

Global sensitivity of aviation NO_x effects to the $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ reaction

K. Gottschaldt^{*}, C. Voigt, P. Jöckel, M. Righi, S. Dietmüller
DLR-Institut für Physik der Atmosphäre Oberpfaffenhofen, Germany

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ABSTRACT: The impact of a recently proposed HNO_3 -forming channel of the $\text{HO}_2 + \text{NO}$ reaction (Butkovskaya et al., 2005, 2007) on atmospheric mixing ratios of ozone, methane and their precursors is assessed with a global stratosphere-troposphere chemistry-climate model. Previous modelling studies applied a rate coefficient that depends only on pressure and temperature. We additionally considered a possible enhancement of the reaction by humidity, as found by a laboratory study (Butkovskaya et al., 2009). This particularly reduces the oxidation capacity of the atmosphere, increasing methane lifetime significantly.

The effects of aircraft NO_x emissions on atmospheric chemistry are altered when considering the above reaction, resulting in a negative net radiative forcing relative to an atmosphere without aviation NO_x . Uncertainties associated with the inclusion of the $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ reaction and with its corresponding rate coefficient propagate a considerable additional uncertainty on estimates of the climate impact of aviation and on NO_x -related mitigation strategies.

This contribution is based on Gottschaldt et al. (2013).

1 INTRODUCTION

Aircraft emissions of reactive nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) peak in the upper troposphere and lower stratosphere (UTLS), and the resulting NO_x increase impacts on the radiatively active trace gases ozone (O_3), methane (CH_4) and stratospheric water vapour. The level of scientific understanding of this contribution to anthropogenic climate forcing has been judged as moderate to poor (Lee et al., 2010, Holmes et al., 2011). This judgement did not include the possible effects of the proposed $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ reaction (Butkovskaya et al., 2005, 2007, 2009, Chen et al., 2009).

The concentration of ozone in the UTLS is determined by transport, mixing and by chemical processes, mainly the ozone destroying, catalytic peroxy radical ($\text{HO}_x = \text{HO}_2 + \text{OH}$) and halogen radical cycles in concert with reactions involving reactive nitrogen oxides (Wennberg et al., 1998). Adding (aviation) NO_x to the chemical system and considering gas phase chemistry only, the effect on ozone changes sign in the altitude range of 12 to 25 km (e.g. Søvde et al., 2007). Above that altitude region of zero net effect, aircraft NO_x emissions intensify the NO_x cycle, enhancing catalytic ozone destruction. This cycle operates more efficiently higher up in the stratosphere, because peroxy radicals (sequestering NO_x into reservoir species such as nitric acid, HNO_3) and NO_2 photolysis are less important at higher altitudes. Below that region, the ozone destroying NO_x cycle is bypassed via peroxy radicals, and direct emissions of NO_x by aircraft can lead to increased ozone production by reducing the abundance of HO_x molecules.

Furthermore, the rates of the major net loss reactions of peroxy radicals, as well as ozone production, all depend nonlinearly and even non-monotonically on NO_x levels (Ehhalt and Rohrer, 1994). However, such chemical nonlinearities are expected to be small for the atmospheric response to aircraft emissions (Holmes et al., 2011).

Methane is emitted from the Earth's surface and lost in the troposphere mainly by the reaction with OH. Thus NO_x emissions affect methane life time via OH. Methane perturbations in turn have

^{*} *Corresponding author:* Klaus Gottschaldt, DLR-Institut für Physik der Atmosphäre, Oberpfaffenhofen, D-82205 Wessling, Germany. Email: klaus-dirk.gottschaldt@dlr.de

an effect on ozone (Ehhalt et al., 2001). Methane oxidation is also a major source of stratospheric water vapour.

Beyond these well-known reactions, the effects of NO_x emissions may be further affected by the recently discovered HNO₃-forming channel of the HO₂ + NO reaction (Butkovskaya et al., 2005, 2007, Chen et al., 2009):



with the rate coefficients k_{1a} and k_{2a} , respectively. Butkovskaya et al. (2009) supposed that HO₂ + NO forms the HOONO intermediate complex that mostly decomposes into OH + NO₂. A small fraction forms nitric acid, possibly involving another molecule (M). We note that reaction R2 is not generally accepted yet (IUPAC, 2008, Sander et al., 2011).

The effects of reaction R2a on atmospheric composition have been studied before (Brühl et al., 2007, Cariolle et al., 2008, Søvde et al., 2011), accounting for pressure and temperature dependence of k_{2a} . We additionally considered that both reaction channels may be modified in the presence of water vapour (Butkovskaya et al., 2009), which will be introduced as reactions R1b and R2b. Unger (2011) reported a negligible impact of R2a on short-lived ozone perturbations due to aviation NO_x. In the following we demonstrate the potential importance of R2 for assessing the climate impact of aviation NO_x, when considering radiative forcing (RF) from perturbations in ozone and methane. The results emphasize the need for further experimental data on the rate coefficient for reaction R2 that are valid in the entire range of atmospheric temperatures, pressures, and water vapour concentrations.

2 METHODOLOGY

2.1 Model setup

This study is based on the global ECHAM/MESSy Atmospheric Chemistry (EMAC) model (Jöckel et al., 2006). The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5, Roeckner et al., 2003). For the present study EMAC was applied (ECHAM5: version 5.3.01, MESSy: modified version 1.10) with a spherical truncation of T42, and 90 vertical hybrid pressure levels up to 0.01 hPa. All simulations cover two years and were nudged in the free troposphere (up to about 200 hPa) to the synoptic meteorological conditions (ECMWF) of the years 2000 and 2001.

Emissions from natural and anthropogenic sources were provided to the model as monthly mean offline fields, representing conditions of the simulated period around the year 2000. Aircraft emissions for the year 2000 were taken from the QUANTIFY project (Lee et al. 2005), and included NO_x only, emitted as 1.815 Tg NO per year. Online emissions of soil NO and isoprene were simulated as a function of specific meteorological conditions.

Gas phase chemistry was calculated with the MECCA1 chemistry submodel (Sander et al., 2005), consistently from the surface to the stratosphere. The applied chemical mechanism included full stratospheric complexity, but neglected the sulphur and halogen families in the troposphere.

Further details about the model setup can be found in Gottschaldt et al. (2013).

2.2 Modifications to the chemical mechanism

A temperature-dependent rate coefficient (Sander et al., 2003),

$$k_0 = k_1 + k_2 \quad (1)$$

was assumed for the HO₂ + NO conversion via both reaction pathways (R1 and R2). The base simulation had $k_1 = k_0$ for reaction R1. Reaction R2 was switched off, i.e. $k_2 = 0$.

Sensitivity simulations with HNO₃ forming channel and no humidity modification differ from the base simulation in the definition of k_1 and k_2 :

$$k_{2a} = \frac{k_0 \cdot \beta}{1 + \beta} \quad (2)$$

$$k_{1a} = k_0 - k_{2a} \quad (3)$$

The factor β has been derived by Butkovskaya et al. (2007) and depends on pressure p and temperature T .

An enhancement of HNO₃ formation in the presence of water has been measured in the laboratory (Butkovskaya et al., 2009), suggesting the following chemical mechanism instead of reactions R1a and R2a:



Humidity effects were considered as a modification of Equations 2 and 3:

$$k_{2b} = \frac{k_0 \cdot \beta \cdot (1 + \gamma \cdot \alpha)}{(1 + \beta) \cdot (1 + \alpha)} \quad \text{and} \quad k_{1b} = k_0 - k_{2b} \quad (4)$$

The term $\alpha = c_{\text{H}_2\text{O}} \cdot K_{eq}$ depends on the equilibrium coefficient K_{eq} (in cm³) of reaction R3 and on the molecular concentration of water, $c_{\text{H}_2\text{O}}$ in cm⁻³, and $\gamma = 42$ is a constant factor (Butkovskaya et al., 2009).

2.3 Simulations

Six simulations were performed for this study that all share the same meteorology, but differ in their atmospheric chemistry. The Base simulation without R2, and with Aircraft emissions (BA) serves as reference for the comparison to simulations DA (Dry = rate coefficient for reaction R2a according to Eq. 2, with Aircraft emissions) and WA (Wet = rate coefficient for R2b with humidity modification according to Eq. 4, with Aircraft emissions). Any pair of a reference and a sensitivity simulation is denoted as “sensitivity block”. The sensitivity blocks (BA versus DA) and (BA versus WA) serve to isolate the effects of R2 on atmospheric HNO₃, HO_x, NO_x and O₃ background mixing ratios.

Each of the above simulations represents a different chemical atmospheric chemical regime, but all three have identical emissions. Thus three more reference simulations are needed to isolate aviation NO_x effects by pairs. B0 (Base simulation, 0 = zero aircraft emissions) is compared to BA. D0 and W0 serve as reference cases for the sensitivities DA and WA, respectively. The corresponding sensitivity blocks are denoted ΔB , ΔD and ΔW .

This study focuses on chemical effects, but small chemical differences cause a divergence of model dynamics in a coupled system. In order to avoid such dynamically induced “noise”, EMAC was operated in Quasi Chemistry Transport Model (QCTM) mode (Deckert et al., 2011) for all simulations, switching off any feedback from chemical perturbations to the dynamical state (meteorology) of the atmosphere. In turn, the meteorological parameters (e.g. temperature, pressure, flow field, radiation, humidity) entering atmospheric chemistry calculations are also identical throughout the suite of simulations. The sensitivity simulations contain only the chemical effects of the applied perturbations.

3 RESULTS

3.1 Effects of the HO₂ + NO → HNO₃ reaction on atmospheric background chemistry

While the relative effects of the HNO₃ forming channel of the HO₂ + NO reaction are pronounced in the UTLS, the absolute effects on [HNO₃]¹, [NO_x], [OH] and [O₃] have their maximum at about 10 hPa. HNO₃ mixing ratios mostly increase compared to an atmosphere without reaction R2. NO_y mixing ratios decrease in the troposphere and increase in the stratosphere. NO_x generally decreases from the ground up to 1 hPa. This leads to less ozone in the troposphere, but enhances it in the altitude range of highest atmospheric ozone mixing ratios. The global annual mean ozone column in the simulation with $k_{2a}(p, T)$ decreases by 0.5 % compared to the simulation without the HNO₃-forming channel. Reaction R2 decreases the oxidizing capacity of the atmosphere, leading to a 10.5 % longer methane lifetime in DA. Our results with $k_{2a}(p, T)$ generally confirm the findings of Cariolle et al. (2008) and Søvde et al. (2011). Humidity enhances the effects of R2, particularly in the lower troposphere with its high water mixing ratios. The ozone burden decreases by 1.8 % and methane lifetime increases by 50 % when comparing the simulation with $k_{2b}(p, T, c_{H_2O})$ to the simulation without R2.

In an attempt to check if any of the chemical regimes yields unrealistic results, HNO₃, NO_x, CO and O₃ profiles from simulations BA, DA and WA were compared to observational profiles of Emmons et al. (2000). However, all simulations match the observed trace gas mixing ratios well and none could be ruled out according to this analysis. Global concentrations of the hydroxyl radical (determining atmospheric oxidizing capacity) were compared to the measurement based values of Spivakovsky et al. (2000). A new modification to NMHC oxidation (Taraborrelli et al., 2012) was not yet included in the chemical mechanism used for this study. It would likely bring the regime with R2 with humidity modification into best agreement with observations, concerning the oxidizing capacity of the atmosphere.

3.2 Chemical and Radiative Forcing effects of aviation NO_x

Aviation NO_x primarily leads to more ozone and more hydroxyl radicals in the altitude-latitude region, where most emissions occur. More tropospheric ozone translates into a positive radiative forcing ($RF_{O_3}^{short}$), i.e. warms the Earth. More hydroxyl radicals destroy more methane, resulting in a negative radiative forcing ($RF_{CH_4}^{long}$). Less methane means less stratospheric water vapour from methane oxidation ($RF_{H_2O}^{long}$). A chemical feedback leads to an ozone decrease in response to less methane, and thus to an additional negative forcing ($RF_{O_3}^{long}$). Correcting for different emissions, all forcing terms from the sensitivity block without reaction R2 agree very well with the results from a recent multi-model aviation study (Holmes et al., 2011), which did not include R2. Positive and negative forcings nearly compensate each other for sustained aircraft NO_x emissions of the year 2000, leaving a positive net RF of about +0.2 mW/m² in our study.

Considering HO₂ + NO → HNO₃ increases the effects of aircraft NO_x emissions on [O₃] and [OH]. $RF_{O_3}^{short}$ is primarily determined by the absolute ozone perturbation due to aviation NO_x. Essentially the same absolute [NO_x] perturbation increases [O₃] more in the regimes with R2 than in the one without. The long lived methane-related forcings $RF_{CH_4}^{long}$, $RF_{O_3}^{long}$ and $RF_{H_2O}^{long}$ are determined by relative methane lifetime changes, and thus by the relative perturbations of OH concentrations. Lower background [OH] due to R2 directly results in enhanced radiative forcing, even for the same absolute [OH] perturbation. However, [OH] increases more in response to aircraft [NO_x] emissions, when the HNO₃ forming channel is considered, thus additionally pronouncing $RF_{CH_4}^{long}$, $RF_{O_3}^{long}$ and $RF_{H_2O}^{long}$ in sensitivity blocks with R2. All in all the negative forcings are more sensitive to the intro-

¹ [] is used as an abbreviation for „mixing ratio“ of the compound in brackets

duction of $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ than the positive short-lived ozone forcing (Figure 1). The net forcing from aviation NO_x effects decreases to -1.6 mW/m^2 in the regime with $k_2(p, T)$, and to -12.1 mW/m^2 in the one with $k_2(p, T, c_{\text{H}_2\text{O}})$.

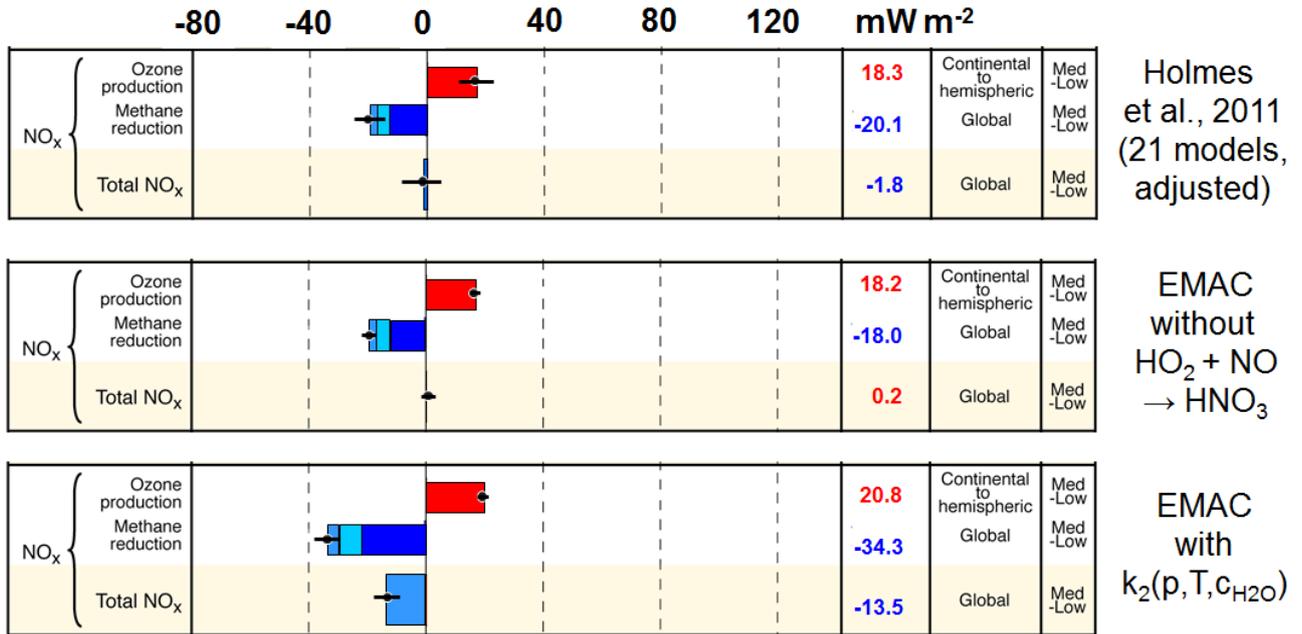


Figure 1: Radiative forcing contributions from aviation NO_x in a recent multi-model study (top), in a pair of EMAC simulations without the HNO_3 forming channel of $\text{HO}_2 + \text{NO}$ (middle), and when considering that reaction (bottom). Colors mark the different forcing components: $\text{RF}_{\text{O}_3}^{\text{short}}$ (red), $\text{RF}_{\text{CH}_4}^{\text{long}}$ (dark blue), $\text{RF}_{\text{O}_3}^{\text{long}}$ (medium blue), $\text{RF}_{\text{H}_2\text{O}}^{\text{long}}$ (light blue). Stratospheric adjusted $\text{RF}_{\text{O}_3}^{\text{short}}$ was calculated directly from the perturbations of the ozone field due to aviation NO_x . The forcings related to methane reduction were derived from perturbations of hydroxyl radical, assuming sustained aviation NO_x emissions of the year 2000. The blue bar at the bottom of each panel illustrates the net radiative forcing from all components. The values of Holmes et al. (2011) were linearly scaled to aircraft NO_x emissions of 0.85 Tg(N)/year , and $\text{RF}_{\text{H}_2\text{O}}^{\text{long}}$ (not considered by Holmes et al., 2011) was calculated from their $\text{RF}_{\text{CH}_4}^{\text{long}}$. Details of the calculations and the error bars are discussed in Gottschaldt et al. (2013).

4 CONCLUSIONS

Considering the regime with $k_2(p, T, c_{\text{H}_2\text{O}})$ to be the most likely one, according to this study, aircraft NO_x emissions are likely to cool the Earth. This tentative conclusion has potentially important implications for strategies, which aim to mitigate aviation RF by NO_x reduction or even trade less NO_x against more CO_2 emissions. We note three effects that might be interesting for strategies, which aim to mitigate aviation RF by changing the emission location: (i) Most aircraft NO_x emissions occur in the UTLS of NH mid-latitudes, while R2 impacts most in the tropical UTLS. Emitting more NO_x in latitude-altitude regions where R2 is more/less important would likely increase/decrease the effects on $[\text{O}_3]$ and $[\text{OH}]$, thereby changing the net forcing. (ii) The current aircraft fleet flies close to the altitude where the $[\text{OH}]$ response to NO_x emissions changes sign. Flying only a little bit higher might drastically reduce OH-induced cooling RF effects. (iii) $\text{RF}_{\text{O}_3}^{\text{short}}$ is concentrated in NH mid-latitudes and perturbations take full effect within weeks, while the methane related forcings act globally on a decadal time scale. The time lag between $\text{RF}_{\text{O}_3}^{\text{short}}$ and methane effects also implies that the short-lived positive forcing becomes more important for increasing air-

craft NO_x emissions, while the long-lived negative forcings would dominate for decreasing emissions.

However, further research is necessary before any recommendation regarding aircraft NO_x emission reduction can be made. Considering the NMHC oxidation mechanism recently introduced by Taraborrelli *et al.* (2012) might increase the $[\text{OH}]$ background, consequently reducing aviation induced relative $[\text{OH}]$ perturbations. This would imply smaller (less negative) methane related RF components in all regimes. Some NO_x related effects are neglected in this study, e.g. formation of nitrate aerosols (Forster *et al.*, 2007), direct RF from NO_2 (Kvalevåg and Myhre, 2007), interaction of O_3 and OH perturbations with the sulphate burden (Unger *et al.*, 2006). We also did not consider plume effects in this study, which might reduce the ozone response to aviation NO_x by 10 to 25 % (Cariolle *et al.*, 2009). Furthermore the robustness of our results should be tested with different models and methodologies. Above all, further experimental work is urgently needed to consolidate parameterizations of the rate coefficient. This need includes stratospheric conditions, and measurements of the effects of humidity on reaction R2 at more than a single configuration of pressure and temperature. Currently, uncertainties associated with the HNO_3 -forming channel of the $\text{HO}_2 + \text{NO}$ reaction just propagate a considerable additional uncertainty on estimates of the radiative forcing due to aircraft NO_x emissions.

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