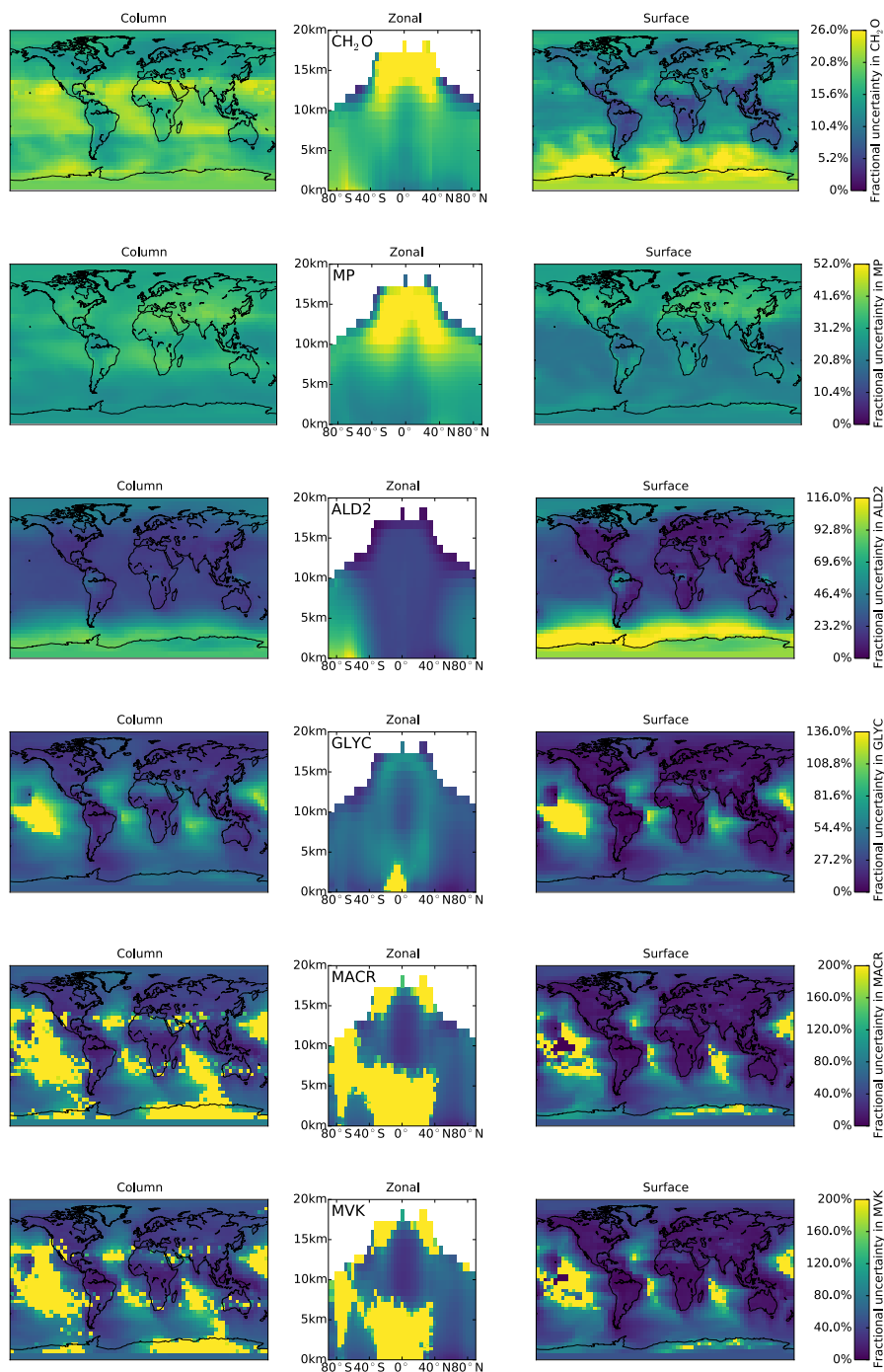
**Figure 4. Monte Carlo simulations to understand model linearity.** Monte Carlo simulations to understand the models linearity. The X axis values shows the percentage change in the metric value of an ensemble member compared to the simulation with no perturbations. The Y axis values show the expected percentage change of the metric based on a linear addition of the individual 1 sigma perturbation experiments weighted by the Monte Carlo perturbation values. Metrics investigates are **a**  $O_3$  tropospheric burden, **b**  $O_3$  mean surface concentration, **c** OH tropospheric burden and **d**  $CH_4$  lifetime. We show the result of 50 Monte Carlo simulations. Each simulation perturbs 10 of the most important reactions (\* reactions in SI-Table 1)  $1\sigma$  by normally distributed random numbers. Black line is the 1 to 1 line, and the green line the orthogonal regression fit.



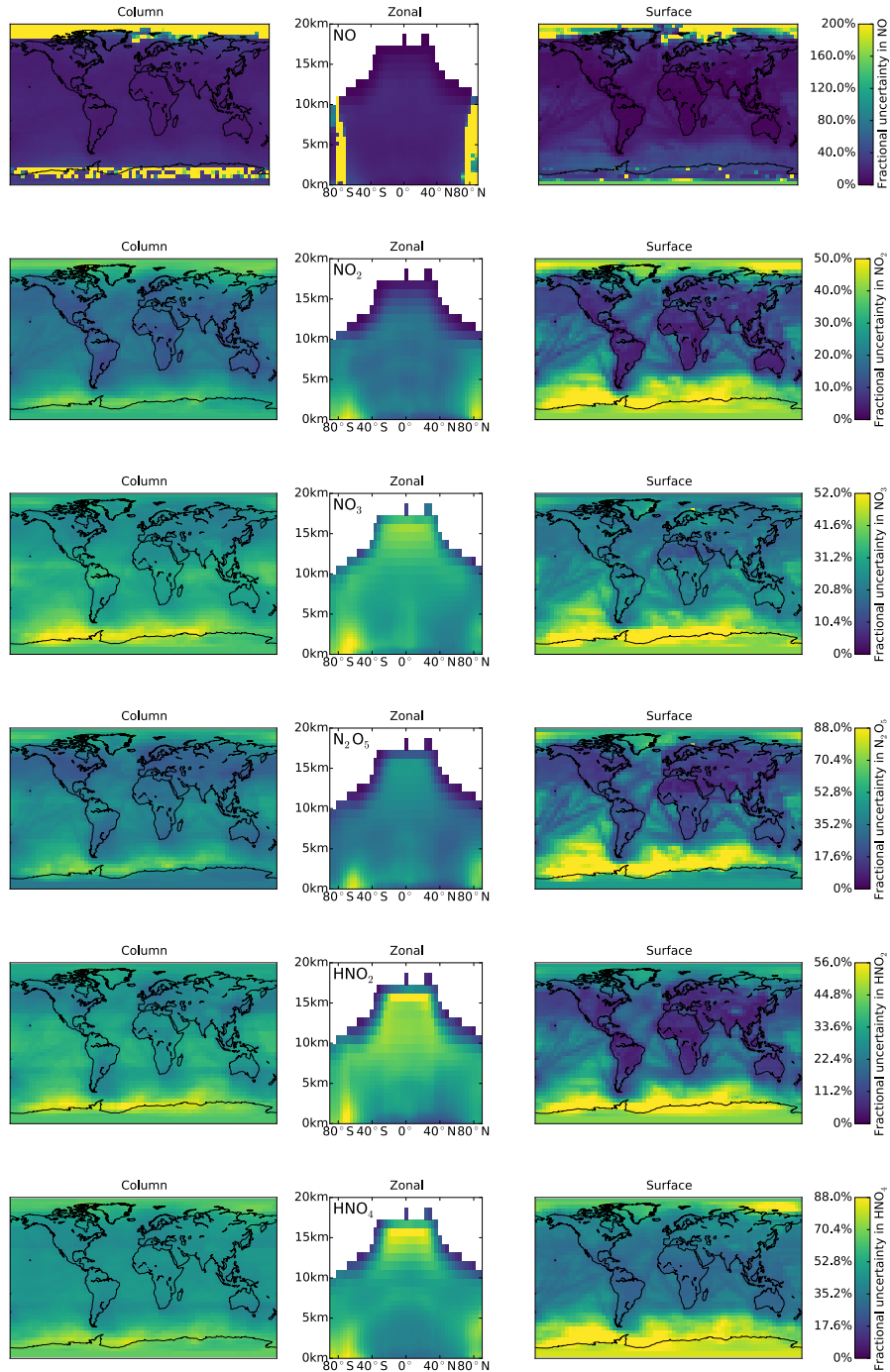
**Figure 5. Spatial distribution of uncertainties.** Fractional uncertainties calculated for  $\text{O}_3$ , OH and CO concentrations for the tropospheric column (left), the zonal mean (centre) and the surface (right) from adding together the individual reaction uncertainties from the 60 reactions studied in quadrature



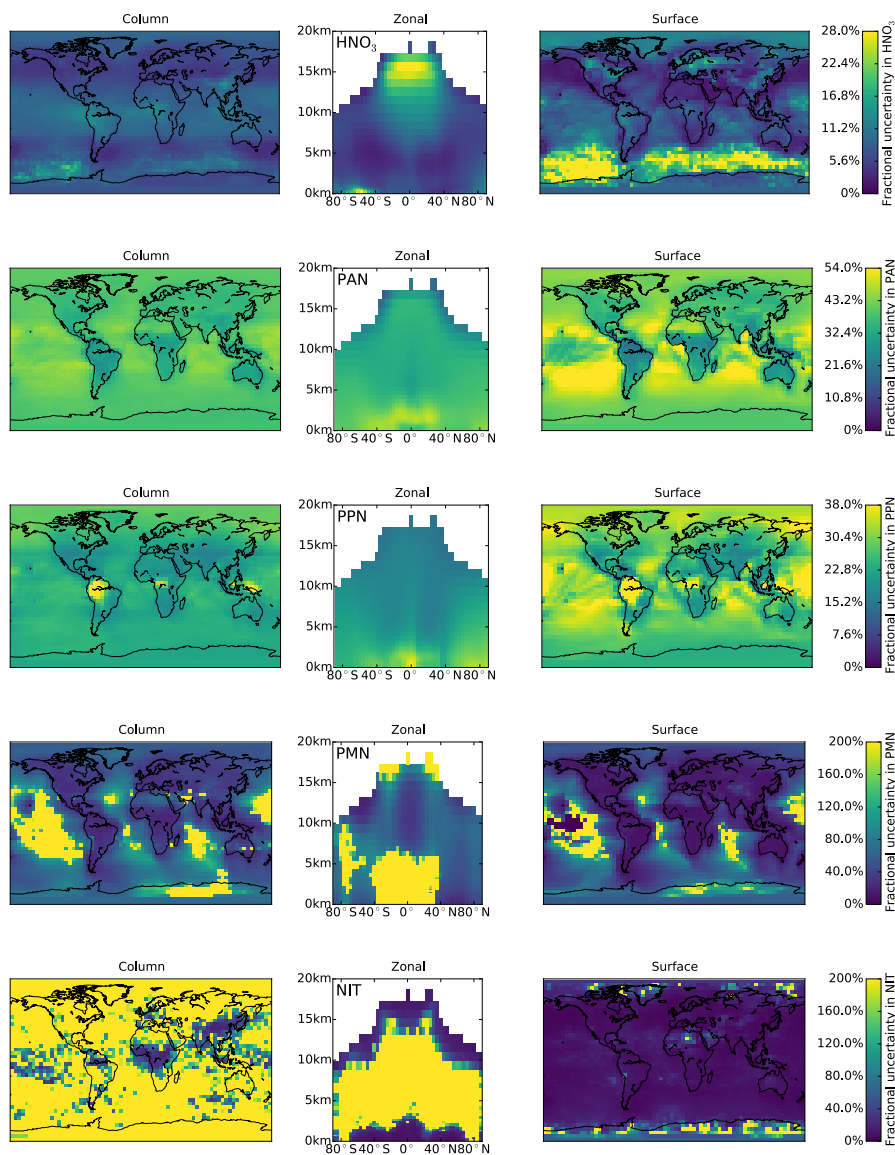
**Figure 6. Primary VOCs.** Total  $1\sigma$  uncertainty in the concentrations of C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, PRPE ( $\geq$  C<sub>3</sub> Alkenes), ALK<sub>4</sub> ( $\geq$  C<sub>4</sub> Alkanes) and ISOP (Isoprene) from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.



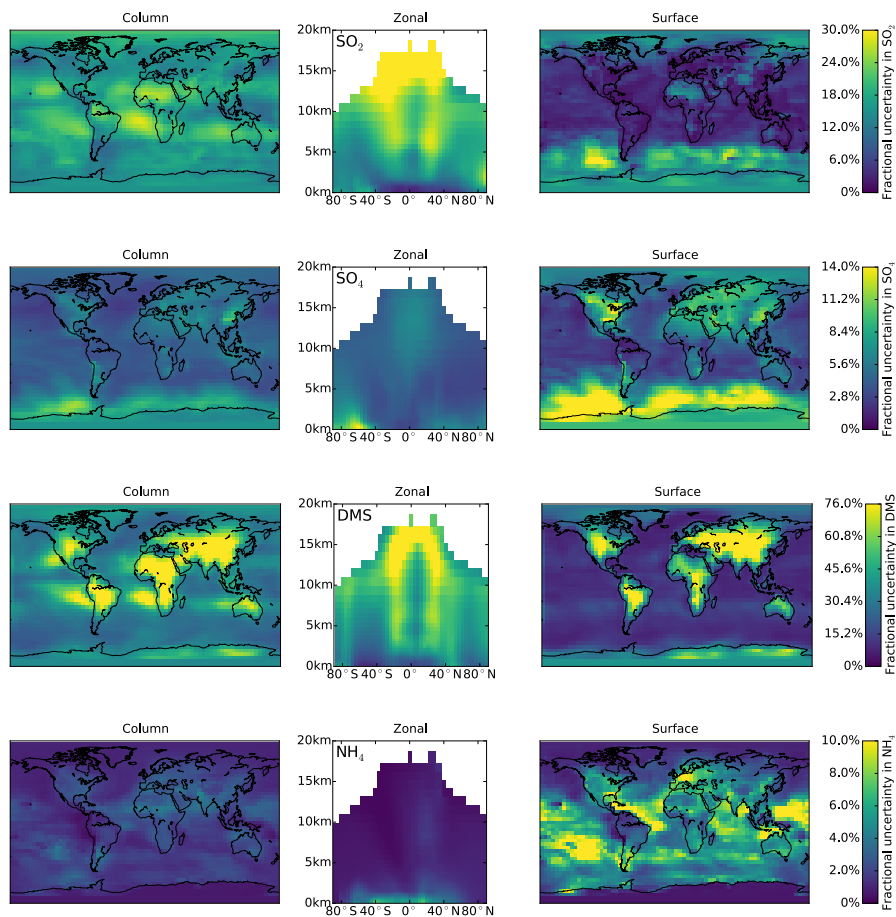
**Figure 7. Other Organics.** Total  $1\sigma$  uncertainty in the concentrations of  $\text{CH}_2\text{O}$ , MP (Methyl Hydro Peroxide), ALD2 (Acetaldehyde), GLYC (Glycoaldehyde), MACR (Methacrolein) and MKV (Methyl Vinyl Ketone) from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.



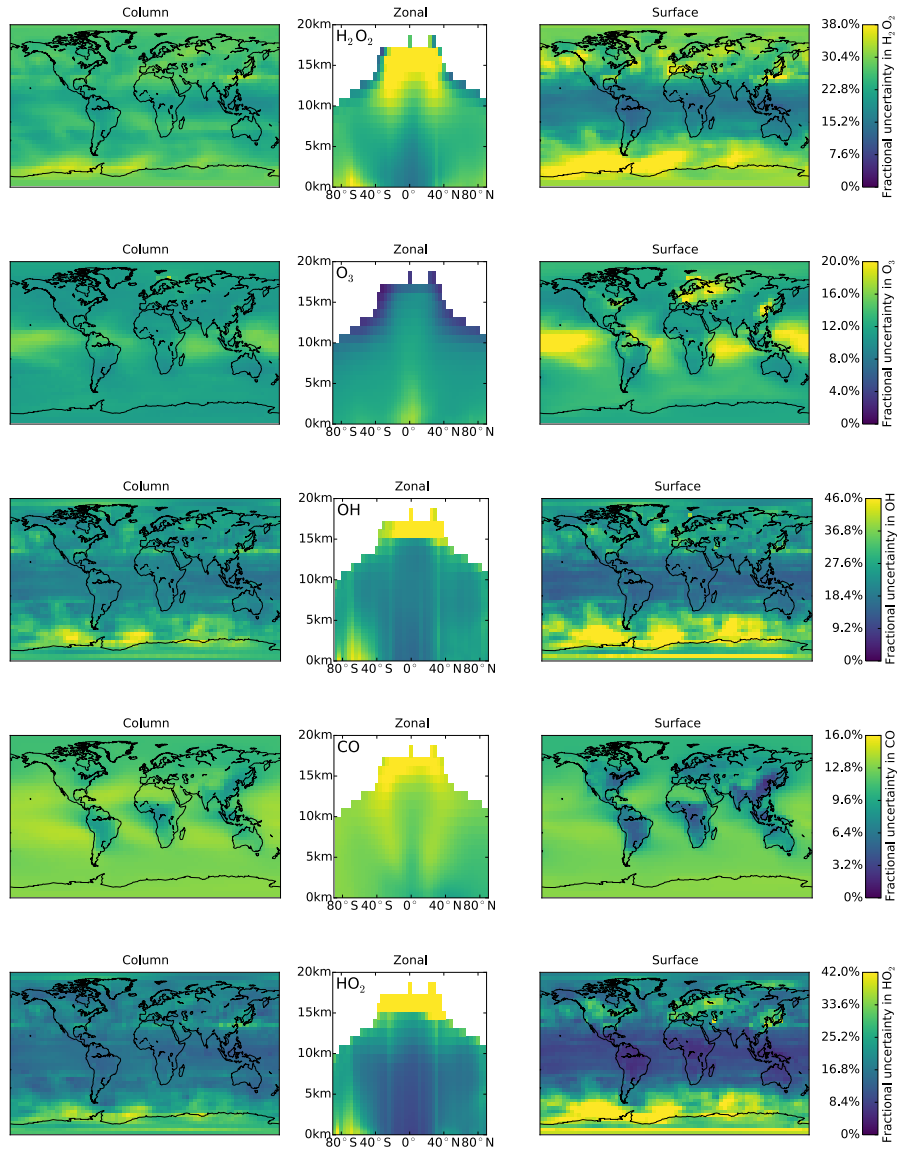
**Figure 8.**  $\text{NO}_x$ . Total  $1\sigma$  uncertainty in the concentrations of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_2$  and  $\text{HNO}_4$  from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.



**Figure 9.**  $\text{NO}_y$ . Total  $1\sigma$  uncertainty in the concentrations of  $\text{HNO}_3$ , PAN (Peroxyacetyl Nitrate), PPN (Peroxypropionyl+Peroxymethacroyl Nitrate), PMN (Peroxymethacroyl Nitrate) and NIT (Inorganic aerosol nitrates) from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.

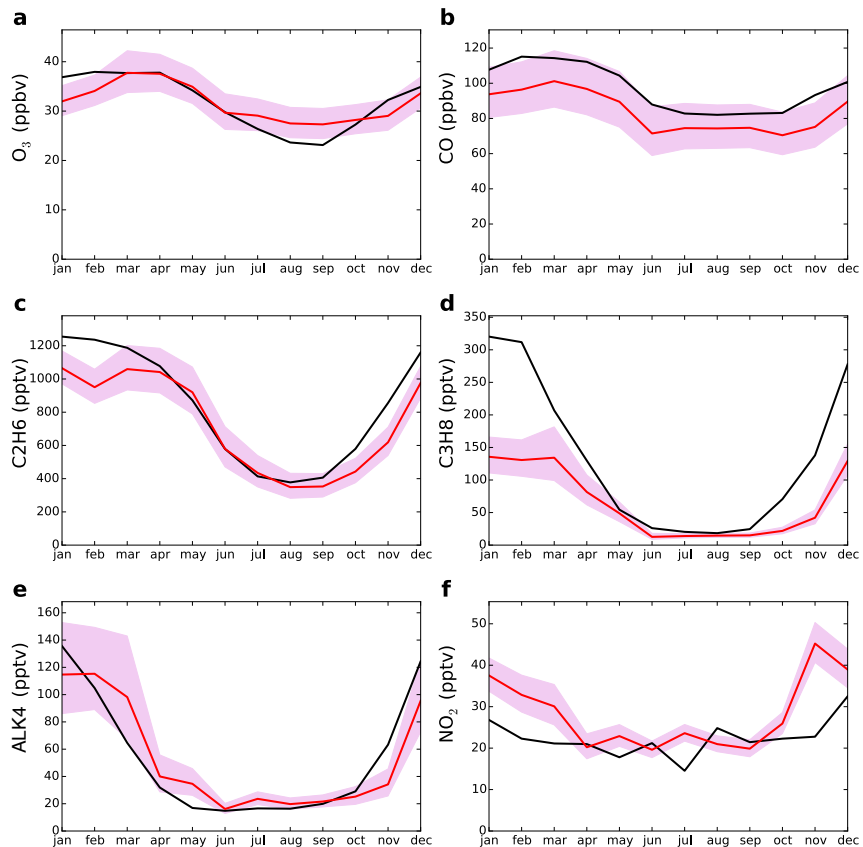


**Figure 10. Sulfur and Aerosols.** Total  $1\sigma$  uncertainty in the concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ , DMS (Dimethyl Sulfide) and  $\text{NH}_4^+$  from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.

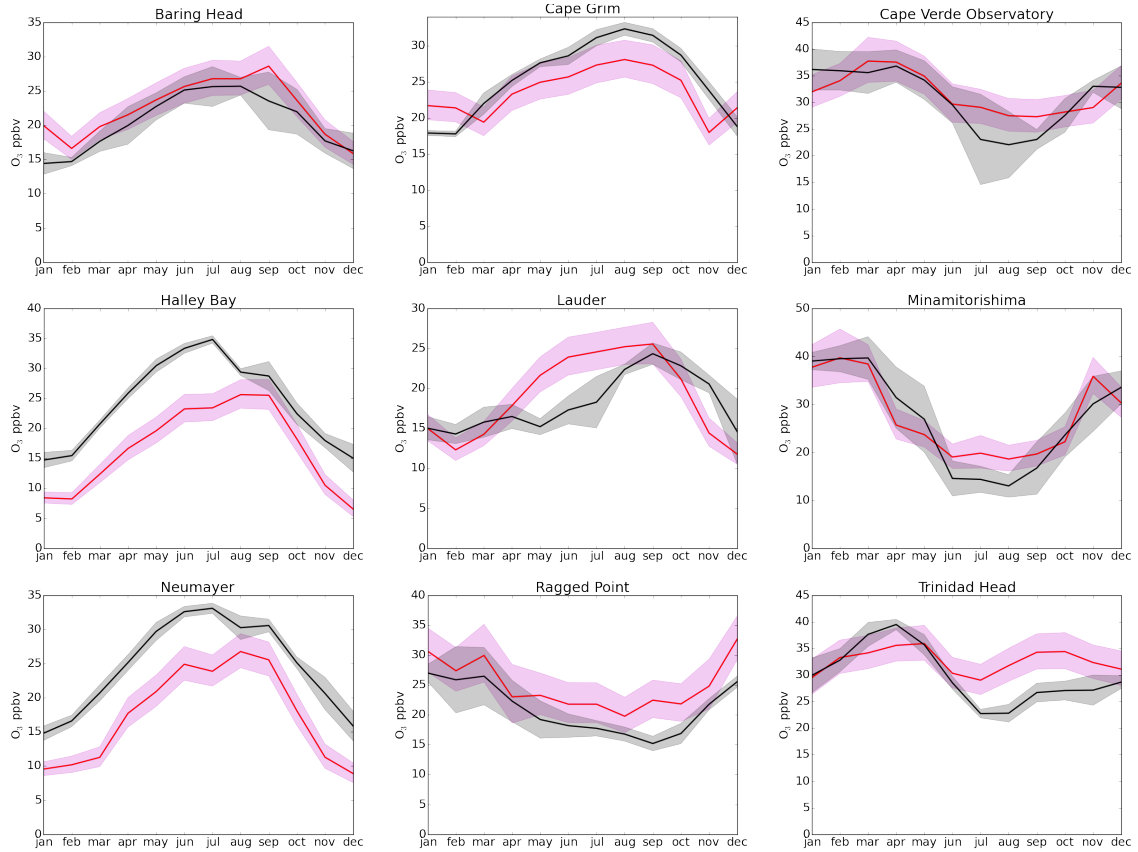


**Figure 11. Inorganics.** Total  $1\sigma$  uncertainty in the concentrations of  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{OH}$ ,  $\text{CO}$  and  $\text{HO}_2$  from the addition in quadrature of the individual reaction uncertainties. Column covers the tropospheric column.

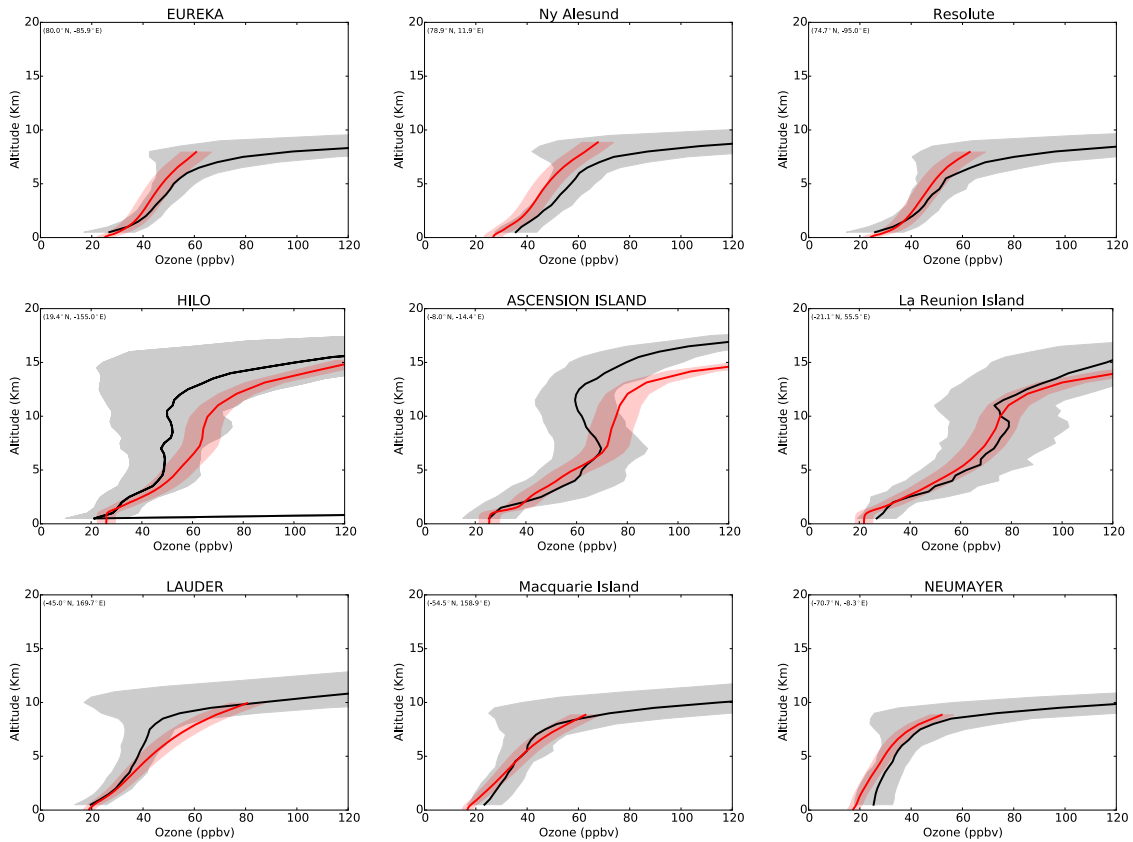




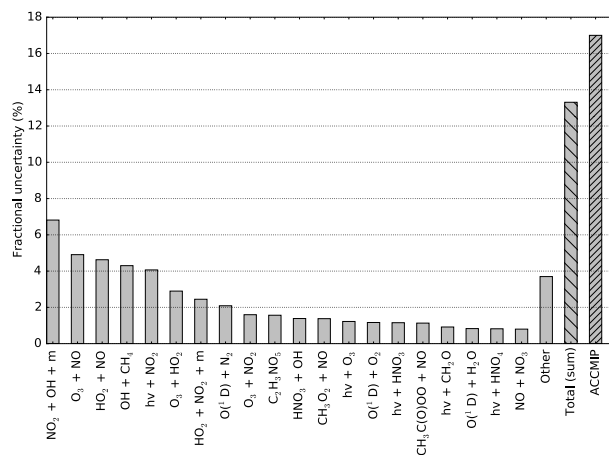
**Figure 12. Impact on model / measurement comparisons.** Modelled (red) and measured (black) annual cycle in monthly mean  $O_3$ , CO,  $C_2H_6$ ,  $C_3H_8$ , ALK4 ( $\geq$  C4 Alkanes) and  $NO_2$  mixing ratios at Cape Verde (?). Shaded area represents the  $1\sigma$  uncertainty from the 60 reactions added together in quadrature.



**Figure 13. Ozone site comparison** Modelled (red) and measured (black) concentrations of ozone at a range of sites. The pink shaded area shows the  $1\sigma$  uncertainty from the chemical kinetics. The error bars represent the  $1\sigma$  variability- $1\sigma$  uncertainty of these observations. Monthly mean observational data obtained from [\(Sofen and Evans, 2015\)](#), using multiple years between 2004 and 2010 to create more complete datasets.



**Figure 14. Ozonesonde** Comparisons between the variability of annual ozonesonde measurements and model data with uncertainties. The black line shows the annual mean observation data and the shaded gray shows the  $\pm 1\sigma$  range of data. The red line shows the model data and the pink shaded line shows the chemical  $\pm 1\sigma$  uncertainty. Observations are obtained from [WUOUDC \(2014\)](#).



**Figure 15. Uncertainties in O<sub>3</sub> radiative forcing.** Absolute fractional uncertainty in tropospheric O<sub>3</sub> radiative forcing between the preindustrial and present day, due to rate constant uncertainty. Shown on the left are the 20 most important reactions. ‘Other’ shows the addition in quadrature of the remaining 40 reactions. ‘Total (sum)’ indicates the total fractional uncertainty calculated by adding together the individual uncertainties in quadrature. ‘ACCMIP’ indicates the inter-model spread found from the ACCMIP (?) study.

**Table 1. Table of reactions studied.** f (298) indicates the JPL or IUPAC panel uncertainty estimate at 298K and g gives the rate at which this uncertainty increases away from 298K (see previous section). Reactions with 0 for the temperature dependence indicates there is zero temperature dependency or not enough information to provide a temperature varying uncertainty. The final column gives the fractional increase in the ozone burden by increasing the rate constant to its  $1\sigma$  value. Reactions with a \* are the 10 reactions used in the Monte Carlo study.

Number	Reaction	f(298)	g (K)	$1\sigma$ O <sub>3</sub> burden change (%)
1*	$\text{NO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HNO}_3$	1.3	100	-6.20
2*	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	1.1	200	-3.61
3*	$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$	1.15	20	3.09
4*	$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	1.1	100	<del>2.79</del> 2.89
5*	$\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2\text{O}_2$	1.15	80	-2.39
6*	$\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$	1.1	20	1.82
7*	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	1.08	20	-1.54
8	$\text{HO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{HNO}_4$	1.06	400	-0.959
9	$\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3$	1.2	0	0.928
10*	$\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$	1.15	150	-0.803
11*	$\text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O} + \text{O}_2$	1.1	10	0.745
12	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2 + \text{CO}_2$	1.5	0	0.721
13*	$\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	1.1	50	-0.693
14	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2$	1.15	100	0.553
15	$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{HO}_2 + \text{CH}_2\text{O}$	1.1	60	0.462
16	$\text{CH}_3\text{C}(\text{O})\text{OONO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OO} + \text{NO}_2$	1.2	200	0.341
17	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_3\text{C}(\text{O})\text{OONO}$	1.2	50	-0.289
18	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	1.05	100	0.282
29	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	1.15	45	0.265
20	$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	1.3	100	0.249
21	$\text{HO}_2 + \text{NO}_3 \rightarrow \text{OH} + \text{NO}_2$	1.5	0	0.248
22	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	1.4	150	-0.243
23	$\text{CH}_3\text{SCH}_3 + \text{OH} \rightarrow \text{SO}_2 + \text{CH}_3\text{O}_2 + \text{CH}_2\text{O}$	1.1	100	0.231
24	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	1.15	50	-0.215
25	$\text{CH}_3\text{CH}_2\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{NO}_2 + \text{HO}_2$	1.2	150	0.211
26	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{OO} + \text{H}_2\text{O}$	1.07	50	0.201
27	$\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$	1.15	50	0.198
28	$\text{HCOOH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{HO}_2$	1.2	100	0.196
29	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_3$	1.25	50	0.195
30	$\text{CH}_3\text{CHO} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{CH}_3\text{C}(\text{O})\text{OO}$	1.3	300	0.193

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31	$\text{HNO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	1.5	200	0.178
32	$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OO} + \text{CH}_2\text{O} + \text{CO} + \text{HO}_2$	1.05	20	0.174
33	$\text{CH}_3\text{SCH}_3 + \text{NO}_3 \rightarrow \text{SO}_2 + \text{HNO}_3 + \text{CH}_3\text{OO} + \text{CH}_2\text{O}$	1.1	150	0.172
34	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{O} + \text{O}_2$	1.2	100	0.170
35	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	1.15	100	0.166
36	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CO} + \text{HO}_2 + \text{H}_2\text{O}$	1.15	50	0.156
37	$\text{NO} + \text{OH} \xrightarrow{\text{M}} \text{HNO}_2$	1.2	50	-0.151
38	$\text{SO}_2 + \text{OH} \xrightarrow{\text{M}} \text{SO}_4 + \text{HO}_2$	1.1	100	0.151
39	$\text{NO}_2 + \text{NO}_3 \xrightarrow{\text{M}} \text{N}_2\text{O}_5$	1.2	100	-0.151
40	$\text{HNO}_4 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$	1.3	500	0.149
41	$\text{OH} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$	1.5	100	-0.146
42	$\text{CO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2$	1.1	100	-0.144
43	$\text{NO}_3 + \text{NO}_3 \rightarrow 2\text{NO}_2 + \text{O}_2$	1.5	500	-0.144
44	$\text{OH} + \text{NO}_3 \rightarrow \text{HO}_2 + \text{NO}_2$	1.5	0	-0.143
45	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	1.1	100	-0.134
46	$\text{HNO}_4 \rightarrow \text{HO}_2 + \text{NO}_2$	1.3	270	0.104
47	$\text{CH}_3\text{O}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	1.3	150	0.0350
48	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2 + \text{OH} \rightarrow \text{HOCH}_2\text{C}(\text{OO})(\text{CH}_3)\text{CH}=\text{CH}_2$	1.07	100	-0.0323
49	$\text{NO}_3 + \text{CH}_2\text{O} \rightarrow \text{HNO}_3 + \text{HO}_2 + \text{CO}$	1.3	0	-0.0145
50	$\text{C}_4\text{H}_{10} + \text{OH} \rightarrow 2\text{H}_2\text{O} + \text{C}_4\text{H}_9$	1.06	100	0.0132
51	$\text{h}\nu + \text{NO}_2 \rightarrow \text{NO} + \text{O}(^3\text{P})$	1.1	0	2.66
52	$\text{h}\nu + \text{O}_3 \rightarrow \text{O}_2 + \text{O}(^1\text{D})$	1.1	0	-1.97
53	$\text{h}\nu + \text{HNO}_3 \rightarrow \text{OH} + \text{NO}_2$	1.1	0	0.559
54	$\text{h}\nu + \text{CH}_2\text{O} \rightarrow \text{CO} + \text{HO}_2 + \text{HO}_2$	1.1	0	0.338
55	$\text{h}\nu + \text{HNO}_4 \rightarrow \text{HO}_2 + \text{NO}_2$	1.1	0	0.262
56	$\text{h}\nu + \text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$	1.1	0	0.223
57	$\text{h}\nu + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}(^3\text{P})$	1.1	0	0.222
58	$\text{h}\nu + \text{HNO}_4 \rightarrow \text{OH} + \text{NO}_3$	1.1	0	0.200
59	$\text{h}\nu + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{OO} + \text{HO}_2 + \text{CO}$	1.1	0	0.199
60	$\text{h}\nu + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$	1.1	0	0.196