Letter to the Editor

ACP Discussions doi: 10.5194/acp-2018-1193
(Editor - Martin Dameris)
‘Mechanism of ozone loss under enhanced water vapour conditions in the mid-latitude lower stratosphere in summer’

Dear Martin Daneris,

many thanks for handling our manuscript. We prepared and submitted a revised version of our manuscript and are confident that we have satisfactorily addressed all comments of referee #1 and #2. A detailed point-by-point response to all referee comments is attached. Further, a document specifying all changes in the revised manuscript compared to the ACPD version is added.

Best wishes,

Sabine Robrecht

Author Comment to Referee #1: page 2-4
Author Comment to Referee #2: page 5-26
All Changes: page 27-74
Author Comment to Referee #1

ACP Discussions doi: 10.5194/acp-2018-1193
(Editor - Martin Dameris)

‘Mechanism of ozone loss under enhanced water vapour conditions in the mid-latitude lower stratosphere in summer’

We thank Referee #1 for guidance on how to revise our paper. Following the reviewers advice we shorten the description of chemical processes and refer to a potential change of stratospheric dynamics due to an enhancement of the stratospheric sulphur abundance. Our reply to the reviewer comments is listed in detail below. Questions and comments of the referee are shown in italics. Passages from the revised version of the manuscript are shown in blue.

This paper presents a detailed chemical study for a potentially significant ozone depletion in the lowermost stratosphere, using a chemical box-model, with 7-day and 19-day back-trajectory analysis. The study is conducted under conditions of low temperatures (<205 K) and an elevated water vapour mixing ratio, up to 20 ppmv (resulting from convective overshooting events, rather frequent for summertime mid-latitude conditions). These convective events can transport ice crystals into the lowermost stratosphere, where the ice evaporates leading to a local water vapour increase. The sensitivity to high Cly mixing ratios is also addressed. The authors analyze with plenty of details the catalytic chemical cycles involving ClOx, NOx, HOx and leading to a perturbed balance of ozone production and destruction taking place in the lowermost stratosphere. The study takes inspiration from previous published works (Anderson et al., 2012; Anderson and Clapp, 2018); the authors conclude that the combined effects of temperature, water vapour and chlorine on the ozone loss process are consistent in their study with respect to these previous ones. I think that this study may help clarify important points regarding the ozone sensitivity to elevated water vapour conditions in the lowermost stratosphere and for this reason I recommend publication on ACP. In my opinion, a few improvements could be made in the manuscript, mainly for completeness and for improving readability.
Specific Comments

(1) Chemical cycles are essentially those leading to polar ozone depletion and widely described in previous literature. For this reason, I suggest moving large part of chemical details from the main text to a specific Appendix or in supplementary material. In particular, section 3.2.2 is in my opinion way too detailed and should be simplified focusing of the evidences of Fig. 5 (which is clear and exhaustive).

As proposed, we decided to shorten following aspects to focus on the analysis of lowermost stratospheric ozone chemistry occurring under enhanced water vapour conditions:

- We removed the chemical formulation of the ClO-Dimer-Cycle and the ClO-BrO-cycle in the description of ozone loss cycles leading to polar ozone loss and moved the formulation of cycle C3 from the introduction to section 3.2.2.

- The description of ozone formation at low water vapour mixing ratios is shortened by removing the formulation of ozone chemistry and NO reactions in Section 3.1.

- The detailed explanations of the water vapour dependence of R12 (OH+O₃) and R19 (OH+CO) in Section 3.2.2 (P.17,1.18-26, ACPD version of the manuscript) is removed.

- The description of the maintenance of activated chlorine is simplified by moving the chemical formulation of cycle C7 and C8 to the appendix. They are substituted by a new scheme (see Fig. of this reply), which illustrates the important relations for the maintenance of elevated chlorine.

(2) The authors clearly state that their box-model ignores mixing with outside air poorer of water vapour, so that their calculated ozone losses should be interpreted as an extreme case. They also suggest a possible use of their findings in global modelling of the atmosphere for future experiment of sulphate geoengineering under changing climate conditions, or in case of major volcanic eruptions. It should be mentioned that in these cases the large scale
latitudinal mixing of atmospheric tracers in the lower branch of the Brewer-Dobson circulation could be significantly affected in sulphate-perturbed conditions due to geoengineering or major tropical eruptions, both leading to a different level of isolation of the tropical pipe with the mid-latitudes. Eddy heat fluxes could also be perturbed, thus affecting mid-latitude temperatures in the lower stratosphere. Recent works have addressed these specific points (e.g., Visioni et al., 2017).


We mention the effect of sulphate geoengineering on lowermost stratospheric dynamics in Section 6 (P.27, l.27–31, revised version of the manuscript). We added the following paragraph.

Figure 1: Scheme to illustrate the balance between chlorine activation and chlorine deactivation (blue, right) and NOx activation and deactivation (green, left). The heterogeneous reaction ClONO2+HCl (R1) links both cycles. Additional reaction pathways balancing radicals are shown in light colour.
Applying solar geoengineering would also affect the temperature in the lowermost stratosphere by perturbing the Eddy-heat fluxes and would change the lower stratospheric dynamic (Visioni et al., 2017). It would affect large scale latitudinal mixing of atmospheric tracers in the lower branch of the Brewer-Dobson-Circulation leading to a different level of isolation of the tropical pipe with mid-latitudes and would result in a different chemical composition of the lower mid-latitude stratosphere.

References

Author Comment to Referee #2

ACP Discussions doi: 10.5194/acp-2018-1193
(Editor - Martin Dameris)
‘Mechanism of ozone loss under enhanced water vapour conditions in the mid-latitude lower stratosphere in summer’

We thank Referee #2 for comprehensive guidance on how to revise our paper. Following the reviewers advice we shortened parts of the paper to improve the readability. Our reply to the reviewer comments is listed in detail below. Questions and comments of the referee are shown in italics. Passages from the revised version of the manuscript are shown in blue.

General comments: The paper by Robrecht et al. investigates a potential ozone loss mechanism in the mid-latitude lower stratosphere under enhanced water vapour conditions and low temperatures, initiated by heterogeneous chlorine activation on liquid aerosol particles. For that purpose the authors conducted box model simulations along 7(19)-days backward trajectories with the CLaMS model. Besides a detailed chemical analysis of their standard case, they investigated the sensitivity of the proposed ozone loss mechanism to water vapour, mixing ratios of Cly, NOy, and Bry, sulphate content and temperature. Overall, I have no doubts that the applied methods and presented findings are valid and of wider interest for the scientific community, and therefore, I recommend this paper for publication in ACP. However, the paper is rather lengthy and the presentation of so many different case studies and sensitivity simulations does not increase the readability of the manuscript. Below I tried to make some suggestions for clarifications. Furthermore, I would like to encourage the authors to address or discuss the overall importance of the discussed ozone depletion mechanism. At the very end it is written that for observed conditions no ozone depletion was simulated, but it would be great to put the presented results more into a global and climatological perspective.
Specific Comments

- Abstract: It is a bit weird that the abstract does not clearly mention that the discussed ozone loss mechanism is initiated by heterogeneous chlorine activation on binary (ternary?) solution droplets. There are only hints in this direction, namely the impact of volcanic eruptions, geoengineering etc.

Following the reviewer’s advice, we mention chlorine activation as initial step for the ozone destruction process in the abstract.

The associated potential ozone loss process requires low temperatures and an elevated water vapour mixing ratio. Since this process is initiated by heterogeneous chlorine activation on liquid aerosols, an increase in sulphate aerosol surface area due to a volcanic eruption or geoengineering could increase its likelihood of occurrence.

Introduction: Again, it would be good to clearly state that the ozone loss process proposed by Anderson et al. involves sulphate aerosol particles. This would put the subsequent description of heterogeneous chlorine activation and catalytic ozone loss cycles much more into perspective.

We revised the first part of the introduction to mention that the mechanism proposed by Anderson et al. involves sulphate aerosols and to make clear, that it is initiated by heterogeneous chlorine activation.

[Anderson et al. (2012)] proposed a potential ozone depletion in the mid-latitude stratosphere in summer on liquid sulphate aerosols under conditions of enhanced water vapour and low temperatures. They proposed this chemical ozone loss to be initiated through heterogeneous chlorine activation and to be driven by catalytic ozone loss cycles related to ozone loss known from polar regions in early spring (e.g. [Groß et al. 2011], [Solomon 1999], [Vogel et al. 2011]).

P2, l15: Is the ClOx definition used here not a bit odd? Why is Cl2 not included? This would also facilitate the understanding of Fig.4f, because then it would be clear where the chlorine released from HCl during the first phase did go. Alternatively, one could also show Cl2 in Fig. 4.
Many thanks for this comment. We added Cl₂ to the definition of ClOₓ and adapted Fig. 4. The sentence discussing the delay between HCl reduction and ClOₓ formation (P. 13 l.11-12 in the ACPD version of this manuscript) is removed.

- P3, l17/18: By how much has water vapour to be enhanced to allow Cl activation at higher temperatures? Can you provide a number?

One question of our study is to estimate how much water vapour has to be enhanced to allow chlorine activation at higher temperatures. For our standard case 10.6 ppmv H₂O are necessary for the occurrence of chlorine activation. To clarify that in the text, we added the following sentence to the introduction.

An aim of our study is to investigate how much water vapour has to be enhanced for chlorine activation to occur at these higher temperatures.

- Model set-up: Why do you neglect NAT and ice in this study? NAT is probably not an issue, but how about ice? Especially since you mention a potential impact of ice particles on the water vapour threshold for Cl activation on liquid aerosol particles due to different heterogeneous reactivities (p32, l3-5).

We decided to calculate heterogeneous chemistry only on liquid particles to have a better comparability with the studies of [Anderson et al.] (2012) and [Anderson and Clapp] (2018). In their studies, they investigate the impact of binary H₂O/sulphate aerosols on mid-latitude ozone chemistry. To clarify this in the text, we added the following sentence to Sec. 2 (Model Setup).

In contrast to the setup in [Groos et al.] (2011), [Müller et al.] (2018) and [Zafar et al.] (2018), only formation of liquid particles (both binary H₂O/H₂SO₄ and ternary HNO₃/H₂O/H₂SO₄ solutions) is allowed (i.e. no NAT or ice particles are formed in this model setup) to enable a better comparability with the studies of [Anderson et al.] (2012, 2017) and [Anderson and Clapp] (2018).

In our study, we mention that chlorine activation on ice has been observed and analysed in former studies (p.31 l.29-31, p.33, l.12–15, ACPD version). We decided to not insert a further case study, which additionally shows the
impact of ice formation, to provide a better readability. We think that to reasonably show the impact of ice formation on the ozone process, however a comprehensive study would be necessary, which is beyond the slope of our current study.

- Model set-up: Could provide a short description of the treatment of liquid aerosol particles in your model? In Table 1 you provide the gas phase equivalent H2SO4 mixing ratio and Fig. 4 ff show the surface area density, but some more information would be great. For example, which H2SO4 wt% in the liquid aerosol particles is reached under the assumed high water vapour/low temperature conditions?

As proposed, we included a description of liquid aerosol treatment in Sec. 2 (P.4, l. 8, revised version of the manuscript).

For heterogeneous particle formation, the initial liquid aerosol number density \( N_0 = 10.0 \text{ cm}^{-3} \), the standard deviation of the logarithmic normal distribution of the particle size \( \sigma = 1.8 \), and the gas phase equivalent of the amount of sulfuric acid in the aerosol (for chosen values see Tab. 1) are set prior to the simulation. The gas phase equivalent is used to calculate the density of liquid particles as described in the study of Shi et al. (2001) (binary solutions) and Luo et al. (1996) (ternary solutions). Particle size and surface area density are calculated based on the density of liquid particles, the aerosol number density, and the standard deviation.

Furthermore, we added an additional plot (in Fig. 8, revised version of the manuscript) as shown in Fig. 1 of this reply, which presents the H2SO4 wt% depending on the water vapour mixing ratio. The following description is included in Section 4.2 (p.19, l.19 revised version of the manuscript).

The particles H2SO4 wt% decreases for all cases with increasing water vapour from more than 50 wt% at 5 ppmv H2O to around 20 wt% at 20 ppmv H2O due to an increasing uptake of H2O in the thermodynamic equilibrium.
Figure 1: Dependence on water vapour of the rate of the main heterogeneous chlorine activation reaction R1, the rate coefficient ($k_{R1}$), the $\gamma$-value $\gamma_{R1}$, the liquid surface area density $A_{\text{liq}}$, and the $\text{H}_2\text{SO}_4$ weight %. Presented parameters correspond to the values after the first chemistry time step of the box-model simulation. Additionally the impact of an enhanced sulphate content (0.8 ppbv $\text{H}_2\text{SO}_4$, yellow), reduced NOy (0.8 NOy, green), reduced Cly (0.8 Cly, black) and enhanced temperatures (red) is shown. The standard case is shown as blue squares.

- P5, l32/33: What was the overall background $\text{H}_2\text{O}$ mixing ratio for the calculated trajectories? And temperature? By how much are the selected trajectories colder?

In the Figure 2 of this reply, we illustrate the water vapour and temperature conditions of the SEAC4RS measurements and the calculated backwards tra-
The top panel shows the distribution of measured water vapour and temperature during the SEAC4RS campaign at a pressure of less than 100 hPa of all flights. This pressure range was chosen to select stratospheric measurements. The overall background water vapour is around 6–7 ppmv.

We calculated trajectories starting at the location of the measurements with enhanced water vapour of at least 10 ppmv H$_2$O. The temperature along these backward trajectories (in total 294) is shown in the bottom panels. The left panel shows the mean temperature and the right panel the minimal temperature of each calculated trajectory. The temperature of our standard trajectory is marked with a red arrow. Most of the trajectories have a mean temperature of 201–202 K and a minimal temperature of 199–200 K. Our standard trajectory has a mean temperature of 199 K and a minimal temperature of 197 K. In total, 28 trajectories with similar low temperatures were calculated. Most of these trajectories correspond to higher measured CH$_4$ mixing ratios and thus very low Cl$_y$ mixing ratios. Only three of the trajectories with very low temperatures and enhanced water vapour correspond to measurements with chlorine high enough to show a visible impact on ozone chemistry.

We added in Sec. 2.2 (p.5, l.1–4, revised version of the manuscript) as follow that Cl$_y$ was a criteria for choosing our standard trajectory in addition to the water vapour mixing ratio and temperature.

A selected example of calculated trajectories is shown in Fig. 1 (revised version). This trajectory was chosen for the chemical analysis, because its initial conditions exhibited enhanced water vapour relative to the overall background, low temperatures and enhanced Cl$_y$ (higher than for comparable water vapour and temperature conditions). Cl$_y$ was calculated from tracer-tracer correlations (see Sec. 2.3).
Sect. 2.3 Initialization: In Table 1 it is mentioned that the ClOx species were initialized with 0. Ok, in the mid-latitude lower stratosphere most chlorine is deactivated, but I am wondering how your initial phase in Fig. 4 would look like, if the trajectories had started with non-zero ClOx? Maybe you could add a short discussion.

We conducted a further simulation, assuming ClO$_x$ counts 1% of total Cl$_y$. This yields slightly more ClO$_x$ in the initial phase. But it changes neither the rate of R1 nor the water vapour threshold or the time, when ozone destruction starts significantly. We added a small discussion in Sec. 2.3.1 after...
the sequence about Cl$_y$ initialization (P.6, l.13–15, revised version of the manuscript).

Since most Cl$_y$ is deactivated in the mid-latitude lowermost stratosphere, the initial mixing ratio of ClO$_x$ species is assumed to be zero. A simulation assuming a ClO mixing ratio of 1% of total Cl$_y$, does not yield a significant difference to our standard case.

- Sect. 2.3.3: I do not really see the point of discussing the MACPEX case. In my view it is just another special case that could be covered by the sensitivity simulations. For the sake of clarity, I would suggest to leave it away.

We agree with the reviewer, that the discussion of the MACPEX case is neither enhancing the readability of the paper nor leading to other results than our standard case based on SEAC$^4$RS measurements. However, we think that presenting a further case, which yields similar sensitivities as the SEAC$^4$RS simulations, complements our results. Hence, we decided to present the MACPEX case in the appendix and adapted the figures and the text in Sec. 2. In Section 4.1, the last sequence (P. 18, l. 4–8, revised version of the manuscript) was changed, but still refers to the MACPEX case:

As a further example for an event with high stratospheric water vapour mixing ratios based on airborne measurements, simulations based on measurements during the Mid-latitude Airborne Cirrus Properties Experiments (MACPEX) were conducted. This campaign was based in Texas during springtime 2011 and hence prior to the formation of the North American Monsoon (NAM). A detailed description of this MACPEX case is given in the appendix (A1). For the MACPEX case, changes in sulphate, Cl$_y$ and NO$_y$ mixing ratios affect the water vapour threshold similarly to that observed for the SEAC$^4$RS trajectory. Thus, the MACPEX results confirm the SEAC$^4$RS findings. Therefore, we conclude that in the considered temperature range ($\sim$197–202 K), an ozone reduction occurs after exceeding a water vapour threshold and that this threshold varies with Cl$_y$, NO$_y$, sulphate content and temperature.

- Fig. 2: What is the rationale behind the chosen H2O mixing ratios of 5 and 15 ppmv? This choice seems a bit arbitrary to me. Why do you not use the 10.6 ppmv H2O of your standard case?
This study is aimed to investigate the sensitivity of mid-latitude lowermost stratospheric ozone chemistry to water vapour and to analyse the chemical mechanisms in detail. The best way to show the differences between the ozone chemistry at low and high water vapour mixing ratios is to choose water vapour mixing ratios, which are clearly in that water vapour regime. To be able to show the chlorine activation phase, we decided to take a water vapour mixing ratio of 15 ppmv instead of 20 ppmv. At 20 ppmv chlorine activation is very fast and reaction rates and mixing ratios are changing strongly. Since the mixing ratio of 10.6 ppmv H$_2$O of the realistic case is elevated comparing to the overall background conditions and close to the threshold, we decided against taking this case to illustrate the chemistry in a low water vapour regime.

To clarify this decision we added the following sentence in Sec. 3 (P.8, L.12, revised version of the manuscript).

These water vapour mixing ratios are chosen, because they are clearly in the regime of the low water vapour background (5 ppmv) of the lower mid-latitude stratosphere and of enhanced water vapour (15 ppmv) as it can be reached through convective overshooting events.

Furthermore, we clarified that choice in the description of Fig.2.

These water vapour mixing ratios are chosen, because they are clearly in the regime of low (5 ppmv) and elevated (15 ppmv) water vapour.

- P10, discussion of Fig. 3: In line 3-5 the water vapour threshold is defined as H$_2$O mixing ratio “at which the end ozone value clearly falls below the end ozone that is reached for low water vapour amounts.” What is meant by “clearly”? That sounds a bit vague. Can you be a bit more quantitative? Furthermore, it is stated that “by 12 ppmv of water vapour, the system is clearly in an ozone destruction regime.” But is 12 ppmv not just the water vapour mixing ratio at which the transition between ozone production to ozone destruction occurs? At lower H$_2$O values, end ozone is higher than initial ozone.

We agree with the reviewer that the description of the threshold is vague formulated. To make the formulation of the threshold more clear, we de-
terminated the lowest water vapour mixing ratio at which chlorine activation occurs to be the threshold. We changed the discussion of Fig. 3 as follows:

Blue squares lying above that line are cases with ozone production, those lying below that line are cases with ozone destruction. The decrease of final ozone with higher water vapour mixing ratios is related to chlorine activation. The time until chlorine activation occurs in the simulation is plotted in Fig. 3 as violet triangles, assuming that chlorine activation occurs when the ClO\textsubscript{x} mixing ratio exceeds 10% of total Cl\textsubscript{y} ([Drda and Müller] 2012). Shown is the time when chlorine activation first occurs in the model. Since the ClO\textsubscript{x}/Cl\textsubscript{y} ratio is dependent on the diurnal cycle, the 24-hours mean value of the ClO\textsubscript{x} mixing ratio was used to determine the chlorine activation time. For low water vapour mixing ratios, no chlorine activation time is plotted, because no chlorine activation occurs. For chlorine activation to occur, a threshold in water vapour has to be reached. Here, we determine the lowest water vapour mixing ratio at which chlorine activation occurs as water vapour threshold (marked by a blue arrow in Fig. 3). In our standard case, this threshold is reached at a water vapour mixing ratio of 10.6 ppmv. Between 10.6 and 12 ppmv H\textsubscript{2}O, chlorine activation leads not to an ozone destruction during the 7-day simulation. For 10.6 to 11.2 ppmv H\textsubscript{2}O, chlorine only remains activated for up to 28 h, because of increasing temperatures, and almost no impact on final ozone is observable. By 12 ppmv of water vapour, chlorine activation yields ozone destruction within the 7-day simulation. Near the water vapour threshold, the activation time is 24 to 36 hours and it decreases with increasing water vapour mixing ratios. It requires only 5 hours at 20 ppmv H\textsubscript{2}O.

-Fig. 4b: Where does the first sharp peak in the light blue line (ClONO\textsubscript{2}+HCl) come from?

In the chosen standard case (15 ppmv), the chlorine activation reaction R1 already occurs significantly within the first diurnal cycle. This would yield an increase in ClO\textsubscript{x}. Since the NO\textsubscript{2} mixing ratio is high at the same time, every formed ClO\textsubscript{x} leads to the formation of ClONO\textsubscript{2}. Hence, the ClONO\textsubscript{2} mixing ratio increases (Fig. 4f) and thus the rate of R1 (ClONO\textsubscript{2}+HCl). The chlorine activation chain (P.13, l. 3–7, ACPD version of the manuscript) requires light to transform Cl\textsubscript{2} to Cl-radicals. During night ClO\textsubscript{x} is accumulated in Cl\textsubscript{2} and Cl\textsubscript{2}O\textsubscript{2}. Hence, there is no ClO from which ClONO\textsubscript{2} could be formed
and the rate of R1 decreases rapidly. This yields the first sharp peak in the 
light blue line in Fig. 4b. For a better readability, we decided to not add this 
discussion to the paper.

- P13, l20ff: Shouldn’t this sentence read: Dependent on temperature and 
water vapour content, the HNO3 formed remains in the condensed phase.? 
And further down: ... 64% of the HNO3 remains in the condensed phase 
on the day with the lowest temperature, while at higher temperatures... 85% 
of HNO3 are released to the gas phase.... Is the HNO3 shown in Fig. 4d 
gas-phase only or total HNO3?

As the reviewer recommended, we revised the text as follows:

Dependent on temperature and water vapour content, the HNO3 formed re-
mains in the condensed particles. In the standard simulation using 15 ppmv 
H2O, 64% of HNO3 remains in the condensed phase on the day with the low-
est temperature (197.3 K, 2 Aug 2013), while at higher temperatures (4–7 
August 2013) 85% of HNO3 are released to the gas phase.

To clarify that HNO3 in Fig. 4d is total HNO3 (gas phase + condensed), we 
revised the description of Fig. 4.

Panels (d), mixing ratio of HNO3 (gas phase + condensed), NOx and ClONO2, ...

- P18/19 cycles C7 and C8: I have a hard time to follow the construction of 
these reaction cycles. My impression is that the authors combined different 
reactions until they ended up with the intended net reaction. For example: 
In R29 NO2 is formed, which in the next step photolyzes (R15). Lower down 
another NO2 is formed (R32), but this time it reacts with ClO to ClONO2 
(R22).

We revised the part about the maintenance of activated chlorine in Sec. 3.2.2. 
The detailed description of the pathways C7 and C8 is moved to the appendix. 
In Sec. 3.2.2, it is substituted by a scheme, which focuses on the main reac-
tions to balance chlorine activation and deactivation as well as HNO3 and 
NO2. This scheme is shown in Fig. [of this reply.}
Figure 3: Reaction scheme to illustrate the balance between chlorine activation and chlorine deactivation (blue, right) and NO\textsubscript{x} activation and deactivation (green, left). The heterogeneous reaction ClONO\textsubscript{2}+HCl (R1) links both cycles. Additional reaction pathways, which balance radicals are shown in light colours.

- P20, l 14-16: I think it would be helpful to mention the reason for the lower H2O threshold under enhanced sulphate conditions, namely the increased SAD. In general, the presentation of the model results would benefit from some more explanation of the underlying processes. This holds also for Sect. 4.2 and the sensitivity of the uptake coefficient to H2O or temperature. By the way, why is the 10xH2SO\textsubscript{4} case not shown in Fig. 7?

The sensitivity of the water vapour threshold to temperature, sulphate, Cl\textsubscript{y} and NO\textsubscript{y} is described in Sec. 4.1 and explained in Sec. 4.2. To clarify this, we added a reference to Section 4.2 in Sec. 4.1 (P.18, l.2, revised version of the manuscript).

The sensitivity of the water vapour threshold to temperature, sulphate abundance and Cl\textsubscript{y} and NO\textsubscript{y} mixing ratio is explained in Section 4.2.

... In general, the presentation of the model results would benefit from some more explanation of the underlying processes. This holds also for Sect. 4.2
and the sensitivity of the uptake coefficient to H2O or temperature. ...

To go into the underlying processes, we mention that the $\gamma$-value depends on the weight-% on sulphuric acid in the particles (which is known from laboratory studies). Therefore a further panel illustrating the dependence of the H$_2$SO$_4$ wt% on the water vapour mixing ratio was included in Fig. 8 of the revised version of the manuscript (Fig. 1 of this reply). We revised the text in Sec. 4.2 (p.19, l.11–23, revised version of the manuscript):

The $\gamma$-value describes the uptake of ClONO$_2$ into liquid particles due to the decomposition of ClONO$_2$ during reaction R1 and is thus a measure of the probability of the occurrence of this heterogeneous reaction ([Shi et al.,] 2001). Laboratory studies showed a dependence of $\gamma_{R1}$ on the solubility of HCl in the droplet, which generally increases for a lower H$_2$SO$_4$ fraction in the particle (H$_2$SO$_4$ wt%) ([Elrod et al.,] 1995 [Hanson,] 1998 [Zhang et al.,] 1994 [Hanson and Ravishankara,] 1994). From Eq. 2 it is obvious that a large surface area $A_{liq}$ and a high $\gamma$-value $\gamma_{R1}$ increase $k_{R1}$ and thus the heterogeneous reaction rate $v_{R1}$.

In Figure 8, the impact of the water vapour content on the H$_2$SO$_4$ weight-percent, $\gamma_{R1}$, $A_{liq}$, $k_{R1}$ and the reaction rate $v_{R1}$ is shown. To avoid the influence of R1 itself on these parameters as much as possible, these parameters are selected for 1 August 2013 at 13:00 UTC. This point in time corresponds to the values after the first chemistry time step during the chemical simulation. The particles H$_2$SO$_4$ wt% decreases for all cases with increasing water vapour from more than 50 wt% at 5 ppmv H$_2$O to around 20 wt% at 20 ppmv H$_2$O due to an increasing uptake of H$_2$O in the thermodynamic equilibrium. The standard case is illustrated in blue squares (Fig. 8) and exhibits a strongly increasing gamma value especially for water vapour mixing ratios between 9 and 14 ppmv due to a lower H$_2$SO$_4$ wt%. In the same water vapour range, the liquid surface area density $A_{liq}$ increases slightly. It increases more for higher water vapour mixing ratios because of HNO$_3$ uptake into the particles.

...By the way, why is the 10xH$_2$SO$_4$ case not shown in Fig. 7?

The aim of Fig. 7 (ACPD version of the manuscript, Fig. 8 of revised version of the manuscript, Fig 1 in this reply) is to illustrate the sensitivity of the water vapour threshold. To focus on this processes, we decided to not
show the 10xH$_2$SO$_4$ case here. The 10xH$_2$SO$_4$ case yields higher values for the surface area, the reaction rate and the rate constant. If we would show also the 10xH$_2$SO$_4$ case, the detailed discussion in Sec. 4.2 would not benefit from Fig. 7 (ACPD version of the manuscript, Fig. 8 of revised version of the manuscript).

- P20, discussion of Fig. 6b: I do not understand the statement that similar conclusions as for the SEAC$^4$RS trajectory hold for the MACPEX trajectory. For almost all cases final O$_3$ is higher than initial O$_3$. And why is there only a subset of sensitivities shown for the MACPEX trajectory? Why not also +1K and 10xH$_2$SO$_4$?

The statement refers to the sensitivity of the water vapour threshold (and thus chlorine activation) to Cl$_y$, NO$_y$, temperature and sulphate. This sensitivity is similar in the MACPEX and SEAC$^4$RS case. In the MACPEX case, final ozone is higher than initial ozone because of the low Cl$_y$ mixing ratio ($\sim$55 pptv). Hence, the catalytic ozone loss cycles have lower rates and ozone is destroyed slower. We added the 10xH$_2$SO$_4$ and +1K case to Fig. 6b (ACPD version of the manuscript, Fig. B2 in the revised version of the manuscript).

- Fig. 6: What is the rationale for the 3xH$_2$SO$_4$ case?

The 3x H$_2$SO$_4$ case is shown here as well, because it is the lowest H$_2$SO$_4$ amount, which would yield ozone destruction in the realistic case (see Sec. 5.2).

- P25, l3-5: I do not fully understand this argumentation. Do you mean that there is no longer enough ClONO$_2$ available to react with the HCl taken up by the condensed particles and that therefore the enhanced HCl uptake does not lead to further chlorine activation and ozone loss?

This argumentation only refers to ozone destruction, not also chlorine activation. After chlorine activation occurred, ozone loss is driven by chlorine catalysed ozone loss cycles. The more chlorine is available in the gas phase, the more ozone can be destroyed by this cycles. An uptake of HCl into the condensed particles reduces gas phase chlorine. Hence, also the chlorine catalysed ozone loss cycles have lower rates and less ozone is destroyed.
- Fig. 8: This figure nicely shows the different ozone regimes as a function of temperature and H2O for two different sulphate conditions. Would it possible to provide such figure also for Cly, Bry, NOy sensitivities? I am aware that this is a multi-dimensional problem, but I think it would be really helpful to get an overview under which conditions ozone formation and ozone depletion occurs. This would also help to get a better understand of the importance of this mechanism on larger scales.

We did the same plot for the 0.8 Cl_y, 0.8 NO_y and 0.5Br_y case (see Fig.5 of this reply). Only minor differences regarding the standard case are observable. For the 0.8 Cl_y and the 0.5 Br_y case, less ozone is destroyed if chlorine activation occurs and the chlorine activation line is slightly shifted. Assuming the 0.8 NO_y case yields a minor shift of the chlorine activation line. Since these tendencies are rather small, we think they are more clear in Fig. 7 of the revised version of the manuscript. Hence, we decided against showing these plots in the paper.

We agree with the reviewer that it would be helpful to apply the processes analysed here on a larger scale also showing the climatological perspective. Therefore, we started a second comprehensive study looking on the likelihood of the occurrence of ozone loss in the WACCM model at mid-latitudes in the lowermost stratosphere that is beyond the slope of our current study. The study here is mainly focused on the mechanisms itself. To enable here already an estimation for the relevance of this process under further conditions, we conducted the sensitivity studies (0.8Cl_y, 0.8NO_y, 0.5Br_y, several H_2SO_4 abundances and temperatures) and case studies (other time duration, observed SEAC4RS conditions, MACPAX case). These additional studies give an estimation for extending the results of this study to a larger scale.
Figure 4: Relative ozone change during the 7-day simulation along the standard trajectory dependent on temperature and H$_2$O mixing ratio for several conditions. The white line corresponds to the water and temperature dependent chlorine activation threshold. In the top-panels, climatological non enhanced (left panel) and enhanced (right panel) sulphate conditions are shown. In the middle panels the impact of a reduction of Cl$_y$ (left) and NO$_y$ (right) and in the bottom panel of Br$_y$ on the ozone change are shown.

- Sect. 5: As mentioned above I think the case studies are too much and do not help to provide further insights into the main chemical mechanism. It’s rather confusing to distinguish the various atmospheric compositions assumed for the individual model simulations. In particular the 19-days case seems
trivial to me: longer time under cold and humid conditions, more ozone loss.

We agree that the sensitivity studies are very detailed and comprehensive. But we think, that they give an insight in the sensitivities of the ozone loss processes and thus enable to apply this processes on a larger scale of realistic conditions than only the chosen example. To make this part less excessive, we moved the chemical details of the ‘Case of high Cl$\gamma$', the ‘Reduced Br$\gamma$ case’ and the ‘19-day Simulation’ to supplemental material. We only show the effect of this cases on the water vapour threshold in a new Figure (see Fig. 5 of this reply, Fig. 11 of the revised version of the manuscript). We did not change the ‘Case based on observations’.

Technical corrections:
- P3, l19: hypothesis hat → hypothesis that
- P4, l8: ans → and
- P4, l20: HNO3+2N2O5
- P8, l3: N2O, 2 should be subscript
- P9, l28: ClOx, x should be subscript
- P16, l3: simultaneous → simultaneous
- P17, l29: HCl-formating → HCl-forming
- P34, l19: and extreme → an extreme

As the reviewer recommended, we revised these sequences in the text.

- Units: The text is a mixture of ppb/ppt and ppbv/pptv. I assume it is always volume mixing ratio?

We revised the text to use only the volume mixing ratio.
- Chemical reactions: It would be nice to mark heterogenous reactions as such.

In the revised version of the manuscript, heterogeneous reactions are marked (het).

- Table 1: I would suggest to add Cly and NOy for completeness. And are 0.6 ppbv and 2.0 ppbv H2SO4 not also sensitivity simulations?
Figure 5: The water dependent final ozone value is shown for (a) the “Case of high Cl$_y$” (see Tab. 1 for NO$_y$ and Cl$_y$ initialisation) assuming background aerosol (light blue) and tripled H$_2$SO$_4$ (yellow), (b) reduced Br$_y$ (light blue, “Reduced Br$_y$ case”), and (c) an extended time period of activated chlorine (light blue, “19-day simulation”). In panel (b) and (c) also final ozone of the standard case is shown (blue). Initial ozone is marked with a grey line. Note that the scale of all y-axis differ.

As proposed by the reviewer, we added Cl$_y$ and NO$_y$ to Table 1 and moved the initialisations with enhanced H$_2$SO$_4$ (0.6 and 2.0 H$_2$SO$_4$) to the column, which presents the sensitivity studies.

- **Fig 1.** It would be nice to mark the time of measurement by a red square or a vertical line also to the left panels. And maybe the tropopause altitude at the location of the airparcel could also be added to the left panel.
As recommended by the reviewer, we mark the time of measurement in the left panels of Fig. 1 with a vertical red line as well as the tropopause at the location of the air parcel with a horizontal grey line.

- Fig. 4, 9, 10, 11, 12: Which time of day do the x-axis tick marks refer to? One can infer night-/day-time from the reactions with OH, but it would be helpful to provide this information, e.g., in the caption.

In the ACPD version of the manuscript, the x-axis tick marks refer to 00:00 UTC. In the revised version of the manuscript, they refer to 00:00 local time, which corresponds to 06:00 UTC on that day. To clarify this in the text, we added the following sentence to the caption of that figures.

The x-axis ticks refer to 00:00 local time (06:00 UTC).

- Fig. 7: units (y-axis) are missing

We added the units in Fig. 7 in the ACPD version of the manuscript (Fig. 8 of the revised version of the manuscript, Fig. [1] in this reply). The $\gamma$-value has no unit.

References


Mechanism of ozone loss under enhanced water vapour conditions in the mid-latitude lower stratosphere in summer

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Abstract. Water vapour convectively injected into the mid-latitude lowermost stratosphere could affect stratospheric ozone. The associated potential ozone loss process requires low temperatures and an elevated water vapour mixing ratio. Since this ozone loss is initiated by heterogeneous chlorine activation on liquid aerosols, an increase in sulphate aerosol surface area due to a volcanic eruption or geoengineering could increase the likelihood of occurrence of this process. However, the chemical mechanism of this ozone loss process has not yet been analysed in sufficient detail and its sensitivity to various conditions is not yet clear. Under conditions of climate change associated with an increase in greenhouse gases, both a stratospheric cooling and an increase in water vapour convectively injected into the stratosphere is expected. Understanding the influence of low temperatures, elevated water vapour and enhanced sulphate particles on this ozone loss mechanism is a key step in estimating the impact of climate change and potential sulphate geoengineering on mid-latitude ozone.

Here, we analyse the ozone loss mechanism and its sensitivity to various stratospheric conditions in detail. Conducting a box-model study with the Chemical Lagrangian Model of the Stratosphere (CLaMS), chemistry was simulated along a 7-day backward trajectory. This trajectory was calculated neglecting mixing of neighbouring air masses. Chemical simulations were initialized using measurements taken during the Study of Emissions and atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC⁴RS) aircraft campaign (2013, Texas), which encountered an elevated water vapour mixing ratio of ¹⁰.⁶ ppmv at a pressure level around 100 hPa. We present a detailed analysis of the ozone loss mechanism, including the chlorine activation, chlorine catalysed ozone loss cycles, maintenance of activated chlorine and the role of active nitrogen oxide radicals (NOₓ). Focussing on a realistic trajectory in a temperature range from ¹⁹⁷–²⁰³ K, a threshold in water vapour of ¹¹.⁰–¹¹.₆ ppmv has to be exceeded and maintained for stratospheric ozone loss to occur. We investigated the sensitivity of the water vapour threshold to temperature, sulphate content, inorganic chlorine (Clᵢ), inorganic nitrogen (NOᵧ) and inorganic bromine (Brᵧ). The water vapour threshold is mainly determined by the temperature and sulphate content. However, the amount of ozone loss depends on Clᵢ, Brᵧ and the duration of the time period over which chlorine activation can be maintained. NOᵧ affects both the potential of ozone formation and the balance between reactions yielding chlorine activation and -deactivation, which determines the water vapour threshold. Our results show that in order to deplete ozone, a
chlorine activation time of 24 to 36 hours for conditions of the water vapour threshold with low temperatures and high water vapour mixing ratios must be maintained. A maximum ozone loss of 9% was found for a 20 ppmv water vapour mixing ratio at North American Monsoon (NAM) tropopause standard conditions with the model run a chemical box-model simulation along a realistic trajectory. For the same trajectory, using observed conditions (of 10.6 ppmv), whether ozone loss occurs was simulated $H_2O$, the occurrence of simulated ozone loss was dependent on the sulphate amount assumed. Detailed analysis of current and future possibilities is needed to assess whether enhanced water vapour conditions in the summertime mid-latitude lower stratosphere leads lead to significant ozone loss.

1 Introduction

The impact of water vapour convectively injected into the lowermost stratosphere on the mid-latitude ozone layer is a matter of current debate (Anderson et al., 2012, 2017; Ravishankara, 2012; Schwartz et al., 2013). Borrmann et al. (1996, 1997) and Solomon et al. (1997) investigated While Anderson et al. (2012) focused on the heterogeneous chemistry of cold liquid sulfate aerosol, earlier studies have focussed on the influence of cirrus clouds on ozone chemistry in the lowermost stratosphere (Borrmann et al., 1996, 1997; Solomon et al., 1997; von Hobe et al., 2011). Anderson et al. (2012) proposed a potential ozone depletion in the mid-latitude stratosphere in summer on liquid sulphate aerosols under conditions of enhanced water vapour and low temperatures. They proposed this chemical ozone loss to occur under these conditions through processes be initiated through heterogeneous chlorine activation and to be driven by catalytic ozone loss cycles related to ozone loss known from polar regions in early spring (e.g. Grooß et al., 2011; Solomon, 1999; Vogel et al., 2011). Here, we present a detailed analysis of this ozone loss mechanism and an extensive investigation of its sensitivity to a variety of conditions. In the bulk and on the surface of cold condensed stratospheric particles, such as binary $H_2SO_4/H_2O$ solutions, ternary solutions, NAT (Nitric Acid Trihydrate) and ice particles (e.g. Spang et al., 2018), inactive chlorine species (HCl, ClONO$_2$) can be converted to active chlorine (ClO$_x$=Cl+ClO+2 $\times Cl_2$O$_2$+2 $\times Cl_2$) through the heterogeneous reactions R1, R2 and R3 (Solomon et al., 1986; Prather, 1992; Crutzen et al., 1992) and the subsequent photolysis of Cl$_2$ and HOCl.

$$ClONO_2 + HCl \xrightarrow{het.} HNO_3 + Cl_2$$ \hspace{1cm} (R1)

$$ClONO_2 + H_2O \xrightarrow{het.} HNO_3 + HOCl$$ \hspace{1cm} (R2)

$$HCl + HOCl \xrightarrow{het.} H_2O + Cl_2$$ \hspace{1cm} (R3)

The heterogeneous reactions R1 and R2 drive the conversion of active nitrogen-oxides (NO$_x$=NO + NO$_2$ + NO$_3$ + 2 $\times N_2O_5$) into HNO$_3$. After chlorine activation, catalytic ozone loss cycles can occur, such as the ClO-dimer-cycle (Molina and Molina, 1987) (Molina and Molina, 1987) and the ClO-BrO-cycle (McElroy et al., 1986). These cycles are responsible for the rapid ozone loss observed in Antarctic spring (e.g. Solomon, 1999). ClO Dimer Cycle (??): $+ \rightarrow + + + \xrightarrow{hv} + + + + + + + + + + + 2 \rightarrow 0$ A third cycle with ClO and HO$_2$ (see Sec. In a third catalytic ozone loss cycle, C2, HOCl is formed and subsequently photolysed yielding OH and Cl radicals leading to stratospheric ozone
destruction) proposed by Solomon et al. (1986) would be expected to play a role in ozone loss in the mid-latitude lower stratosphere (e.g. Daniel et al., 1999; Ward and Rowley, 2016). This cycle was originally proposed by Solomon et al. (1986) as an ozone depleting cycle in the Antarctic lower stratosphere, but for polar ozone destruction, this cycle turned out to be of minor importance (Solomon, 1999). Nevertheless, C2 would be expected to play a role in ozone loss in the mid-latitude lower stratosphere (e.g. Daniel et al., 1999; Ward and Rowley, 2016).

Under the very dry conditions in the polar stratosphere, very low temperatures (below ~195 K) are required for heterogeneous chlorine activation through reactions R1–R3 (Solomon, 1999; Shi et al., 2001). An enhancement of water vapour above background values would allow chlorine activation at higher temperatures (200–205 K) (Drdla and Müller, 2012), which led to the hypothesis that chlorine activation and subsequent ozone loss could occur at mid-latitudes in summer in the lowermost stratosphere (Anderson et al., 2012, 2017; Anderson and Clapp, 2018). The aim of our study is to investigate for a variety of conditions by how much water vapour has to be enhanced for chlorine activation to occur at these higher temperatures.

An enhanced stratospheric sulphate aerosol content increases heterogeneous chlorine activation by increasing the surface area of the condensed particles (Drdla and Müller, 2012; Solomon, 1999). As an example, the aerosol surface area density in the lower stratosphere ranges between ~0.5 and 1.5 \( \mu \text{m}^2 \text{cm}^{-3} \) under non-volcanic conditions (Thomason and Peter, 2006), while the perturbation of Mt. Pinatubo yielded peak values of more than 40 \( \mu \text{m}^2 \text{cm}^{-3} \) (Thomason et al., 1997). In the stratosphere, water vapour increases with altitude, primarily due to methane oxidation (LeTexier et al., 1988; Rohs et al., 2006). The upper branch of the Brewer Dobson circulation (BDC) transports higher stratospheric water vapour mixing ratios down to lower altitudes at mid to high latitudes, and this air mixes with the low water vapour containing air from the tropics that has moved poleward in the lower branch of the BDC (e.g. Brewer, 1949; Randel et al., 2004; Schwartz et al., 2013; Konopka et al., 2015; Poshyvailo et al., 2018), giving typical mid-latitude lowermost stratosphere values of 2–6 ppmv H2O. However, above North America in summer, enhanced water vapour mixing ratios of 10–18 ppmv at an altitude of ~16.5 km (380 K potential temperature, ~ 100 hPa) (Smith et al., 2017) have been observed, which were connected with deep convective storm systems penetrating the tropopause (Homeyer et al., 2014; Herman et al., 2017; Smith et al., 2017). These convective overshooting events can transport ice crystals into the lowermost stratosphere, where the ice evaporates leading to a local enhancement of water vapour (Hanisco et al., 2007; Schiller et al., 2009; Herman et al., 2017).

As greenhouse gases increase in the atmosphere, models predict that more water may be convectively transported into the stratosphere (Trapp et al., 2009; Klooster and Roebber, 2009). This increases the possibility that the ozone loss process proposed by Anderson et al. (2012) will occur, especially in the case of an additional enhancement of stratospheric sulphate particles caused by volcanic eruptions or sulphate geoengineering. However, the occurrence of this ozone loss process requires halogens to be present, which are decreasing in the stratosphere due to the Montreal Protocol and its amendments and adjustments (WMO, 2014) (WMO, 2018). However, for assessing the impact of geoengineering on the ozone layer, also the impact of very short lived halogens needs to be taken into account (Tilmes et al., 2012). For estimating the impact of both climate change and a possible sulphate geoengineering on the mid-latitude ozone layer, it is necessary to consider the influence of enhanced water vapour and sulphate content on mid-latitude ozone chemistry in the lowermost stratosphere in more detail.
In the study by Anderson et al. (2012), a range of initial mixing ratios for HCl and ClONO$_2$ with rather high concentrations of 850 pptv HCl and 150 pptv ClONO$_2$ was assumed. Here, we investigate ozone loss in mid-latitude summer based on measurements from flights by the NASA ER-2 aircraft during the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC$^4$RS) campaign, which was based in Houston, Texas in 2013 (Toon et al., 2016). Conducting box-model simulations with the Chemical Lagrangian Model of the Stratosphere (CLaMS, McKenna et al., 2002a, b), the ozone loss mechanism is analysed in greater detail. The model setup is described in Section 2. In Sec. 3, the chlorine activation step, catalytic ozone loss cycles and the maintenance of activated chlorine levels in the mid-latitude stratosphere are investigated in detail. The sensitivity of this mechanism to water vapour, sulphate content, temperature, Cl$_y$ mixing ratio (Cl$_y$=HCl+ClONO$_2$+ClO$_x$), reactive nitrogen (NO$_y$=NO$_x$+HNO$_3$+) and inorganic bromine (Br$_y$) is explored in Sec. 4. Case studies, which extend the simulated time period and assume conditions based on both SEAC$^4$RS and MACPEX (Mid-latitude Airborne Cirrus Properties Experiment) measurements as well as conditions used in the study of Anderson et al. (2012), further illustrate these sensitivities in Sec. 5.

2 Model setup

The simulations presented here were performed with the box-model version of CLaMS (McKenna et al., 2002a, b). Stratospheric chemistry is simulated based on a setup used in previous studies (Grooß et al., 2011; Müller et al., 2018; Zafar et al., 2018) for single air parcels along trajectories including diabatic descent and neglecting mixing between neighbouring air masses. A full chemical reaction scheme comprising gas phase and heterogeneous chemistry is applied using the SVODE-solver (Brown et al., 1989). Chemical reaction kinetics are taken from Sander et al. (2011), photolysis rates are calculated for spherical geometry (Becker et al., 2000), and heterogeneous reaction rates for R1–R3 were calculated based on the the study of Shi et al. (2001), and photolysis rates are calculated for spherical geometry (Becker et al., 2000). For heterogeneous particle formation, the initial liquid aerosol number density ($N_0=10.0\,\text{cm}^{-3}$), the standard deviation of the logarithmic normal distribution of the particle size ($\sigma=1.8$), and the gas phase equivalent of the amount of sulfuric acid in the aerosol (for chosen values see Tab. 1) are set prior to the simulation. The gas phase equivalent is used to calculate the density of liquid particles as described in the study of Shi et al. (2001) (binary solutions) and Luo et al. (1996) (ternary solutions). Particle size and surface area density are calculated based on the density of liquid particles, the aerosol number density, and the standard deviation. In contrast to the setup in Grooß et al. (2011), Müller et al. (2018) and Zafar et al. (2018), only formation of liquid particles (both binary H$_2$O/H$_2$SO$_4$ and ternary HNO$_3$/H$_2$O/H$_2$SO$_4$ solutions) is allowed (i.e. no NAT or ice particles are formed in this model setup) to enable a better comparability with the studies of Anderson et al. (2012, 2017) and Anderson and Clapp (2018). Note that this is also different from the study of and the study of Borrmann et al. (1996, 1997), who investigated lowermost stratospheric ozone chemistry on cirrus clouds.
2.1 Measurements

The box model simulations were initialized using water vapour, ozone and CH$_4$ measurements taken during the SEAC$^4$RS aircraft campaign and water vapour, ozone and measurements taken during MACPEX campaign (more information on the chemical initialization is provided in Section 2.3). The investigation of mid-latitude ozone chemistry presented here is primarily based on SEAC$^4$RS conditions, while simulations based on MACPEX data were conducted to complement the results of the investigation by showing a further measurement-based example. The SEAC$^4$RS campaign took place during the North American summertime, while the MACPEX campaign was in spring, prior to the build up of the North American Monsoon (NAM) anticyclone. The SEAC$^4$RS campaign It was based in Houston, Texas, and took place during August and September 2013 (Toon et al., 2016). One aim of this campaign was to investigate the impact of deep convective clouds on the water vapour content and the chemistry in the lowermost stratosphere. We initialized the model using measurements taken on 8 August 2013 by the Harvard Lyman-α–Lyman-α photofragment fluorescence hygrometer (HWV, Weinstock et al., 2009), which flew on the NASA ER-2 high altitude research aircraft. Ozone was initialized in our simulations using O$_3$ measurements from the National Oceanic and Atmospheric Administration (NOAA) UAS-O$_3$-instrument (Gao et al., 2012). Initial Cl$_y$ and NO$_y$ were determined using tracer-tracer correlations (for more informations see Sec. 2.3) based on methane measurements with the Harvard University Picarro Cavity Ring down Spectrometer (HUPCRS) (Werner et al., 2017). The simulation results initialized with SEAC$^4$RS measurements were compared with a case of enhanced lower stratospheric water sampled during the spring 2011 MACPEX campaign (Rollins et al., 2014) also based in Houston, Texas. The water vapour values used here were measured by the Fast In-situ Stratospheric Hygrometer (FISH), which employs the Lyman-α photofragment fluorescence technique (Meyer et al., 2015). MACPEX ozone was measured by the UAS-instrument (Gao et al., 2012). Initial and were assumed based on tracer-tracer correlations with that was measured by the Jet Propulsion Laboratory’s Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument (Webster et al., 1994).

2.2 Trajectories

Diabatic trajectories were calculated using wind and temperature data from the ERA-Interim reanalysis (Dee et al., 2011) with $1^\circ \times 1^\circ$ resolution provided by the European Centre for Medium-Range Weather Forecasts (ECMWF). The vertical velocities were calculated from the total diabatic heating rates derived from ERA-Interim data (Ploeger et al., 2010). Trajectories (7-day 7-day forward and backward) were initialized at locations during MACPEX and SEAC$^4$RS where stratospheric water vapour was over 10 ppmv. Selected examples A selected example of calculated trajectories are is shown in Fig. 1. These trajectories were This trajectory was chosen for the chemical analysis, because the initial conditions exhibited enhanced water vapour relative to the overall background and the temperatures were very low. These are then low temperatures and enhanced Cl$_y$ (higher than for comparable water vapour and temperature conditions). Cl$_y$ was calculated from tracer-tracer correlations (see Sec. 2.3). This trajectory is then most suitable for the occurrence of the mechanism proposed by Anderson et al. (2012). In the left panel, backward trajectories are a backward trajectory is presented in the range of −7 to 0 days from the time of measurement and
forward trajectories (red line) and a forward trajectory in the range from 0 to 7 days. In the right panel, the location of the measurement is shown by a red square. The black trajectory refers to a measurement on 11 April 2011 during the MACPEX campaign. The potential temperature level of this trajectory is around 380 and above the tropopause located at \( \sim 350 \), which was deduced from the temperature profile measured during the flight on 11 April 2011. The backward trajectory reaches very low temperatures with a minimum temperature of 191. The forward trajectory shows a strongly increasing temperature and pressure level due to a decrease in altitude. Coming from the Western Pacific, this air parcel passes the North American continent briefly. For this study numerous water measurements of the MACPEX campaign were analysed, but only few values of more than 10 were observed above the tropopause. The trajectory marked in blue in Fig.

The shown trajectories (Fig. 1, a forward and a backward trajectory) are based on measurements on 8 August 2013 during the SEAC\(^4\)RS campaign. With a potential temperature of 380 to 390 K, this trajectory is above the tropopause of \( \sim 370\text{ \(K\)} \) (Fig. 1 left, grey line), deduced from the temperature profile measured during the flight. Both, the forward and backward trajectories stay in the region of the North American continent. For the SEAC\(^4\)RS campaign, the temperature range of the backward trajectory varies between 197 and 202 K and the forward trajectory exhibits increasing temperatures. In addition, we considered trajectories based on other SEAC\(^4\)RS measurements with enhanced water vapour, however most of them exhibit higher mean temperatures of at least 200 K. Since low temperatures are expected to push stratospheric ozone depletion in mid-latitudes (Anderson et al., 2012) due to faster heterogeneous chemical reactions and thus faster chlorine activation, the SEAC\(^4\)RS backward trajectory (Fig.1, blue day \(-7\) to \(0\)) is selected here as the standard trajectory.

This trajectory is used to analyse the chemical mechanisms affecting lower stratospheric ozone under various water vapour conditions, and to explore the sensitivity of these processes to different initial conditions.

### 2.3 Initialization

Important trace gases for ozone chemistry – \( \text{O}_3 \), \( \text{Cl}_y \) and \( \text{NO}_y \) – are initialized based on measurements during the SEAC\(^4\)RS and MACPEX aircraft campaigns, aircraft campaign over North America (see Sec. 2.1). Ozone and water vapour were measured directly during the aircraft campaigns. \( \text{Cl}_y \) and \( \text{NO}_y \) are inferred from tracer-tracer relations using either correlations using \( \text{CH}_4 \) (SEAC\(^4\)RS) or (MACPEX) measured on the aircraft employed. The initialization of all further trace gases except of water vapour were taken from the full chemistry 3D-CLaMS simulation (Vogel et al., 2015, 2016) for summer 2012 at the location of the measurement. Chemistry was initialized 7 days before the measurement. However, this time shift does not affect the sensitivities and the mechanism investigated here, because the trace gases \( \text{Cl}_y \) and \( \text{NO}_y \) were initialized based on measured \( \text{CH}_4 \) and mixing ratios, which are not significantly changing during a 7-day box-model simulation.

#### 2.3.1 Standard case

In the standard case, the initial values of \( \text{O}_3 \), \( \text{Cl}_y \) and \( \text{NO}_y \) are determined based on an observation with an enhanced water vapour content of 10.6 ppmv (measured by the HWV-instrument) from the SEAC\(^4\)RS (Toon et al., 2016) aircraft campaign. A gas phase equivalent mixing ratio for background sulphuric acid (\( \text{H}_2\text{SO}_4 \)) of 0.20 ppbv is assumed. Initial \( \text{CO} \) (49.6 ppbv) is taken from the 3D-CLaMS simulation (Vogel et al., 2015), which is higher than the measured value of 34.74 ppbv (measured
by the HUPCRS instrument). Simulations assuming the measured CO mixing ratio showed only a minor difference to the results presented here. The initial values for the main trace gases for the standard case are summarized in Table 1. Note, in the 3D-CLaMS simulation, the mixing ratios of HCl (131 ppt, CLaMS), O₃ (206 ppb, CLaMS) and HNO₃ (354 ppt, CLaMS) are at the location of the SEAC⁴RS measurement lower than in the standard initialization (see Tab. 1).

Since Clₙ and NOₙ were not measured during the SEAC⁴RS ER2-flights in the lowermost stratosphere, values for Clₙ and NOₙ are calculated through tracer-tracer correlations (Groß et al., 2014, see Appendix C for equations) based on a SEAC⁴RS CH₄ measurement (of 1.776 ppmv) on 8 August 2013. The Clₙ-CH₄ correlation was calculated from measurements of the Airborne Chromatograph for Atmospheric Trace Species (ACATS) during flights of the ER-2 aircraft and from measurements by the cryogenic whole air sampler (Tripleof the university of Frankfurt (on board of the TRIPLE balloon gondola) during balloon flights at mid and high latitudes in the year 2000 (Groß et al., 2002). Between the year 2000 and 2013 stratospheric CH₄ increased and Clₙ decreased. Hence, the change of both lowermost stratospheric CH₄ and Clₙ has to be taken into account when using this tracer-tracer correlation. The increase in CH₄ was estimated to be equivalent to the growth rate for tropospheric CH₄. This growth rate was calculated to be 45.8 ppb/ppbv from the year 2000 to 2013 by determining and adding every annual mean of the tropospheric CH₄ growth rate given in GHG Bulletin (2014). Subtracting this increase of CH₄ from the measured CH₄ mixing ratio yields an equivalent CH₄ equivalent for the year 2000. From the CH₄ equivalent, an equivalent Clₙ mixing ratio for the year 2000 was calculated using the tracer-tracer correlation (Groß et al., 2014). The annual decrease of Clₙ is assumed to be 0.8% (WMO, 2014) from the year 2000 to 2013, and thus the initial Clₙ is calculated to be 156 ppt. Since most

**Figure 1.** Pressure, potential temperature, temperature and location of the selected 7-day trajectories (forward and backward) calculated based on measurements with enhanced water vapour during the MACPEX (black) and SEAC⁴RS (blue) aircraft campaigns. Red In the left panels, the grey line marks the approximate tropopause altitude, deduced from the temperature profile measured during the flight. The red line (left panel) marks the time of measurement and red squares (right panels) mark the location of the measurement (right). For the right panels, the bottom panel exhibits a zoom from the top panel. In the bottom panel, and the MACPEX trajectory consists of single squares due to a faster movement begin of the air parcel in that region. Backward-trajectory (1 August) is marked by a green arrow.
Cl$_y$ is deactivated in the mid-latitude lowermost stratosphere, the initial mixing ratio of ClO$_x$ species is assumed to be zero. A simulation assuming a ClO mixing ratio of 1% of total Cl$_y$, does not yield a significant difference to our standard case. Initial NO$_y$ was calculated through a N$_2$O correlation. Since no N$_2$O was measured on the ER2-flights during SEAC$^4$RS, stratospheric N$_2$O-N$_2$O was first estimated through a methane correlation (Grooß et al., 2002), which is based on measurements from the year 2000. Hence, the equivalent CH$_4$ mixing ratio for the year 2000 (see above) was used to calculate an N$_2$O equivalent. Considering an estimated increase in N$_2$O of 10.4 ppb from 2000 to 2013, which was determined in the same way as the CH$_4$ change (GHG Bulletin, 2014), the N$_2$O mixing ratio related to the time of the measurement in 2013 was calculated. Afterwards NO$_y$ is calculated with a correlation from Grooß et al. (2014) to be 782.9 ppt.

This standard case initialization is shown in Table 1. Because of the uncertain conditions in convective overshooting plumes, sensitivity box-model simulations are conducted. Furthermore, testing the impact of various parameters on chemical ozone loss is intended to yield a better understanding of the balance between stratospheric ozone production and ozone loss, which is a key aspect for potential mid-latitude ozone depletion. The assumed water vapour content in a simulation is varied from 5 to 20 ppmv. In addition, simulations assuming the same water vapour range and a constant temperature in a range from 195–220 K are conducted assuming sulphate background conditions with a gas phase equivalent of 0.20 ppbv and 10×enhanced sulphate (2.00 ppbv) for illustrating the dependence of ozone loss on water vapour and temperature. Furthermore, sensitivity simulations are conducted, assuming 80% Cl$_y$, 80% NO$_y$ or 50% Br$_y$, and a standard case simulation along a 19-day trajectory is calculated.

### 2.3.2 Case of high Cl$_y$

Simulations conducted assuming high Cl$_y$ and NO$_y$ concentrations taken from Fig. 2 in Anderson et al. (2012) are referred to as “Case of high Cl$_y$”, which constitutes a worst case scenario. In the case of high Cl$_y$, HNO$_3$ is determined as 1.19 ppb assuming the same ratio for HNO$_3$ (63% of total NO$_y$) and NO+NO$_2$ (37% of total NO$_y$) as in the standard case. An overview of the important trace gases in the initialization is given in Tab. 1. The results of the case initialized with high Cl$_y$ are compared with the results obtained from standard case simulations.

### 2.3.3 MACPEX Case

Similar to the standard case, a simulation based on measurements during the MACPEX aircraft campaign 2011 (Rollins et al., 2014) was conducted, referred to as “MACPEX Case”. This case presents a further example for an event with high stratospheric water vapour based on airborne measurements and complements the results obtained from the standard case. All trace gases except for ozone, , and water vapour are taken from a 3D CLaMS simulation (Vogel et al., 2015, 2016). Initial and is calculated based on as and tracer-tracer correlations (Grooß et al., 2014) with corrections considering a increase from 2009 to 2013 and a increase from 2000 to 2009, is determined using the same correlation with as for the standard case. Therefore is first calculated using measured of 320.28 ppbv and a correlation based on measurements from 2009 (Grooß et al., 2014). The increase of stratospheric and is considered as described for the standard case (GHG Bulletin, 2014). First, an increase in of 1.6 ppb from 2009 to 2011 is estimated to adjust. Furthermore calculated is adjusted considering a difference between in 2000 and 2009 of
Table 1. Mixing ratios and sources used for initialization of relevant trace gases. The standard initialization is based on SEAC^4RS measurements. Cl\textsubscript{y} and NO\textsubscript{y} values were determined based on tracer-tracer correlations (see Sec. 2.3.1) for the standard and the MACPEX case. The high Cl\textsubscript{y} case is based on Fig. 2 from Anderson et al. (2012). Initial mixing ratios of ClO\textsubscript{x} species were assumed to be zero for all cases.

<table>
<thead>
<tr>
<th>Species</th>
<th>Standard case</th>
<th>Case of high Cl\textsubscript{y}</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{3}</td>
<td>303.2 ppbv UAS-O\textsubscript{3}</td>
<td>303.2 ppbv UAS-O\textsubscript{3}</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>1.76 ppmv CLaMS-3D</td>
<td>1.76 ppmv CLaMS-3D</td>
</tr>
<tr>
<td>CO</td>
<td>49.6 ppbv CLaMS-3D</td>
<td>49.6 ppbv CLaMS-3D</td>
</tr>
<tr>
<td>Cl\textsubscript{y}</td>
<td>149.5 pptv tracer corr.</td>
<td>80% Cl\textsubscript{y} 850 pptv Anderson et al. (2012)</td>
</tr>
<tr>
<td>HCl</td>
<td>52.7 pptv tracer corr.</td>
<td>850 pptv Anderson et al. (2012)</td>
</tr>
<tr>
<td>ClONO\textsubscript{2}</td>
<td>6.2 pptv tracer corr.</td>
<td>150 pptv Anderson et al. (2012)</td>
</tr>
<tr>
<td>NO\textsubscript{y}</td>
<td>2.497829 pptv tracer corr.</td>
<td>80% NO\textsubscript{y} 1.89 ppbv</td>
</tr>
<tr>
<td>HNO\textsubscript{3}</td>
<td>439.234932 pptv tracer corr.</td>
<td>80% 1.19 ppbv see section 2.3.2</td>
</tr>
<tr>
<td>NO</td>
<td>144.8 pptv tracer corr.</td>
<td>325 pptv Anderson et al. (2012)</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>144.8 pptv tracer corr.</td>
<td>375 pptv Anderson et al. (2012)</td>
</tr>
<tr>
<td>Br\textsubscript{y}</td>
<td>6.9 pptv CLaMS-3D</td>
<td>50% Br\textsubscript{y} 6.9 pptv CLaMS-3D</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>5–20 ppmv</td>
<td>5–20 ppmv</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.2 ppbv</td>
<td>0.6 ppbv, 2.0 ppbv</td>
</tr>
<tr>
<td>Temperature</td>
<td>195–220 K standard trajectory</td>
<td>const. temp (195–220 K) standard trajectory</td>
</tr>
</tbody>
</table>

0.026 ppm. The annual decrease of from 2000 to 2011 is assumed to be 0.8% (WMO, 2014). A summary of the initial values for main tracers assumed in the MACPEX case are given in Table 1.

3 Mid-latitude ozone chemistry

Mid-latitude ozone chemistry in the lowermost stratosphere depends on water vapour abundance and temperature. This study focuses on the water vapour dependence of stratospheric ozone chemistry by analysing chemical processes occurring in a box-model simulation along a realistic trajectory in the temperature range from 197–203 K under several water vapour conditions. In Figure 2, the mixing ratio of ozone, ClO\textsubscript{x} and NO\textsubscript{x} is shown for two simulations assuming 5 ppmv (dashed line) and 15 ppmv (solid line) H\textsubscript{2}O. These water vapour mixing ratios are chosen, because they are clearly in the regime of the low water vapour background (5 ppmv) of the lower mid-latitude stratosphere and of enhanced water vapour (15 ppmv) as it can be reached through convective overshooting events. For the low water vapour (5 ppmv) case, net ozone formation occurs, the ClO\textsubscript{x} mixing ratio remains low and the NO\textsubscript{x} mixing ratio high. In contrast, assuming a water vapour mixing ratio of 15 ppmv, ozone depletion occurs, accompanied by a decrease in NO\textsubscript{x} and coupled with chlorine activation as indicated by the increasing ClO\textsubscript{x} ClO\textsubscript{x} mixing ratio. The sensitivity to variations in water vapour conditions on stratospheric ozone is tested
Figure 2. Volume mixing ratio of $O_3$ (panel-a), ClO$_x$ (panel-b) and NO$_x$ (panel-c) during a simulation with 15 ppmv H$_2$O and 5 ppmv H$_2$O. These water vapour mixing ratios are chosen, because they are clearly in the regime of low (5 ppmv) and elevated (15 ppmv) water vapour. The x-axis ticks refer to 00:00 local time (06:00 UTC).

here by conducting simulations with standard conditions but varying the assumed water vapour mixing ratio from 5 to 20 ppmv in varying increments, with the resolution increased near the changeover from ozone production to destruction.

In Figure 3, the ozone values reached at the end of the 7-day simulation (end-final ozone, blue squares) are plotted as a function of the assumed water vapour mixing ratio. The initial ozone value, of 303.2 ppbv, is shown by the grey line. Blue squares lying above that line are cases with ozone production, those lying below that line are cases with ozone destruction. The threshold is determined as the water vapour mixing ratio at which the end ozone value clearly falls below the end ozone that is reached for low water vapour amounts. For the standard case shown in Fig. 3, this threshold is reached at a water vapour mixing ratio in the range of 11.0 to 11.6 ppmv. By 12 ppmv of water vapour, the system is clearly in an ozone destruction regime. The occurrence of the water vapour threshold and ozone depletion decrease of final ozone with higher water vapour mixing ratios is related to chlorine activation. The time until chlorine activation occurs in the this simulation is plotted in Fig. 3 as violet triangles.
Assuming that chlorine activation occurs when the ClO$_x$ mixing ratio exceeds 10% of total Cl$_y$ (Drdla and Muller, 2012), plotted here. Shown is the time when chlorine activation first occurs in the model. Since the ClO$_x$/Cl$_y$ ratio is dependent on the diurnal cycle, the 24-hours mean value of the ClO$_x$ mixing ratio was used to determine the chlorine activation time. For low water vapour mixing ratios, no chlorine activation time is plotted, because no chlorine activation occurs. Chlorine activation only occurs when the For chlorine activation to occur, a threshold in water vapour has to be reached. Here, we determine the lowest water vapour mixing ratio at which chlorine activation occurs as water vapour threshold is exceeded (marked by a blue arrow in Fig. 3). In our standard case, this threshold is reached at a water vapour mixing ratio of 10.6 ppmv. Between 10.6 and 11.8 ppmv H$_2$O, chlorine activation leads not to an ozone destruction during the 7-day simulation. For 10.6 to 11.2 ppmv H$_2$O, chlorine only remains activated for up to 28 h, because of increasing temperatures, and almost no impact on final ozone is observable. By 12.0 ppmv of water vapour, chlorine activation yields ozone destruction within the 7-day simulation. Near the water vapour threshold, the activation time is 24 to 36 hours and it decreases with increasing water vapour mixing ratios. It requires 5 hours at 20 ppmv H$_2$O. The shorter the chlorine activation time, the longer activated chlorine exists during the simulation yielding greater ozone depletion. The processes yielding ozone depletion at high water vapour conditions as well as ozone formation at low water vapour are analysed in detail in the subsequent sections. For this investigation we use the simulated reaction rates for each chemical reaction along the course of the calculation. For high water vapour mixing ratios the roles of both chlorine activation and a decrease in the NO$_x$ mixing ratio (Fig. 2) are discussed.

3.1 Ozone formation at low water vapour mixing ratios

At water vapour mixing ratios up to 11.8 ppmv, net ozone formation occurs during the 7-day simulation (see Fig. 3). This ozone formation is mainly driven by the photolysis of O$_2$→and the subsequent reaction →Additionally, photolysis of →followed by R8 leads to ozone formation. NO radicals, which are formed in R7, mainly react with ozone as well as ClO and BrO forming Cl and Br radicals.→Since these radicals react with ozone in reaction R16 () and ?? (), not all of the formed in R7 yields a net ozone formation. However, R7 is part of →Additionally the “Ozone Smog Cycle” (Haagen-Smit, 1952) known from tropospheric chemistry →which has also an impact on stratospheric chemistry →can yield ozone formation in the lower stratosphere (Grenfell et al., 2006; Grooß et al., 2011).

\[
\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{CO}_2 + \text{H} \quad \text{(R4)} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \quad \text{(R5)} \\
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \quad \text{(R6)} \\
\text{NO}_2 + \hbar \nu & \rightarrow \text{NO} + \text{O}^{(3}\text{P)} \quad \text{(R7)} \\
\text{O}_2 + \text{O}^{(3}\text{P)} + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad \text{(R8)} \\
\text{net: CO} + 2 \text{O}_2 & \rightarrow \text{CO}_2 + \text{O}_3 \quad \text{(C1)}
\end{align*}
\]

The rate of this cycle is determined by reaction R4 at low water vapour mixing ratios, and its net reaction is the oxidation of CO. The ozone formation through this cycle contributes around 40% to the total ozone formation at 5 ppmv in our box model.
3.2 Ozone loss at high water vapour mixing ratios

For higher water vapour mixing ratios than 11 ppmv, net ozone depletion is simulated (Fig. 3) in the 7-day standard simulation. The ozone loss mechanism generally consists of two steps: a chlorine activation step transferring inactive chlorine (HCl) into active ClO\textsubscript{x} followed by catalytic ozone loss processes (Anderson et al., 2012). We analyse both the chlorine activation step and subsequent catalytic ozone loss cycles potentially occurring in mid-latitudes in the lower stratosphere under enhanced water vapour conditions. Since ozone depletion is larger at high water vapour mixing ratios, conditions with a water vapour mixing ratio of 15 ppmv are chosen here to analyse the chemical ozone loss mechanism. Figure 4 shows an overview of the development of important mixing ratios and reaction rates during the 7-day simulation. Panel a illustrates temperature (black line) and surface area density of liquid particles (blue line).

The first phase of the ozone loss mechanism (dark grey background in Fig. 4) is dominated by the occurrence of heterogeneous reactions. The most important heterogeneous chlorine activation reaction is R1 (Fig. 4b), which leads to the chlorine activation

---

**Figure 3.** Impact of the water vapour content on the ozone mixing ratio (final ozone, blue squares) reached at the end of the 7-day simulation along the standard trajectory and assuming standard conditions. The initial ozone amount is marked by the grey line. The arrow marks the water vapour threshold, which has to be exceeded for chlorine activation at standard conditions to occur. In the bottom panel, violet triangles show the time until chlorine activation occurs. For low water vapour mixing ratios no chlorine activation occurs. 

standard simulation. Hence, the ozone formation which occurs in the simulations assuming low water vapour mixing ratios is due to both the photolysis of O\textsubscript{2} and cycle C1.
chain (von Hobe et al., 2011)

\[
\begin{align*}
\text{ClO} + \text{NO}_2 + M & \rightarrow \text{ClONO}_2 + M \\
\text{ClONO}_2 + \text{HCl} & \rightarrow \text{het.} \rightarrow \text{Cl}_2 + \text{HNO}_3 \\
\text{Cl}_2 + h\nu & \rightarrow 2\text{Cl} \\
2 \times (\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2) \\
\text{net: HCl} + \text{NO}_2 + 2\text{O}_3 & \rightarrow \text{ClO} + \text{HNO}_3 + 2\text{O}_2.
\end{align*}
\]

This chlorine activation chain yields a transformation of inactive HCl into active ClO\textsubscript{x} as well as of NO\textsubscript{x} into HNO\textsubscript{3}. The ozone loss due to this reaction chain is negligible and no depleting effect on ozone occurs during the first phase (Fig. 4c). In Fig. 4gf, the NO\textsubscript{x} mixing ratio is seen to decrease and HNO\textsubscript{3} increases due R1. Further, in the first phase the HCl mixing ratio decreases, yielding an increase of ClO\textsubscript{x} (Fig. 4f). The delay between HCl reduction and formation (Fig. 4f) is caused by the combination of the diurnal cycle and the accumulation of and during night. Both decreasing NO\textsubscript{x} and increasing ClO\textsubscript{x} have an impact on ozone during the second phase of the ozone loss mechanism (light grey background in Fig. 4), which is characterized by a decreasing ozone mixing ratio (Fig. 4c). The role of NO\textsubscript{x} and ClO\textsubscript{x} is discussed in detail in the next sections.

3.2.1 Role of NO\textsubscript{x}

The transformation of NO\textsubscript{x}-radicals into HNO\textsubscript{3} is due to R9 (ClO+NO\textsubscript{2}) and subsequent the occurrence of the heterogeneous reactions R1 (ClONO\textsubscript{2} + HCl) and R2 (ClONO\textsubscript{2} + H\textsubscript{2}O), which form HNO\textsubscript{3}. This behaviour was also found in former studies (e.g. Keim et al., 1996; Pitari et al., 2016; Berthet et al., 2017), investigating the impact of volcanic aerosols on stratospheric ozone chemistry. Dependent on temperature and water vapour content, the HNO\textsubscript{3} formed is taken up into remains in the condensed particles. In the standard simulation using 15 ppmv H\textsubscript{2}O, an uptake of 64\% is reached of HNO\textsubscript{3} remains in the condensed phase on the day with the lowest temperature (197.3 K, 2 Aug 2013), while at higher temperatures (4–7 August 2013) 85\% of HNO\textsubscript{3} remain in are released to the gas phase. After the transformation of NO\textsubscript{x} into HNO\textsubscript{3}, the NO\textsubscript{x} mixing ratio remains low in the second phase of the mechanism (Fig. 4d, light grey region) while the HNO\textsubscript{3} mixing ratio (cond.+gas) remains high.

The transformation of NO\textsubscript{x} radicals into HNO\textsubscript{3}, due to the occurrence of heterogeneous reactions at elevated water vapour amounts, affects stratospheric ozone chemistry. In the presence of a high NO\textsubscript{x} concentration (as at low water vapour mixing ratios), ozone chemistry is dominated by radicals (see Sec. 3.1) and the ozone formation in cycle C1 is determined by the rate of R4 (OH+CO). But if the NO\textsubscript{x} concentration is low (as in the second phase of the mechanism), this ozone formation cycle is rate limited by R6 (NO + HO\textsubscript{2}). For the standard case at 15 ppmv H\textsubscript{2}O, both rates are shown in Fig. 4e. In the first phase before NO\textsubscript{x} is transferred into HNO\textsubscript{3}, cycle C1 is limited by R4 (OH+CO) which peaks on 1 August 2013 with a maximum rate of 1.0·10\textsuperscript{5} cm\textsuperscript{-3}s\textsuperscript{-1}. In the second phase at low NO\textsubscript{x} concentrations, cycle C1 is limited by R6 (NO + HO\textsubscript{2}) which peaks.
Figure 4. Reaction rates and mixing ratios important for the ozone loss mechanism in the standard simulation using 15 ppmv H$_2$O. The chlorine activation phase is shaded in dark grey, while the phase of ozone loss has a light grey background. Panel (a) shows the temperature of the trajectory and the liquid surface area density, the ozone mixing ratio is presented in panel (c). Heterogeneous reaction rates are shown in panel (b) as well as the rate of the gas phase reaction CH$_4$ + Cl. Panels (d), mixing ratio of HNO$_3$ (gas phase + condensed), NO$_x$ and ClONO$_2$, and (e) are relevant to show the role of NO$_y$ for the ozone loss process. Reaction R4 (OH+CO, panel e) limits ozone formation in cycle C1 at high NO$_x$ mixing ratios and R6 (HO$_2$ + NO) at lower NO$_x$ concentrations. Panels (f)–(h) illustrate the role of chlorine for ozone loss by showing the mixing ratio of HCl, ClO$_x$ and ClONO$_2$ (panel f), main reaction rates (R17 (ClO+ClO), R18 (ClO+BrO), R13 (ClO + HO$_2$)) for catalytic ozone loss cycles (panel g) and potential reaction pathways for the OH-radical (R4 (OH+CO), R19 (OH+ClO), R15 (OH+O$_3$)) as possible reaction chains following R13 (ClO+HO$_2$) (panel h). The x-axis ticks refer to 00:00 o’clock local time (06:00 UTC).
on 3 August 2013 with a maximum rate of $1.5 \times 10^4 \, \text{cm}^{-3} \text{s}^{-1}$. Hence, due to the occurrence of the heterogeneous reaction R1 the net ozone formation decreases by at least $3.5 \times 10^4 \, \text{cm}^{-3} \text{s}^{-1}$ from 1 August to 3 August.

### 3.2.2 Role of ClO$_x$

In the first phase of the mechanism, chlorine activation yields a transformation of inactive chlorine into active ClO$_x$. Net chlorine activation occurs when the rates of the heterogeneous reactions R1 (ClONO$_2$ + HCl), R2 (ClONO$_2$ + H$_2$O) and R3 (HCl+HOCl) exceed the gas phase HCl formation dominated by the reaction

$$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3. \quad (R12)$$

Enhanced ClO$_x$ concentrations induce catalytic ozone loss cycles at low temperatures, as the ClO-Dimer-cycle (Molina et al., 1987), the ClO-BrO-cycle (McElroy et al., 1986) and cycle C2 (Solomon et al., 1986).

$$\begin{align*}
\text{ClO} + \text{HO}_2 &\rightarrow \text{HOCI} + \text{O}_2 \\
\text{HOCI} + \hν &\rightarrow \text{Cl} + \text{OH} \\
\text{OH} + \text{O}_3 &\rightarrow \text{HO}_2 + \text{O}_2
\end{align*} \quad (R13)$$

$$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad (R16)$$

$\text{net:} \ 2\text{O}_3 + \hν \rightarrow 3\text{O}_2. \quad (C2)$

Under conditions of low water vapour (stratospheric background), the rate limiting steps of these cycles are the reactions

$$\begin{align*}
\text{ClO} + \text{ClO} + \text{M} &\rightarrow \text{ClOOCl} + \text{M}, \quad (R17) \\
\text{ClO} + \text{BrO} &\rightarrow \text{Br} + \text{Cl} + \text{O}_2 \quad (R18)
\end{align*}$$

and $\text{ClO} + \text{HO}_2 \rightarrow \text{HOCI} + \text{O}_2. \quad (R13)$

The rates of the reactions R17, R18 and R13 increase strongly in the second phase of the mechanism (light grey area in Fig. 4g) and thus catalytic ozone loss cycles can occur. Under the assumed conditions, ozone depletion is mainly driven by reaction pathways following both R18 and R13. The reaction rates peak on August 3 with a value of $7.8 \times 10^4 \, \text{cm}^{-3} \text{s}^{-1}$ for R13 (ClO+HO$_2$), $6.8 \times 10^4 \, \text{cm}^{-3} \text{s}^{-1}$ for R18 (ClO+BrO) and $2.7 \times 10^4 \, \text{cm}^{-3} \text{s}^{-1}$ for R17 (ClO+ClO). In contrast the rate of ozone loss due to the reactions net: $2\text{O}_3 + \hν \rightarrow 3\text{O}_2$ are not important here, as the peak values or $25$ are only about $0.35 \times 10^4$ (not shown). Additionally the sensitivity of various reaction rates to the water vapour mixing ratio was tested. In Figure 5, the mean reaction rates on 3 August are plotted against the water content assumed during the simulation. Panel (a) shows an acceleration of the ozone loss cycles ClO-BrO-cycle (based on R18) and C2 (based on R13) beginning from a water vapour mixing ratio of 11ppmv. In contrast, the rate determining reaction of (R17, ClO+ClO) the ClO-Dimer-Cycle (R17) increases at a higher water vapour mixing ratio. In contrast, the rate of ozone loss due to the reactions between ClO$_x$ and O$_x$ (O$_x$=O$_3$, O)
Figure 5. Average reaction rates and volume mixing ratios from the standard simulations on 3rd of August dependent on water vapour content. Panel (a) shows the reaction rates of R17 (ClO+ClO), R18 (ClO+BrO), R13 (ClO+HO2) and R16 (ClO+O(3P)) → Cl+O2 resulting in ozone reduction, panel (b) possible reaction pathways for the OH radical (R4 (OH+CO), R19 (OH+ClO) and R15 (OH+O3)), panel (c) reactions yielding depletion of HNO3 (R20 (HNO3+OH), R21 (HNO3+hv)), panel (d) reactions of the H3COO-radical R23 (H3COO+ClO) and R22 (H3COO+NO), panel (e) important heterogeneous reactions (R1 (ClONO2+HCl), R2 (ClONO2+H2O)), and panel (f) the balance between R1 (ClONO2+HCl) and R12 (CH4+Cl). Panel (g) shows the mixing ratios of NOx, ClOx and 10-Cl and panel (h) the mixing ratios of OH and HO2.

species is negligible here (as shown by the low rate of the reaction ClO+O(3P) → Cl+O2, Fig. 5a).

At stratospheric background conditions with a low water vapour mixing ratio, the rate determining step of cycle C2 is R13 (Solomon et al., 1986; Ward and Rowley, 2016). For the conditions with enhanced water vapour of 15 ppmv in the standard simulation, the rate of R15 (OH+O3) is limiting this cycle (Fig. 4f). An investigation of possible reaction pathways of the OH-radical yields that reactions of OH with CO (R4) and ClO (R19) exhibit a rate similar to the reaction with ozone (R15,
Based on these reactions, two further reaction chains affecting ozone can be deduced. In cycle C3, the OH-radical reacts with CO yielding CO$_2$ and a hydrogen radical, from which HO$_2$ is formed. Subsequently HOCl can be formed via R13 (ClO+HO$_2$) and photolysed in reaction R14. Thus, the net reaction of this pathway is the oxidation of CO to CO$_2$ and the simultaneous destruction of ozone (C3).

\[
\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \quad \text{(R4)}
\]

In the cycles C2 and C4 two ozone molecules are destroyed, while one ozone molecule is destroyed in C3. To assess the effectiveness regarding ozone loss of C2 and C3—C4, the rate of R4 (limiting C3) is compared with two times the rate of R15 (limiting C2) and R19 (limiting C4). This comparison shows that cycle C2 is more relevant for ozone loss than C3 and C4 (Fig. 5b). Reaction R15 (C2) and R4 (C3) accelerate with increasing water vapour mixing ratio, due to an increasing formation of OH (Fig. 5h), and peak in the threshold range of ~11 ppmv. When the threshold region is reached, the OH mixing ratio decreases due to a declining mixing ratio (Fig. 5g) and thus a lower rate of the reaction. The lower OH concentration results in a decrease of the reaction rates of R15 (OH+) and R4 (OH+CO) shown in Fig. 5b, since R15 (OH+) and R4 (OH+CO) are limited through the OH mixing ratio. The limiting step of cycle C4 (R19) is negligible for low water amounts and starts to increase in the range of the threshold region due to the strong gain of both (Fig. 5g-h). Accordingly, the relevance of C4 for catalytic ozone destruction increases for higher water vapour mixing ratios.
A requirement for the effectiveness of the ozone loss cycles \(\text{C2} \text{and C3} \text{C4}\) is a high mixing ratio of \textit{active activated} chlorine (\(\text{ClO}_x\)). In Fig. 4b, the rate of the main \textit{HCl-forming \textit{HCl-formation}} reaction \(R12\) (\(\text{Cl}+\text{CH}_4\), dark blue) shows a formation of \textit{HCl}, which \textit{has to be balanced (by HCl destroying reactions) to hold} is \textit{mainly balanced by the heterogeneous HCl-destruction} reaction \(R1\) (\(\text{ClONO}_2 + \text{HCl}\)) \textit{holding} the \textit{HCl mixing ratio low and thus \textit{ClO}_x \textit{values high}}. \textit{For conditions of the Antarctic polar night in the lower stratosphere this balance between This balance between \textit{chlorine activation (R1, ClONO}_2+\textit{HCl) and \textit{chlorine deactivation (R12, Cl+CH}_4) is schematically illustrated with blue arrows in Fig. 6 and similar to HCl-null-cycles (Müller et al., 2018), which balance gas phase HCl-formation and heterogeneous HCl-destruction can be described through HCl-null-cycles (Müller et al., 2018)} under Antarctic polar night conditions. \textit{In these polar HCl-null-cycles each HCl formed in reaction R12 is depleted through the heterogeneous reaction R3 (HCl+HOCl). For the formation of HOCl in reaction R13 (+ClO), the generation of radicals through R23 is essential for Antarctic polar night conditions. For the conditions in the mid-latitudes during summer considered here, a higher \textit{NO}_x mixing ratio prevails than under Antarctic ozone hole conditions due to a lower uptake into the condensed particles. As a consequence R1 (\(\text{ClONO}_2 + \text{HCl}\)) is \textit{here} mainly responsible for the \textit{HCl loss and hence the pathway AC1} represents a more probable reaction chain to balance the \textit{HCl formation}. Since the reactions R12, R20 and R1 hold the lowest rates in AC1, these reactions are \textit{essential for constituting AC1}. In R12 \textit{HCl is formed and afterwards instantly a methylperoxy radical (} is formed (AR1), which reacts with \textit{NO (})). This reaction yields an \textit{H radical, which is rapidly converted into an OH radical by formation and photolysis of HOCl (R13 and R14)}). Through the reaction between the \textit{OH radical and (R20)} and the subsequent photolysis of (AR4), a \textit{radical is released from}. The photolysis of \textit{HCl-depletion. Reaction R1 combined with R9 (ClO + NO}_2) \textit{yields additionally the transformation of NO}_x \textit{into HNO}_3. \textit{This HNO}_3 \textit{formation is balanced by reaction}

\[
\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3
\]

(see Fig. 6, green), leading to a \textit{steady HNO}_3 \textit{mixing ratio (Fig. 4d)}.

\textit{A further option to convert HNO}_3 \textit{into active NO}_x \textit{may be the HNO}_3-\textit{photolysis}

\[
\text{HNO}_3 + \text{hv} \rightarrow \text{NO}_2 + \text{OH},
\]

but the rate of reaction \textit{OH}+(R20) \textit{R20} is more than 2.5 times larger than the rate of the \textit{HNO}_3 \textit{photolysis (R21, Fig. 5c)}.

\textit{The radical, which is generated in AR4, reacts with ClO (R9) forming , which heterogeneously reacts with HCl (R1). As a consequence the HCl, formed in Hence, the heterogeneous reaction R1 couples two pathways: A pathway \textit{balancing HCl-destruction in R1} and \textit{HCl-formation in R12 (Cl+CH}_4) and thus \textit{maintaining a high ClO}_x \textit{mixing ratio, and a pathway balancing HNO}_3-\textit{formation in R1} and \textit{HNO}_3 \textit{destruction in R20} and thus \textit{maintaining a low NO}_x \textit{mixing ratio}. \textit{The balance of radical species, which are converted in both pathways, additionally links both pathways (Fig. 6, light colours). In reaction R12, is mainly destroyed in reaction R1 following pathway AC1, which yields the oxidation of as the net reaction. In cycle AC1 the radical reacts with NO (??). As an alternative the besides HCl a methylperoxy radical (H}_3\text{COO) is formed,}
Figure 6. Reaction scheme to illustrate the balance between chlorine activation and chlorine deactivation (blue, right) and NOx activation and deactivation (green, left). The heterogeneous reaction ClONO$_2$ + HCl (R1) links both cycles. Additional reaction pathways, which balance radicals are shown in light colours.

which reacts either with NO or with ClO leading to HO$_x$-formation (HO$_x$ = H, OH, HO$_2$).

\[
\begin{align*}
H_3COO + NO &\rightarrow HCHO + H + NO_2 \\
H_3COO + ClO &\rightarrow HCHO + HO_2 + Cl
\end{align*}
\]  

(R22) (R23)

In reaction R20, HNO$_3$ is depleted in a reaction with an HO$_x$-radical can also react with ClO (R23). In Fig. 5d the rates of ?? and R23 are compared with each other dependent on the water vapour mixing ratio assumed during the simulation. For the (yellow), how the H$_3$COO-radical reacts, depends on the mixing ratios of ClO$_x$ and NO$_x$. For water vapour mixing ratio of the threshold region, reaction ?? dominates and AC1 mainly balances the HCl formation and destruction. At higher water vapour mixing ratios (more than 15 ppmv) ratios around the water vapour threshold, reaction R23 (+ClO) becomes more important than ?? (NO). The NO$_x$ mixing ratio is higher than the ClO$_x$ mixing ratio (Fig. 5g). Hence, the methylperoxy radical rather reacts with NO than with ClO (Fig. 5e), because of a lower and a higher concentration. The lower mixing ratio is due to a stronger conversion of into as well as a higher uptake into the liquid particles at a higher water vapour mixing ratio. Hence for very high d) leading to pathway (a) in Fig. 6. At higher water vapour mixing ratios (here, greater than 15 ppmv), cycle AC2 mainly balances HCl formation. The net reaction of AC2 is the oxidation of methane () into formaldehyde () with a simultaneous ozone destruction. Since the ozone destruction rather reacts with ClO (R23) leading to pathway (b) in Fig. 6. The balance between HCl-formation and -destruction as well as HNO$_3$-formation and -destruction due to the catalytic ozone loss cycles ?? and C3 is much faster, the ozone destruction in AC2 is negligible compared to the ozone loss cycles discussed above. Occurrence of the heterogeneous reaction R1 is analysed in detail in the
Appendix A.

However, in this example the heterogeneous HCl-destruction (R1, ClONO2+HCl) does not balance the HCl-formation (R12, Cl + CH4) (Fig. 4b) due to completely because of increasing temperatures (Fig. 4a). Higher temperatures decelerate the heterogeneous HCl-destruction and thus result in the slightly increasing HCl-mixing ratio from 4 August–7 August 2013 (Fig. 4f). Such temperature fluctuations (Fig. 4a) affect the balance between HCl formation and destruction less at higher water vapour mixing ratios, because the heterogeneous HCl-destruction rate (R1) increases for both low temperatures and high water vapour mixing ratios (see Sec. 4). Thus, regarding the balance between HCl formation and HCl destruction (and hence the balance between chlorine deactivation and chlorine activation), a high water vapour mixing ratio can compensate a small range of temperature fluctuations. This balance can be described by the cycles AC1 and AC2 and maintains activated chlorine levels, which is essential for the catalytic ozone loss cycles C2 and C3–C4 to proceed.

4 Analysis of chlorine activation

In the previous section we showed that in the temperature range of 197–203 K there is a threshold for water vapour, which has to be exceeded to yield chlorine activation and thus enables substantial ozone destruction. Here, we investigate the sensitivity of this threshold on sulphate content, temperature, Cl, and NO mixing ratio.

4.1 Sensitivity of the water vapour threshold

Modifying temperature, sulphate amount or the mixing ratios of Cl, or NO yields a shift of the water vapour threshold. Figure 7 shows the ozone values reached at the end of the 7-day simulation (final ozone) for a variety of sensitivity cases assuming the standard trajectory of the SEAC4RS case (left) and the MACPEX trajectory (right). For each case, the water vapour threshold is marked with an arrow in the colour of the corresponding case.

The water vapour dependent final ozone values for the standard case are plotted as blue squares (Fig. 7, left) with a water vapour threshold of 10.6 ppmv (see Sec. 3). Raising the trajectory temperature by 1 K over the standard case leads to a higher water vapour threshold of 13.5–14.0 ppmv (open red squares), while increasing the sulphate content by a factor of 3 results in a lower threshold region of ~9.0–9.5 ppmv (yellow diamonds). An even larger enhancement of the sulphate content (10× H2SO4, magenta diamonds) lowers the water vapour threshold further to a value near 7–8 ppmv. Reducing the NO mixing ratio to 80% of the standard case yields a shift of the threshold to a lower water vapour mixing ratio (green filled triangles), while an equivalent reduction in the Cl mixing ratio shifts the threshold to higher water vapour mixing ratios (black circles). A reduction in Cl also reduces ozone destruction and hence results in higher ozone mixing ratios at the end of the simulation. While the preceding analysis was based on a single SEAC4RS trajectory, similar conclusions are reached when the analysis is conducted using a trajectory from the MACPEX campaign. Results of the analysis using the MACPEX initialization and backward trajectory (Fig. 4) for the sensitivity of the water vapour threshold to temperature, sulphate abundance and Cl, and NO mixing ratio is explained in the next section (Sec. 4, black) are shown in the right panel of Fig. 7. A critical water vapour range of 12–13 ppmv is required to produce a reduction of the final ozone value. In the MACPEX case, the final ozone is mostly for...
Figure 7. Impact of the water vapour content on the ozone mixing ratio (final ozone) reached at the end of the 7-day simulation along the standard trajectory (SEAC$^4$RS, left) and the MACPEX trajectory (right). The standard case is shown in blue and the initial ozone amount is marked by the grey line. An impact on the final ozone mixing ratios is observable after exceeding a critical threshold in water vapour, which is marked with an arrow for the different cases. This threshold changes with a shift in trajectory temperature (+1K, red), the Cl$_y$ mixing ratio to 0.8 Cl$_y$ (black), the NO$_y$ mixing ratio (0.8 NO$_y$, green) and the sulphate content (3 × standard H$_2$SO$_4$, yellow and 10 × standard H$_2$SO$_4$, magenta).

As a further example for an event with high stratospheric water vapour mixing ratios based on airborne measurements, simulations based on measurements during the Mid-latitude Airborne Cirrus Properties Experiments (MACPEX) were conducted. This campaign was based in Texas during springtime 2011 and hence prior to the formation of the North American Monsoon (NAM). A detailed description of this MACPEX case is given in the Appendix (App. pptv) assumed in the MACPEX case, which yields lower rates for catalytic ozone loss after chlorine activation occurred. For the MACPEX case, changes in sulphate (Fig. 7, left, yellow diamonds), Cl$_y$ (black circles) or and NO$_y$ (green triangles) mixing ratios affect the catalytic ozone destruction water vapour threshold similarly to that observed for the SEAC$^4$RS trajectory. Thus, the MACPEX results confirm the SEC$^4$RS findings. Therefore, we conclude that in the considered temperature range (∼197–203 K), an ozone reduction occurs after exceeding a water vapour threshold and that this threshold varies with Cl$_y$, NO$_y$, sulphate content and temperature.
4.2 Explanation of the water vapour threshold

The sensitivity of the water vapour threshold to Cl\(_y\), NO\(_x\), sulphate loading and temperature is investigated, focussing on the balance between heterogeneous chlorine activation mainly due to R1 (ClONO\(_2\) + HCl) and gas phase chlorine deactivation mainly due to R12 (Cl + CH\(_4\)). Net chlorine activation takes place when the chlorine activation rate exceeds the chlorine deactivation rate. Reaction R1 is the key reaction in the chlorine activation process. Therefore, in the following, first the dependence of R1 on the water vapour content is analysed in detail. Second, the balance between chlorine activation and deactivation is investigated, also considering the impact of Cl\(_y\), NO\(_x\), sulphate and temperature on the water vapour threshold.

In general the rate of R1 (ClONO\(_2\) + HCl) \(v_{R1}\) is determined through:

\[
v_{R1} = k_{R1} \cdot c_{ClONO_2} \cdot c_{HCl}
\]

The concentrations of ClONO\(_2\) \(c_{ClONO_2}\) and HCl \(c_{HCl}\) are associated with the gas phase mixing ratio and the rate constant \(k_{R1}\), as a measure of the reactivity of the heterogeneous reaction, depends in this case on the \(\gamma\)-value \(\gamma_{R1}\), the surface area of the liquid particle \(A_{liq}\), the temperature \(T\) and \(c_{HCl}\) (Eq. 2) (Shi et al., 2001).

\[
k_{R1} \propto \frac{\gamma_{R1} \cdot A_{liq} \cdot \sqrt{T}}{1 + c_{HCl}}
\]

The \(\gamma\)-value describes the uptake of ClONO\(_2\) into liquid particles due to the decomposition of ClONO\(_2\) during reaction R1 and is thus a measure of the probability of the occurrence of this heterogeneous reaction (Shi et al., 2001). Laboratory studies showed a dependence of \(\gamma_{R1}\) on the solubility of HCl in the droplet, which generally increases for a lower H\(_2\)SO\(_4\) fraction in the particle (H\(_2\)SO\(_4\) wt%) (Elrod et al., 1995; Hanson, 1998; Zhang et al., 1994; Hanson and Ravishankara, 1994). From Eq. 2 it is obvious that a large surface area \(A_{liq}\) and a high \(\gamma\)-value \(\gamma_{R1}\) increase \(k_{R1}\) and thus the heterogeneous reaction rate \(v_{R1}\).

In Figure 8, the impact of the water vapour content on the H\(_2\)SO\(_4\) weight-percent \(\gamma_{R1}\), \(A_{liq}\), \(k_{R1}\) and the reaction rate \(v_{R1}\) is plotted. To avoid the influence of R1 itself on these parameters as much as possible, these parameters are selected for 1 August 2013 at 13:00 UTC. This point in time corresponds to the values after the first chemistry time step during the chemical simulation. The particles H\(_2\)SO\(_4\) wt% decreases for all cases with increasing water vapour from more than 50 wt% at 5 ppmv H\(_2\)O to around 20 wt% at 20 ppmv H\(_2\)O due to an increasing uptake of H\(_2\)O in the thermodynamic equilibrium. The standard case is illustrated in blue squares (Fig.8) and exhibits a strongly increasing gamma value especially for water vapour mixing ratios between 9 and 14 ppmv as well as an almost constant liquid surface area \(A_{liq}\) due to a lower H\(_2\)SO\(_4\) wt%.

In the same water vapour range, the slight increase in the liquid surface area density \(A_{liq}\) is caused by formation in R1 and the subsequent uptake increases slightly. It increases more for higher water vapour mixing ratios because of HNO\(_3\) into the condensed particles, especially for high water values uptake into the particles. Due to the increasing \(\gamma\)-value with increasing water vapour, the rate constant \(k_{R1}\) increases (Shi et al., 2001) and thus induces a larger reaction rate \(v_{R1}\) with an increasing water vapour mixing ratio.

At low water vapour mixing ratios, not only the rate of R1 (ClONO\(_2\) + HCl) but also of R12 (CH\(_4\) + Cl) increases with an increasing water content (Fig. 5f). An increasing heterogeneous reaction rate (R1) results in both a lower NO\(_x\) mixing ratio and
more HCl converted into ClO\textsubscript{x}. A higher ClO\textsubscript{x} concentration yields a higher Cl mixing ratio and thus an increase in the rate of R12 (CH\textsubscript{4} + Cl). Since both the rates of R1 and R12 increase, no significant net chlorine activation occurs. In Around the water vapour threshold region, the Cl-mixing ratio peaks (Fig. 5g), because less ClO is converted into Cl through R24 (ClO + NO → Cl + NO\textsubscript{2}).

\begin{equation}
\text{ClO + NO} \rightarrow \text{Cl + NO}_2
\end{equation}

(R24)

due to the decreasing NO\textsubscript{x} mixing ratio. The lower Cl mixing ratio reduces the HCl formation in R12 (CH\textsubscript{4} + Cl). Hence, the increasing heterogeneous reactivity \(k_{R1}\) yields a higher rate of R1 and in the same way it impedes R12 by reducing the NO\textsubscript{x}
mixing ratio. **In the same way, an increase in** \( k_{R1} \) **yields a higher rate of** \( R1 \). As a consequence the rate of \( R1 \) exceeds the rate of \( R12 \) and a net chlorine activation takes place, leading to a reduction of HCl. The decline in both HCl and NO\(_x\) yields smaller rates of \( R1 \) and \( R12 \) at high water amounts and thus the peak of \( R1 \) and \( R12 \) **occurs in the water vapour threshold region** (Fig. 5f). Hence, the increasing heterogeneous reactivity (**promotes destabilizes the balance between chlorine activation and deactivation by promoting the chlorine activation (due to an increasing rate of** \( R1 \) and impedes impeding chlorine deactivation (due to a reduction of \( R12 \)). This yields heterogeneous chlorine activation to exceed gas phase HCl-formation in the water vapour threshold region. The increase in \( k_{R1} \) yields a net chlorine activation in the water vapour threshold region by destabilizing the balance between chlorine activation and deactivation.

For an enhanced sulphate content (Fig. 8, yellow diamonds), the particle surface area density (**illustrated by** \( A_{liq} \)) is larger, leading to both a stronger increase of the heterogeneous reactivity (**promotes destabilizes the balance between chlorine activation and deactivation by promoting the chlorine activation (due to an increasing rate of** \( R1 \) and impedes impeding chlorine deactivation (due to a reduction of \( R12 \)). This yields heterogeneous chlorine activation to exceed gas phase HCl-formation in the water vapour threshold region. The increase in \( k_{R1} \) yields a net chlorine activation in the water vapour threshold region by destabilizing the balance between chlorine activation and deactivation.**

In summary, the **water vapour** threshold is determined by the balance between chlorine activation and deactivation and is thus in a certain temperature range especially sensitive to the water dependence of the heterogeneous reactivity (**promotes destabilizes the balance between chlorine activation and deactivation by promoting the chlorine activation (due to an increasing rate of** \( R1 \) and impedes impeding chlorine deactivation (due to a reduction of \( R12 \)). This yields heterogeneous chlorine activation to exceed gas phase HCl-formation in the water vapour threshold region. The increase in \( k_{R1} \) yields a net chlorine activation in the water vapour threshold region by destabilizing the balance between chlorine activation and deactivation.**

**But,**

**an increase in** \( k_{R1} \) **yields a higher rate of** \( R1 \). As a consequence the rate of \( R1 \) exceeds the rate of \( R12 \) and a net chlorine activation takes place, leading to a reduction of HCl. The decline in both HCl and NO\(_x\) yields smaller rates of \( R1 \) and \( R12 \) at high water amounts and thus the peak of \( R1 \) and \( R12 \) **occurs in the water vapour threshold region** (Fig. 5f). Hence, the increasing heterogeneous reactivity (**promotes destabilizes the balance between chlorine activation and deactivation by promoting the chlorine activation (due to an increasing rate of** \( R1 \) and impedes impeding chlorine deactivation (due to a reduction of \( R12 \)). This yields heterogeneous chlorine activation to exceed gas phase HCl-formation in the water vapour threshold region. **The increase in** \( k_{R1} \) **yields a net chlorine activation in the water vapour threshold region by destabilizing the balance between chlorine activation and deactivation.**
4.3 Temperature dependence

The water vapour threshold, which has to be exceeded for chlorine activation and stratospheric ozone loss to occur, is mainly dependent on the temperature. To illustrate the impact of both temperature and water vapour mixing ratio on stratospheric ozone, the relative ozone change occurring after a 7-day simulation, in which a constant temperature and water vapour concentration and the Cl\textsubscript{y} and NO\textsubscript{y} values of the standard case are assumed, is shown in Fig. 9. In the left panel, ozone change as a function of temperature and water vapour is plotted for non-enhanced sulphate amounts. In the right panel, the relative ozone change is shown for 10× standard sulphate to estimate a potential impact of volcanic eruptions or sulphate geoengineering on stratospheric ozone. Since mixing of neighbouring air parcels is neglected in the box-model study, the relative ozone change calculated corresponds to the largest possible ozone change for the conditions assumed. A mixing of moist tropospheric air with dry stratospheric air is expected to reduce the water vapour mixing ratio during the time period of the 7-day trajectory and hence could stop ozone depletion before the end of the trajectory is reached. In addition to the relative ozone change, the threshold for chlorine activation is shown as a white line in both panels. When temperature is held constant, this threshold corresponds to the water vapour threshold discussed above. Chlorine activation occurs at higher water mixing ratios and lower temperatures relative to the white line plotted. Here, chlorine is defined to be activated, if the ClO\textsubscript{x}/Cl\textsubscript{y} ratio exceeds 10%.

For climatological non-enhanced sulphate amounts (Fig. 9, left), the temperature has to fall below 203 K for chlorine activation to occur, even for high water vapour mixing ratios of 20 ppmv. For the simultaneous presence of high water vapour and low temperatures an ozone loss of 9% (max. 27 ppbv O\textsubscript{3}) was found. This maximal ozone loss occurs for a range of low temperatures (195–200 K) and enhanced water vapour mixing ratios (10–20 ppmv), because of a similar time until chlorine activation occurs. If the temperatures are higher and water vapour mixing ratios lower than the chlorine activation line, the ozone mixing ratio increases around 3.5% (∼ 10 ppbv O\textsubscript{3}). At enhanced sulphate conditions (Fig. 9, right) an ozone loss of max. 10% (30 ppmv O\textsubscript{3}) occurs for low temperatures and high water vapour mixing ratios. For a water vapour mixing ratio of 20 ppmv the temperature has to fall below 205 K for ozone loss to occur. If the temperatures are very low (195–200 K) and the water vapour is high (10–20 ppmv) ozone loss is slightly reduced. This turnaround occurs, because at a high sulphate loading in combination with high water and low temperatures more HCl is taken up by condensed particles. This leads to less Cl\textsubscript{y} in the gas phase and thus lower rates of catalytic ozone loss.

In summary, the combination of low temperatures, enhanced sulphate concentrations and high water vapour mixing ratios promotes an ozone decrease of up to ∼10% (max. corresponding to maximum −30 ppbv O\textsubscript{3}) for high water vapour mixing ratios, low temperatures and enhanced sulphate conditions. In comparison to the study of Anderson et al. (2012), the temperatures have to fall below 203 K (here) instead of 205 K (in Anderson et al. (2012)) for non enhanced sulphate conditions and below 205 K instead of 208 K (in Anderson et al. (2012)) for enhanced sulphate conditions and a water vapour mixing ratio of 20 ppmv for chlorine activation and thus ozone loss to occur. Hence, Anderson et al. (2012) found ozone loss in mid-latitudes at high water vapour mixing ratios for temperatures 2 to 3 K higher than in our simulations.
5 Case studies

Case studies were conducted to illustrate the sensitivities described above on ozone loss and to estimate the impact of realistic conditions and an upper boundary on the ozone loss process. As a kind of worst case study (upper boundary), the “Case of high” was simulated using and mixing ratios based on the study of Anderson et al. (2012), which uses and much larger than inferred from tracer-tracer correlations (Table 1). In the “case based on observations”, standard conditions and the measured water vapour mixing ratio of 10.6 ppmv were assumed using both the low sulphate content of the standard case and a slightly enhanced sulphate content, which represents the possible impact of volcanic eruptions or geoengineering conditions. As a kind of worst case study (upper boundary), the “Case of high Cl$_y$” was simulated using Cl$_y$ and NO$_y$ mixing ratios based on the study of Anderson et al. (2012), which uses Cl$_y$ and NO$_y$ much larger than inferred from tracer-tracer correlations (Table 1). In the “reduced Br$_y$ case”, standard conditions with a 50% reduced Br$_y$ mixing ratio were assumed to test uncertainties in current observations of stratospheric bromine burden. Additionally the previously noted standard 7-day trajectory was extended to a 19-day trajectory to infer the dependence of ozone loss on the simulated time period.

5.1 Case of high based on observations
Figure 10. Behaviour under “Case of high” conditions assuming high values for and (see Tab. 1). Left panel shows the dependence of ozone values reached at the end of the 7-day simulation on water vapour for reference (blue) and 3× enhanced sulphate contents (yellow); the grey line corresponds to the initial ozone value. Right panel presents the volume mixing ratio of ozone, temperature, liquid surface area density, ozone mixing ratio, reaction rates of R1 (scaled by 0.5ClONO$_2$ + HCl, cyan), HClR18 (ClO+BrO, and and reaction rates of reactions essential black) (as an example for chlorine activation and catalytic ozone loss cycles), R6 (R1 and R18-NO + HO$_2$, violet) which limits ozone formation at low NO$_x$ concentrations as well as volume mixing ratios of HCl (ClO+BrOred), R17 ClO$_x$ (ClO+ClOlight blue), NO$_x$ (black) and R13 HNO$_3$ (scaled with 0.5) for the “Case based on observations” with 10.6 ppmv H$_2$O and 0.20 ppbv H$_2$SO$_4$. The panels on the right show the same quantities, but for enhanced sulphate conditions (0.60 ppbv H$_2$SO$_4$). The x-axis ticks refer to 00:00 local time (06:00 UTC) of that day.

The simulation of the case based on observations during the SEAC$^4$RS aircraft campaign corresponds to the most realistic case for today’s chemical conditions. It is identical to that of the standard case but assumes a fixed water vapour mixing ratio of 10.6 ppmv observed on 8 August 2013. Under these conditions, neither relevant heterogeneous chlorine activation due to R1 (ClONO$_2$ + HCl) nor catalytic ozone loss cycles (e.g., based on ClO+BrO) can be observed in the simulation (Fig. 10, left). Instead, ozone is formed. In comparison, the same simulation with 0.6 ppbv gas phase equivalent H$_2$SO$_4$ instead of 0.2 ppbv was conducted (Fig. 10, right). The enhanced sulphate content yields a larger liquid surface area density and thus an increased heterogeneous reactivity. Hence, reaction R1 occurs in the 3×H$_2$SO$_4$ simulation significantly, leading to a slightly increasing ClO$_x$ mixing ratio and a decrease of the NO$_x$ mixing ratio. Both a reduced ozone formation in C1 (which is at decreased NO$_x$ concentrations limited by R6) and ozone loss cycles (e.g., based on the reaction ClO+BrO or ClO+HO$_2$) can be observed, resulting in a reduction of ozone.
Using initial conditions, the trajectory corresponding to the SEAC4RS observations shows ozone loss with sulphate enhanced by a factor of 3. However, we note that this was an unusually cold trajectory. A more common case with higher mean temperatures would require a higher sulphate content to enhance the heterogeneous reactivity that chlorine activation can occur. Thus under current chemical conditions in the UTLS (upper troposphere, lower stratosphere), it is most unlikely to get significant ozone loss by convectively injected water vapour in mid-latitudes.

5.2 Case of high Cl\textsubscript{y}

Under conditions of substantially higher initial Cl\textsubscript{y} and NO\textsubscript{x} mixing ratios (see Tab. 1) than in the standard case used in Anderson et al. (2012), a larger ozone loss up to 265 ppbv during the 7-day simulation is simulated (Fig. 11a). Since these high Cl\textsubscript{y} conditions have been criticised in other studies (e.g. Schwartz et al., 2013; Homeyer et al., 2014) as being unrealistically high, they are assumed here as a worst case scenario. Under high chlorine conditions, and for a high water vapour content (more than \(\approx 18\) ppmv), an almost complete ozone destruction with an end a final ozone value of less than 50 ppbv is simulated (Fig. ??, left 11a), which corresponds to parcel ozone loss of 85%. During the 3.5-day simulation in the study of Anderson et al. (2012), an ozone loss of 20% with respect to initial ozone occurs for 18 ppmv H\textsubscript{2}O. This difference in relative ozone loss for similar conditions here and in the study of Anderson et al. (2012) is caused by a longer assumed ozone destruction period in our simulation. Since the Cl\textsubscript{y}-mixing ratio is much higher than in the standard case, the catalytic ozone loss cycles are dominated by the Cl\textsubscript{O}-Dimer cycle (see S1 in the Supplements for chemical details). Assuming the measured water vapour content of 10.6 ppmv for high chlorine conditions would lead to an ozone depletion of 57% during the 7-day simulation. In comparison, in the standard case an ozone loss of 8% is reached when a high water vapour mixing ratio of 20 ppmv is assumed. However, even for the standard trajectory and a high chlorine content, a water vapour amount of 8 ppmv has to be exceeded to yield any ozone reduction. This threshold shifts from 8 ppmv to 7 ppmv for the case where stratospheric sulphate is tripled (Fig. ??, left 11a, yellow triangles). Comparing the standard case and the high case using 15 ppmv water vapour conditions, in the high case more inactive chlorine is converted into active on the first day of the simulation (Fig. ??, right). This higher mixing ratio results in faster catalytic ozone loss cycles with peak values of \(2 \cdot 10^5\) for R13 (ClO\textsuperscript{+}), \(2.0 \cdot 10^5\) for R18 (ClO\textsuperscript{+}Br\textsuperscript{O}) and \(10.9 \cdot 10^5\) for R17 (ClO\textsuperscript{+}ClO) on 3 Aug 2013. Since the Cl\textsubscript{y}-mixing ratio is much higher than in the standard case, the catalytic ozone loss cycles are dominated by the Cl\textsubscript{O}-Dimer cycle and result in a much larger ozone loss than in the standard case assuming realistic and mixing ratios.

5.3 Case-based on observations

The simulation of the case-based on observations during the SEAC4RS aircraft campaign corresponds to the most realistic case for today's climate. It is identical to that of the standard case but assumes a fixed water vapour mixing ratio of 10.6 ppmv observed on 8 August 2013. Under these conditions, neither heterogeneous chlorine activation due to R1 (CI) nor catalytic ozone loss cycles (e.g. based on ClO\textsuperscript{+}Br\textsuperscript{O}) can be observed in the simulation (Fig. 10, left). Instead, ozone is formed due to cycle Cl. In comparison, the same simulation with 0.6 gas phase equivalent instead of 0.2 was conducted (Fig. 10, right). The enhanced sulphate content yields a larger liquid surface area density and thus an increased heterogeneous reactivity. Hence, reaction
Figure 11. Left panels present the temperature, liquid surface area density. The water dependent final ozone mixing ratio, reaction rates value is shown for (a) the “Case of R1-high Cl,” (e.g., see Tab. 1 for NOy and Cly initialisation). R18 assuming background aerosol (ClO+BrO, blacklight blue) and tripled H2SO4 (as an example for ozone loss cycles yellow), R6 (violet) which limits ozone formation at low concentrations as well as volume mixing ratios of HCl reduced Bry (redlight blue, “Reduced Bry case”), and (c) an extended time period of activated chlorine (light blue, “19-day simulation”). In panel (black) and (scaled with 0.5c) for conditions also final ozone of the measurement-standard case is shown (blue). Initial ozone is marked with 10.6 and 0.20 a grey line. The panels on the right show Note that the same quantities, but for enhanced sulphate conditions (0.60) scale of all y-axis differ.

R1 occurs in the 3× simulation significantly, leading to a slightly increasing mixing ratio and a decrease of the mixing ratio. Both a reduced ozone formation in Cl (which is at decreased concentrations limited by R6) and ozone loss cycles (e.g., based on the reaction ClO+BrO or ClO +) can be observed, resulting in a reduction of ozone. Using initial conditions, the trajectory corresponding to the SEAC4RS observations shows ozone loss with sulphate enhanced by a factor of 3. However, we note that this was an unusually cold trajectory. A more common case with higher mean temperatures would require a higher sulphate content to enhance the heterogeneous reactivity enough for chlorine activation to occur.

5.3 Reduced Bry Case
Impact of a reduction on the water vapour threshold and the ozone loss process. Left panel shows the dependence of ozone values reached at the end of the 7-day simulation on water vapour for the standard case (blue) and a simulation assuming the half of (light blue); the grey line corresponds to the initial ozone value. Right panel presents the volume mixing ratio of ozone, the mixing ratio of (scaled by 0.5), HCl, and and reaction rates of reactions essential for chlorine activation and catalytic ozone loss cycles (R1 () and R18 (ClO+BrO), R17 (ClO+ClO) and R13 ()). The mixing ratio of inorganic bromine (Br,) has a high uncertainty in the lowermost stratosphere due to the influence of very short lived bromine containing substances. For example, during the CONTRAST field campaign (Jan-Feb 2014, western Pacific region), Koenig et al. (2017) observed a Br mixing ratio in the lower stratosphere of 5.6–7.3 pptv and the contribution of Br, which crosses the tropopause, was estimated to be 2.1±2.1 pptv (Wales et al., 2018). Navarro et al. (2017) found somewhat different bromine partitioning depending on the ozone, NO, and Cl concentrations, using very short lived bromine species observations in the eastern and western Pacific ocean from the ATTREX campaign. Because our Br–Br values are not based on measurements for this specific case modeled, we tested the sensitivity to a value that is half of our standard case. The impact of this Br reduction is illustrated in Fig. ?? assuming a water vapour mixing ratio of 15 ppmv11b.

Comparing the end final ozone value for the 0.5 Br simulations (Fig. ??, left11b, light blue triangles) with those of the standard case (blue squares), a higher water vapour threshold and a reduced ozone loss of about 30% at high water vapour mixing ratios is simulated. The reduction shift of the water vapour threshold is due to the impact of Br reduces a slightly longer time period of chlorine activation. At high HCl and low mixing ratios at the start of the simulation, the formation of on the NO/NO-ratio.

Due to the reaction

\[ \text{BrO + NO} \rightarrow \text{Br + NO}_2, \quad (\text{R25}) \]

reduced Br yields a smaller NO/NO-ratio and hence less ClONO formation in R9 (ClO+NO). Since ClONO formation is essential for maintaining the chlorine activation reaction R1 (). Hence, the chlorine activation is dependent on the formation of chlorine activation in R1 (ClONO and thus on the /NO-ratio (von Hobe et al., 2011). A higher /NO-ratio yields a higher rate of R9 and enhances the rate of R1. A +HCl), reduced Br –mixing ratio leads to a smaller /NO-ratio due to R25 (BrO+NO) and thus to yields a lower chlorine activation rate (von Hobe et al., 2011). A reduction of the chlorine activation rate (R1) would change the balance between chlorine activation and chlorine deactivation, which determines and thus a shift of the water vapour threshold region. Thus, this reduction would lead to the shift of the water vapour threshold, which is illustrated in Fig. ?? (left panel). With less- to higher water vapour mixing ratios. In the case of reduced Br, the catalytic, less ozone is destroyed regarding the standard case. The ozone destruction in the ClO-BrO-cycle (??) is reduced(Fig. ??, right panel) is reduced, while the rates of R17 (ClO+ClO) and R13 (ClO+HO) are similar to those of the standard case (Fig. 4e; for chemical details of the reduced Br-case see Suppl. S2). This results in the reduced ozone destruction in the 0.5 Br case.

5.4 19-day-simulationExtended time period

Impact of the simulated time period on ozone loss. Left panel shows the dependence of ozone values reached at the end of the simulation on water vapour for the standard case (7-day, blue) and the 19-day simulation (cyan); the grey line corresponds to
the initial ozone value. Right panel presents temperature, liquid surface area, the mixing ratio of ozone, (scaled by 0.5), HCl, and reaction rates of reactions essential for chlorine activation and catalytic ozone loss cycles (R1 ( ) and R18 (ClO + BrO), R17 (ClO + ClO) and R13 ( ) for the 19-day simulation.

Since the occurrence of the ozone loss process analysed in this study is strongly dependent on a variety of parameters, the time period over which the ozone loss might occur is very uncertain. The impact of this time period on ozone loss was tested by extending the 7-day trajectory used in the sections above to span the entire period with temperatures low enough to maintain chlorine activation. The temperature development of this trajectory is shown in Fig. ???. On 27 July 2013, the 19-day simulation starts at a temperature of 208 K (Fig. ???, right), decreasing until 29 July 2013 to lower than In this time extended simulation, temperatures are well below 200 K. The temperatures remain lower than at the begin of the simulation and remain below 201 K until 11 August and increase to over 205 K on for 14 August 2013. Assuming a water vapour mixing ratio of 15 ppmv days, Hence, chlorine activation occurs on 30 July 2013, after the temperatures fall below 200 K (Fig. ???, right). The mixing ratio of remains low and remains high until 11 can be maintained for a longer time period than in the standard case and breaks up due to increasing temperatures for details regarding chemical processes and temperature development along the extended trajectory see Suppl. August, when the heterogeneous reaction rate of R1 ( ) decreases due to higher temperatures. For this reason chlorine activation cannot anymore be maintained by cycle AC1. This, the time span holding a mixing ratio high enough for the occurrence of catalytic ozone loss cycles ( ??–C2, C3–C4) comprises 14 days and ozone destruction stops on 12 August (S3).

Because of the extended time period, the final ozone values using the enhanced water vapour mixing ratios for 49 days the longer trajectory (cyan triangles Fig. ???, left panel11c) are much lower than those of the standard 7-day simulation (blue squares). Additionally, more ozone is formed when using low water vapour concentrations. Comparing the water vapour threshold of the 7-day trajectory (∼11.0–11.6 ppmv) and the 19-day simulation (∼10.6 ppmv), a shift to lower water vapour mixing ratios occurs in the 19-day trajectory. This shift is likely due to an extended time period with a temperature well below 200 K at the begin of this trajectory, which allows a chlorine activation to occur even for slightly lower water vapour amounts. Simulations along a trajectory starting on the same day as the 7-day trajectory, but finishing on 15 August, yield the same water vapour threshold as the 7-day simulation (not shown), indicating that the shift in the threshold shown in Fig. ??–11 is associated with the very cold conditions at the start of the 19-day simulation. Hence, the length of the chosen trajectory has no impact on the water vapour threshold, but does effect the final ozone.

6 Discussion

Many uncertainties affect the assessment of the extent of ozone loss that occurs in the lowermost stratosphere at mid-latitudes under elevated enhanced water vapour conditions. The number and depth of convective overshooting events as well as the area and duration affected by enhanced water vapour mixing ratios is a subject of recent research (e.g. Homeyer et al., 2014; Smith et al., 2017). The mixing ratio ratios of important trace gases (O3, Cl2, Br2, NO2) in overshooting plumes and the possibility probability that water vapour mixing ratios high enough for chlorine activation meet temperatures low enough is a matter of
In this study, we examined the sensitivity to different water vapour mixing ratios, temperature, content, and trajectory duration.

The ozone loss mechanism investigated here requires the occurrence of the heterogeneous reaction R1, which leads to enhanced ClOx and reduced NOx mixing ratios and thus maintains effective catalytic ozone loss cycles. Enhanced ClO and reduced NO concentrations were observed by Keim et al. (1996) and Thornton et al. (2007) close to the mid-latitude tropopause under conditions with elevated both enhanced water vapour and enhanced concentrations of condensation nuclei, such as sulphate particles. These observations were attributed to the occurrence of the heterogeneous reactions R1 (ClONO2+HCl) and R2 (ClONO2 + H2O, Thornton et al., 2007; Keim et al., 1996). For the temperature and the water vapour range observed in the studies of Keim et al. (1996) (15 ppmv H2O, ~207 K) and Thornton et al. (2007) (15–22 ppmv H2O, ~213–215 K), a heterogeneous chlorine activation would not occur in the box-model simulation conducted here, not even in a sensitivity simulation assuming a high sulphate gas phase equivalent of 7.5 ppbv H2SO4 (not shown). At low temperatures (≤196 K), heterogeneous chlorine activation may occur in the tropical stratosphere (Solomon et al., 2016; von Hobe et al., 2011). Von Hobe et al. (2011) observed enhanced ClO mixing ratios during aircraft campaigns over Australia (SCOUT-O3, 2005) and Brazil (TROCCINOX, 2005) in combination with low temperatures and the occurrence of cirrus clouds. Analysing the balance between chlorine activation and deactivation von Hobe et al. (2011) showed an increase of the chlorine activation rate (R1) with a higher ClO, BrO and O3 mixing ratio. Thus, once started, R1 accelerates due to higher ClO-mixing ratios subsequently yielding a fast conversion of NOx into HNO3 (von Hobe et al., 2011), comparable to the NOx repartitioning found in the present study. Von Hobe et al. (2011) found a threshold in ozone mixing ratio, which has to be exceeded for chlorine activation to occur. Hence, the water vapour threshold discussed here is expected to depend on the ozone mixing ratio, as well. Furthermore a potential occurrence of ice particles in the lowermost mid-latitude stratosphere (Spang et al., 2015) might affect the water vapour threshold due to a different heterogeneous reactivity on ice than on liquid particles (Solomon, 1999).

An elevated sulphate content enhances enhanced sulphate content increases the heterogeneous reaction rate caused by an increased enlarged liquid surface. Due to this relation, an impact of stratospheric albedo modification (by applying solar geoengineering) on the ozone loss process proposed by Anderson et al. (2012) is discussed (Dykema et al., 2014). Applying solar geoengineering would also affect the temperature in the lowermost stratosphere by perturbing the Eddy-heat fluxes and would change the lower stratospheric dynamics (Visioni et al., 2017). It would also affect large scale latitudinal mixing of atmospheric tracers in the lower branch of the Brewer-Dobson-Circulation leading to a different level of isolation of the tropical pipe with mid-latitudes and would result in a different chemical composition of the lower mid-latitude stratosphere (Visioni et al., 2017).

Varying the sulphate content in this our study showed that for temperatures and water vapour conditions of the case based on observations, a moderate enhancement of 3×H2SO4 is sufficient to yield ozone depletion. Considering the temperature and water vapour dependence of the chlorine activation line (Fig. 9, white line), a 10× enhancement of stratospheric sulphate yields a shift of chlorine activation to slightly lower water vapour mixing ratios and higher temperatures. However, even for enhanced sulphate and a water vapour mixing ratio of 20 ppmv, the temperature has to fall below 205 K for chlorine activation (and hence ozone depletion) to occur at the assumed Cl2 and NO2 conditions of the standard case.

After the chlorine activation step, catalytic ozone loss cycles can occur: the ClO-Dimer cycle(1), the ClO-BrO-cycle (2) and
cycles subsequent to R13 (ClO + HO2, C2–C4). Cycle C2 is reported to have an impact on stratospheric ozone in mid-latitudes in previous studies (e.g. Johnson et al., 1995; Kovalenko et al., 2007; Ward and Rowley, 2016). Here, C2 was found to be the dominate cycle based on R13 under standard conditions. Nevertheless, simulating the “0.5 Br2 and” and “high Cl2” case has shown that the relevance of (ClO+ClO) and (ClO+BrO) depends on the ClO-Dimer-cycle and the ClO-BrO-cycle depends on the assumed initial values of Cl2 and Br2. Anderson and Clapp (2018) discussed the occurrence of the ClO-Dimer cycle (22) and the ClO-BrO-cycle (22)-dependent on water vapour, the Cl2 mixing ratio and temperature. They illustrate a significant increase in the rate of R17 (ClO+ClO) and R18 (ClO+BrO) if the combination of elevated enhanced water vapour and low temperatures is sufficient for chlorine activation to occur. If chlorine activation occurs in their model study, a higher Cl2 mixing ratio yields higher catalytic ozone loss rates (R17, R18). Their finding regarding the effect of temperature, water vapour and chlorine on the ozone loss process is consistent with the results found here. The occurrence of net chlorine activation is determined by temperature and water vapour mixing ratio, while the Cl2 mixing ratio controls how much ozone is destroyed. A measure for the effect of temperature and water vapour on stratospheric chlorine activation and ozone chemistry is the temperature and water vapour dependent chlorine activation line (Fig. 9, white line). Anderson et al. (2012) estimates reported that lower temperatures than 205 K are necessary for chlorine activation to occur at a water vapour mixing ratio of 20 ppmv and a climatological non enhanced sulphate content. In comparison, assuming standard conditions for Cl2 and NOy but a constant temperature here, temperatures lower than 203 K are required for ozone loss to occur at similar H2O and sulphate concentrations. The standard trajectory was chosen here to hold for conditions most likely for chlorine activation based on SEAC4RS measurements and at. For the temperature range of this trajectory, and the measured water vapour mixing ratio (10.6 ppmv) is slightly lower than the water vapour threshold no significant ozone depletion occurs. Hence, for all SEAC4RS and MACPEX trajectories calculated (not only the shown examples), no trajectory produced ozone loss. A further requirement for the occurrence of chlorine activation is the maintenance of the conditions, which yield chlorine activation, during the entire time of chlorine activation. Assuming standard conditions and a water vapour mixing ratio of 20 ppmv, chlorine activation takes 5 hours, but for conditions of. However for a water vapour content close to the water vapour threshold, low temperatures and enhanced water vapour mixing ratios have to be maintained 24–36 hour hours for chlorine activation and thus to have an impact on stratospheric ozone chemistry to occur. For the occurrence of ozone depletion, temperatures have also to remain low and water vapour mixing ratios high after the chlorine activation step.

The maximum ozone depletion at standard conditions occurs here for a water vapour mixing ratio of 20 ppmv. Final ozone at assuming 20 ppmv H2O in the 7-day simulation is 11% lower than the final ozone reached under atmospheric background conditions of assuming 5 ppmv H2O. For the 19-day simulation at assuming 20 ppmv H2O, the final ozone is 22% reduced compared to the 19-day simulation at assuming 5 ppmv H2O. Anderson and Clapp (2018) calculated a similar ozone reduction of 17% in a 14-day simulation and the same potential temperature range of 380 K assuming 20 ppmv H2O and similar somewhat higher Cl2 conditions (≈0.2 ppbv) than as used here in the realistic case. In contrast assuming the high Cl2 and NOy of mixing ratios employed by Anderson et al. (2012) in the case of high Cl2 would lead to an ozone loss of 85% (265 ppbv) during the 7-day simulation. This ozone loss would occur in the lower stratosphere.

Borrmann et al. (1996, 1997) and Solomon et al. (1997) conducted a study about the impact of cirrus clouds on chlorine ac-
tivation and ozone chemistry in the mid-latitudes lowermost stratosphere. They found a significant impact of heterogeneous processes occurring on cirrus clouds for ozone chemistry of the lowermost stratosphere but a minor effect for column ozone. Anderson and Clapp (2018) calculated a fractional loss in the total ozone column of 0.25–0.27% assuming a full Cl\(y\) profile in the altitude range of 12–18 km with a constant water vapour mixing ratio of 20 ppmv and the mixing ratio of Cl\(y\) similar to somewhat higher (∼0.2 ppbv at a potential temperature of 380 K) than in our standard case. However, the simulations of us and Anderson and Clapp (2018) assume a constant high water vapour mixing ratio and neglect mixing with the stratospheric background, which is characterized by much lower water vapour mixing ratios and subsequent dilution of convective uplifted air masses. Ozone loss would only occur in the specific volume of stratospheric air, that is directly affected by the convectively injected additional water. Hence, the ozone loss presented here corresponds to the maximal possible ozone loss for rather realistic convective overshooting conditions.

7 Conclusions

We investigated in detail the ozone loss mechanism at mid-latitudes in the lower stratosphere occurring under enhanced water vapour conditions and the sensitivity of this ozone loss mechanism on a variety of conditions. A CLaMS box-model study was conducted including a standard assumption and a variety of sensitivity cases regarding the chemical initialisation, temperatures and the duration of the simulated period. The assumed standard conditions (155.7 pptv Cl\(y\), 728.8 pptv NO\(y\), 197–203 K and an \(H_2SO_4\) gas phase equivalent of 0.20 ppbv) were determined based on measurements in an \(H_2O\) environment showing strongly enhanced \(H_2O\) values compared to the stratospheric background during the SEAC\(^4\)RS aircraft campaign in Texas 2013.

The ozone loss mechanism consists of two phases: The first step is chlorine activation due to the heterogeneous reaction ClONO\(_2\) + HCl (R1), which yields both an increase of ClO\(x\) and a decrease of NO\(x\). When chlorine is activated, enhanced ClO\(x\) mixing ratios lead to catalytic ozone loss cycles in the second phase of the mechanism. Our findings show that besides the ClO-Dimer-cycle and the ClO-BrO-cycle, three ozone loss cycles (C\(_2\)–C\(_4\)) based on the reaction ClO+HO\(_2\) (R13) have to be taken into account. The relevance of the cycles C\(_2\) and C\(_3\)–C\(_4\) for ozone loss depends on the different ozone loss cycles for ozone destruction depends on water vapour, Cl\(y\) and Br\(y\) mixing ratios. Reduced NO\(x\) mixing ratios yield a decreasing chemical net ozone formation in cycle C\(_1\). This reduced ozone formation at high water vapour mixing ratios is in the box-model simulation amounts to around 20% as high as of the ozone destruction in catalytic ozone loss cycles. Furthermore a detailed analysis of chemical processes revealed the occurrence of pathways, which maintain high ClO\(x\) and low NO\(x\) mixing ratios after the chlorine activation step but do not reduce ozone, similar to HCl-null-cycles in the lower stratosphere (Müller et al., 2018) in Antarctic early spring (Müller et al., 2018).

Focussing on the dependence of chlorine activation on temperature and water vapour mixing ratio, we found that the temperature has to fall below 203 K for chlorine activation to occur at a water vapour mixing ratio of 20 ppmv and Cl\(y\) and NO\(y\) for our standard case. Testing the water vapour dependence of ozone loss along a realistic trajectory that experienced very low
temperatures between 197 and 202 K, we observed a water vapour threshold of 11.0–11.6 ppmv H2O, which has to be exceeded for ozone reduction chlorine activation to occur. An ozone loss occurs in these simulations for at least 12 ppmv H2O. For our assumed standard conditions, a maximum ozone loss of 9% (27 ppbv) was calculated for a water vapour mixing ratio of 20 ppmv. In contrast, a simulation assuming the observed conditions (10.6 ppmv H2O) yielded ozone formation; but a tripling of background sulphate gas phase equivalent (as it can be reached under geoengineering conditions or volcanic eruptions) is sufficient for a slight ozone loss to occur under these unusually cold conditions for the chosen standard trajectory. Simulating a high Cl\textsubscript{y} case assuming initial Cl\textsubscript{y} and NO\textsubscript{y} based on the study of Anderson et al. (2012) results in both a lower water vapour threshold of 7–8 ppmv and a larger ozone depletion of 85% (265 ppbv) at high water vapour mixing ratios. The model runs described here assume an air parcel moving along the trajectory, which does not mix with neighbouring air masses. In the case of water, this mixing would likely reduce the concentration. Because that mixing was neglected, the runs discussed here are likely and an extreme case, and the ozone loss modelled simulated provides an upper bound to the process described. Considering the duration for which low temperatures and high water vapour mixing ratios have to be maintained to activate chlorine and deplete stratospheric ozone, a chlorine activation time of 24 to 36 hours when the water vapour abundance is near the close to the water vapour threshold and of 5 h at assuming 20 ppmv H2O was calculated. The water vapour threshold shifts strongly with depends strongly on a changing temperature and sulphate content as well as with on Cl\textsubscript{y}, NO\textsubscript{y} and Br\textsubscript{y} mixing ratios. The dependence of the water vapour threshold is explained here by focussing on the water dependence of the heterogeneous reactivity (R1) and the balance between heterogeneous chlorine activation (R1, Cl\textsubscript{y}NO\textsubscript{2} + HCl) and gas phase chlorine deactivation (R12, Cl + CH\textsubscript{4}).

The ozone loss mechanism was investigated here by conducting box-model simulations along a trajectory, which was calculated based on measurements of elevated enhanced water vapour. Sensitivity and case studies, which cover a range of uncertainties, illustrate the impact of the Cl\textsubscript{y}, NO\textsubscript{y}, Br\textsubscript{y} and H2O mixing ratios, the temperature, the sulphate gas equivalent and the duration of the simulated period on the ozone loss process. While the water vapour threshold which has to be exceeded for chlorine activation to occur is mainly determined by the temperature, water vapour mixing ratio and sulphate content, the intensity of ozone loss depends on Cl\textsubscript{y}, NO\textsubscript{y}, Br\textsubscript{y} and the duration of the time period, for which a chlorine activation can be maintained. Our comprehensive sensitivity studies are a basis to assess the impact of enhanced water vapour mixing ratios in the lower mid-latitude stratosphere on ozone under sulphate geoengineering conditions and in a changing climate. However, for the conditions observed during SEC\textsuperscript{4}RS (in particular H2O=10.6 ppmv), we did not simulate ozone depletion for the observed conditions. Further global any ozone depletion Global modelling studies are needed to establish whether the mechanism analysed here is of concern for the future.

Code and data availability. The complete SEAC\textsuperscript{4}RS data are available at https://www-air.larc.nasa.gov/cgi-bin/ArcView/seac4rs. The CLaMS box model calculations can be requested from Sabine Robrecht (sa.robrecht@fz-juelich.de).
Appendix A: Maintenance of activated chlorine

In Sec. 3.2.2 chlorine catalysed ozone loss cycles are analysed and the maintenance of activated chlorine is described schematically based on Fig. 6. Here, we describe the pathways yielding the maintenance of activated chlorine and balancing the NO\textsubscript{x} mixing ratio in more detail, including all radical balancing reactions. Since the pathway balancing HCl-formation and -destruction is coupled with the pathway balancing HNO\textsubscript{3}-formation and -destruction, both are combined here. In total, two pathways are described here, which balance HCl-formation and -destruction as well as HNO\textsubscript{3}-formation and -destruction, and which mainly differ in the reaction of the methylperoxy radical (H\textsubscript{3}COO + NO, R22, or H\textsubscript{3}COO + ClO\textsubscript{2}, R23).

At water vapour mixing ratios slightly higher than the water vapour threshold, H\textsubscript{3}COO reacts rather with NO. Hence, pathway AC1 mainly balances HCl and ClO\textsubscript{2} as well as HNO\textsubscript{3} and NO\textsubscript{x}.

\[
\begin{align*}
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \text{CH}_3 & \text{(R12)} \\
\text{CH}_3 + \text{O}_2 & \rightarrow \text{H}_3\text{COO} & \text{(AR1)} \\
\text{H}_3\text{COO} + \text{NO} & \rightarrow \text{NO}_2 + \text{H}_3\text{CO} & \text{(R22)} \\
\text{H}_3\text{CO} + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 & \text{(AR2)} \\
\text{ClO} + \text{NO}_2 + \text{M} & \rightarrow \text{ClONO}_2 + \text{M} & \text{(R9)} \\
\text{ClONO}_2 + \text{HCl} & \rightarrow \text{HNO}_3 + \text{Cl}_2 & \text{(R1)} \\
\text{OH} + \text{HNO}_3 & \rightarrow \text{H}_2\text{O} + \text{NO}_3 & \text{(R20)} \\
\text{Cl}_2 + \text{h}ν & \rightarrow \text{2Cl} & \text{(AR3)} \\
\text{2} \times (\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2) & \text{(R16)} \\
\text{NO}_2 + \text{h}ν & \rightarrow \text{NO} + \text{O}(^3\text{P}) & \text{(R7)} \\
\text{NO}_3 + \text{h}ν & \rightarrow \text{NO}_2 + \text{O}(^3\text{P}) & \text{(AR4)} \\
\text{HO}_2 + \text{ClO} & \rightarrow \text{HOC}_2 + \text{O}_2 & \text{(AR5)} \\
\text{HOC}_2 + \text{h}ν & \rightarrow \text{OH} + \text{Cl} & \text{(R14)} \\
\text{2} \times (\text{O}(^3\text{P}) + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}) & \text{(AR5)} \\
\text{net:} \text{CH}_4 + \text{O}_2 & \rightarrow \text{HCHO} + \text{H}_2\text{O} & \text{(AC1)}
\end{align*}
\]

In pathway AC1, HCl is formed in R12. The methyl radical formed in R12 reacts fastly with oxygen in AR1 yielding a methylperoxy radical H\textsubscript{3}COO, which reacts with NO in R22. In reaction R9 ClONO\textsubscript{2} is formed, which reacts with HCl heterogeneously in R1 (and thus leads to an HCl depletion). HNO\textsubscript{3} formed in R1 is depleted in R20. These reactions constitute the balance between HCl and HNO\textsubscript{3}-formation and -destruction. The reactions AR3 and R16 balance the ClO\textsubscript{x}-species, R7 and AR4 the NO\textsubscript{x}-species, reactions R13 and R14 the HO\textsubscript{x}-species and AR5 odd oxygen (O\textsubscript{3}) All of these radical reactions are
significantly faster than the reactions, which constitute the balance between HCl and HNO₃ formation and destruction. Hence, the net reaction of this pathway is the oxidation of CH₄ to HCHO (formaldehyde).

In cycle AC1 the \text{H₃COO}-radical reacts with NO (R22). As an alternative the \text{H₃COO}-radical reacts with ClO (R23) at high water vapour mixing ratios yielding to cycle AC2 as balance between HCl and HNO₃ formation and destruction.

\[
\begin{align*}
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \text{CH}_3 & \text{(R12)} \\
\text{CH}_3 + \text{O}_2 & \rightarrow \text{H}_3\text{COO} & \text{(AR1)} \\
\text{H}_3\text{COO} + \text{ClO} & \rightarrow \text{HCHO} + \text{HO}_2 + \text{Cl} & \text{(R23)} \\
\text{ClO} + \text{NO}_2 + \text{M} & \rightarrow \text{ClONO}_2 + \text{M} & \text{(R9)} \\
\text{ClONO}_2 + \text{HCl} & \xrightarrow{\text{het}} \text{HNO}_3 + \text{Cl}_2 & \text{(R1)} \\
\text{OH} + \text{HNO}_3 & \rightarrow \text{H}_2\text{O} + \text{NO}_3 & \text{(R20)} \\
\text{Cl}_2 + \text{hv} & \rightarrow 2\text{Cl} & \text{(AR3)} \\
3 \times (\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2) & \text{(R16)} \\
\text{HO}_2 + \text{ClO} & \rightarrow \text{HOC}_2 + \text{O}_2 & \text{(R13)} \\
\text{HOCI} + \text{hv} & \rightarrow \text{OH} + \text{Cl} & \text{(R14)} \\
\text{O}(\text{^3P}) + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} & \text{(AR6)} \\
\text{net: CH}_4 + 2\text{O}_3 & \rightarrow \text{HCHO} + \text{H}_2\text{O} + 2\text{O}_2 & \text{(AC2)}
\end{align*}
\]

The main difference between pathway AC1 and AC2 is the reaction of the \text{H₃COO}-radical. The reactions R12, AR1, R9, R1 and R20 balance HCl and ClOₓ as well as HNO₃ and NOₓ. The reactions AR3, R16, R13, R14 and AR5 convert the radical species and are very fast. The net reaction of this pathway is the oxidation of methane (CH₄) into formaldehyde (HCHO) with a simultaneous ozone destruction. Since the ozone destruction due to the catalytic ozone loss cycles discussed in Sec. 3.2.2 is much faster, the ozone destruction in AC2 is negligible compared to the ozone loss cycles discussed above.

Appendix B: \textbf{MACPEX case}

The MACPEX case (Mid-latitude airborne Cirrus Properties Experiment) was conducted to complement the results obtained from the standard case as a further example for an event with high stratospheric water vapour based on airborne measurements. In this section, first the model setup for the MACPEX case is described. In a second step, the results of model calculations of the MACPEX case are presented, comprising the chosen trajectory for chemical simulations and the sensitivity of ozone chemistry to various conditions.
B1 Model Setup

Simulations are performed similar to the SEAC4RS case (see, Sec. 2) based on measurements with enhanced water vapour of at least 10 ppmv taken during the MACPEX campaign (Rollins et al., 2014). Chemistry is calculated for single air parcels along trajectories including diabatic descent. Trajectories are calculated as described in Sec. 2.2. For chemical initialization, important trace gases for ozone chemistry — O₃, Clₓ and NOₓ — are initialized based on MACPEX measurements. Ozone and water vapour were measured directly during the aircraft campaign. Clₓ and NOₓ are inferred from tracer-tracer relations using N₂O measured on the aircraft employed. The initialization of all further trace gases except of water vapour were taken from the full chemistry 3D-CLaMS simulation (Vogel et al., 2015, 2016) for summer 2012 at the location of the measurement. Chemistry was initialized 7 days before the measurement.

The MACPEX campaign (Rollins et al., 2014) took place during the spring 2011 and was based in Houston, Texas. The water vapour values used here were measured by the Fast In-situ Stratospheric Hygrometer (FISH), which employs the Lyman-α photofragment fluorescence technique (Meyer et al., 2015). MACPEX ozone was measured by the UAS-O₃ instrument (Gao et al., 2012). Initial Clₓ and NOₓ were assumed based on tracer-tracer correlations with N₂O that was measured by the Jet Propulsion Laboratory’s Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument (Webster et al., 1994).

Initial Clₓ and NOₓ is calculated based on N₂O tracer-tracer correlations (Groos et al., 2014, see also App. C) with corrections considering a N₂O increase from 2009 to 2013. Clₓ is determined using the same correlation with CH₄ as for the standard case (see Sec. 2.3). Therefore CH₄ is first calculated using measured N₂O of 320.28 ppbv and a correlation based on measurements from 2009 (Groos et al., 2014). The increase of stratospheric CH₄ and N₂O is considered as described for the standard case (GHG Bulletin, 2014). First, an increase in N₂O of 1.6 ppbv from 2009 to 2011 is estimated to adjust N₂O. Furthermore calculated CH₄ is adjusted considering a difference between CH₄ in 2000 and 2009 of 0.026 ppm. The annual decrease of Clₓ from 2000 to 2011 is assumed to be 0.8% (WMO, 2014). A summary of the initial values for main tracers assumed in the MACPEX case are given in Table B1. Furthermore sensitivity studies assuming only 80% of initial Clₓ (0.8 Clₓ), 80% of initial NOₓ (0.8 NOₓ), and an elevated H₂SO₄-background (0.6 ppbv H₂SO₄) are conducted.

B2 Results of MACPEX simulations

During the MACPEX campaign only few cases with enhanced stratospheric water vapour were observed. Here we present an example for a trajectory calculated based on such a case. This trajectory is used to test the sensitivity of lowermost stratospheric ozone in mid-latitudes on the water vapour, Clₓ and NOₓ mixing ratio and on an enhancement of stratospheric sulphate.

B2.1 MACPEX Trajectory

The selected trajectory for the MACPEX case is shown in Fig. B1. It refers to a measurement on 11 April 2011 during the MACPEX campaign. In the left panel, a backward trajectory is presented in the range of −7 to 0 days from the time of measurement and a forward trajectory in the range from 0 to 7 days. In the right panel, the location of the measurement is
Table B1. Mixing ratios and sources used for initialization of relevant trace gases for the MACPEX case. Cl\textsubscript{y} and NO\textsubscript{y} values were determined based on tracer-tracer correlations (see text). Initial mixing ratios of ClO\textsubscript{x} species were assumed to be zero.

<table>
<thead>
<tr>
<th>Species</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{3}</td>
<td>283.0 ppbv</td>
<td>UAS-O\textsubscript{3}</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>1.68 ppmv</td>
<td>CLaMS-3D</td>
</tr>
<tr>
<td>CO</td>
<td>19.0 ppbv</td>
<td>CLaMS-3D</td>
</tr>
<tr>
<td>Cl\textsubscript{y}</td>
<td>55 pptv</td>
<td>tracer corr.</td>
</tr>
<tr>
<td>HCl</td>
<td>52.7 pptv</td>
<td>tracer corr.</td>
</tr>
<tr>
<td>ClONO\textsubscript{2}</td>
<td>2.19 pptv</td>
<td>tracer corr.</td>
</tr>
<tr>
<td>NO\textsubscript{y}</td>
<td>620 pptv</td>
<td>tracer corr.</td>
</tr>
<tr>
<td>HNO\textsubscript{3}</td>
<td>390.3 pptv</td>
<td>tracer corr.</td>
</tr>
<tr>
<td>NO</td>
<td>114.6 pptv</td>
<td>tracer corr.</td>
</tr>
<tr>
<td>NO\textsubscript{2}</td>
<td>114.6 pptv</td>
<td>tracer corr.</td>
</tr>
<tr>
<td>Br\textsubscript{y}</td>
<td>1.2 pptv</td>
<td>CLaMS-3D</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>5–20 ppmv</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.2 ppbv, 0.6 ppbv</td>
<td></td>
</tr>
</tbody>
</table>

shown by a red square.

The potential temperature level of this trajectory is around 380 K and above the tropopause located at \(\sim 350\) K, which was deduced from the temperature profile measured during the flight on 11 April 2011. The forward trajectory shows a strongly increasing temperature and pressure level due to a decrease in altitude. Coming from the Western Pacific, this air parcel passes the North American continent briefly. The backward trajectory reaches very low temperatures with a minimum temperature of 191 K. Because of its low temperature, which pushes the occurrence of heterogeneous reactions, the backwards trajectory is chosen to test the sensitivity of lowermost stratospheric ozone to a variety of conditions.

5 B2.2 Sensitivity studies

Chemical simulations assuming the MACPEX initialization (Tab. B1) and a water vapour mixing ratio varying between 5 and 20 ppmv are performed along the MACPEX 7-day backwards trajectory. Final ozone, reached at the end of this simulations, is shown as blue squares in Fig. B2. The water vapour threshold necessary for chlorine activation to occur is reached at 8 ppmv H\textsubscript{2}O. It is a lower water vapour mixing ratio than for the SEAC\textsuperscript{4}RS case, because of the very low temperatures reached.

For the MACPEX trajectory and 8 ppmv H\textsubscript{2}O, the time until chlorine is activated takes 63 h from the beginning of the trajectory. Because of increasing temperatures (see Fig. B2), chlorine activation can be maintained for 14 h at this water vapour mixing ratio. Hence, no decrease of final ozone can be observed during this simulation. For higher water vapour mixing ratios, chlorine activation is maintained for a longer time and final ozone is reduced comparing with final ozone reached for low water vapour
Figure B1. Pressure, potential temperature, temperature and location of the selected trajectory calculated based on measurements with enhanced water vapour during the MACPEX aircraft campaign. The red line (left panels) marks the time of measurement and the red squares (right panels) mark the location of the measurement. Since the tropopause is very low, it is not plotted here. In the right panel, the begin of the trajectory (4. April 2011) is at the left edge of the panel. In the bottom panel (left), the MACPEX trajectory consists of single squares due to a faster movement of the air parcel in that region.

mixing ratios. In general, the decrease in final ozone is much lower for the MACPEX case than for the SEAC4RS case. In the MACPEX initialization, $\text{Cl}^+$ is a third of $\text{Cl}^+$ in the SEAC4RS initialization. Hence, catalytic ozone loss has lower rates for MACPEX conditions and ozone is less affected by chlorine activation. Even assuming high water vapour of 20 ppmv yields higher final ozone than initial ozone for MACPEX conditions. Although chlorine is activated in the MACPEX case, no net ozone destruction occurs.

The impact of changes in sulphate, $\text{Cl}^+$ and $\text{NO}_3$ is tested for the MACPEX case, as well. The changes affect the water vapour threshold in the same way as in the SEAC4RS case. A enhancement of sulphate (Fig. 7, left, yellow diamonds), and a reduction of $\text{NO}_3$ (green triangles) shifts the water vapour threshold to lower water vapour mixing ratios. A reduction of $\text{Cl}^+$ (black circles) shifts it to higher water vapour mixing ratios.
Figure B2. Impact of the water vapour content on the ozone mixing ratio (final ozone) reached at the end of the 7-day simulation along the MACPEX trajectory. The standard case is shown in blue and the initial ozone amount is marked by the grey line. An impact on the final ozone mixing ratios is observable after exceeding a critical threshold in water vapour. This threshold changes with a shift in the temperature (+1K, red), the Cl\textsubscript{y} mixing ratio to 0.8 Cl\textsubscript{y} (black), the NO\textsubscript{y} mixing ratio (0.8 NO\textsubscript{y}, green), the sulphate content (3 × standard H\textsubscript{2}SO\textsubscript{4}, yellow, 10 × standard H\textsubscript{2}SO\textsubscript{4}, pink).
Appendix C: Tracer-Tracer Correlations

The mixing ratios of Cl\textsubscript{y} and NO\textsubscript{y} were initialized based on stratospheric tracer-tracer correlations from Grooß et al. (2014). Cl\textsubscript{y} and NO\textsubscript{y} were initialized based on a CH\textsubscript{4} measurement during the SEAC\textsuperscript{4}RS aircraft campaign. Initial Cl\textsubscript{y} was calculated using the tracer-tracer correlation (Grooß et al., 2014)

\[
[\text{Cl}_y] = 2.510 + 3.517 \cdot [\text{CH}_4] - 3.741 \cdot [\text{CH}_4]^2 + 0.4841 \cdot [\text{CH}_4]^3 + 0.03042 \cdot [\text{CH}_4]^4. \quad (C1)
\]

The volume mixing ratio of Cl\textsubscript{y} ([Cl\textsubscript{y}]) is here in pptv and the mixing ratio of methane ([CH\textsubscript{4}]) in ppmv.

To determine NO\textsubscript{y} based on the CH\textsubscript{4} measurement, first N\textsubscript{2}O was calculated through

\[
[N_2O] = -124.9 + 311.9 \cdot [\text{CH}_4] - 158.1 \cdot [\text{CH}_4]^2 + 146.6 \cdot [\text{CH}_4]^3 - 43.92 \cdot [\text{CH}_4]^4 \quad (C2)
\]

assuming [N\textsubscript{2}O] in ppbv and [CH\textsubscript{4}] in ppmv (Grooß et al., 2002). Subsequently NO\textsubscript{y} (in ppt) was calculated in a correlation with N\textsubscript{2}O.

\[
[\text{NO}_y] = 11.57 + 0.1235 \cdot [N_2O] - 1.013 \cdot 10^{-3} \cdot [N_2O]^2 + 1.984 \cdot 10^{-6} \cdot [N_2O]^3 - 1.119 \cdot 10^{-9} \cdot [N_2O]^4 \quad (C3)
\]

In the MACPEX case NO\textsubscript{y} and Cl\textsubscript{y} were initialized based on N\textsubscript{2}O measurements. NO\textsubscript{y} was calculated using correlation C3. Cl\textsubscript{y} was calculated using C1. Therefore first CH\textsubscript{4} (in ppmv) had to be calculated based on a correlation with N\textsubscript{2}O (in ppbv)

\[
[\text{CH}_4] = 0.1917 + 0.01333 \cdot [N_2O] - 8.239 \cdot 10^{-5} \cdot [N_2O]^2 + 2.840 \cdot 10^{-7} \cdot [N_2O]^3 - 3.376 \cdot 10^{-10} \cdot [N_2O]^4 \quad (C4)
\]

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