

**Global sensitivity of
aviation**

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Global sensitivity of aviation NO_x effects to the HNO_3 -forming channel of the $\text{HO}_2 + \text{NO}$ reaction

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Abstract

The impact of a recently proposed HNO₃-forming channel of the HO₂ + 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 HO₂ + NO → HNO₃ 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.

1 Introduction

Aircraft emissions of reactive nitrogen oxides (NO_x = NO + NO₂) peak in the upper troposphere and lower stratosphere (UTLS), and the resulting NO_x increase impacts on the radiatively active trace gases ozone (O₃), methane (CH₄) 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., 2009, 2010; Holmes et al., 2011). This judgement did not include the possible effects of the proposed HO₂ + NO → HNO₃ 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 (HO_x = HO₂ + OH) and halogen radical cycles in concert with reactions involving

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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 (Kawa et al., 1998; Penner et al., 1999; Søvde et al., 2007; Köhler et al., 2008; Fichter, 2009). 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 (Grewe et al., 1999; 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 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 (i) the uptake of HNO_3 into ubiquitous super-cooled aerosol particles, in particular in the stratosphere (Fahey et al., 1993; Schreiner et al., 1999; Voigt et al., 2000), or into ice (e.g. Voigt et al., 2006, 2007; Kärcher and Voigt, 2006), but also by (ii) the recently discovered HNO_3 -forming channel of the $\text{HO}_2 + \text{NO}$ 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 $\text{HO}_2 + \text{NO}$ forms the HOONO intermediate complex that mostly decomposes into $\text{OH} + \text{NO}_2$. A small fraction forms nitric acid, possibly involving another molecule (M).

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) in Sect. 2.3. The combinations of (R1a) with (R2a) and of (R1b) with (R2b) are two alternative formulations for the net reaction of HO_2 with NO, forming NO_2 , OH and HNO_3 . For the sake of readability, the HNO_3 forming channel in general (R2a or R2b) is denoted by (R2), whereas (R1) indicates the other channel (R1a or R1b). Likewise, k_2 refers to k_{2a} or k_{2b} , and k_1 to k_{1a} or k_{1b} .

We note that Reaction (R2) is not generally accepted yet, according to IUPAC (2008): “Although the possibility for HNO_3 formation via rearrangement of an initially formed HOONO adduct has been confirmed in the theoretical study of Zhang and Donahue (2006), further studies of the formation of HNO_3 in the title reaction are urgently required to reduce uncertainties”, and according to Sander et al. (2011): “Until the results have been confirmed by other groups and are better understood, no recommendation can be made”.

Hoor et al. (2009) already mentioned Reaction (R2) in the context of air traffic NO_x effects. Unger (2011) reported a negligible impact of (R2a) on short-lived ozone perturbations due to aviation NO_x . Søvde et al. (2011) investigated the response of ozone and methane to the difference between pre-industrial and modern emissions of ozone precursors (NO_x , CH_4 , CO, NMHC). The consideration of (R2a) affected their results, but they did not separate out the effects of NO_x emissions. In this paper 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

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Reaction (R2) that are valid in the entire range of atmospheric temperatures, pressures, and water vapour concentrations.

The paper is organized as follows: Sect. 2 describes the base model configuration and the changes to the chemical mechanism when including Reaction (R2) for sensitivity simulations. The results of the base simulation and of two sensitivity simulations with different rate coefficients are presented in Sect. 3. All three simulations were repeated with aircraft NO_x emissions switched off exclusively, to isolate the perturbations from aviation. Chemical effects of aviation NO_x are discussed in Sect. 4, and Sect. 5 deals with the corresponding radiative forcings. Finally, Sect. 6 provides a discussion of our results and the conclusions.

2 Methodology

2.1 Base model configuration, no additional HNO₃ forming channel

This study is based on the global ECHAM/MESSy Atmospheric Chemistry (EMAC) model. EMAC is a numerical chemistry and climate simulation system that includes submodels describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al., 2006). It uses the first version of the Modular Earth Submodel System (MESSy1, Jöckel et al., 2005) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5, Roeckner et al., 2003 and 2006). For the present study EMAC was applied (ECHAM5: version 5.3.01, MESSy: modified version 1.10) in the T42L90MA-resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic gaussian grid of approx. 2.8 by 2.8 degrees in latitude and longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa. The model setup comprised the submodels listed in Table 1.

Dynamics in the free troposphere (up to about 200 hPa) was nudged towards the analysed ECMWF meteorology. This results in realistic atmospheric dynamics, as was

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shown for the “S2” setup of Jöckel et al. (2006). Gravity wave forcing was treated as in S2, and clouds with a standard EMAC scheme (Sundqvist, 1978; Lohmann and Roeckner, 1996). An aerosol climatology (Tanre et al., 1984) was used for the calculation of the radiation field and other climatologies (troposphere: Kerkweg, 2005, stratosphere: H₂SO₄ from Stratospheric Aerosol and Gas Experiment – SAGE) to provide aerosol surfaces for heterogeneous chemistry. The chemical setup considered 13 heterogeneous reactions, some of them on different surface types: 11 on nitric-acid trihydrate particles, 11 on polar stratospheric ice clouds, 8 on liquid stratospheric aerosol, and one on liquid tropospheric sulphate aerosol.

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. It has been evaluated by Jöckel et al. (2006). A temperature-dependent rate coefficient,

$$k_0 = k_1 + k_2 = A \cdot \exp\left(-\frac{B}{T}\right) \quad (1)$$

was assumed for the HO₂ + NO conversion via both reaction pathways (R1 and R2). All simulations for this paper were carried out with the Arrhenius factor $A = 3.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, and activation temperature $B = 250 \text{ K}$ (Sander et al., 2003). Temperature T is in K. The base simulation had $k_1 = k_0$ for Reaction (R1). Reaction (R2) was switched off, i.e. $k_2 = 0$. The scavenging submodel accounted for 41 aqueous reactions in rain and Langmuir uptake of nitric acid on ice. The code was modified with respect to the standard version to avoid unrealistically high convective liquid and ice water contents. Compared to Tost et al. (2010), this particularly reduced uptake and subsequent removal of nitric acid in the tropical UTLS.

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. Transient biomass burning data stem from GFED 3.1 (van der Werf et al.,

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2010). Anthropogenic non-traffic emissions were taken from the inventory by Lamarque et al. (2010) in support of IPCC 5th Assessment Report. Shipping emissions are based on the same dataset, but were rescaled to the time period 1998–2007 using the scaling factors of Eyring et al. (2010). Road traffic and aircraft emissions for the year 2000 were taken from the QUANTIFY project (Lee et al., 2005; QUANTIFY, 2008). Aircraft emissions included NO_x only, emitted as 1.815 Tg NO per year. Other sources included NH_3 emissions from the EDGAR3.2FT database (van Aardenne et al., 2005), SO_2 volcanic emissions from AeroCom (Dentener et al., 2006), terrestrial DMS (Spiro et al., 1992) and biogenic emissions (Ganzeveld et al., 2006). Speciation of Non-Methane Hydro Carbons (NMHCs) was realized following von Kuhlmann et al. (2001), as described also in Hoor et al. (2009).

Online emissions of soil NO and isoprene were simulated as a function of specific meteorological conditions. Note that isoprene oxidation in the chemical mechanism used for this study does not include the recently described recycling of the hydroxyl radical (Taraborrelli et al., 2012). The implications of this simplification will be discussed later. Lightning NO_x production was parameterized following the scheme by Grewe et al. (2001), resulting in 5.5 Tg nitrogen (N) per year in all simulations of this study for the year 2001. This value is close to the observation-based estimate of 5 Tg N yr^{-1} (Schumann and Huntrieser 2007). Boundary conditions for long-lived species (CO_2 , CH_4 , N_2O , CFCs, HCFCs, Halons and H_2) were nudged to prescribed surface mixing ratios as in Jöckel et al. (2006). Finally, external fields for oceanic DMS, isoprene and ocean salinity were provided in order to simulate the exchange between ocean and atmosphere.

All simulations cover two years and were nudged to the synoptic meteorological conditions of the years 2000 and 2001. A slightly negative ENSO index (Wolter and Timlin, 2011) indicates that atmospheric dynamics was not particularly distinct in those years. Furthermore, atmospheric mixing ratios of the hydroxyl radical (OH) seem to be well buffered against interannual variability on a global scale (Montzka et al., 2011). OH will be important for the subsequent discussion. The initial chemical mixing ratios stem

from output on 31 December 1999 of a previous simulation with the chemistry mechanism as in Jöckel et al. (2006). The first year was discarded as chemical spin-up time.

All simulations shown were performed on the IBM Power6 system “Blizzard” at Deutsches Klimarechenzentrum (DKRZ Hamburg), using 4 nodes with 64 tasks each, a Rosenbrock-3 solver with the chemistry submodel MECCA1, 12 min model time step, and 5-hourly output. It took about 4.5 h real time to calculate one model month per simulation. This high computational cost was the reason for limiting the simulation period to 24 months.

2.2 Sensitivity simulations with HNO₃ forming channel, no humidity modification

These simulations differ from the base simulation in the definition of k_1 and k_2 :

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

$$k_1 = k_0 - k_2 \quad (3)$$

i.e. $k_{1a} = k_0 - k_{2a}$ or $k_{1b} = k_0 - k_{2b}$. Butkovskaya et al. (2007) proposed

$$\beta(p, T) = 0.01 \cdot \left(\frac{530}{T} + p \cdot 4.8 \times 10^{-6} - 1.73 \right) \quad (4)$$

with pressure p in Pa and T in K. Equation (4) is based on an empirical fit to laboratory data and is valid for dry conditions, in the pressure range 93–800 hPa and the temperature range 223–298 K. Consequently both reaction rates depend on temperature and pressure in this case. Brühl et al. (2007) applied Eq. (4) for atmospheric conditions up to a pressure altitude of 0.01 hPa, and concluded that it brings nitric acid in the upper atmosphere of EMAC into better agreement with MIPAS observations. We adopted Eq. (4) like Brühl et al. (2007), although Butkovskaya et al. (2009) stated that β remains uncertain at low pressure and requires further experimental work. The focus of our study is on the UTLS, which is well within the claimed validity range of Eq. (4).

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2.3 Sensitivity simulations with HNO₃ forming channel, with humidity modification

An enhancement of HNO₃ formation in the presence of water has been measured in the laboratory for the range of 0–70% relative humidity with respect to liquid water (Butkovskaya et al., 2009). The enhancement of HNO₃ formation in the presence of water vapour may be due to the formation of an H₂O·HO₂ complex:



suggesting the following chemical mechanism instead of Reactions (R1a) and (R2a):



By fitting the enhancement factor of HNO₃ formation as a function of H₂O concentration, Butkovskaya et al. (2009) derived the ratio $\gamma = k_{2b}/k_{2a}$ at 298 K and 267 hPa. Then, humidity effects can be considered as a modification of Eq. (2):

$$k_{2b} = \frac{k_0 \cdot \beta \cdot (1 + \gamma \cdot \alpha)}{(1 + \beta) \cdot (1 + \alpha)} \quad (5)$$

Butkovskaya et al. (2009) infer that the effect of water vapour on HNO₃ formation depends only weakly on pressure in the range of 133 to 933 hPa, while the temperature dependence is unknown (LeBras, 2011). A constant factor $\gamma = 42$ (Adams, 1979; Butkovskaya et al., 2009) is assumed in the simulations featuring Reaction (R2b) (and thus k_{2b}). Equation (5) allows us to build on the representation of (R1a) and (R2a) in the code, instead of explicitly implementing Reactions (R3), (R1b) and (R2b). The term

$$\alpha = c_{\text{H}_2\text{O}} \cdot K_{\text{eq}} \quad (6)$$

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depends on the equilibrium coefficient (in cm^3)

$$K_{\text{eq}} = 6.6 \times 10^{27} \cdot T \cdot \exp\left(\frac{3700}{T}\right) \quad (7)$$

of Reaction (R3) (Kanno et al., 2006) and on the molecular concentration of water, $c_{\text{H}_2\text{O}}$ in cm^{-3} .

The total rate coefficient $k_0 = k_1 + k_2$ of the $\text{HO}_2 + \text{NO}$ reaction does not depend on $c_{\text{H}_2\text{O}}$ in this formulation, consistent with Bohn and Zetzsch (1997).

2.4 Interpretation of sensitivity simulations and methodological limitations

Six simulations will be discussed in this study that all share the same meteorology, but differ in their atmospheric chemistry (Table 2). The **B**ase simulation without (R2), and with **A**ircraft emissions (BA) serves as reference for the comparison to simulations DA (**D**ry = rate coefficient for Reaction (R2a) according to Eq. (2), with **A**ircraft emissions) and WA (**W**et = rate coefficient for R2b with humidity modification according to Eq. (5), with **A**ircraft 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) are discussed to isolate the effects of (R2) on atmospheric HNO_3 , HO_x , NO_x and O_3 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 (**B**ase 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 .

Sensitivity method: Considering aviation NO_x as a small chemical perturbation, the deviations of a simulation with aircraft NO_x emissions from one without are evaluated. The response to the perturbation may weakly depend on background NO_x mixing ratios. Aircraft NO_x emissions change the NO_x background and therefore affect their own

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effects. Furthermore, buffering in the chemical system may partially compensate the effects of switched-off emissions (Grewe et al., 2012). Thus the sensitivity method is inappropriate for source attribution, but well suited to evaluate the atmospheric impact of changed emissions (Grewe et al., 2010). We refer to the differences between otherwise identical simulations with and without aviation NO_x as “effects of aviation NO_x ”. The term is ambiguous though and may have a different physical meaning with other methodologies, e.g. tagging. Since we only apply the sensitivity method, “effects of . . .” is still used throughout the paper for brevity. The sensitivity method shows the net response of the chemical system to a perturbation, including all chemical nonlinear and buffering effects without discrimination. It is discussed for sensitivity blocks ΔB , ΔD and ΔW how each hypothetical atmosphere would change without aircraft NO_x emissions.

QCTM mode: This study focuses on chemical effects, but not on the potential feedbacks between perturbed chemistry and dynamics. Small chemical differences cause a divergence of model dynamics in a coupled system. In such cases, the strategy to compare a base simulation with a chemically modified sensitivity simulation would require very long integration times to find a statistically significant chemical signal, due to the dynamically induced “noise”. For small perturbations this might not be possible at all. Therefore 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. Model configuration here is largely similar to the one used for Deckert et al. (2011). The same predefined climatologies (for radiatively active gases, nitric acid and chemical water vapour tendencies) were used in all simulations to calculate chemical feedbacks on model dynamics. 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. Statistical analyses to extract a chemical signal are therefore not necessary. Model meteorology and emissions in the simulations do both depend on time though. However, a statistical evaluation of interannual variability of the chemical

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signal is not possible for one simulation year. At the most, variation throughout the year may give some indication of the sensitivity of the chemical signal to different states of the background atmosphere.

The analysis of chemical signals from QCTM simulations neglects any potential differences that might occur in response to the feedbacks from chemical perturbations on dynamics, and back from dynamics on atmospheric chemistry. However, aviation induced chemical perturbations are too small to modify meteorology enough to change the chemistry response (Grewe et al., 2002).

3 Effects of the $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ reaction on atmospheric chemistry

In this section it will be discussed how Reactions (R2a) or (R2b) (summarized as R2) affect background atmospheric chemistry, without considering aviation effects. Two simulations (DA, WA) with different reaction rate coefficients for (R2) are compared to a reference simulation (BA) without (R2). All three simulations have identical emissions (including aviation) and meteorology.

The left column of Fig. 1 shows the 12-month average of zonal mean mixing ratios of HNO_3 , HO_x , NO_x and O_3 for simulation BA. Mixing ratios of trace gas X are denoted [X] in the following text. These plots serve as a reference when interpreting plots of absolute or relative deviations in the sensitivity simulations. Absolute and relative deviations of annual zonal mean $[\text{HNO}_3]$, $[\text{NO}_x]$, $[\text{OH}]$, $[\text{HO}_2]$ and $[\text{O}_3]$ of WA with respect to BA are shown in the middle and right columns of Fig. 1, respectively. Differences to simulation DA will be discussed in the text but not shown.

In an attempt to check if any of the chemical regimes yields unrealistic results, $[\text{HNO}_3]$, $[\text{NO}_x]$, $[\text{CO}]$ and $[\text{O}_3]$ 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 (see Supplement). Neither the regime without the HNO_3 -forming channel of $\text{HO}_2 + \text{NO}$, nor the two regimes with it can be ruled out according to this test.

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3.1 Reaction rates

Figure 2 (left) shows the cumulative rate of Reactions (R1a) and (R2a). It peaks in the tropics between 10 and 1 hPa, at $0.94 \text{ pmol mol}^{-1} \text{ s}^{-1}$. There is also a smaller local maximum in the tropical UTLS. (R2a) is favoured at low temperatures and high pressures. This causes a local maximum in the cold spot of the tropical UTLS, where about 1 % of the $\text{HO}_2 + \text{NO}$ reaction proceed via the HNO_3 forming channel (Fig. 2, middle). NO_x is reused in the catalytic cycle involving (R1). Each time a NO_x molecule passes through this cycle, it has a small chance of getting lost via (R2). The small branching ratio will consequently be amplified by the cycling. Humidity is highest near the surface, decreasing by nearly 4 orders of magnitude towards the UTLS. This makes the humidity modification (Eq. 5) most important in the troposphere, where up to 5.5 % of the $\text{HO}_2 + \text{NO}$ reaction form HNO_3 (Fig. 2, right). Humidity effects might be slightly underestimated, because all water vapour leading to relative humidity higher than 100 % is immediately transferred into clouds.

In the following $[\text{HNO}_3]$, $[\text{HO}_x]$, $[\text{NO}_x]$ and $[\text{O}_3]$ in simulations DA and WA are compared to BA, isolating the impact of (R2) on background mixing ratios of those species. A more detailed analysis of the spatial and temporal patterns for the relevant reaction rates (rate coefficients and concentration of educts) would be necessary to fully understand the observed sensitivity patterns. This might be warranted once reaction (R2) and its rate coefficient are fully accepted.

3.2 Effects of the HNO_3 -forming channel on $[\text{HNO}_3]$ background

Reaction (R2) is the only major source of HNO_3 above about 40 km, putting the relative effect off the scale at altitudes with near zero background $[\text{HNO}_3]$ (Fig. 1, 1st row). However, absolute deviations from BA are small there. They have a maximum at 10 hPa, where high absolute $\text{HO}_2 + \text{NO}$ reaction rates meet high HNO_3 background mixing ratios. This is an indication for more effective HNO_3 loss processes in the altitude range of maximum HNO_3 production via (R2). There is a local $[\text{HNO}_3]$ increase in the tropical

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UTLS, due to the maximum of the branching ratio. $[\text{HNO}_3]$ increases by more than 50% there in the dry case, confirming the results of Cariolle et al. (2008). The local maximum is even more pronounced when considering humidity. While directly producing HNO_3 , Reaction (R2) also indirectly reduces the educts for HNO_3 formation via $\text{NO}_2 + \text{OH}$. The latter effect may prevail in the tropical lower troposphere and at an altitude of about 14 km at high latitudes, leading to lower HNO_3 mixing ratios than in the reference simulation. There is a strong seasonal dependence of the HNO_3 response to (R2) (not shown), with reductions at high latitudes only occurring during autumn and spring in the respective hemispheres. Please note that the above discussion refers to HNO_3 calculated online by the chemistry submodel MECCA1, while all simulations used the same HNO_3 offline climatology for partitioning in polar stratospheric clouds (PSCs). This inconsistency in PSC chemistry must be accepted in order to use the QCTM mode.

3.3 Effects of the HNO_3 -forming channel on $[\text{HO}_x]$ background

The $[\text{HO}_x]$ response to (R2b) is dominated by $[\text{HO}_2]$, varying from -0.18 to $+0.38 \text{ pmol mol}^{-1}$ in DA and by $\pm 1.1 \text{ pmol mol}^{-1}$ in WA, both with respect to BA (Fig. 1, 2nd row). HO_2 mixing ratios decrease in WA in the lower troposphere, in the tropics more than at high latitudes. Above is a change of sign in the response, followed by a local $[\text{HO}_2]$ increase, reaching more than 50% in the tropical UTLS. Although positive and negative perturbations are higher in WA, the magnitude of the negative perturbation increases more, due to higher humidity at lower altitudes. $[\text{HO}_2]$ changes are close to zero for the next 14 km, to rise again locally at 10 hPa. Above is another change of sign and $[\text{HO}_2]$ decreases again throughout the uppermost part of the atmosphere. This response pattern is similar for DA, with nearly identical altitudes of zero net response, but lower magnitude in the troposphere. Relative $[\text{HO}_2]$ changes are most pronounced in the troposphere, where there is little background $[\text{HO}_2]$. Primarily the HNO_3 producing channel of $\text{HO}_2 + \text{NO}$ weakens the OH producing channel of this

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reaction. Therefore [OH] decreases in DA and WA all over, by more than 0.1 pmol mol⁻¹ at 10 hPa across all latitudes (Fig. 1, 3rd row). This coincides with the maximum absolute impact of Reaction (R2) on [HNO₃] and NO_x. There is a local maximum of absolute [OH] decrease in the tropical UTLS, matching the local maximum of [HNO₃] deviations. The local maximum in DA reaches only about 50 % of the corresponding feature in WA. Relative [OH] deviations from BA match those of [NO_x]. [OH] decreases by more than 15 % throughout the troposphere in WA. Reaction (R2) shifts the OH/HO₂ ratio towards HO₂ (Fig. 4, 2nd row). This effect is most pronounced in the upper troposphere, reaching 29 % in DA and 57 % in WA, both compared to BA.

Following Lawrence et al. (2001), the global OH burden for the tropospheric domain with a climatological tropopause is calculated as

$$\rho = 300 - 215(\cos(\phi))^2, \quad (8)$$

where ρ is pressure in hPa and ϕ is latitude. The OH concentrations in Table 3 are annual mean values, computed from global monthly mean concentrations (c_{OH}):

$$\langle c_{\text{OH}} \rangle = \frac{\sum (w \cdot [\text{OH}] \cdot c_{\text{air}})}{\sum w}, \quad (9)$$

where $\langle \rangle$ denotes the global spatial integral, the sum \sum is over all grid cells in the tropospheric domain, [OH] is a 3-D field of monthly mean OH mixing ratios, c_{air} is the corresponding 3-D field of the concentration of air (in cm⁻³), and w is a 3-D field of weighting factors. Weighting with the reaction rate coefficient k_{CH_4} of



is most relevant to this study, because it determines the methane related radiative forcing terms from aviation NO_x. This reaction is responsible for about 90 % of the global methane breakdown, and accounts for nearly all methane losses in the troposphere (Stenke et al., 2012). Values of the global OH concentration critically depend on the

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weighting factor and on the domain used for the computation, hampering comparisons between different studies (Lawrence et al., 2001). In order to facilitate comparability, results with grid cell air mass as weighting factor are also provided.

The global OH concentrations ($\langle c_{\text{OH}}^{\text{mass}} \rangle$, $\langle c_{\text{OH}}^k \rangle$) of simulation BA are higher than in other modelling studies (Spivakovsky et al., 2000; Jöckel et al., 2006, 2010) that also did not consider (R2). Spivakovsky et al. (2000) utilize a top-down approach, starting from observations of precursors for HO_x-NO_x photochemistry. The global mean OH concentration is then derived from simulations with an accuracy of $\pm 15\%$. BA falls within this uncertainty range. Jöckel et al. (2006) suggest that the differences to Spivakovsky et al. (2000) may lay in the representation of convection (via lightning NO_x and transport of HO_x precursors), or in missing heterogeneous chemical processes. Simulation BA was done with a newer version of EMAC and different emissions, but with an otherwise similar setup as in Jöckel et al. (2006). They prescribed biomass burning CO emissions of 452.36 Tgyr⁻¹, simulations of this study had only 254.79 Tgyr⁻¹. The reaction CO + OH → CO₂ + H accounts for approximately 41 % of all tropospheric OH losses (von Kuhlmann et al., 2003). Biomass burning CO emissions in the simulation of Jöckel et al. (2010) ranged from 335.77 to 588.39 Tgyr⁻¹, corresponding to a variation of -21 % to +38 % for the period 1997 to 2006. Montzka et al. (2011) show $\langle c_{\text{CO}}^{\text{mass}} \rangle$ variations of -3.5 % to +9 % for that simulation, and $\langle c_{\text{OH}}^{\text{mass}} \rangle$ is roughly anticorrelated, with +3 % to -2.5 %. We have not tested the sensitivity of global [OH] to CO emissions in our model, but lower CO mixing ratios might at least partially explain the higher OH levels. An update in the scavenging parameterisation might also have contributed to the differences between EMAC simulations for previous studies (Jöckel et al., 2006, 2010) and the current study.

Reaction (R2) decreases $\langle c_{\text{OH}} \rangle$ by about 10 % in DA and by 33 % in WA, both with respect to BA. Are the OH concentrations in DA and WA realistic? Values based on simulations using chemical mechanisms without (R2) may no longer serve as a benchmark here. Direct observations are not suitable for deriving a global climatology or average, due to the short lifetime of OH and spatial variability of [OH]. Indirect estimates

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of (c_{OH}) are based on measurements of longer lived trace gases that are removed from the atmosphere mainly through reactions with OH. Spivakovsky et al. (2000) verify their results with measurements of CH_3CCl_3 , HCFC-22, and others. Global mean OH concentrations derived from the mass balance of these species have an uncertainty of -20% to $+28\%$ with respect to their preferred value (Table 3). BA and DA are within this range, WA is just outside.

Although only important close to the surface, the recently discovered OH recycling during NMHC oxidation increased global $\langle c_{\text{OH}}^{\text{mass}} \rangle$ from 1.08 to $1.22 \times 10^6 \text{ cm}^{-3}$ in a simulation with the EMAC model (Taraborrelli et al., 2012). Only one simulation year has been evaluated to obtain these numbers, but little interannual variability is expected (Montzka et al., 2011). The new chemical mechanism has not yet been available for this study, but assuming a similar impact of 13% in our simulations would bring $\langle c_{\text{OH}}^{\text{mass}} \rangle$ to 1.44, 1.27 and 0.96 cm^{-3} in BA, DA and WA, respectively. Then all three simulations would be within the range given by Spivakovsky et al. (2000), i.e. compatible with observations.

Note that the combination of the new NMHC oxidation mechanism (Taraborrelli et al., 2012) and (R2) including humidity effects (WA) might yield the most realistic global OH concentration.

3.4 Effects of the HNO_3 -forming channel on methane lifetime with respect to background [OH]

Methane is a long-lived greenhouse gas, playing an important role in global climate change. Top-down methods for the quantification of methane fluxes are constrained mainly by uncertainties in the sink estimates and the choice of lifetime used in the mass balance calculations (Denman et al., 2007). The lifetime of a gas is essentially its atmospheric mass burden divided by the loss rate. Reaction (R4) mainly determines the lifetime of methane (τ_{CH_4}), which is very sensitive to modifications of OH mixing ratios and distributions. The above uncertainties in [OH] propagate considerable uncertainties

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on τ_{CH_4} with respect to Reaction (R4) ($\tau_{\text{CH}_4}^{\text{OH}}$). Recent model based estimates range from $9.72_{-2.81}^{+5.33}$ yr (Shindell et al., 2006), $9.9_{-3.0}^{+5.2}$ yr (Stevenson et al., 2006)¹, or 7.23 to 11.43 yr (Hoor et al., 2009). These values are only comparable to simulation BA, because none of those previous works considered (R2). Independent estimates of $\tau_{\text{CH}_4}^{\text{OH}}$ are based on methane and methyl chloroform (MCF = CH_3CCl_3) observations, giving $9.6_{-1.6}^{+2.4}$ yr (Denman et al., 2007)² or 11.2 ± 1.3 yr (Prather et al., 2012). Thus it may serve as a reference for simulations with and without (R2).

Methane lifetime was calculated according to Lawrence et al. (2001), with

$$\tau_{\text{CH}_4}^{\text{OH}} = \frac{\sum m_{\text{CH}_4}}{\langle c_{\text{OH}}^k \rangle \cdot \sum (k_{\text{CH}_4} \cdot m_{\text{CH}_4})} \quad (10)$$

for the tropospheric domain defined by Eq. (8). The sums are over all grid boxes in the domain, m_{CH_4} is the methane mass per grid cell, k_{CH_4} is the reaction rate coefficient of (R4), and $\langle c_{\text{OH}}^k \rangle$ is the global mean concentration of OH (Eq. 9), weighted by k_{CH_4} . Before calculating the annual mean, Eq. (9) is evaluated with monthly mean 3-D fields of k_{CH_4} and m_{CH_4} , and monthly mean values for $\langle c_{\text{OH}}^k \rangle$. About a decade of simulation time would be needed for methane mixing ratios to adjust to a perturbation, while the short-lived [OH] almost immediately adjusts. The actual m_{CH_4} from each simulation entered Eq. (9). However, using methane from BA would reduce $\tau_{\text{CH}_4}^{\text{OH}}$ in DA and WA by negligible 0.1 yr, compared to the values in Table 3.

¹ $\tau_{\text{CH}_4}^{\text{OH}}$ was not given by Stevenson et al. (2006). The given value is based on their scenario S1, minimum, mean and maximum for all models, a soil sink for methane of 30 Tgyr^{-1} , and a stratospheric sink of 40 Tgyr^{-1} .

²This value follows from a global methane burden of 4929 Tg , and a loss due to (R4) of $511 \pm 103 \text{ Tgyr}^{-1}$.

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Simulation BA is on the low side of estimates for $\tau_{\text{CH}_4}^{\text{OH}}$ (7.6 yr, Table 3). Methane lifetime increases to 8.4 yr in DA, and to 11.4 yr in BA. All values are in the range of other estimates. Uncertainties in the rate coefficient of (R4) impose uncertainties of up to -30% and $+44\%$ on methane lifetime in the simulations of this study, though the corresponding uncertainties of $\langle c_{\text{OH}}^k \rangle$ are small (see Supplement). Methane lifetime changes moderately, if an upper domain boundary of 100 hPa is considered instead of the climatological tropopause (Eq. 8), because (R4) is most important in the troposphere (Stenke et al., 2012). The rate coefficient formulation of Atkinson (2003), as used in this study, is in between the recommendations of IUPAC (2007) and Sander et al. (2011). However, the recommended temperature dependent rate coefficients ($k_{\text{CH}_4}^{\text{best}}$) of the different studies agree remarkably well (Supplement, Fig. S5).

The methane lifetime change of 10.5 % from BA to DA is in good agreement with Søvde et al. (2011), who found 10.9 % for a similar comparison with a different model. Cariolle et al. (2008) reported only about 5 %. Müller (2011) found $\tau_{\text{CH}_4}^{\text{OH}} = 7.7$ yr in a simulation without (R2), 8.8 yr when considering (R2) similar to DA, and 9.8 yr for the equivalent to simulation WA. Considering humidity in the rate coefficient of (R2) has a bigger effect in this study. More details about the methodology of Müller (2011) would be needed for an attempt to pinpoint the causes of this difference. Taraborrelli et al. (2012) reported a decrease of methane lifetime from 8.02 yr to 7.2 yr when taking into account OH recycling during NMHC oxidation. Assuming a similar 10 % reduction of methane lifetime in simulations BA, DA and WA would bring $\tau_{\text{CH}_4}^{\text{OH}}$ in WA closest to the observation based value of Denman et al. (2007). WA is the only regime consistent with the MCF-derived $\tau_{\text{CH}_4}^{\text{OH}}$ of Prather et al. (2012), with and without 10 % reduction.

3.5 Effects of the HNO_3 -forming channel on $[\text{NO}_x]$ background

As for $[\text{HNO}_3]$ and $[\text{OH}]$, the biggest absolute effects on annual zonal mean $[\text{NO}_x]$ manifest themselves at about 10 hPa. Compared to BA, $[\text{NO}_x]$ decreases by up to

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251 pmol mol⁻¹ in DA and by up to 245 pmol mol⁻¹ in WA (Fig. 1, 4th row). There is an altitude of less [NO_x] changes around 70 hPa, followed by a region of again pronounced [NO_x] reduction at 100 hPa in the tropics. Humidity effects are bigger there, with the maximum decrease above the equator being 60 pmol mol⁻¹ in DA and 100 pmol mol⁻¹ in WA. [NO_x] is reduced throughout the troposphere, except between 30° N and 70° N, near emission sources at the ground. This indicates a non-monotonic response, depending on NO_x background mixing ratios. The [NO_x] response to the introduction of (R2) becomes positive at NO_x mixing ratios higher than about 200 pmol mol⁻¹ near the ground, both in DA and WA. The region of zero response is shifted to NO_x mixing ratios of 100 pmol mol⁻¹ at 750 hPa in DA, but not shifted in WA. Thus (R2) seems to modify the chemical response function not only quantitatively, but also qualitatively. Peak [NO_x] perturbations in the planetary boundary layer lie between -4 and +20 pmol mol⁻¹ in DA, and between -18 and +79 pmol mol⁻¹ in WA. The minimum and maximum extreme values are located at 20° N and 52° N, respectively. There is another region of zero net [NO_x] change around 3 hPa, corresponding to the highest NO_x background concentrations.

The relative NO_x effect most pronounced in the troposphere, reaching -35% in DA and -60% in WA. It is skewed towards the less polluted Southern Hemisphere, as noted already by Cariolle et al. (2008).

In addition to the overall NO_x decrease, Reaction (R2) shifts the NO/NO₂ ratio towards NO throughout the troposphere and UTLS (Fig. 4, 1st row). The lower NO_x background created by (R2) seems to slow down OH- and NO₂-formation by (R1), because the OH/HO₂ ratio is also being shifted towards the educt of (R2).

The response of atmospheric chemistry to aircraft NO_x emissions depends on NO_x background mixing ratios (Ehhalt and Rohrer, 1994). This nonlinear effect will ultimately impact on estimates of radiative forcing due to aviation NO_x, independent of the causes for the modified NO_x background.

3.6 Effects of the HNO₃-forming channel on [O₃] background

As shown in the last row of Fig. 1, the decrease in NO_x near 10 hPa corresponds to increased ozone mixing ratios in DA and WA. However, the effect of (R2) on [O₃] changes sign in this sensitivity block at altitudes of 14 km above the poles and 26 km above the equator. Reaction (R1) produces NO₂, and the subsequent photolysis of NO₂ is a major source of O₃ in the troposphere. NO_x mixing ratios decrease due to Reaction (R2), and the NO/NO₂ ratio is additionally shifted towards NO. Both effects result in less ozone production via NO₂ photolysis. Ozone production depends nonlinearly on NO_x levels, and the [NO_x] perturbation due to (R2) is superimposed on the vertical background [NO_x] gradient. The local [NO_x] minimum at 100 hPa in the tropics might translate into increased ozone production (Lin et al., 1988; Wu et al., 2007), leading to a less negative ozone response than at the altitude of 22 km. There is a monotonic ozone response to [NO_x] perturbations at aircraft flight altitudes and the reduced [NO_x] background in DA and WA moves the chemical system away from the nonlinear region. Transport is superimposed on these chemical effects: compared to a simulation without (R2), there is less ozone in the tropical upwellings, and more ozone in the downwellings at high latitudes. Ozone decreases below the altitude of zero net change throughout the troposphere, by more than 10 nmol mol⁻¹ at 9 km at all latitudes in WA. The tropospheric ozone decrease reaches only 4 nmol mol⁻¹ at all latitudes in DA, and more than 10 nmol mol⁻¹ just in a small spot in the tropics. The relative impact on ozone is most pronounced in the troposphere, where background concentrations are low. It reaches -11 % in DA and -32 % in WA. Following the NO_x response to (R2), the ozone effect is larger in the Southern Hemisphere. There is no big difference between the stratospheric ozone effects in DA and WA. Mixing ratios increase by up to 1.5 % there.

Butkovskaya et al. (2009) note the difficulty of quantifying the importance of the humidity effect on the reaction rate coefficient of (R2) at higher altitudes. Water concentration progressively decreases with altitude, which is partially compensated by the

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increase of K_{eq} due to decreasing temperature (Eq. 7, Fig. 2). Ozone increases by up to 94 nmol mol^{-1} in the tropical stratosphere in DA, but only by 89 nmol mol^{-1} in WA. According to Eq. (5) humidity should always enhance the effects of (R2) (given $\alpha > 0$). Possibly the humidity effect is negligible in that altitude, and enhanced ozone loss from below the zone of no change in zonal mean mixing ratios prints through via atmospheric transport.

Higher atmospheric density in the troposphere over-compensates higher absolute ozone increases in the stratosphere. Thus the global annual mean ozone column decreases, from 316 DU in simulation BA, by 0.5% in DA, and by 1.8% in WA (Table 2). A comparison to TOMS total ozone (http://toms.gsfc.nasa.gov/ftpdata_v8.html, not shown) revealed a slight high bias of model O_3 , as already noted by Jöckel et al. (2006). Compared to their coupled simulations, using a HNO_3 climatology for decoupling tends to average out individual PSC events, and impairs denitrification and ozone destruction further. The effects of (R2) act in the right direction.

4 Chemical effects of aviation NO_x

In this section the effects of identical aircraft NO_x emissions in three different atmospheric chemical regimes are isolated. The three background regimes were discussed in the previous section. Three different reference cases without aircraft NO_x emissions are introduced (Table 2: B0, D0, W0), one for each regime. Here each sensitivity block refers to a pair of simulations within the same chemical regime: ΔB refers to BA versus B0, ΔD to DA versus D0, and ΔW to WA versus W0. This notation applies to absolute and relative deviations between the two simulations of each pair.

4.1 Chemical effects of aviation NO_x on $[\text{NO}_x]$

The plots for aviation effects (Fig. 3a and 3b) are cut at the 50 hPa level to zoom into the altitude range where aircraft fly. The colour bar does not cover the full range of values

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in each picture to improve the visibility of the interesting features. The subsequent discussion refers to annual zonal mean values for the simulation year 2001.

Aircraft NO_x emissions peak in the mid-latitudes of the Northern Hemisphere (NH), between 8 and 12 km altitude. Compared to simulation B0, annual zonal mean $[\text{NO}_x]$ increases in simulation BA by up to 66 pmol mol^{-1} due to aircraft emissions. Reaction (R2) generally decreases $[\text{NO}_x]$ in the simulations, which also affects NO_x from aviation. Thus $[\text{NO}_x]$ increases slightly less when Reaction (R2) is included, by up to 64 pmol mol^{-1} in sensitivity block ΔD , and only 61 pmol mol^{-1} in ΔW (Fig. 3a, 1st column). In contrast, the relative effect of aviation NO_x increases when background NO_x is lower due to Reaction (R2) (Fig. 3b, 1st column). It reaches 73 % for sensitivity block ΔB , 83 % for ΔD , and 97 % for ΔW . The lowering effect of (R2) on $[\text{NO}_x]$ affects the background chemistry more than the perturbation by emissions.

In northern mid latitudes near the ground, aircraft NO_x emissions decrease NO_x mixing ratios in all sensitivity blocks. This corresponds to the only tropospheric region, where Reaction (R2) increases $[\text{NO}_x]$ (as discussed in Sect. 3.5).

4.2 Chemical effects of aviation NO_x on $[\text{O}_3]$

Ozone mixing ratios in the troposphere rise in response to the additional NO_x from aviation, by up to $4.2 \text{ nmol mol}^{-1}$, $4.7 \text{ nmol mol}^{-1}$ and $5.4 \text{ nmol mol}^{-1}$ for ΔB , ΔD , and ΔW , respectively (Fig. 3a, 3rd column). The annual mean peak ozone perturbation in sensitivity block ΔB agrees well with those found by other studies: $4.5 \text{ nmol mol}^{-1}$ (Fichter, 2009), about 4 nmol mol^{-1} (Grewe et al., 2002), $4.3 \text{ nmol mol}^{-1}$ (Gauss et al., 2006), $2.8 \text{ nmol mol}^{-1}$ (Hoor et al., 2008), 6 to 9 nmol mol^{-1} (Koehler et al., 2008).

Relative effects on ozone are additionally pronounced when (R2) is considered, because (R2) lowers $[\text{O}_3]$ in the troposphere. Ozone mixing ratios increase by up to 3.6 % in ΔB , 3.9 % in ΔD , and 4.7 % in ΔW (Fig. 3b, 3rd column). Absolute and relative ozone perturbations are transported further, and are thus not as localized as the shorter lived $[\text{NO}_x]$ perturbations. There are regions in the stratosphere, where ozone mixing ratios

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decrease in response to aviation NO_x (Fig. 3a). This is expected from photochemical considerations (Sect. 1), but difficult to interpret here. There are no direct aircraft NO_x emissions from the inventory into the altitude range of negative ozone response. Ozone perturbations in Fig. 3 show the integrated results of photochemistry and the transport of species with different lifetimes. The annual global mean ozone burden increases due to aviation NO_x in all sensitivity blocks, but most in ΔW (Table 2). This is consistent with the known increase in ozone production as $[\text{NO}_x]$ decreases (Lin et al., 1988; Wu et al., 2007).

4.3 Chemical effects of aviation NO_x on $[\text{HO}_x]$

The relative $[\text{HO}_2]$ response (not pictured) is nearly identical in ΔB , ΔD and ΔW , reaching -23% . This corresponds to respective absolute peak perturbations of -0.43 , -0.45 and $-0.48 \text{ pmol mol}^{-1}$ in the region of maximum aviation NO_x . Below an altitude of about 7 km the $[\text{HO}_2]$ perturbation becomes positive ($\sim 0.07 \text{ pmol mol}^{-1}$ in ΔB , ΔD , ΔW). The crossover between positive and negative response to aviation NO_x occurs at the same altitude as in the background response to (R2) (Fig. 1), but with reversed signs. Thus the pattern of $[\text{HO}_2]$ perturbations in Fig. 1 also primarily reflects the inherent response of the photochemical system to $[\text{NO}_x]$ perturbations, which were caused by the introduction of Reaction (R2).

Mixing ratios of the hydroxyl radical, $[\text{OH}]$, increase in the troposphere in response to aircraft NO_x emissions. The peak perturbation in ΔB is 19 fmol/mol or 17% . Additional NO_x in the troposphere enhances (R1), shifting the $[\text{OH}]/[\text{HO}_2]$ ratio towards $[\text{OH}]$. Furthermore, OH production is increased, due to additional O_3 photolysis and the subsequent reaction with water vapour. Note a small spot of decreasing $[\text{OH}]$ at high northern latitudes, just above the tropopause. The $[\text{OH}]$ response to aviation NO_x changes sign in the same altitude in all sensitivity blocks, regardless of different NO_x and HO_x background mixing ratios. Only the meteorology is identical in all simulations, and there is the same emission perturbation in all sensitivity blocks. Thus pressure- and

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temperature dependence of reaction rate coefficients in the base photochemical mechanism (i.e. independent of R2) dominate the non-monotonic response of [OH].

Both, absolute and relative effects on [OH] are stronger, when (R2) is considered: peaking at 20 fmol/mol (20 %) for ΔD , and 21 fmol/mol (25 %) for ΔW (Fig. 3a, b, 2nd column). Perturbation patterns for the OH concentration, c_{OH}^k , look similar to [OH] perturbations in Fig. 3. Peak values are $0.167 \times 10^6 \text{ cm}^{-3}$ (18 %) for ΔB , $0.169 \times 10^6 \text{ cm}^{-3}$ (20 %) for ΔD , and $0.173 \times 10^6 \text{ cm}^{-3}$ (25 %) for ΔW . The altitude of the peak [OH] perturbation is lower than that of $[\text{NO}_x]$, but higher than that of $[\text{O}_3]$. This reflects the superposition of ozone and NO_x perturbations, both interacting with OH.

Global annual mean OH concentrations (Eq. 9) for the region below 50 hPa are given in Table 4. About a decade of simulation time would be needed for methane mixing ratios to adjust to a perturbation. The corresponding methane lifetimes were calculated according to Eq. (10), always taking $[\text{CH}_4]$ from simulation BA. Using the same distribution for all sensitivity blocks is methodologically cleaner for analysing the differences between them, although using other $[\text{CH}_4]$ would change $\tau_{\text{CH}_4}^{\text{OH}}$ only by $\sim 1\%$. Methane lifetime in Table 4 was derived from monthly mean values. Aviation NO_x increases $\langle c_{OH}^k \rangle$ in ΔD more than in ΔB , but most in ΔW (Table 5). Methane lifetime reduces accordingly, most in ΔW (Table 5).

4.4 Contrasts between aviation NO_x effects for different implementations of the $\text{HO}_2 + \text{NO}$ reaction

Summarizing the chemical effects, aviation NO_x increases $[\text{NO}_x]$, [OH] and $[\text{O}_3]$ in all sensitivity blocks. Absolute and relative effects on [OH] and $[\text{O}_3]$ are more pronounced when considering Reaction (R2), most in sensitivity block ΔW .

Why is (R2) enhancing the effects on [OH] and $[\text{O}_3]$? Production and loss of peroxy radicals and ozone depend nonlinearly on temperature, pressure and ambient concentrations of other chemical species (e.g. NO_x). Generally, (R2) changes the response function of those production and loss terms to a $[\text{NO}_x]$ perturbation. In addition the

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changed chemical background due to (R2) will shift the response depending on ambient concentrations. Both effects change production and loss rates, translating into modified mixing ratios. Differences between sensitivity blocks ΔB , ΔD and ΔW are consequently due directly to the different chemical mechanisms, and indirectly to the resulting different background mixing ratios. The sensitivity method used for this study provides only one final response of $[\text{NO}_x]$, $[\text{OH}]$ and $[\text{O}_3]$ to a $[\text{NO}_x]$ perturbation. In order to find the response functions for each sensitivity block, production and loss terms for OH and O_3 would have to be evaluated for the relevant atmospheric conditions and for a range of different ambient concentrations. A box modelling approach would be suited for this and might be warranted for a future study, if Reaction (R2) becomes established. Tagging (Grewe et al., 2010) or small perturbation methods (Hoor et al., 2008) might then help to disentangle the different nonlinear effects leading to the final response of $[\text{NO}_x]$, $[\text{OH}]$ and $[\text{O}_3]$.

For the current study we do not attempt a thorough analysis, and note selected aspects only. Reaction (R2) shifts the ratios $[\text{OH}]/[\text{HO}_2]$ and $[\text{NO}]/[\text{NO}_2]$ towards $[\text{HO}_2]$ and $[\text{NO}]$ (Fig. 4). Ambient $[\text{HO}_2]$ increases in the UTLS and dominates the $[\text{HO}_x]$ response to (R2). Background $[\text{NO}_x]$ decreases due to (R2). More ambient $[\text{HO}_x]$ and less $[\text{NO}_x]$ may make the coupled catalytic cycles involving those species more sensitive to additional NO_x , which is more of a limiting factor in ΔD and ΔW . Simulations BA, B0, WA and W0 were repeated for short periods of time to diagnose the rates of the main reactions affecting the HO_x and NO_x catalytic cycles. Reactions with HO_2 as educt become less effective above 7 km and more effective below. All other reactions are enhanced by aviation NO_x . The rates of all reactions involving OH, HO_2 , NO or NO_2 as an educt are more affected by aviation NO_x in ΔB than in ΔW . Aviation NO_x increases NO_x mixing ratios absolutely more in ΔB than in ΔW , while the relative response is stronger in ΔW . Relative differences between reaction rates in ΔB and ΔW are small, except for the reactions involving OH as an educt. The Reactions (R4), $\text{O}_3 + \text{OH} \rightarrow \text{HO}_2$ and $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$ are much more enhanced by aviation NO_x in sensitivity block ΔB than in ΔW . Particularly the relative $[\text{OH}]$ response to aviation NO_x

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is stronger in ΔW , because the main OH loss reactions are weaker in ΔW than in ΔB . Ozone destruction by $O_3 + OH \rightarrow HO_2$ is enhanced in response to aviation NO_x in general. The reaction of OH with O_3 is less effective in an atmosphere with (R2), due to decreased OH availability. Thus less ozone is destroyed, leading to a stronger ozone signal in sensitivity blocks ΔD and ΔW , compared to sensitivity block ΔB . In turn, more OH is formed by photolysis of the additional ozone, also causing a bigger [OH] perturbation in ΔW . However, the above should be regarded as preliminary ideas that might help to design a thorough analysis.

5 Radiative forcing effects

Four radiative forcing (RF) effects due to aviation NO_x chemical perturbations are considered here: (i) the short-lived O_3 response as discussed in Sect. 4.2, (ii) the long-lived methane response due to modified [OH] (Sect. 4.3), (iii) a long-lived ozone response due to $[CH_4]$ changes, and (iv) modifications to stratospheric water vapour from methane oxidation. The net RF is the relatively small sum of larger positive (i) and larger negative (ii, iii, iv) components. Like in other studies (Hoor et al., 2010; Myhre et al., 2011), radiative forcing calculations are limited to the chemical perturbations in the altitude range between the surface and 50 hPa. This is within the validity range of the applied rate coefficient parameterisations for (R2) and captures almost all aviation NO_x effects. Tests using the top of the computational domain (0.01 hPa) as upper boundary show that compared to the 50-hPa-top, methane related RFs decrease by less than 3% and the short-lived ozone forcing by about 0.1%.

5.1 Radiative forcing from the short-lived ozone response to aviation NO_x

Simulations B0, D0 and W0 were repeated in purely dynamical mode with a modified version of the EMAC radiation module (Dietmüller, 2011, based on Stuber et al., 2001). The radiation module is called twice during the model integration: (i) online for the

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reference case, and (ii) as offline diagnostic for the perturbed case. Monthly mean 3-D fields of $[O_3]$ from B0 were provided to the module together with the ozone perturbation ($\Delta B = BA - B0$) due to aviation NO_x . All perturbations above 50 hPa were set to zero, then using B0 + ΔB to calculate radiation for the perturbed case.

5 The shortwave radiative forcing is purely determined by the ozone perturbation. Longwave radiative fluxes are influenced by temperature, which within the troposphere remains unchanged from the reference to the perturbed radiative flux profile. A second diagnostic temperature field is determined for the perturbed case, which represents the new radiative equilibrium induced by the ozone perturbation in the stratosphere
10 (Hansen et al., 1997; Stuber et al., 2001). These diagnostic temperatures are allowed to adjust to changing $[O_3]$ perturbations constantly. The additional radiative flux change induced by the stratospheric temperature adjustment is taken as an integral part of the longwave ozone radiative forcing.

A monthly tropopause climatology was derived from BA according to the WMO definition (WMO, 1992) based on the temperature lapse rate for latitudes equatorward of 30° .
15 The climatological value (Eq. 8) was used when no lapse rate was found. At latitudes poleward of 30° the potential vorticity isosurface of 3.5 PVU defined the tropopause. In addition to $[O_3]$, monthly mean climatologies of the radiatively active substances CH_4 , N_2O , $CFCl_3$ and CF_2Cl_2 were derived from the year 2001 output of the reference simulations to use the radiation module without online chemistry. Dynamics was nudged
20 for 2000 and 2001, and the first year was discarded for spin-up of the stratospheric temperature adjustment to the perturbed ozone field in the radiation module.

The stratospheric-adjusted radiative forcing from short-lived ozone perturbations was then calculated as the global mean of

$$25 \quad RF_{O_3}^{short} = (\Phi_A^{sw} + \Phi_A^{lw}) - (\Phi_0^{sw} + \Phi_0^{lw}) \quad (11)$$

Φ^{sw} is the net shortwave radiation flux at the tropopause and Φ^{lw} is the longwave flux. Index A denotes a simulation with aircraft NO_x emissions (i.e. BA, DA or WA) and index 0 refers to the corresponding reference simulation (B0, D0 or W0). Annual mean values

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for $RF_{O_3}^{\text{short}}$ are listed in Table 5, and monthly mean integrals are shown in Fig. A1 for the three sensitivity blocks (ΔB , ΔD and ΔW). Assuming less interannual than seasonal variability, $RF_{O_3}^{\text{short}}$ might not change by more than 10 % from year to year (Appendix A).

We also applied the methodology of Holmes et al. (2011) to estimate the radiative forcing for sensitivity blocks ΔB , ΔD and ΔW . The results are given in Table 5. Holmes et al. (2011) derive uncertainty ranges of more than 30 % from an ensemble of simulations, which characterise inter-model uncertainty, but do not apply to our single-model study. Only the first term of their equation

$$RF_{O_3}^{\text{short}} = \frac{\Delta \langle [O_3]^{\text{short}} \rangle}{\Delta E} \cdot \frac{dF}{d \langle [O_3] \rangle} \quad (12)$$

was extracted from our simulations. $\Delta \langle [O_3]^{\text{short}} \rangle = \langle [O_3]_A^{\text{short}} \rangle - \langle [O_3]_0^{\text{short}} \rangle$ is the change of the global mean short-lived ozone burden (in Dobson units) due to aviation NO_x emissions. It was calculated from monthly mean ozone fields. The term $\Delta E = 0.8473 \text{ Tgyr}^{-1}$ is equal to the total N emissions of the QUANTIFY (2008) inventory (Lee et al., 2005), as they were switched off completely in the control simulations B0, D0 and W0. $RF_{O_3}^{\text{short}}$ depends on the spatial distribution of the ozone perturbation and on the method to determine RF. Both are hidden in the pre-calculated RF efficiency of tropospheric ozone ($dF/d \langle [O_3] \rangle$). Holmes et al. (2011) adopt the value of Myhre et al. (2011), who also used the QUANTIFY (2008) aviation NO_x inventory (Lee et al., 2005) and stratospheric-adjusted RF, but not the EMAC model.

Applying both methods to our simulations, the corresponding results for $RF_{O_3}^{\text{short}}$ agree remarkably well, within 5 % of each other. Note that $RF_{O_3}^{\text{short}}$ from both methods agrees least well in sensitivity block ΔW , where the ozone perturbation is expected to differ most from the ones considered by Holmes et al. (2011). Furthermore, modifications of background ozone due to (R2) also affect the radiation available for interacting with

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the aviation perturbation. In contrast, the direct calculation of $RF_{O_3}^{short}$ captures such deviations and tends to provide a more accurate result here.

Applying Eq. (12) to 21 different simulations from other recent studies (Holmes et al., 2011), then scaling the results linearly to the total aircraft NO_x emissions in our simulations, leads to $RF_{O_3}^{short} = 18.3 \pm 6.1 \text{ mW m}^{-2}$. Reaction (R2) was not considered in any of these simulations, and applying Eq. (12) to sensitivity block ΔB gives a nearly identical result (18.2 mW m^{-2}). The ozone response to aviation NO_x calculated in ΔB is reasonable for an atmosphere without the HNO_3 -forming channel of $HO_2 + NO$.

Equation (12) illustrates that $RF_{O_3}^{short}$ is determined essentially by absolute $[O_3]$ perturbations. Those are shown in Fig. 3b for sensitivity blocks ΔB and ΔW , and summarized in Table 4 for all sensitivity blocks. Aviation NO_x causes $\langle [O_3]^{short} \rangle$ to increase least in ΔB and most in ΔW . This is reflected by $RF_{O_3}^{short}$, which is up to 3.9 mW m^{-2} higher when considering Reaction (R2) (Table 5).

5.2 Methane related radiative forcings

Decadal simulations would be required to reach a steady state response of CH_4 to any chemical perturbation, due to the long atmospheric lifetime of methane (Tables 2 and 3). For this study just one year was evaluated per simulation. Furthermore, the setup features prescribed surface mixing ratios for CH_4 . It does not include CH_4 emissions explicitly, inhibiting the attribution of methane changes to chemical perturbations. Thus methane perturbations cannot be quantified from the simulations of this study directly. However, in the troposphere and UTLS methane is almost exclusively affected by Reaction (R4) (Sects. 3.3 and 3.4), governed by

$$\frac{d[CH_4]}{dt} = -[CH_4] \cdot [OH] \cdot k_{CH_4} \quad (13)$$

Methane perturbations due to aircraft NO_x emissions may be estimated from the corresponding $[OH]$ perturbations, which almost immediately adjust due to the short lifetime

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of OH. Methane effects trail the time of NO_x emission by τ_{CH_4} , and previous emissions determine the actual methane related RF. However, we do not make any assumptions about previous emissions, but analyse the projected steady state response of the atmosphere to sustained aircraft NO_x emissions of the year 2000 instead. Considering the smaller pre-2000 emissions would reduce methane effects by about 30 % (Grewe and Stenke, 2008).

The long lifetime of methane implies that the spatial distribution of [CH₄] perturbations is determined by atmospheric mixing, and thus almost independent of the original [OH] perturbation. This would not be captured by translating localized [OH] perturbations (Fig. 3) directly into 3-D methane perturbations. Thus we do not attempt to estimate $\text{RF}_{\text{CH}_4}^{\text{direct}}$ from 3-D methane fields with radiative transfer calculations, but prefer the approaches of Ramaswamy et al. (2001) and Holmes et al. (2011) that rely on globally integrated quantities for methane perturbations. Note that [OH] perturbations and thus methane related forcings still critically depend on the location of the original [NO_x] perturbation. The global mean methane mixing ratio at the surface in a simulation with aviation is $M_A = \langle [\text{CH}_4]_A \rangle$, in the reference simulation M_0 , and $N = \langle [\text{N}_2\text{O}] \rangle$, all in nmol mol⁻¹. Following Ramaswamy et al. (2001):

$$\text{RF}_{\text{CH}_4}^{\text{direct}} = a \left(\sqrt{M_A} - \sqrt{M_0} \right) - b \cdot \ln \left\{ \frac{1 + c \cdot (M_A N)^{0.75} + d \cdot M_A \cdot (M_A N)^{1.52}}{1 + c \cdot (M_0 N)^{0.75} + d \cdot M_0 \cdot (M_0 N)^{1.52}} \right\} \quad (14)$$

in W m⁻², with $a = 0.036$, $b = 0.47$, $c = 2.01 \times 10^{-5}$, $d = 5.31 \times 10^{-15}$. The second term on the right hand side is a correction for the overlap with N₂O (Berntsen et al., 2005). Monthly global mean methane mixing ratios for 2001 were estimated from NOAA/GMD data (Forster et al., 2007) by applying a cosine variation of ± 7 nmol mol⁻¹ to an annual mean value of 1770 nmol mol⁻¹. Those observation based values were assigned to M_A in each sensitivity block (i.e. to BA, DA, WA; Table 4), since observations are affected by aircraft NO_x emissions. Monthly combined nitrous oxide data are from the NOAA/ESRL global monitoring division (HATS_Global_N2O in

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ftp://ftp.cmdl.noaa.gov/hats/n2o/combined/HATS_global_N2O.txt), giving a mean value of $316.338 \text{ nmol mol}^{-1}$ for 2001. Only the global methane mixing ratios for hypothetical atmospheres without aviation were derived from simulations B0, D0 and W0 (Table 4):

$$M_0 = M_A - \Delta\tau_{\text{CH}_4}^{\text{OH}} \cdot M_A \quad (15)$$

5 The relative methane lifetime change,

$$\Delta\tau_{\text{CH}_4}^{\text{OH}} = \frac{\left(\tau_{\text{CH}_4}^{\text{OH}}\right)_A - \left(\tau_{\text{CH}_4}^{\text{OH}}\right)_0}{\left(\tau_{\text{CH}_4}^{\text{OH}}\right)_0} \quad (16)$$

was calculated by applying Eq. (10) to monthly mean fields. Methane oxidation (R4) causes [OH] to increase when [CH₄] decreases, leading to a further [CH₄] loss. This chemical feedback would lead to a different M_0 in a decadal long-term simulation than an estimate based on the initial perturbation. It is thus considered as an additional term of the total long-lived methane RF here, estimated as a fraction of the direct forcing:

$$\text{RF}_{\text{CH}_4}^{\text{long}} = \text{RF}_{\text{CH}_4}^{\text{feedback}} + \text{RF}_{\text{CH}_4}^{\text{direct}} = (1 + f_1) \cdot \text{RF}_{\text{CH}_4}^{\text{direct}} \quad (17)$$

A feedback factor of $f_1 = 0.4 \pm 0.1$ (Holmes et al., 2011) is used here, which is slightly higher than earlier estimates (Ramaswamy et al., 2001: $f_1 = 0.3 \pm 0.05$). Tropospheric ozone decreases due to the enhanced methane oxidation, caused by aviation NO_x. This long-lived ozone effect enhances the methane forcing by another 30 % to 40 % (Ramaswamy et al., 2001), i.e. $f_2 = 0.35 \pm 0.05$:

$$\text{RF}_{\text{O}_3}^{\text{long}} = f_2 \cdot \text{RF}_{\text{CH}_4}^{\text{long}} \quad (18)$$

Oxidation of methane is a major source of stratospheric water vapour. The radiative forcing from a water vapour perturbation is estimated to be 15 to 20 % of the direct methane forcing (Myhre et al., 2007), i.e. $f_3 = 0.175 \pm 0.025$:

$$\text{RF}_{\text{H}_2\text{O}}^{\text{long}} = f_3 \cdot \text{RF}_{\text{CH}_4}^{\text{long}} \quad (19)$$

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The results for all forcings in all sensitivity blocks are given in Table 5, together with the relative changes of methane lifetime, the relative perturbation of $\langle c_{\text{OH}}^k \rangle$ and the sum of all RF terms. $\text{RF}_{\text{CH}_4}^{\text{long}}$ is only affected by uncertainties from f_1 . The biggest possible uncertainty due to f_1 and f_2 is assumed for $\text{RF}_{\text{O}_3}^{\text{long}}$, due to f_1 and f_3 is for $\text{RF}_{\text{H}_2\text{O}}^{\text{long}}$. Uncertainties associated with the rate coefficient of (R4) (see Supplement) translate into an additional uncertainty for $\Delta\tau_{\text{CH}_4}^{\text{OH}}$ and all subsequently derived RF related to methane. The best estimates were calculated with $k_{\text{CH}_4}^{\text{best}}$ from Atkinson (2003) and the extremes cover results obtained with $k_{\text{CH}_4}^{\text{min}}$ or $k_{\text{CH}_4}^{\text{max}}$ from IUPAC (2007), see Supplement. Seasonal variations of meteorological and chemical situations seem to have little impact on forcings that are due to [OH] perturbations (Appendix A). Interannual variation of the long-lived RF terms is expected to be small.

For comparison, we additionally calculated $\text{RF}_{\text{CH}_4}^{\text{long}}$ and $\text{RF}_{\text{O}_3}^{\text{long}}$ according to Holmes et al. (2011):

$$\text{RF}_{\text{CH}_4}^{\text{long}} = \frac{\Delta\tau_{\text{CH}_4}^{\text{OH}}}{\Delta E} \cdot f_1 \cdot M_A \cdot \frac{dF}{d\langle[\text{CH}_4]\rangle} \quad (20)$$

$$\text{RF}_{\text{O}_3}^{\text{long}} = \frac{\Delta\tau_{\text{CH}_4}^{\text{OH}}}{\Delta E} \cdot f_1 \cdot M_A \cdot \frac{d\langle[\text{O}_3]\rangle}{d\langle[\text{CH}_4]\rangle} \cdot \frac{dF}{d\langle[\text{O}_3]\rangle} \quad (21)$$

Holmes et al. (2011) excluded stratospheric water vapour from their analysis and $\text{RF}_{\text{CH}_4}^{\text{long}}$ was calculated according to Eq. (19), based on the results from Eq. (20). Only the relative change of methane lifetime and the aircraft emissions were derived from our simulations. Note that from all the chemical perturbations in the sensitivity blocks ΔB , ΔD and ΔW , only relative variations of $\tau_{\text{CH}_4}^{\text{OH}}$ enter Eqs. (17) to (21). Consequently the relative response of [OH] to aviation NO_x determines the methane related radiative forcing terms. This is in contrast to $\text{RF}_{\text{O}_3}^{\text{short}}$, which is determined by absolute $[\text{O}_3]$ perturbations.

The pre-calculated RF efficiency of tropospheric methane ($dF/d\langle[\text{CH}_4]\rangle$) and the coupling term $d\langle[\text{O}_3]\rangle/d\langle[\text{CH}_4]\rangle$ were adopted from Holmes et al. (2011). The results are given in Table 5, but no uncertainty analysis was attempted. $\text{RF}_{\text{CH}_4}^{\text{long}}$ and $\text{RF}_{\text{O}_3}^{\text{long}}$ from both methods (Ramaswamy et al., 2001 versus Holmes et al., 2011) agree even better than $\text{RF}_{\text{O}_3}^{\text{short}}$, indicating little methodological uncertainties.

Linear scaling of the results of Holmes et al. (2011) to $0.847 \text{ Tg N yr}^{-1}$ leads to $\text{RF}_{\text{CH}_4}^{\text{long}} = -13.3 \pm 3.0 \text{ mW m}^{-2}$ and $\text{RF}_{\text{O}_3}^{\text{long}} = -4.5 \pm 1.9 \text{ mW m}^{-2}$. Values from sensitivity block ΔB are not as negative, but well within the uncertainty ranges given by Holmes et al. (2001).

5.3 Net radiative forcing from aviation NO_x effects

Net RF from aviation NO_x induced perturbations is the sum from large positive and large negative terms, giving a small net forcing with relatively big uncertainty ranges. The ranges given in this study include only uncertainties inherited from the rate coefficient (k_{CH_4}) for $\text{CH}_4 + \text{OH}$, and from the factors (f_1, f_2, f_3) applied to estimate radiative forcings that could not be calculated directly. Modifications to f_1, f_2, f_3 or k_{CH_4} would apply to all sensitivity blocks in the same way and shift all RF results in one direction. Thus the net forcing for the three sensitivity blocks ($\Delta\text{B}, \Delta\text{D}, \Delta\text{W}$) could be minimal ($-2.4, -4.6, -16.7$) mW m^{-2} , or maximal ($+2.8, +1.4, -7.5$) mW m^{-2} . According to this analysis, the total radiative forcing from aviation NO_x is near zero for ΔB and gradually decreases to significantly negative values for ΔW . Interannual variations of the different radiative forcing terms are likely to shift net RF in the same direction in all sensitivity blocks (Appendix A), retaining the differences between the chemical regimes. Net RF would still be negative in ΔW considering 10 % uncertainty of $\text{RF}_{\text{O}_3}^{\text{short}}$.

None of the models evaluated by Holmes et al. (2011) considered the reaction $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$, and thus a fair comparison is only possible to sensitivity block ΔB . We linearly scaled their results to the aircraft NO_x emissions used here, and additionally

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estimated $RF_{H_2O}^{long}$ according to Eq. (19) from their $RF_{CH_4}^{long}$. Then their model ensemble leads to a net RF of 1.4 mW m^{-2} , with 10 models attributing a cooling effect to aviation NO_x . Without $RF_{H_2O}^{long}$ only 3 models would diagnose a negative net RF. The result for ΔB supports the conclusion that RF from aviation NO_x is about zero when not including (R2). Note that considering transient historical emissions to get the instantaneous RF in 2000 would reduce all long-lived forcings by about 35% (Grewe and Stenke, 2008; Myhre et al., 2011), compared to the steady state response discussed here.

Another recent study (Unger, 2011) also found a cooling effect from $RF_{O_3}^{short} + RF_{CH_4}^{long} + RF_{O_3}^{long}$. (R2) was included there with $k_{2a}(p, T)$, resulting in a remarkably low specific $RF_{O_3}^{short}$ of $0.8 \times 10^{-11} \text{ W m}^{-2} \text{ kg}^{-1} (\text{N}) \text{ yr}^{-1}$, versus $2.2 \times 10^{-11} \text{ W m}^{-2} \text{ kg}^{-1} (\text{N}) \text{ yr}^{-1}$ (Holmes et al., 2011), $2.1 \times 10^{-11} \text{ W m}^{-2} \text{ kg}^{-1} (\text{N}) \text{ yr}^{-1}$ (sensitivity block ΔB), and $2.3 \times 10^{-11} \text{ W m}^{-2} \text{ kg}^{-1} (\text{N}) \text{ yr}^{-1}$ (sensitivity block ΔD). Considering the relatively small difference between the short-lived ozone forcing even in ΔB and ΔD , low specific $RF_{O_3}^{short}$ might explain the reporting of a negligible impact of (R2) on that term by Unger (2011). Sensitivity block ΔD yields a negative net RF for a different reason: methane related forcings are more sensitive to aircraft NO_x emissions, overcompensating increased $RF_{O_3}^{short}$. Reasons for this discrepancy might include that Unger (2011) used a different aviation inventory, included the formation of nitrate aerosols, and did not consider stratospheric temperature adjustment for RF.

We are not aware of any aviation study for comparison that included (R2) with a humidity dependent rate coefficient. If our assumptions about $k_{2b}(p, T, c_{H_2O})$ are correct, aircraft NO_x emissions are likely to cool the Earth. Limitations and uncertainties of this result will be summarized in the next section and should be considered, before attaching any practical importance to it.

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6 Summary and conclusions

We discussed the global impact of the $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ Reaction (R2) on atmospheric trace gases, particularly on ozone, methane, and their precursors. Previous modelling studies (Brühl et al., 2007; Cariolle et al., 2008; Søvde et al., 2011; Unger, 2011) applied a rate coefficient $k_{2a}(p, T)$ that depends only on pressure and temperature. This study additionally considered a humidity modification to the rate coefficient, i.e. $k_{2b}(p, T, c_{\text{H}_2\text{O}})$. Furthermore, we isolated aviation NO_x effects, and compared the respective radiative forcings in an atmosphere with the above reaction to an atmosphere without it.

While the relative effects of the HNO_3 forming channel of the $\text{HO}_2 + \text{NO}$ reaction are pronounced in the UTLS, the absolute effects on HNO_3 , NO_x , OH and O_3 have their maximum at about 10 hPa. HNO_3 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 HNO_3 -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 $k_{2b}(p, T, c_{\text{H}_2\text{O}})$ to the simulation without (R2).

The simulations discussed in the previous paragraph (BA, DA, WA) include aircraft NO_x emissions. All agree reasonably well with observations, and neither the two regimes with the HNO_3 -forming channel, nor the one without could be ruled out on that grounds. Since we cannot decide which background chemistry is correct, we cannot

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entirely rule out that the differences between the aviation NO_x effects in the three regimes are to some degree artefacts of possibly wrong background mixing ratios. 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. However, the dependence on temperature of the humidity modification to the rate coefficient of (R2), and to a lesser degree on pressure, is still uncertain (LeBras, 2011). This should be kept in mind when interpreting the results of simulations with $k_2(p, T, c_{\text{H}_2\text{O}})$.

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 ($\text{RF}_{\text{O}_3}^{\text{short}}$), i.e. warms the Earth. More hydroxyl radicals destroy more methane, resulting in a negative radiative forcing ($\text{RF}_{\text{CH}_4}^{\text{long}}$). Less methane means less stratospheric water vapour from methane oxidation ($\text{RF}_{\text{H}_2\text{O}}^{\text{long}}$). A chemical feedback leads to an ozone decrease in response to less methane, and thus to an additional negative forcing ($\text{RF}_{\text{O}_3}^{\text{long}}$). 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 $+0.2 \text{ mW m}^{-2}$ in our study.

Considering $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ increases the effects of aircraft NO_x emissions on $[\text{O}_3]$ and $[\text{OH}]$. $\text{RF}_{\text{O}_3}^{\text{short}}$ is primarily determined by the absolute ozone perturbation due to aviation NO_x . Essentially the same absolute $[\text{NO}_x]$ perturbation increases $[\text{O}_3]$ more in the regimes with (R2) than in the one without. This is consistent with the nonlinear effect of higher ozone production at lower $[\text{NO}_x]$ background (Lin et al., 1988; Wu et al., 2007), which had been caused by (R2). The long lived methane-related forcings

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$RF_{CH_4}^{long}$, $RF_{O_3}^{long}$ 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 HNO_3 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 introduction of $HO_2 + NO \rightarrow HNO_3$ than the positive short-lived ozone forcing. 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 $k_2(p, T, c_{H_2O})$.

Considering the regime with $k_2(p, T, c_{H_2O})$ 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 $[O_3]$ and [OH], thereby changing the net forcing. (ii) The current aircraft fleet flies close to the altitude where the [OH] response to NO_x emissions changes sign. Flying only a little bit higher might drastically reduce OH-induced cooling RF effects. (iii) $RF_{O_3}^{short}$ 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 $RF_{O_3}^{short}$ and methane effects also implies that the short-lived positive forcing becomes more important for increasing aircraft NO_x emissions, while the long-lived negative forcings would dominate for decreasing emissions.

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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, e.g. with a small perturbation approach like in Hoor et al. (2009). 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. The uncertainties associated with the HNO_3 -forming channel of the $\text{HO}_2 + \text{NO}$ reaction propagate a considerable additional uncertainty on estimates of the radiative forcing due to aircraft NO_x emissions.

Appendix A

Monthly variation of radiative forcing

The simulations of this study were evaluated for only one year, prohibiting a direct statistical analysis of interannual variability of the radiative forcing terms. Here RF variation throughout the year is evaluated to give some indication of the sensitivity of the chemical signal to different states of the background atmosphere. This may serve as a proxy for possible interannual variability.

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Global monthly mean values of $RF_{O_3}^{short}$ deviate by about -16% to $+13\%$ from the annual mean values (Table 5) in all sensitivity blocks (Fig. A1). This is partly due to the monthly variation of aircraft emissions in the inventory. Those range for NO_2 from 7.16 Gg day^{-1} in January to 7.97 Tg day^{-1} in September, which is -5% and $+4\%$ with respect to the annual mean of 7.61 Tg day^{-1} . Scaling monthly RF values with the respective emissions leaves a variation from -11% to $+9\%$ with respect to the annual mean. This may include any nonlinear dependence of RF on the amount of aircraft emissions, as well as the effects of seasonal weather changes on RF. Assuming less interannual than seasonal variability, $RF_{O_3}^{short}$ might not change by more than 10% from year to year. Note that $[NO_x]$ perturbations are reflected in $RF_{O_3}^{short}$ with a delay of about 10 days (lifetime of NO_x in the UTLS).

Perturbations of $[OH]$ affect methane and thus the above RF terms with a delay of about decade (τ_{CH_4}). $RF_{CH_4}^{long}$, $RF_{H_2O}^{long}$ and $RF_{O_3}^{long}$ in Fig. A1 reflect the variations of C_{OH}^k , $\langle [CH_4]_A \rangle$ and $\langle [N_2O] \rangle$ throughout the year, expressed as radiative forcing. However, the actual radiative forcing from any $[NO_x]$ perturbation would be smeared over years. There is little variation of $RF_{CH_4}^{long}$, $RF_{H_2O}^{long}$ and $RF_{O_3}^{long}$ throughout the year. Seasonal variations of meteorological and chemical situations seem to have little impact on forcings that are due to $[OH]$ perturbations. Interannual variation for the long-lived RF components is expected to be small.

Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys-discuss.net/12/24287/2012/acpd-12-24287-2012-supplement.pdf>.

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**Table 1.** Applied processes and respective submodels of EMAC.

Submodel	Process	Ref.
AIRSEA	Air-sea exchange	Pozzer et al. (2006)
CLOUD	Large-scale condensation	see Lohmann and Roeckner (1996), Roeckner et al. (2003)
CONVECT	Convection	Tost et al. (2006b)
CVTRANS	Convective tracer transport	see Jöckel et al. (2006)
DRADON	Diagnostic for ^{222}Rn	Jöckel et al. (2010)
DRYDEP, SEDI	Dry deposition	Kerkweg et al. (2006a)
H2O	Stratospheric H_2O and feedback	see Jöckel et al. (2006)
HETCHEM	Heterogeneous reaction rates	see Jöckel et al. (2006)
JVAL	Photolysis rate calculations	see Jöckel et al. (2006)
LNOX	Lightning NO_x emissions	Grewe et al. (2001), Tost et al. (2007)
MECCA1	Gas phase chemistry	Sander et al. (2005)
OFFLEM, ONLEM	Emissions	Kerkweg et al. (2006b)
NCREGRID	Automatic grid transformations	Jöckel (2006)
PSC	Partitioning (H_2O , HNO_3) in PSCs	Kirner et al. (2011)
QBO	QBO nudging	Jöckel et al. (2006)
RAD4ALL	Radiation	see Jöckel et al. (2006)
SCAV	Scavenging, aqueous phase chemistry	Tost et al. (2006a, 2007)
TIMEPOS	Diagnostic tracer output	unpublished data
TNUDGE	Tracer boundary conditions	Kerkweg et al. (2006b)
TRACER, PTRAC	Prognostic tracers	Jöckel et al. (2008)
TROPOP	Tropopause diagnostics	Jöckel et al. (2006)

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Table 2. Simulations performed for this study. They differ only in the rate coefficient for the HNO_3 -forming channel of $\text{HO}_2 + \text{NO}$ (Reaction R2) and aircraft NO_x emissions. The rate coefficient k_2 may be zero (**Base**), depend on pressure and temperature (**Dry**), or additionally on water vapour concentration (**Wet**). Aviation may be on or zero (**0**). Each pair of simulations with identical treatment of (R2) defines a sensitivity block (ΔB : BA vs. B0, ΔD : DA vs. D0, ΔW : WA vs. W0) for the discussion of aviation NO_x effects in the corresponding chemical regime. The annual mean ozone burden $\langle [\text{O}_3] \rangle$ was calculated from the surface to 0.01 hPa.

Simulation	BA	B0	DA	D0	WA	W0
Sensitivity block	ΔB		ΔD		ΔW	
Rate coefficient for (R2)	$k_2 = 0$		$k_2(\rho, T)$		$k_2(\rho, T, c_{\text{H}_2\text{O}})$	
Aircraft NO_x emissions	on	off	on	off	on	off
$\langle [\text{O}_3] \rangle$, in DU	316.12	315.62	314.59	314.06	310.29	309.72

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Table 3. Global mean hydroxyl radical concentrations (in 10^6 cm^{-3}) and corresponding tropospheric methane lifetimes (τ_{CH_4} , in years) with respect to $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ (Reaction R4). Methane lifetimes for BA, DA and WA were calculated with the recommended reaction rate coefficient for (R4) from Atkinson et al. (2003). The upper boundary is the climatological tropopause defined by Eq. (8). The values of Spivakovsky et al. (2000) are based on observations of CH_3CCl_3 , HCFC-22, and precursors for $\text{HO}_x\text{-NO}_x$ photochemistry.

Reference or simulation	Year(s)	CO emissions in Tgyr^{-1}	$\langle c_{\text{OH}}^{\text{mass}} \rangle$	$\langle c_{\text{OH}}^k \rangle$	$\tau_{\text{CH}_4}^{\text{OH}}$
Spivakovsky et al. (2000)	1986–1989	n.a.	1.14	1.32	8.23
Jöckel et al. (2006)	1998–2005	452.36	1.08	1.31	8.02
Jöckel et al. (2010)	2001	364.06	1.06	1.26	8.54
BA	2001	254.79	1.27	1.42	7.6
DA	2001	254.79	1.13	1.29	8.4
WA	2001	254.79	0.85	0.95	11.4

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Table 4. Global annual mean parameters relevant for radiative forcing calculations. All were evaluated for the region below an upper boundary of 50 hPa. $\Delta \langle [\text{O}_3]^{\text{short}} \rangle$ is the short-lived increase of the ozone burden due to aircraft NO_x emissions, compared to the respective base case. $\langle c_{\text{OH}}^k \rangle$ is the hydroxyl radical concentration. Methane lifetime ($\tau_{\text{CH}_4}^{\text{OH}}$) was calculated from the $[\text{OH}]$ field of the respective simulation, but $[\text{CH}_4]$ is always from BA. $\langle [\text{CH}_4] \rangle$ is the methane burden, derived independently for each sensitivity block from monthly mean values of relative methane lifetime change. The same observation based value of $\langle [\text{CH}_4] \rangle$ is assumed for BA, DA and WA as a reference to calculate a hypothetical methane burden for B0, D0 and W0, respectively.

Simulation	BA	B0	DA	D0	WA	W0
$\Delta \langle [\text{O}_3]^{\text{short}} \rangle$, in DU	0.4933	0	0.5238	0	0.5653	0
$\langle c_{\text{OH}}^k \rangle$, in 10^6 cm^{-3}	1.41	1.39	1.28	1.26	0.947	0.924
$\tau_{\text{CH}_4}^{\text{OH}}$, in years	8.38	8.49	9.25	9.40	12.49	12.81
$\langle [\text{CH}_4] \rangle$, in nmol mol^{-1}	1770	1793	1770	1797	1770	1813

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Table 5. Changes in methane concentration and lifetime, as well as radiative forcing for 0.847 Tg aviation N per year in an atmosphere without Reaction (R2) (ΔB), with (R2a) (ΔD), and (R2b) (ΔW). Values in brackets were obtained with the factor decomposition method of Holmes et al. (2011), i.e. Eqs. (12), (19), (20) and (21). The other $RF_{O_3}^{short}$ values are based on the stratospheric adjusted RF diagnostic of Dietmüller (2011), i.e. Eq. (11). All other long-lived forcing terms reflect the steady state response of the atmosphere to sustained aircraft NO_x emissions of the year 2000, based on methane lifetime changes due to $[OH]$ perturbations. $RF_{CH_4}^{long}$ and $RF_{O_3}^{long}$ were calculated according to IPCC (2001), $RF_{H_2O}^{long}$ according to Myhre et al. (2007): Eqs. (11), (17), (18) and (19). All results refer to the global domain with an upper boundary at 50 hPa. Uncertainties are discussed in Sect. 5, including those terms without explicitly given error margin.

	ΔB	ΔD	ΔW
$\Delta \langle C_{OH}^k \rangle$, in %	+1.51	+1.83	+2.58
$\Delta \tau_{CH_4}^{OH}$, in %	$-1.28_{-0.03}^{+0.01}$	$-1.52_{-0.03}^{+0.01}$	$-2.45_{-0.03}^{+0.01}$
$RF_{CH_4}^{long}$, in $mW m^{-2}$	-11.6 ± 1.1 (–11.9)	-13.8 ± 1.2 (–14.1)	-22.2 ± 1.8 (–22.6)
$RF_{O_3}^{long}$, in $mW m^{-2}$	-4.1 ± 1.0 (–4.0)	-4.8 ± 1.2 (–4.8)	-7.8 ± 1.8 (–7.7)
$RF_{H_2O}^{long}$, in $mW m^{-2}$	-2.0 ± 0.5 (–2.1)	-2.4 ± 0.6 (–2.5)	-3.9 ± 0.9 (–4.0)
$RF_{O_3}^{short}$, in $mW m^{-2}$	+17.9 (+18.2)	+19.4 (+19.3)	+21.8 (+20.8)
net RF, in $mW m^{-2}$	$+0.2 \pm 2.6$ (+0.2)	-1.6 ± 3.0 (–2.0)	-12.1 ± 4.6 (–13.5)

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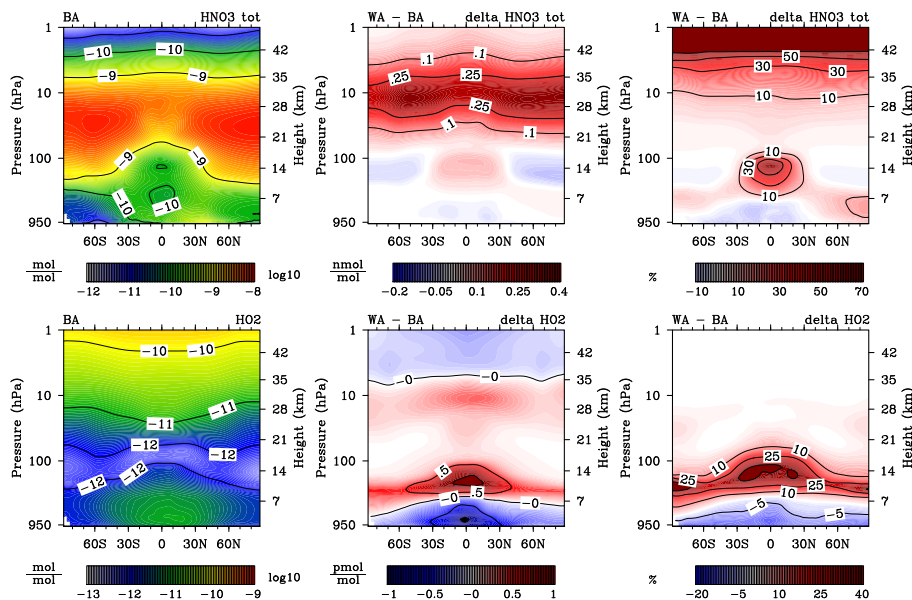


Fig. 1. Comparison of $[\text{HNO}_3]$, $[\text{HO}_2]$, $[\text{OH}]$, $[\text{NO}_x]$ and $[\text{O}_3]$ in a simulation with the HNO_3 -forming channel to a reference simulation without $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$. Both simulations have identical aviation NO_x emissions. The left column shows the logarithm of annual zonal mean mixing ratios in the reference simulation (BA). The middle and right columns show absolute (WA-BA) and relative ($100 \cdot \frac{\text{WA}-\text{BA}}{\text{BA}}$) deviations when including the HNO_3 -forming channel with a rate coefficient depending on pressure, temperature and humidity (simulation WA). The plots are cut at 1 hPa to zoom into the region of interest, although the uppermost model level is at 0.01 hPa.

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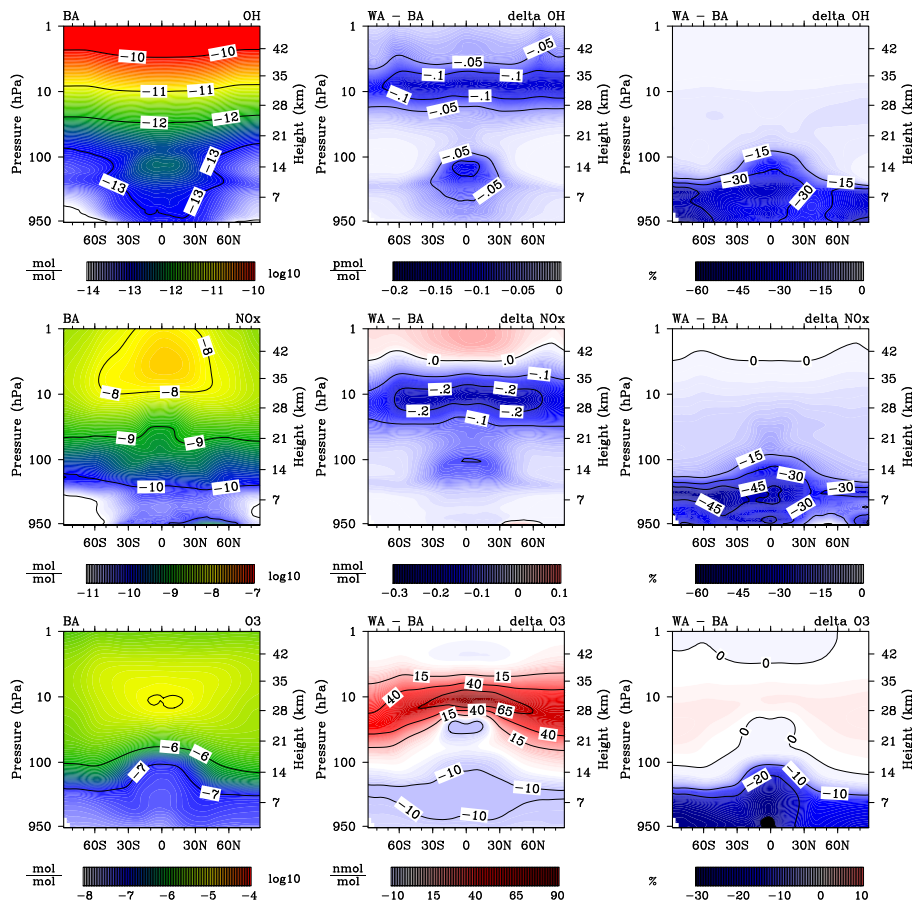


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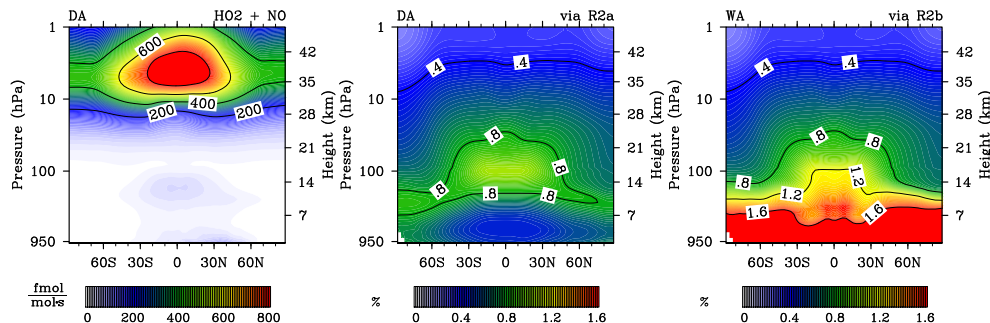


Fig. 2. Annual zonal mean reaction rate for $\text{HO}_2 + \text{NO}$ in $\text{fmol mol}^{-1} \text{s}^{-1}$ (left) in simulation DA. This is similar in the three considered chemical regimes (neglecting feedback via modified educt concentrations). No HNO_3 is formed by the above reaction in simulation BA. The percentage proceeding via the HNO_3 forming channel assuming a rate coefficient only depending on pressure, temperature (DA) is shown in the middle, and on the right if the rate coefficient additionally depends on humidity (WA).

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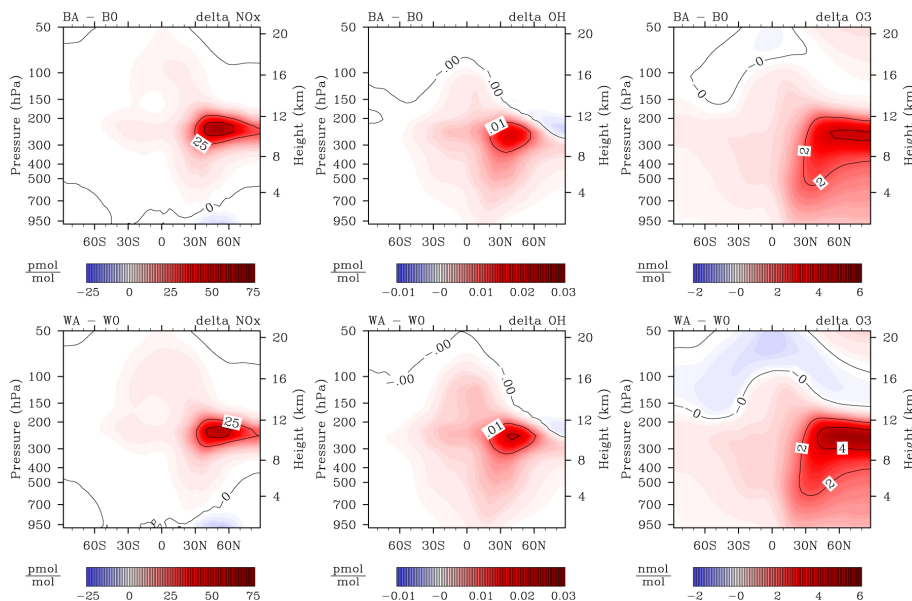


Fig. 3a. Absolute deviations of annual zonal mean mixing ratios of NO_x , OH and O_3 in a simulation with aviation NO_x from one without. Simulations without (top), and with $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$ assuming a rate coefficient depending on pressure, temperature and humidity (bottom).

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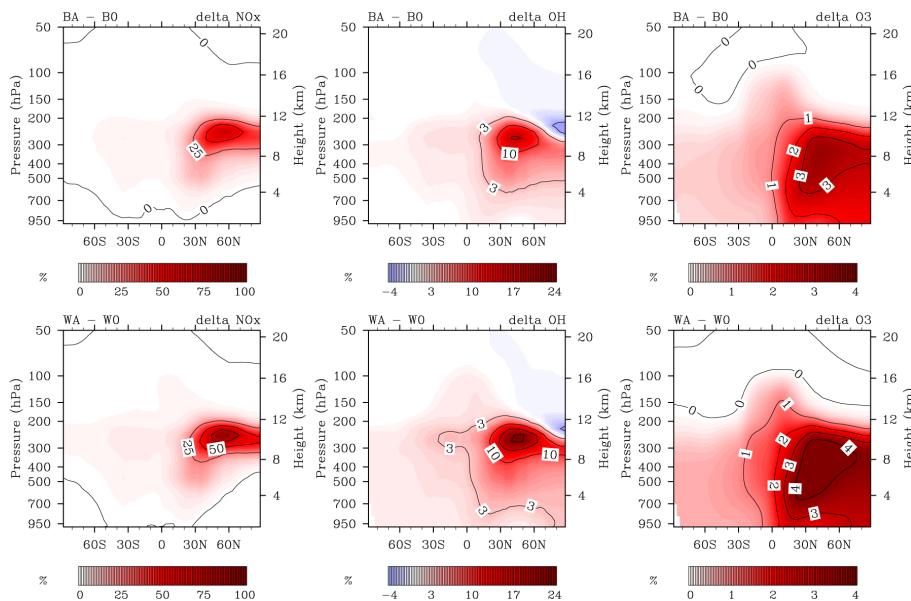


Fig. 3b. As Fig. 3a, but percental deviations relative to the respective simulation without aviation NO_x .

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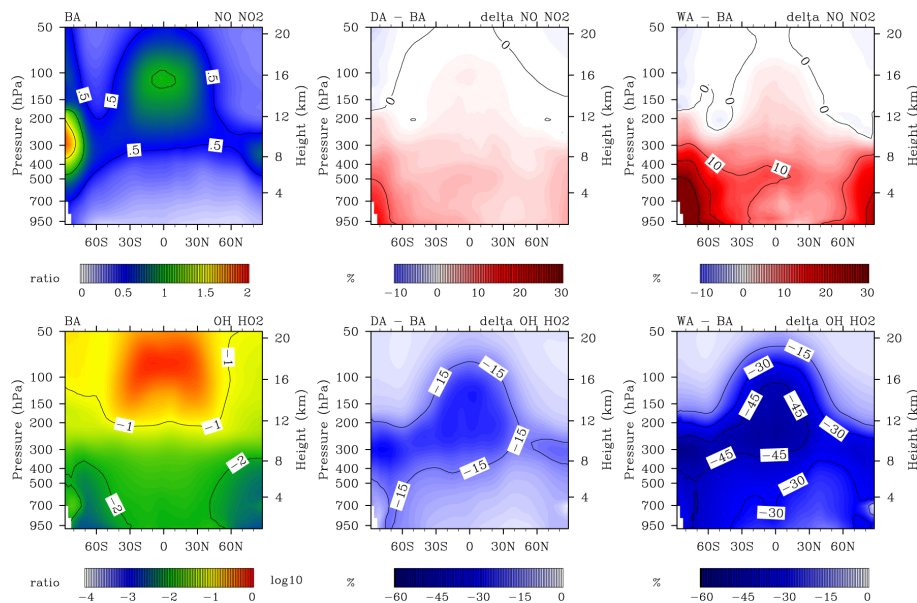


Fig. 4. Annual zonal mean ratio of $[\text{NO}]/[\text{NO}_2]$ (top) and $[\text{OH}]/[\text{HO}_2]$ (bottom) in simulations with aviation NO_x . The left column shows the reference case without $\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$. Middle and right panels give the relative change of the ratios when considering the HNO_3 -forming channel with rate coefficients $k_2(p, T)$ and $k_2(p, T, c_{\text{H}_2\text{O}})$, respectively.

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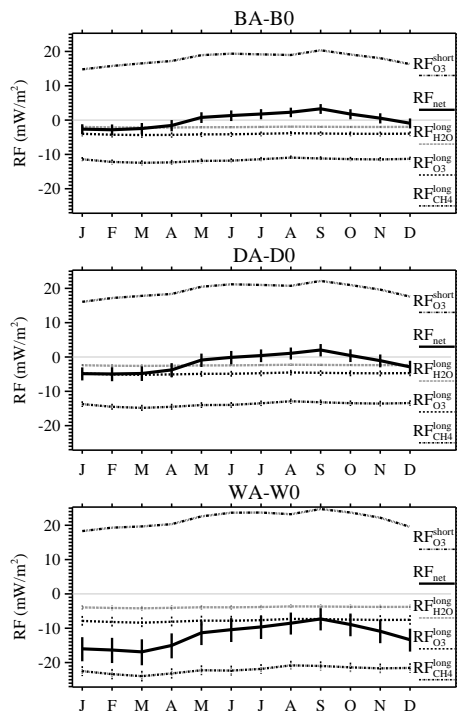


Fig. A1. Monthly mean radiative forcing terms according to Eq. (11) (Dietmüller, 2011), (17), (18) (IPCC, 2001), and (19) (Myhre et al., 2007). Note that $RF_{CH_4}^{long}$, $RF_{H_2O}^{long}$ and $RF_{O_3}^{long}$ reflect the almost instantaneous response of [OH] to the $[NO_x]$ and $[O_3]$ perturbations here, but the actual radiative forcing would rather be determined by the long-term methane response and the seasonal variation of methane mixing ratios. $RF_{O_3}^{short}$ is the actual RF at the time, but aircraft NO_x emissions are not immediately reflected by an ozone perturbation. The error bars are discussed in Appendix A and in Sect. 5.