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Heterogeneous chlorine activation on stratospheric aerosols and clouds in the Arctic polar vortex

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Abstract. Chlorine activation in the Arctic is investigated by examining different parameterizations for uptake coefficients on stratospheric aerosols, high-resolution in-situ measurements and vortex-wide satellite observations. The parameterizations for heterogeneous chemistry on liquid aerosols are most sensitive to temperature with the reaction rates doubling for every 1 K increase in temperature. However, differences between the currently available parameterizations are negligible. For Nitric Acid Trihydrate particles (NAT) the major factors of uncertainty are the number density of nucleated particles and different parameterizations for heterogeneous chemistry. These two factors induce an uncertainty that covers several orders of magnitude on the reaction rate. Nonetheless, since predicted reaction rates on liquid aerosols always exceed those on NAT, the overall uncertainty for chlorine activation is small. In-situ observations of ClO_x from Arctic winters in 2005 and 2010 are used to evaluate the heterogeneous chemistry parameterizations. The conditions for these measurements proved to be very different between those two winters with HCl being the limiting reacting partner for the 2005 measurements and $ClONO_2$ for the 2010 measurements. Modeled levels of chlorine activation are in very good agreement with the in-situ observations and the surface area provided by Polar Stratospheric Clouds (PSCs) has only a limited impact on modeled chlorine activation. This indicates that the parameterizations give a good representation of the processes in the atmosphere. Back-trajectories started on the location of the observations in 2005 indicate temperatures on the threshold for PSC formation, hence the surface area is mainly provided by the background aerosol. Still, the model shows additional chlorine activation during this time-frame, providing cautionary evidence for chlorine activation even in the absence of PSCs. Vortex-averaged satellite observations by the MLS instrument also show no definite connection between chlorine activation and PSC formation. The inter -and intra-annual variability of vortex-average HCl and HNO_3 based on MLS observations is examined for the Arctic winters 2004/2005 to 2010/2011. These observations show that removal of HCl and HNO_3 from the gas-phase are not correlated. HNO_3 loss exhibits great inter-annual variability depending on prevailing temperatures while HCl loss is continuous through December without considerable inter- or intra-annual variability. Only the recovery of HCl in late winter depends on the level of denitrification. Hence, the occurrence of HNO_3 containing PSC particles does not seem to have a significant effect on the speed of initial chlorine activation on a vortex-wide scale.

1 Introduction

During polar night in the stratosphere the main chlorine reservoir species HCl and $ClONO_2$ are converted to photolabile species through heterogeneous reactions on liquid and solid particles (Solomon et al., 1986), a process known as chlorine activation. Under the influence of sunlight, these

photo-labile species are converted to ClO_x ($ClO + 2 \cdot Cl_2O_2$), which is referred to as "active chlorine", as ClO_x drives the catalytic ozone loss cycles which lead to severe depletion of ozone in polar spring (Molina and Molina, 1987; Solomon, 1999). The liquid and solid particles acting as reactions sites for heterogeneous chemistry are provided by Polar Stratospheric Clouds (PSCs) and the ubiquitous background sulfate aerosol layer. PSCs are composed of mixtures of Supercooled Ternary Solution (STS), Nitric Acid Trihydrate (NAT) and ice (e.g. Peter and Grooß (2012)). Clouds composed of STS and low number density NAT ($3 \times 10^{-4}\,cm^{-3}$–$10^{-3}\,cm^{-3}$) are the most common type in cold Arctic winters and STS with high number density NAT ($> 10^{-3}\,cm^{-3}$) are more common for the Antarctic (Pitts et al., 2011). Ice formation is usually only observed over the Antarctic as the polar vortex over the Arctic tends to be warmer. An exception was the Arctic winter of 2009/2010, which was exceptionally cold leading to ice formation (Pitts et al., 2011; Khosrawi et al., 2011). An overview of our current understanding of PSC processes is given in Lowe and MacKenzie (2008) and Peter and Grooß (2012).

The greatest uncertainty in PSC formation is the nucleation mechanism for NAT which directly influences the NAT number density. However, based on CALIPSO observations (Pitts et al., 2011) and in-situ measurements (Fahey et al., 2001), NAT number densities can be constrained to values between 10^{-1} and $10^{-4}\,cm^{-3}$. Background aerosol surface area density depends on the COS and SO_2 fluxes into the stratosphere and is significantly enhanced only after large volcanic eruptions (Robock, 2000). The influence of the sulfate aerosol on stratospheric ozone was particularly observable after the eruptions of El Chichón (Hofmann and Solomon, 1989) and Mt. Pinatubo (Portmann et al., 1996; Tilmes et al., 2008b).

The importance of PSCs and the sulfate aerosol layer on heterogeneous chemistry is well established (e.g. Solomon (1999)), with the impact of an unperturbed aerosol layer on heterogeneous processing first discussed by Rodriguez et al. (1988). But recently Drdla and Müller (2012) suggested that even during volcanic quiescent times chlorine activation in polar night is dominated by reactions on cold binary sulfate aerosol. However, elevated levels of active chlorine usually coincide with the presence of PSCs which makes it difficult to attribute chlorine activation to heterogeneous processing on a particular aerosol or cloud type.

Kawa et al. (1997) reported in-situ measurements of active chlorine from the Antarctic during the ASHOE/MAESA campaign in 1994 where backtrajectories indicated that during the ten days prior to the measurements, temperatures had been too high for PSC formation and therefore concluded that the observed chlorine activation must have occurred on the background aerosol. With the current high chlorine loading in the stratosphere and one option to counter a temperature increase at the surface being the deliberate enhancement of the stratospheric aerosol layer (e.g. Crutzen (2006); Rasch
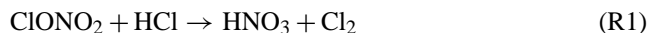
et al. (2008); Tilmes et al. (2008a)), understanding the role of the background aerosol for chlorine activation is essential.

The following sections will discuss the existing parameterizations for heterogeneous chemistry on the various aerosol types and their uncertainty. These parameterizations are validated with in-situ measurements and the role of the background aerosol is constrained with model simulations and satellite observations.

2 Chlorine Activation

Following Portmann et al. (1996) the evolution of chlorine species in the polar regions can be divided into four phases. The "setup phase" preceding the polar winter when Cl_y is partitioned between the reservoir species (HCl and $ClONO_2$), the "activation phase" during polar night when the reservoir species are partly converted into ClO_x, the "maintenance/further activation phase" when activation and deactivation are in competition and further activation occurs if temperatures are sufficiently low and finally the "termination phase" when active chlorine is converted back into the reservoir species.

The three heterogeneous reactions mainly responsible for chlorine activation are (Solomon, 1999; Peter and Grooß, 2012):

$$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2 \qquad (R1)$$
$$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl \qquad (R2)$$
$$HOCl + HCl \rightarrow Cl_2 + H_2O \qquad (R3)$$

Of minor importance for the activation of chlorine is the heterogeneous reaction of N_2O_5, the night-time reservoir species of NO_x, with HCl. This reaction only occurs on NAT (Hanson and Ravishankara) and ice (Tolbert et al., 1988). However, N_2O_5 is usually hydrolyzed on sulfuric acid aerosols before temperatures are low enough for NAT or ice formation (Hanson and Lovejoy, 1994; Müller et al., 1994).

$$N_2O_5 + H_2O \rightarrow 2 \cdot HNO_3 \qquad (R4)$$
$$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3 \qquad (R5)$$

In the Arctic active chlorine is principally deactivated into $ClONO_2$, the speed of deactivation is thus limited by the availability of NO_x ($NO + NO_2 + NO_3$) (Müller et al., 1994; Douglass et al., 1995)

$$ClO + NO_2 \rightarrow ClONO_2 \qquad (R6)$$

The production of NO_x in the polar stratosphere occurs primarily due to the photo-dissociation of HNO_3; thus, it is a function of solar zenith angle and the availability of gas-phase HNO_3.

$$HNO_3 + h\nu \rightarrow OH + NO_2 \qquad (R7)$$
$$OH + HNO_3 \rightarrow NO_3 + H_2O \qquad (R8)$$

Other sources of NO_x are the production through galactic cosmic rays (Nicolet, 1975) and energetic particle precipitation (Solomon et al., 1982; Vogel et al., 2008). Except for the sporadic occurrence of solar proton events (Randall et al., 2005; Jackman et al., 2008), these processes are only a minor source of NO_x compared to the photolysis of HNO_3. However, they provide a steady supply of NO_x, independent of solar zenith angle.

Large NAT particles can effectively remove HNO_3 from the lower stratosphere (Fahey et al., 2001) which results in suppressed deactivation and prolongs the availability of ClO_x into late winter and spring (Harris et al., 2010). In the illuminated polar vortex in spring, ClO_x rapidly depletes ozone, causing the creation of the ozone hole over the Antarctic and severe depletion of ozone over the Arctic for very cold winters. Extensive denitrification of the lower polar stratosphere through sedimentation of NAT particles is more common in the Antarctic than in the Arctic. Temperatures in the Antarctic are lower and remain below the NAT equilibrium temperature (T_{NAT}, Hanson and Mauersberger, 1988) for longer periods than in the Arctic and thus, allow NAT particles to grow and sediment. In the Arctic temperatures are higher and more variable than in the Antarctic which results in less pronounced denitrification and faster deactivation of chlorine through Reaction (R6). In the Antarctic, the almost complete destruction of ozone in polar spring causes the production of ClO from the reaction of Cl with O_3 to slow down. The subsequent increase in Cl concentrations allows the rapid deactivation of Cl into HCl to occur (Douglass et al., 1995).

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (R9)$$

Recently, Grooß et al. (2011) reported that in the Antarctic, for very low ozone values (<0.5 ppmv) a balance is maintained for a certain period between rapid gas-phase production of HCl and HOCl and rapid heterogeneous reaction between these two compounds. This period ends when the almost complete destruction of ozone causes very rapid (on the order of one day), irreversible deactivation Cl into HCl.

The speed of the heterogeneous Reactions (R1) to (R3) is described by the rate constant k which depends on the uptake coefficient γ, aerosol surface area density SAD and mean gas velocity c_{gas}.

$$k = 0.25 \cdot \gamma \cdot c_{gas} \cdot \text{SAD} \qquad (1)$$

The uptake coefficient γ describes the fraction of collisions of gas molecules with the particle surface which lead to a reaction. The uptake coefficient and the surface area density are the main factors controlling the heterogeneous reaction rate and both strongly depend on temperature.

In this work we use parameterizations of the uptake coefficient to model heterogeneous chemistry on liquid aerosols derived by Shi et al. (2001) and Hanson (1998), and for NAT particles the work of Carslaw and Peter (1997), which is based on laboratory measurements by Hanson and Ravishankara (1993) and Abbatt and Molina (1992). NAT reac-
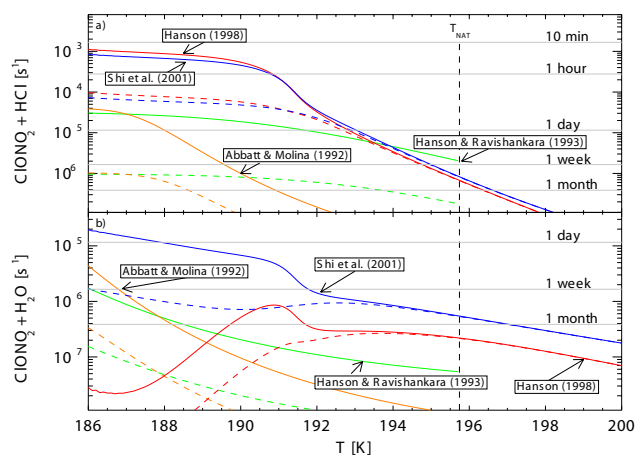

Fig. 1. First order loss rates for $ClONO_2 + HCl$ **(a)** and $ClONO_2 + H_2O$ **(b)** for different parameterizations and aerosol types for typical stratospheric conditions (50 hPa, 5 ppmv H_2O, 1 ppbv HCl, 0.5 ppbv $ClONO_2$, 10 ppbv HNO_3, 0.15 ppbv H_2SO_4 and 10 background aerosol particles cm^{-3}). Solid red and blue lines depict ternary aerosol, dashed lines binary aerosol. Solid green and orange lines represent NAT particles with density 10^{-1} cm^{-3}, dashed lines 10^{-4} cm^{-3}. Adapted from Dameris et al. (2007).

tion probabilities based on the scheme by Hanson and Ravishankara (1993) represent an upper limit while the scheme by Abbatt and Molina (1992) represents the lower limit. For liquid aerosols the parameterizations yield very similar reaction rates, with Shi et al. (2001) reporting an uncertainty of 40% for reaction R1 and 32% for reaction R2. As the parameterization by Shi et al. (2001) has only been derived for binary aerosols it has been extended to STS particles by assuming that there is no difference in the uptake coefficient for STS particles and binary aerosol particles that would exist in the absence of HNO_3, as shown by Elrod et al. (1995). The background aerosol surface area depends on the stratospheric H_2SO_4 content. This surface area increases only for temperatures below about 192 K with the uptake of HNO_3 and the formation of STS (Carslaw et al., 1994). The surface area density for NAT particles depends primarily on the assumed particle density.

Figure 1 shows the first order loss rates in these two species for typical stratospheric conditions for Reactions (R1) and (R2) on liquid aerosols and NAT particles. NAT surface area density is calculated assuming a uniform distribution of spherical particles and the liquid aerosol surface area assuming a log-normal distribution. The main reaction channel for chlorine activation is Reaction (R1) (Fig. 1a). Other reactions are less important for the initial chlorine activation phase as $ClONO_2$ constitutes the second largest reservoir and is quantitatively removed (Müller et al., 1994; Douglass et al., 1995; Portmann et al., 1996). When $ClONO_2$ starts to regenerate and HCl falls below $ClONO_2$ mixing ratios, reaction R2 gains importance if temperatures

are low enough. The various heterogeneous chemistry parameterizations and possible number densities for NAT particles cover several orders of magnitude in first order loss rates, indicating a large uncertainty concerning their ability to act as reaction sites for chlorine activation. However, over most of the temperature range heterogeneous reaction rates on NAT are slower than on the background aerosol, even when a high NAT number density of $10^{-1}\,cm^{-3}$ (Fig. 1) is assumed. Only at temperatures around the thermodynamic equilibrium temperature for NAT, reaction rates on NAT are faster than on the background aerosol. With the formation of STS or a NAT number density less than $10^{-1}\,cm^{-3}$, reaction rates on the liquid aerosol always exceed those on NAT. While chlorine activation on liquid aerosols is not sensitive to the parameterizations, it is very sensitive to temperature. The reaction rate doubles for every 1 K cooling and increases tenfold over a 2 K temperature range around 192 K with the uptake of HNO_3 on the background aerosol (Carslaw et al., 1994; Peter, 1997). This causes high sensitivity of simulated chlorine activation to small variabilities in the temperature field. Therefore, for heterogeneous reactivity on liquid aerosols even a small bias in the temperature field has larger effects than the uncertainty of the uptake coefficients itself.

3 In situ observations

During a flight into the Arctic vortex by the high-altitude research aircraft Geophysica on 7 March 2005, high concentrations of active chlorine compounds (ClO and Cl_2O_2) were observed by the HALOX instrument (von Hobe et al., 2005), and back-trajectories from the flightpath indicate that temperatures 24 h prior to the measurements were low enough for several hours to cause heterogeneous activation of chlorine. Prior to this, temperatures were too high for efficient heterogeneous chemistry which makes chlorine activation unlikely. For the analysis of chlorine activation, chemistry and PSC microphysics are simulated along trajectories starting on 3rd March 2005 and ending on the flightpath. Trajectory and chemistry simulations are performed using the CLaMS Model (McKenna et al., 2002a,b) driven by ERA-INTERIM meteorological fields (Dee et al., 2011). To calculate the reaction rates JPL 2006 recommendations (Sander et al., 2006) are used. STS growth is simulated with the thermodynamic model developed by Carslaw et al. (1995), dynamic NAT growth with the model of Carslaw et al. (2002) and the NAT nucleation rate is taken from Voigt et al. (2005).

The initialization of these trajectories is based on in-situ measurements of N_2O and CH_4 from HAGAR (Homan et al., 2010; Werner et al., 2010), H_2O from the FISH instrument (Zöger et al., 1999) and aerosol number density (size range: 10 nm–5 μm in diameter) from the COPAS instrument (Weigel et al., 2009). Additional details of this flight can be found in von Hobe et al. (2006). CH_4 observations by HAGAR indicate that a homogeneous airmass was sampled al-
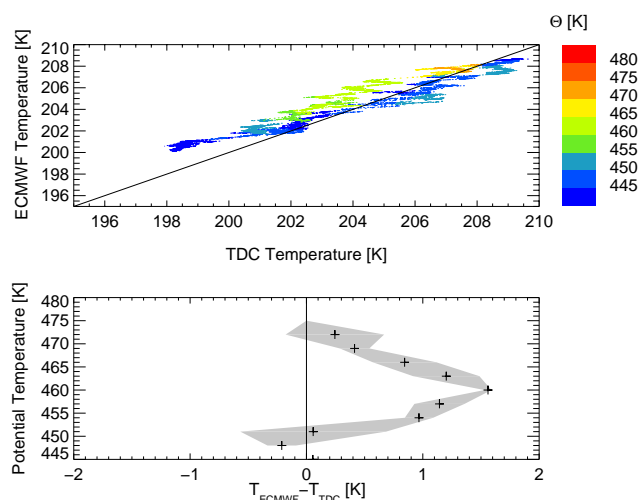

Fig. 2. Top: Temperatures interpolated from ERA-INTERIM data on the flightpath versus TDC temperature measurements on board the Geophysica as function of potential temperature for the flight on 7 March 2005. Bottom: Vertical profile of temperature differences averaged into 3 K bins.

though the flight covered 65°–85° equivalent latitude. From these measurements we derive the total inorganic chlorine loading Cl_y using the CH_4-Cl_y tracer correlation reported in Grooß et al. (2002) as a function of potential temperature and equivalent latitude. $ClONO_2$, HCl, and HNO_3 mixing ratios are taken from ACE-FTS v2.2update (Bernath et al., 2005) observations on 3 and 4 March, interpolated on the trajectory positions on 3 March 12:00 UTC as a function of potential temperature and equivalent latitude. The difference between the concentrations of Cl_y and the sum of $ClONO_2$+HCl is initialized as ClO_x. For most of the flightpath HNO_3 values, initialized from ACE-FTS, are between 6 and 7 ppbv. Calculated with the passive tracer subtraction method (Grooß et al., 2002), this yields a denitrification of ∼50% corroborating the conclusion by von Hobe et al. (2006) that the observed air masses were highly denitrified. All other chemical species are interpolated from the hemispheric CLaMS simulation for the Arctic winter 2004/2005 (Grooß and Müller, 2007). The background aerosol surface area is taken from the climatology compiled by David Considine (Eyring et al., 2010).

The uncertainty of this initialization can be described as a composite of the measurement error of the instruments, accuracy of the CH_4–Cl_y correlation and the uncertainty in interpolating the average of several satellite profiles on the backward-trajectory positions. Accuracy of the HAGAR CH_4 measurements is typically about 2 %, while CH_4 from ACE-FTS in the lower stratosphere is about 10 % (De Mazière et al., 2008). The accuracy of HCl and $ClONO_2$ from ACE-FTS is about 10 % (Mahieu et al., 2008; Wolff et al., 2008).

To estimate the error of the CH_4-Cl_y tracer correlation we correlate ACE-FTS measurements of CH_4 and Cl_y. In the
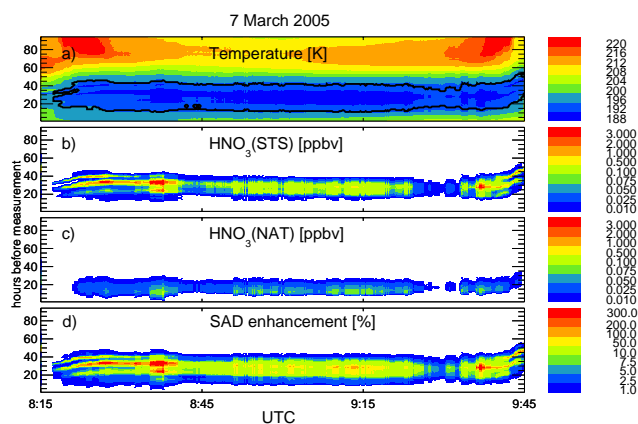
Fig. 3. Temperature history (**a**), simulated condensation of HNO$_3$ on STS (**b**), NAT (**c**) and corresponding enhancement of the surface area density over the background aerosol (**d**) along 92 h back-trajectories ending on the Geophysica flightpath on 7 March 2005. Areas under T_{NAT} are enclosed by the black line.

absence of heterogeneous processing, Cl$_y$ can be assumed to mainly consist of HCl and ClONO$_2$. During the main part of the flight HAGAR-CH$_4$ is around 850 ppbv, which yields an inorganic chlorine content of 3.11 ppbv according to the correlation of Grooß et al. (2002). The sum of HCl and ClONO$_2$ as measured by ACE-FTS in November 2004, poleward of 65° at CH$_4$ mixing ratios between 825–875 ppbv yields a Cl$_y$ value of 3.18 ± 0.16 ppbv. This indicates the correlation of Grooß et al. (2002) is in good agreement with ACE-FTS observations and that the uncertainty introduced by the use of the CH$_4$-Cl$_y$ tracer correlation is similar to the uncertainty of the ACE-FTS observations.

The uncertainty introduced on the initialization by interpolating the average of several satellite profiles on the backward-trajectory positions is estimated by interpolating the satellite measurements on the potential temperature of the Geophysica observations and subsequently calculating the range of observations of the three nearest neighbors in the equivalent latitude space. This introduces the largest error on the initialization since the range of the three nearest neighbors is typically within 0.2 ppbv.

Therefore, the overall uncertainty of our initialization on chlorine activation is estimated by varying initial HCl, ClONO$_2$ and ClO$_x$ by ± 0.2 ppbv while total Cl$_y$ is kept constant.

However, the largest uncertainty for modeling heterogeneous chemistry is not the initialization but temperatures along the trajectories. Since heterogeneous chemistry is highly sensitive to temperature, accurate knowledge of it is necessary to model the activation of chlorine on stratospheric aerosols. For example, Brakebusch et al. (2012) have shown that temperatures for the Arctic winter of 2004/05 in the specified dynamics version of the Whole Atmosphere Community Climate Model tend to be warm biased compared to

MLS observations and that agreement between model and satellite observations improves when a -1.5 K bias is applied to the heterogeneous chemistry calculations. Similarly, Wohltmann et al. (2012) reported that a large part of the discrepancy between their model and observations of chlorine compounds can be explained by a 1 K temperature bias in the temperature fields.

Ambient temperature on board Geophysica is measured by the Thermodynamic Complex (TDC, Shur et al., 2006). These measurements similarly, show a ~ 1.5 K bias when compared to ERA-INTERIM temperatures (Fig. 2). To allow a direct comparison, ERA-INTERIM data is first interpolated on isentropic coordinates and temperature is subsequently linearly interpolated in space and time on the measurement positions of the TDC. Between 455–470 K ERA-INTERIM temperatures are consistently higher than the observations. ERA-INTERIM also shows better agreement at higher temperatures and the warm bias appears to be limited to temperatures below 205 K. In Fig. 2b the vertical profile for the temperature bias is shown. The maximum of the warm bias is located at 460 K, on flight altitude, with 1.5 K. No in-situ temperature measurements exist over the course of the trajectories so we assume the warm bias exists for the whole trajectory length and adjust the temperatures below 205 K according to the kernel shown in Fig. 2.

Modeling PSCs along the trajectories indicates (Fig. 3) the presence of NAT and STS 24 h prior to the measurements. On the trajectories ending between 08:45 and 09:30 UTC typically less than 0.1 ppbv HNO$_3$ condenses on STS. This enhances the surface area density by about a factor of 1.5 compared to the background aerosol. The maximum calculated enhancement is about a factor of 2. For trajectories ending before 8:45 and after 9:30 all available HNO$_3$ is predicted to condense to STS, with a maximum enhancement of the surface area density by a factor of 5. However, these maximum enhancements only occur for a few hours along the trajectories. For most of the time when the trajectories experience temperatures below T_{NAT}, PSCs enhance the surface area by less than 10 % over the background aerosol. As temperatures are below T_{NAT} for only about 20 h modeled NAT particles cannot reach thermodynamic equilibrium. With temperatures below T_{NAT} for such a short time, NAT number density is on the order of 10^{-3} cm^{-3}, which leads to a negligible increase in surface area density by NAT. Therefore, any modeled increase in surface area density is caused by STS and not NAT particles.

To assess the ability of the model to reproduce the measured extent of chlorine activation two simulations are performed. The first calculates the heterogeneous reaction rates with a surface area density that includes all PSCs (Full PSC) and the second uses only the surface area density of the background aerosol without any enhancement due to STS or NAT (Binary only). Temperatures are well above the frost point so ice PSCs do not form in either of these simulations. Figure 4 shows that the difference between initialized and measured
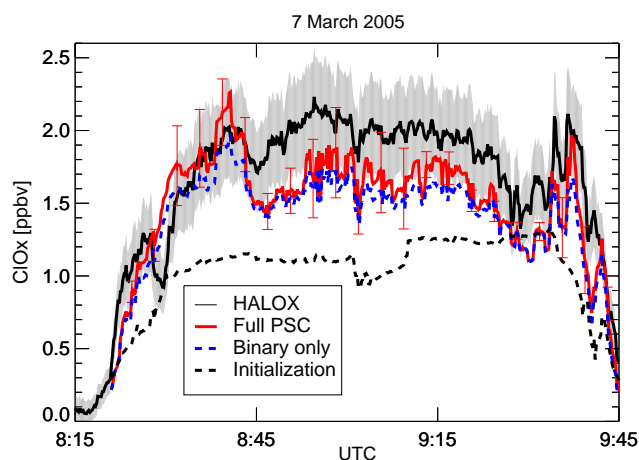
Fig. 4. Comparison of HALOX in-situ data and CLaMS simulations for the flight on 7 March 2005. The solid black line marks the HALOX measurements ($ClO+2 \cdot Cl_2O_2$) with its accuracy shaded grey and blue the simulations with the error bars showing their uncertainty.

ClO_x on the flight path is on average about 1 ppbv. Maximum activation is simulated for trajectories ending before 08:45 and after 09:30 UTC. These trajectories also exhibit the maximum uptake of HNO_3 on PSCs as minimum temperatures are about 1–2 K lower than for the other trajectories. For trajectories ending between 08:45 and 09:30 about 0.7 ppbv additional chlorine is activated within 92 h. The model cannot reproduce all of the fine structures of the measurements which is likely due to the coarse initialization and resolution of the ERA-INTERIM meteorological fields. However, overall both model simulations show good agreement with measured ClO_x, within the uncertainty of initialization and measurements. For trajectories ending before 08:45 modeled chlorine activation tends to be at the upper limit of uncertainty and afterwards at the lower limit. The difference between both simulations is minimal with the "Full PSC" simulation activating slightly more chlorine than the "Binary only" simulation. However, this difference is on the order of 10% indicating that the heterogeneous reactivity provided by the binary aerosol in the model is sufficient to produce an activation that corresponds to most of the observed activation of chlorine within the considered time-frame. Even though modeled PSCs increase the surface area density by up to 500 % the effect on chlorine activation is limited, as this maximum increase only lasted for a short time-frame. In the model, neither HCl nor $ClONO_2$ are completely depleted thus, chlorine activation along the trajectories is limited by the heterogeneous reaction rates and not by the availability of either reservoir species. As the model results overlap with the observations, within the uncertainties of this simulation and measurements, the temperature dependence of the current parameterizations for heterogeneous chlorine activation is in agreement with the processes in the real atmosphere.

Since heterogeneous reaction rates depend non-linearly on temperature, the modeled chlorine activation is highly sensitive on the assumed temperature bias. A larger bias at lower temperatures leads to more activation of chlorine and increased agreement between 8:45 and 9:30 UTC. However, a larger temperature bias is not supported by our measurements.

In addition to the Geophysica flight from 7 March 2005 we examined three Geophysica flights in January 2010 from the RECONCILE campaign in the Arctic (Fig. 5). The temperature histories along 7 day back-trajectories ending on the flightpath of these flights indicate temperatures low enough for efficient heterogeneous chemistry. Temperatures are below T_{NAT} at the beginning of the trajectories and during the flights. In between temperatures exceed 200 K so all PSCs that formed initially very likely evaporated. Prior to the flights temperatures for most trajectories are below T_{NAT} for about 30 h consecutively with some trajectories during flight 2 residing below T_{NAT} over 50 h. Trajectories for flight 3 are the longest time below T_{NAT}. Here temperatures are below T_{NAT} for 40 h at the beginning of the trajectories and again for 30 h prior to the flight. In contrast to the 2005 flight, minimum temperatures for all three flights are below 190 K, low enough for extensive PSC formation and thus low enough for extensive HNO_3 uptake from the gasphase. Measurements during the three considered flights in January 2010 from the up -and downward facing LIDAR MAL (Matthey et al., 2003) on-board Geophysica show that backscatter ratios are elevated by a factor of 3–4 and a depolarization of less than 4%. The high backscatter combined with the low depolarization is an indicator that PSCs mostly consisted of STS droplets and that no or only very few NAT particles were present. Chlorine activation is simulated by running box-model calculations along these 7 day trajectories. The initialization is taken directly from a hemispheric 3D-CLaMS simulation. Total Cl_y is estimated from measured CH_4 by HAGAR via the CH_4-Cl_y correlation (Grooß et al., 2002). Model HCl and $ClONO_2$ are then scaled accordingly so that model Cl_y agrees with observations. Generally, model Cl_y has to be scaled up by about 15% to agree with observations.

For all three flights the model activates significant amounts of chlorine over the 7 day period considered. For flights 1 and 2 additional chlorine is activated along the majority of trajectories during the 7 days of simulation, generally around 0.4 ppbv with some trajectories showing up to 0.8 ppbv additional ClO_x. Only a minor fraction of the trajectories shows no additional chlorine activation. The trajectories for flight 3 all show additional chlorine activation, generally around 0.5 ppbv with maximum additional ClO_x of 1.2 ppbv. The limiting factor for chlorine activation for these three flights is the availability of $ClONO_2$. The model simulates that $ClONO_2$ is completely depleted at the time of the flights, hence, the additionally available surface area density provided by PSCs cannot have an effect on ClO_x
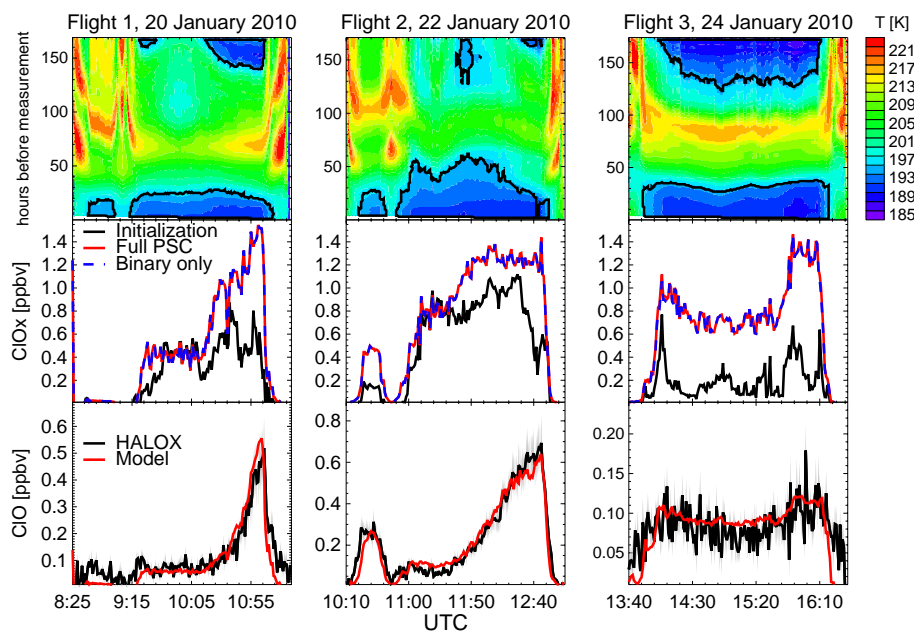
Fig. 5. Top: Temperature history along 7 day back-trajectories from HALOX measurements for 3 flights in January 2010. Middle: ClO_x initialization (black) and modeled ClO_x on the flightpath with full PSC surface area density (red) and background aerosol only (blue dashed). Bottom: Measured (black) and modeled values of ClO (red).

levels. Consequently, the simulation only using the background aerosol surface area density to calculate heterogeneous reaction rates produces the same results as the "Full PSC" simulation.

In contrast to the flight on 7 March 2005, no reliable Cl_2O_2 measurements exist for the flights in January 2010 so we are limited to comparing modeled and measured ClO. ClO possesses a distinct diurnal cycle and the parameters describing the equilibrium between ClO and Cl_2O_2 are still subject to some uncertainty (von Hobe et al., 2007). To calculate ClO from simulated ClO_x we use the results from Sumińska-Ebersoldt et al. (2012) who constrained the ClO/Cl_2O_2 equilibrium parameters to in-situ observations. The thermal equilibrium constant is taken from Plenge et al. (2005) and the Cl_2O_2 absorption cross-section from von Hobe et al. (2009) scaled to the absolute measurements of Lien et al. (2009). Figure 5 shows modeled and measured ClO for the three flights in January 2010. The first two flights have decreasing solar zenith angles leading to increasing ClO values and the third flight was carried out in darkness. Overall, the model shows excellent agreement with the measurements with flights 1 and 2 showing the dependence of ClO on the solar zenith angle and flight 3 showing nighttime, thermal equilibrium measurements.

4 Vortex average

To further examine, which effect the surface area enhancement caused by the HNO_3 uptake has on chlorine activation

vortex averaged satellite observations from MLS for the Arctic winters 2004/2005 to 2010/2011 are analyzed. We focus on the vortex core, described by equivalent latitudes poleward of 75° N. A high inter-annual variability, common for the Arctic, is evident in the observations of HCl and HNO_3 (Fig. 6). The winters 2004/2005, 2007/2008 and 2010/2011 had very cold and stable vortices leading to strong denitrification and depressed values of gas-phase HCl extending into spring. The observations for the winters 2005/2006 and 2008/2009, on the other hand, show hardly any denitrification and HCl starts increasing in the middle of January. The onset of chlorine activation at the beginning of winter is controlled by the quantitative titration of the available $ClONO_2$ through the heterogeneous reaction R1. Thus, a decrease in gas-phase HCl can serve as an indicator for chlorine activation.

$$\frac{d[ClO_x]}{dt} \approx -\frac{d[HCl]}{dt} - \frac{d[ClONO_2]}{dt} \approx -2\frac{d[HCl]}{dt} \quad (2)$$

Although HCl shows high inter-annual variability for the period of January to April, observations show only little variability in December when chlorine begins to become activated. At the end of December HCl has decreased by about 1 ppbv, 50% of the initially available HCl. Significant differences in HCl depletion between the different winters emerge not until the middle of January. In winters 2005/06 and 2008/09 HCl starts recovering in January, while in winters 2004/05 and 2007/08 the final recovery does not begin until February. This corresponds to observations of HNO_3. A decrease in gas-phase HNO_3 can serve as an indicator for
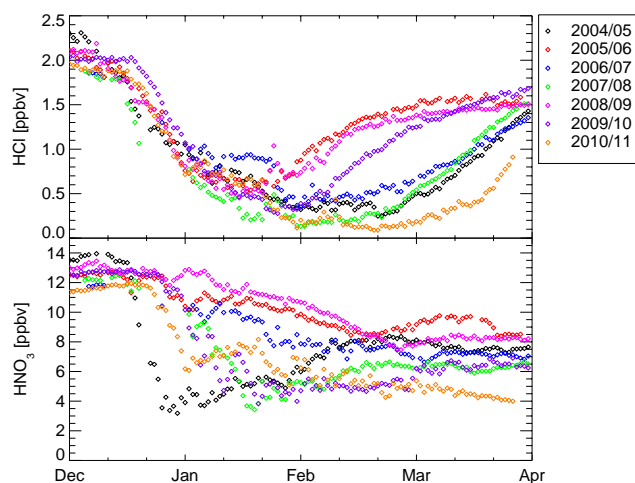
Fig. 6. HCl and HNO$_3$ observations by MLS for the Arctic winters 2004/2005 to 2010/2011 on 500 K potential temperature in the vortex core (equivalent latitude > 75° N).

Fig. 7. Probability density distribution of maximum surface area density enhancement by STS along 7 day back-trajectories starting on MLS observations poleward of 75° N equivalent latitude.

the presence of PSC or irreversible denitrification. Pitts et al. (2009, 2011) have shown that the first PSCs forming in Arctic winter are mainly composed of STS and low number density NAT ($<10^{-3}$ cm^{-3}). Therefore, the observed decrease in gas-phase HNO$_3$ in December can mostly be attributed to condensation of HNO$_3$ on STS and a lesser extent to NAT and, possibly irreversible denitrification.

In early winter, HNO$_3$ shows, in contrast to HCl, high inter-annual variability indicating that the additional surface area provided by PSCs has no detectable direct influence on the rate of chlorine activation on a vortex wide scale. For the winters 2004/2005 and 2009/2010 75 % of gas-phase HNO$_3$ are removed throughout the winter. Gas-phase HNO$_3$ shows a steep decline in the middle of December 2004 and at the end of December in 2009. For 2004 we can assume that the surface area density was significantly enhanced through HNO$_3$ uptake throughout December while for 2009 surface area density was for most of the time at background levels. In winters 2005/2006 and 2008/2009 observations show only a gradual decrease of gas-phase HNO$_3$. This decrease of gas-phase HNO$_3$ indicates that PSCs formed only to a minor extent compared to the winters 2004/05 and 2009/2010. Pitts et al. (2011) show that maximum PSC coverage in the winter 2008/2009 was only one third of the maximum coverage in 2009/2010. Still, the decrease of HCl in December is very similar for all winters despite the high variability in gas-phase HNO$_3$.

Figure 7 shows the probability density distribution of the maximum enhancement of the surface area by STS in the absence of NAT formation for the winters 2004, 2008 and 2009. These three winters cover the whole spectrum in HCl and HNO$_3$ variability. STS formation is calculated according to Carslaw et al. (1995) along 7 day back-trajectories from MLS observations in December 2005, 2008 and 2009
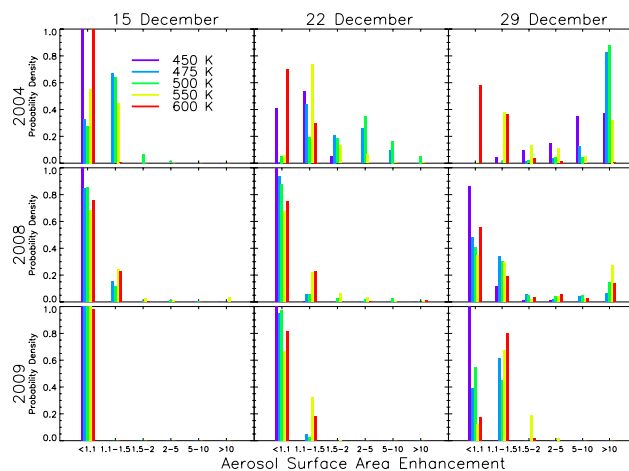
poleward of 75° N equivalent latitude, assuming that no irreversible denitrification or dehydration has occurred yet. We show the fraction of trajectories that fall into 6 different bins. The first bin contains the fraction of trajectories with a maximum enhancement of the surface area density of less than 1.1, i.e. showing no significant enhancement over background aerosol levels. For the next two bins (maximum enhancement factor 1.1–1.5 and 1.5–2) only a small fraction of gas-phase HNO$_3$ has condensed on STS but has already significantly enhanced the surface area density. In the bins with an enhancement factor of 2–5 and 5–10 most available gas-phase HNO$_3$ is condensed on STS and in the last bin virtually all HNO$_3$ is in STS leading to an increase of surface area density over the background aerosol of more than a factor of 10. Figure 7 shows this distribution on 3 different days in December and for 5 altitudes. The trajectories ending 15 December show no or only a minor increase of surface area density but already some differences emerge between the different winters. In 2009 none of the trajectories show any increase in SAD and for 2008 less than 20 % show a small enhancement. In 2004, however, only less than 30 % between 475 and 550 K show no increase in surface area density.

Differences between the winters become more apparent for 22 December. For 2008 and 2009 the distribution hardly changes compared to 15 December, most trajectories still show little enhancement of surface area density. In 2004, however, most trajectories show some enhancement of surface area density and between 475 and 550 K all do. At 500 K more than 50 % of the trajectories already show an enhanced surface area density by more than a factor of 2. The difference between these three winters becomes most obvious for the trajectories started on December 29th. In 2004 the distribution has completely shifted from trajectories only showing minor enhancement of surface area density on 15 December

to the majority showing an enhancement of a factor greater than 10. On the 450 and 475 K isentropes more than 80 % of the backward trajectories exhibit temperatures which lead to a more than tenfold increase in surface area density. This is also visible in the sharp drop in MLS gas-phase HNO_3 at the end of December 2004 (Fig. 6). Nonetheless, MLS HCl measurements show no drastic change in the loss rate suggesting that the heterogeneous loss of HCl is not connected to the available surface area density. The change in probability density for 2008 and 2009 towards the end of December is less pronounced. Most trajectories show only a minor increase in surface area density but still their distribution is shifted towards higher surface area densities. This is more apparent in 2008 than in 2009, on 29 December 2009 the maximum increase in surface area density for almost all trajectories was less than a factor 1.5.

These three winters show the huge variability in PSC occurrence and HNO_3 uptake for December in the Arctic. Nevertheless, HCl loss rates observed by MLS are fairly constant throughout December with little inter -and intra-annual variability. Only the vertical extent of HCl loss shows inter-annual variability which is correlated with the vertical extent of the low temperatures necessary for efficient heterogeneous chemistry.

5   Conclusions

We have examined the importance of the stratospheric background aerosol for chlorine activation. The evaluation of heterogeneous chemistry parameterizations has shown that uncertainties in NAT microphysics contribute most to the overall uncertainty in modeling heterogeneous chemistry. The uncertainties for NAT reactivity cover several orders of magnitude. However, using the most commonly observed NAT number densities, heterogeneous processing on these particles is significantly slower than on the background aerosol. For modeling chemistry on the binary background aerosol the greatest uncertainty results from temperature uncertainties as the reaction rate doubles for every 1 K increase in temperature and increases tenfold with the formation of STS over a 2 K temperature range. To study heterogeneous chemistry on a synoptic timescale we analyzed backtrajectories from the flightpath of the Geophysica flight on 7 March 2005. These trajectories show chlorine reactivation about 30 h before the flight. With the initialization derived from satellite data, simulating chlorine activation along trajectories ending on the flightpath allows the influence of the various aerosols on modeled chlorine activation to be assessed. Even though NAT and STS could form under the prevailing conditions the additional surface area provided by PSCs does not significantly enhance chlorine activation. 90% of additionally activated chlorine during this time-frame originate from heterogeneous chemistry on a surface area provided by the background aerosol. This shows that for modeling heterogeneous

chemistry the increase in reaction rate with decreasing temperature is more important than the increase of surface area density and that to correctly model heterogeneous chemistry on synoptic timescales accurate knowledge about the prevailing temperatures is essential. This flight also showed that a considerable amount of chlorine can be activated on a timescale of hours when both HCl and $ClONO_2$ are available. The three flights from January 2010 corroborate these results albeit under very different ambient conditions. For the 2005 flight neither HCl nor $ClONO_2$ are completely depleted in the model and therefore, the temperature is the decisive factor determining the level of chlorine activation. In 2010, however, $ClONO_2$ is the limiting factor as it is completely depleted while temperatures remain low enough for efficient heterogeneous chemistry. Thus, heterogeneous chemistry on the background aerosol surface area yields identical results as calculations with full PSC surface area and both simulations show excellent agreement with observations.

Not only can heterogeneous processing on the background aerosol surface area explain the bulk of chlorine activation on synoptic timescales along individual trajectories, but based on satellite observations we demonstrate that the vortex-average chlorine activation rate for the Arctic winters 2004/05 to 2010/11 is not correlated with the occurrence of PSCs and the associated uptake of HNO_3 from the gasphase. The observed HCl loss rate in December is similar for all considered Arctic winters despite their high variability in PSC occurrence. Even intra-annual variability of gasphase HNO_3 is not reflected in observed HCl. During the December 2004 gas-phase HNO_3 dropped sharply while the HCl loss rate remained constant. Thus, the vortex-average observations confirm the findings from the in-situ observations that the surface area provided by PSCs does not significantly impact chlorine activation rates.

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