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# Temperature thresholds for polar stratospheric ozone loss

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## Abstract

Low stratospheric temperatures are known to be responsible for heterogeneous chlorine activation that leads to polar ozone depletion. Here, we discuss the temperature threshold below which substantial chlorine activation occurs. We suggest that the onset of chlorine activation is dominated by reactions on cold binary aerosol particles, without formation of polar stratospheric clouds (PSCs), i.e. without significant uptake of $HNO_3$ from the gas-phase. Using reaction rates on cold binary aerosol, a chlorine activation threshold temperature, $T_{ACL}$, is derived. At typical stratospheric conditions, $T_{ACL}$is similar in value to $T_{NAT}$ the highest temperature at which nitric acid trihydrate (NAT) can theoretically condense to form PSCs. $T_{NAT}$ is still in use as parameterization for the threshold temperature for the onset of chlorine activation. However, perturbations can cause $T_{ACL}$ to differ from $T_{NAT}$: $T_{ACL}$ is dependent upon $H_2O$, potential temperature, and the sulphate aerosol loading, but unlike $T_{NAT}$ is not dependent upon $HNO_3$. A parameterization of $T_{ACL}$ is provided here, allowing it to be calculated over a comprehensive range of stratospheric conditions. Although considering $T_{ACL}$ as a proxy for chlorine activation can be no substitute for a detailed model calculation, $T_{ACL}$ provides a more accurate description of the temperature conditions necessary for polar ozone depletion than $T_{NAT}$ and can readily be used in place of $T_{NAT}$.

## 1 Introduction

For more than two decades most of the stratospheric ozone over Antarctica has disappeared each spring in a phenomenon commonly known as the “ozone hole” (Farman et al., 1985; Stolarski et al., 1986; Jones and Shanklin, 1995); similar but more variable and less severe ozone loss has occurred in the Arctic (e.g., Manney et al., 2003; Rex et al., 2004; Tilmes et al., 2004). It is well established that polar ozone is lost through rapid, gas-phase catalytic cycles involving chlorine atoms (McElroy et al., 1986; Molina and Molina, 1987; Solomon, 1999), which are primarily derived from man-

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made chemicals such as chlorofluorocarbons (CFCs). Although chlorine is present throughout the stratosphere, usually it is tied up in relatively inert “reservoir” species, in particular HCl and $ClONO_2$. It was first suggested by Solomon et al. (1986) that during polar winter the ozone-destroying potential of chlorine is realized through the reactions on particle surfaces activating the chlorine tied up in reservoir species. This activation determines the location and magnitude of the subsequent springtime polar ozone depletion.

This paper revisits the processes controlling the onset of heterogeneous chlorine activation, which are important for reliable assessments of future polar ozone loss, when climate change (IPCC/TEAP, 2005; WMO, 2007) or its mitigation (Crutzen, 2006; Tilmes et al., 2008a; Rasch et al., 2008) may alter the pattern of chlorine activation.

The most important heterogeneous reactions for chlorine activation are:

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \quad \text{(R1)}$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \quad \text{(R2)}$$

$$HCl + HOCl \rightarrow Cl_2 + H_2O \quad \text{(R3)}$$

In each case, reservoir species ($ClONO_2$, HCl) are converted into less stable species ($Cl_2$, HOCl) that photolyze readily in springtime, initiating gas-phase ozone destruction. Reactions (R1)–(R3) are very slow in the gas phase, but efficient both in the liquid phase and on solid particle surfaces. The efficiency of each reaction varies depending upon the type of particle and the prevailing temperature (Ravishankara and Hanson, 1996; Carslaw and Peter, 1997; Peter, 1997; Solomon, 1999; Sander et al., 2006; Lowe and MacKenzie, 2008). Multiple particle compositions exist simultaneously in the stratosphere (e.g., Solomon, 1999; Pitts et al., 2009, 2010). Sulfate aerosol, composed of binary $H_2SO_4/H_2O$ solutions, is ubiquitous in the stratosphere. More limited in extent are polar stratospheric clouds (PSCs), which only form at the low temperatures of polar winter. The most prevalent PSC types are composed of $HNO_3$, either the more stable solid-phase compound nitric acid trihydrate (NAT), or liquid supercooled ternary solutions (STS) of $HNO_3/H_2SO_4/H_2O$. The transition from binary $H_2SO_4/H_2O$ particles to STS particles, in principle, is continuous; however, the uptake of $HNO_3$ and the resulting growth in particle volume increases rapidly below ~ 193 K at typical stratospheric conditions (Carslaw et al., 1994; Peter, 1997; Lowe and MacKenzie, 2008). At the lowest temperatures (below the ice frost point) water ice PSCs will form. Multiple factors, in particular temperature, determine the mixture of different PSC particles present at any location.

The onset of chlorine activation will be determined by the particles which, upon cooling of the polar stratosphere, first provide surfaces for efficient heterogeneous reactions. Because of the formation of solid NAT PSCs is difficult under stratospheric conditions and, therefore, requires substantial supercooling, liquid-phase particles will likely control the onset of chlorine activation.

PSCs frequently contain liquid-phase STS particles (Carslaw et al., 1997a; Peter, 1997; Solomon, 1999; Pitts et al., 2009) and laboratory studies have revealed that chemistry on liquid PSCs is efficient (Hanson et al., 1994; Shi et al., 2001). Studies have increasingly emphasized the importance of STS PSCs for chlorine activation (e.g., Hanson et al., 1994; Ravishankara and Hanson, 1996; Kawa et al., 1997; Hanisco et al., 2002) Further, binary $H_2SO_4/H_2O$ aerosol particles have been discussed for many years as a potentially important contributor to chlorine chemistry and polar ozone loss (Hofmann and Solomon, 1989; Wolff and Mulvaney, 1991; Hofmann and Oltmans, 1993; Cox et al., 1994; Hanson et al., 1994; Portmann et al., 1996; Wegner et al., 2010).

In the late eighties and early nineties, as an explanation for the Antarctic ozone hole and polar ozone loss, the picture had emerged that chlorine activation occurs on the surfaces of solid PSCs consisting of either NAT or ice (e.g., Solomon, 1999). Models designed to explain observations of a perturbed polar chlorine chemistry were based on the assumption that chlorine activation occurs on NAT and ice surfaces (e.g., Jones et al., 1990; Crutzen et al., 1992; Prather, 1992; Müller et al., 1994; Chipperfield et al., 1994; Kettleborough et al., 1994). Further, observations indicated that the onset of chlorine activation occurs at 195 K (Toohey et al., 1993; Webster et al., 1993; Santee et al., 1997; Kühl et al., 2004), coinciding with $T_{NAT}$, the temperature below which NAT can exist. $T_{NAT}$ is the highest PSC formation temperature that is thermodynamically possible.

Although it is well established for more than a decade that polar chlorine activation is caused to a large extent by heterogeneous reactions on liquid-phase particles (e.g., Solomon, 1999), $T_{NAT}$ (or, alternatively, 195 K) is still being used as a first-oder approximation to parameterize the onset of heterogeneous chlorine activation in models (Geer et al., 2006; Kiesewetter et al., 2010).

Further, measurements have shown that the total volume of air exposed to temperatures below $T_{NAT}$ (labelled $V_{PSC}$) is quantitatively related to springtime ozone loss (Rex et al., 2004; Tilmes et al., 2004). This relationship has been used to estimate future ozone loss (Knudsen et al., 2004) and to evaluate model performance (Chipperfield et al., 2005; Douglass et al., 2006). However, variability in $V_{PSC}$ values from one study to another has raised questions about the definitions of $T_{NAT}$ and $V_{PSC}$ (Chipperfield et al., 2005). Answering these questions requires an understanding of the physical and chemical processes linking $T_{NAT}$ to ozone loss.

Here, we will examine the factors controlling the onset of chlorine activation, and by implication ozone loss, in polar winter. We suggest that heterogeneous reactions on liquid, cold binary aerosols are effective at temperatures near 195 K, without PSC formation, i.e., without a significant depletion of $HNO_3$ in the gas-phase. Using liquid reactivities, a temperature threshold for chlorine activation, $T_{ACL}$, is derived, and its behaviour under varying stratospheric conditions is described. Inaccuracies introduced by using $T_{NAT}$ as a proxy for the chlorine activation threshold temperature are explored, demonstrating that $T_{ACL}$ will provide a more accurate description than $T_{NAT}$ of the onset of polar chlorine activation and ozone loss.

In recent years, based on presentations of the concept of $T_{ACL}$ at conferences (Drdla, 2005), $T_{ACL}$ as a threshold temperature for polar chlorine activation has already been employed to study the effect of a possible future hydrogen economy on polar ozone loss (Feck et al., 2008), to evaluate the performance of chemistry climate models (Tilmes et al., 2007), and to estimate the possible effect of a mitigation of climate change by artificial injection of sulfur into the stratosphere (Crutzen, 2006; Rasch et al., 2008) on Arctic ozone loss and on the recovery of the ozone hole (Tilmes et al., 2008a, 2009).

## 2 Heterogeneous chemistry on nitric acid trihydrate

Because NAT is the most stable composition for condensed phase $HNO_3$ under stratospheric conditions, $T_{NAT}$ is the highest temperature at which $HNO_3$ can theoretically condense to form polar stratospheric clouds. Based on laboratory measurements (Hanson and Mauersberger, 1988; Worsnop et al., 1993), $T_{NAT}$ can be calculated in a simple way, as a function of pressure and of $H_2O$ and $HNO_3$ partial pressures. Comparison of $T_{NAT}$ with temperatures of meteorological analyses allows an assessment of where polar stratospheric clouds can potentially form.

The temperature dependence of chlorine activation resulting from assuming that chlorine activation occurs at $T_{NAT}$ is illustrated in Fig. 1 where the line labelled “NAT, Original” provides the chlorine reactivity on NAT particles as a function of temperature. The rate of an individual heterogeneous reaction on a given particle type is determined from

$$k = \frac{1}{4}\gamma \cdot \mathrm{SA} \cdot v \tag{1}$$

(Hofmann and Solomon, 1989), where $\gamma$ is the (dimensionless) reaction probability (also called sticking coefficient) for the reaction on the particle type, SA is the total surface area of the particle type, and $v$ is the velocity of the gas-phase reactant. A model (Drdla et al., 2002; Drdla and Schoeberl, 2002) has been used to calculate surface areas and reaction probabilities as a function of temperature. For the “NAT, Original” reactivity, NAT is assumed to form at $T_{NAT}$, and the surface area is calculated assuming a NAT concentration of $1\,\mathrm{cm}^{-3}$. This yields a large surface area ($\sim 7\,\mu\mathrm{m}^2\mathrm{cm}^{-3}$).

The reaction probabilities on NAT are assumed to be constant, specifically 0.2 for (R1), 0.004 for (R2), and 0.1 for (R3) (Sander et al., 2006). The resultant loss rates of both $ClONO_2$ and HCl due to Reactions (R1)–(R3) have been summed, and divided by the concentration of $ClONO_2$ and HCl to provide the normalized chlorine reactivity shown in Fig. 1. The normalization reduces the sensitivity to the assumed chlorine levels (1 ppbv for $ClONO_2$ and 2 ppbv for HCl).

For the "NAT, Original" calculation, a step increase in reactivity occurs at $T_{NAT}$. Above $T_{NAT}$ there is no chlorine activation but 1 K below $T_{NAT}$ complete activation takes only one day. However, the "NAT, Original" reactivity is contingent upon three distinct assumptions, all of which must be satisfied for $T_{NAT}$ to provide a reliable indicator of chlorine activation: (1) NAT particles are usually present at and below $T_{NAT}$ (2) NAT particles always have a large surface area, and (3) chlorine activation on NAT is rapid at temperatures near $T_{NAT}$.

The first assumption, that reaction probabilities on NAT are fast near $T_{NAT}$, is true when the reaction probabilities are assumed to be constant instead of temperature-dependent. Laboratory measurements (Abbatt and Molina, 1992; Hanson and Ravishankara, 1993) have shown that on NAT all three Reactions (R1)–(R3) are sensitive to the relative humidity, which increases rapidly at lower temperatures. However, Carslaw and Peter (1997) found that the laboratory measurements by Abbatt and Molina (1992) and by Hanson and Ravishankara (1993) lead to very different reactive uptake coefficients for Reaction (R1) (up to factors of 50 to 100, Carslaw and Peter, 1997; WMO, 1999). Carslaw et al. (1997b) suggested considering two schemes for Reactions R1–R3 on NAT particles, one based on the measurements by Hanson and Ravishankara, 1993 as an upper limit, and one based on the measurements by Abbatt and Molina (1992) as the lower limit. Incorporating this humidity dependence (Carslaw and Peter, 1997), adopting the lower limit scheme based on Abbatt and Molina (1992), and assuming the same large NAT surface areas as "NAT, Original" decreases chlorine reactivities at $T_{NAT}$ by three orders of magnitude ("NAT, New $\gamma$"). The reactivity exceeds 0.1 $day^{-1}$ only 5 K or more below $T_{NAT}$ and cooling to the ice frost point is necessary to approach the “NAT, Original” values.

Further, PSCs are often not present at temperatures below $T_{NAT}$ (Schlager et al., 1990; Dye et al., 1990; Pitts et al., 2009) and the PSCs that do form frequently are liquid-phase STS PSCs instead of NAT (Carslaw et al., 1997a; Peter, 1997; Solomon, 1999). In laboratory experiments in the AIDA simulation chamber, NAT does not form even when supersaturations up to $S = 26$ prevail for up to four hours (Wagner et al., 2005). The microphysical processes hindering NAT formation remain uncertain, but the freezing mechanism that converts liquid particles to NAT probably plays a critical role. Finally, the large surface areas in the “NAT, Original” calculation are controlled by the assumed NAT particle concentration (Fig. 2a) and are only possible for NAT concentrations greater than 1 $\mathrm{cm}^{-3}$. However, the primary evidence for these large NAT concentrations comes from PSC observations (Dye et al., 1990) that have since been identified as liquid-phase STS, not NAT (Carslaw et al., 1997a). The observations specifically of NAT particles frequently find much lower concentrations, $<10^{-2}\,\mathrm{cm}^{-3}$ (Northway et al., 2002; Pitts et al., 2009).

The discovery of very large NAT particles (>5 µm radius), commonly referred to as “NAT rocks” (Fahey et al., 2001), was crucial because these measurements provided the first conclusive evidence of large NAT particles with very low concentrations ($<10^{-3}\,\mathrm{cm}^{-3}$). In Arctic winter 1999/2000, “NAT rocks” were observed over many days and over large geographical regions, implying that such particles are probably widespread at low enough temperatures, but had been undetectable with previous instrumentation. (See Supplement for a more detailed discussion of observed particle concentrations of NAT PSC).

The occurrence of “NAT rocks” is important for denitrification i.e., for the permanent removal of $HNO_3$ from the stratosphere. Large NAT particles sediment rapidly, enabling efficient denitrification even above the ice frost point. But low NAT concentrations also have implications for heterogeneous chemistry. As the NAT particle concentration decreases, the maximum surface area also decreases (Fig. 2a). For NAT concentrations below $10^{-2}\,\mathrm{cm}^{-3}$, the liquid surface area density always exceeds the NAT surface area density. Furthermore, NAT particles are increasingly unlikely to reach the theoretically possible maximum surface areas at low concentrations because of slow growth (Fig. 2b). For concentrations of ∼$10^{-4}$ cm$^{-3}$, more than five days below $T_{NAT}$ are necessary for NAT surface areas to approach the maximum values. Observations show that NAT surface areas are ∼0.005 µm$^2$cm$^{-3}$ in a 20-h old PSC (Voigt et al., 2005). With such slow growth, particles start sedimenting appreciably before all the available gas-phase $HNO_3$ condenses. Therefore, for sufficiently low particle concentrations, the theoretical maximum surface area is unlikely to be reached under stratospheric conditions.

Separately, either reduced surface areas or humidity-dependent reaction probabilities are each sufficient to prevent NAT particles from dominating the heterogeneous chemistry. When combined (“NAT, Current” in Fig. 1), these two factors imply that NAT particles cannot be responsible for the onset of chlorine activation observed near $T_{NAT}$. “NAT, Current” assumes a NAT surface area of 0.1 µm$^2$cm$^{-3}$, consistent with a NAT concentration of $10^{-4}$cm$^{-3}$ after five days of continuous growth (Fig. 2a). The NAT reaction probabilities are the same as in the “NAT, New $\gamma$” case. Even after five days below $T_{NAT}$, NAT particles solely activate less than 0.1% of the available chlorine. Over longer timescales, larger NAT surface areas may be possible but their chemical relevance is limited because, in the meantime, a substantial fraction of the chlorine tied up in reservoir species will have been activated by other particles.

## 3 Heterogeneous chemistry on liquids

Stratospheric liquid sulfate aerosol provides a large, ubiquitous surface area (∼1µm$^2$cm$^{-3}$) for heterogeneous reactions (e.g., Portmann et al., 1996; Carslaw et al., 1997a; Solomon, 1999). Chlorine activation reactions on liquid aerosol are humidity-dependent (Hanson et al., 1994; Carslaw and Peter, 1997; Shi et al., 2001), resulting in a steady increase in reactivity with decreasing temperature (Fig. 1, “Liquid”): at ∼195 K, the reactivity exceeds 0.1 day$^{-1}$. For the “Liquid” simulation in Fig. 1, the aerosol composition was calculated using the parameterization of Carslaw et al. (1995). The liquid reactivities used the formulation by Shi et al. (2001). This formulation provides the reactivity of binary $H_2SO_4/H_2O$ aerosol only. To calculate ternary aerosol reactivities, the reactivity was assumed to be the same as that for the binary aerosol particles that would form under the same conditions (i.e., with the same water activity). Therefore, differences between binary and ternary reactivities are caused solely by surface area differences.

Measurements of chlorine enhancements initiating at 195 K can only be explained by liquid aerosol activation (Solomon, 1999). Simultaneous measurements of stratospheric particles and chlorine activation (Kawa et al., 1997; Del Negro et al., 1997) showed no NAT particles or corresponding surface area increase. Thus, while liquid aerosol chlorine activation may occur near the theoretical PSC formation threshold $T_{NAT}$, the two activation mechanisms are distinct. With the constant reaction probabilities in the "NAT, Original" formulation, chlorine reactivity is controlled by particulate surface area alone. For liquid aerosol, in contrast, the controlling factors are reversed: the onset of activation is caused solely by reaction probability changes, while the surface area is nearly constant. Near $T_{NAT}$ the aerosol contains a negligible fraction of gas-phase $HNO_3$. The $H_2O$ content is higher than at midlatitudes (thus, enabling efficient chlorine reactions) but the surface area has increased by less than 2%. Large liquid surface area enhancements only occur 4 K below $T_{NAT}$, when $HNO_3$ uptake converts the aerosol into an STS PSC. The reactivity for binary aerosol (Fig. 1, "Liquid (binary)"), where STS formation is disabled, is identical to the "Liquid" value at temperatures above 192 K. The divergence between the two curves at low temperatures isolates the contribution of PSC formation (i.e., the enhancement of surface area) to chlorine activation. Even without PSCs, the aerosol reactivity exceeds 1 $day^{-1}$.

Simulations of winter-long evolution in a detailed PSC and chemistry models (Drdla et al., 2002; Drdla and Schoeberl, 2002, see Supplement for more detailed information) corroborate these conclusions. Over an entire Arctic winter, NAT particles caused 2% of the total chlorine activation and STS PSCs 12%; the remaining 86% were caused by cold binary aerosol. A second model simulation with only binary sulfate aerosol (i.e., with PSC formation suppressed) had chlorine activation that was nearly identical to the simulation with full PSCs (63.8% versus 63.4%). Even in the Antarctic, 58% of all chlorine activation is caused by binary aerosol in a simulation with full PSC formation; without PSCs, aerosol replaces the PSC contribution and the total chlorine activation is almost unchanged (68.6% versus 68.1%). The differences in ozone depletion between the full PSC simulation and the binary aerosol simulation are caused by denitrification and dehydration, not by variations in chlorine activation. PSCs contribute to chlorine activation because they happen to be present for periods in winter, but under the same conditions cold binary aerosol reactivity is sufficient to rapidly activate any available chlorine. By the time PSCs form, activation is limited by the availability of reactants, not by the reaction rate, so a reactivity of 1 day$^{-1}$ on cold binary aerosol has the same effect on chlorine activation as a reactivity of 10 day$^{-1}$ on a PSC.

Although chlorine activation on cold binary aerosol may initiate near $T_{NAT}$ (Fig. 1a), the similarity should not be used to estimate chlorine activation under other conditions, such as the denitrified conditions common in Antarctic springtime. When $HNO_3$ is depleted, PSC formation is suppressed (Fig. 1b): $T_{NAT}$ and the STS onset temperature are lower by ~3 K and for the PSCs that do form, their reduced surface area limits the reactivities. In contrast, the binary aerosol reactivity is unaffected by denitrification and, therefore, is identical for the conditions shown in Fig. 1a and b. Consistent with the liquid aerosol reactivities, observations confirm that chlorine activation is efficient under denitrified conditions, in both the Arctic (Hanisco et al., 2002; Wegner et al., 2010) and Antarctic (Shindell and de Zafra, 1997). Since chlorine activation does not require NAT formation, $T_{NAT}$ does not provide a reliable predictor of chlorine activation and subsequent ozone loss.

## 4 The chlorine activation threshold: $T_{ACL}$

To describe how the onset of chlorine activation responds to changing conditions, it is useful to define a temperature threshold for the onset of chlorine activation, $T_{ACL}$. The definition put forward here is based on liquid aerosol reactivities by requiring that a critical reactivity threshold must be exceeded for efficient activation. We adopt a reactivity threshold of 0.1 $\text{day}^{-1}$, which is the point at which detectable levels of active chlorine (∼10%) are produced on time scales of a day. Modelled ozone loss enhancements also occur starting at this threshold (see Supplement).

This formulation does not take into account chlorine deactivation, which counteracts chlorine activation, if the activation does not occur in polar night. While the formation of HCl from the reaction of atomic chlorine with $CH_4$ only becomes significant for very low ozone concentrations (Douglass et al., 1995; Grooß et al., 1997) and is, therefore, not relevant for the onset of chlorine activation, the reformation of $ClONO_2$ from activated ClO counteracts chlorine activation. However, for the low solar elevation conditions during polar winter, the formation of $ClONO_2$ is also strongly suppressed because of low concentrations of $NO_2$. The reservoir species for $NO_2$, $N_2O_5$, is converted to $HNO_3$ via heterogeneous reactions on background sulfate aerosol and the reformation of $NO_2$ from $HNO_3$ via the reaction with OH and photolysis is rather slow for low solar elevation.

If one assumes a simple model to estimate the extent to which chlorine activation counteracts heterogeneous chlorine activation by reformation of $ClONO_2$ by subtracting the rate of $ClONO_2$ formation from the rate of chlorine activation ($p = 50$ hPa, $H_2O$=0.5 ppmv, HCl=1.0 ppbv, $ClONO_2$=0.5 ppbv, $HNO_3$=10 ppbv, $H_2SO_4$=0.15 ppbv) results in no substantial change of $T_{ACL}$ for a zenith angle of 90° (held constant over 24 h) and in a temperature shift by −0.5 K for a zenith angle of 80° (T. Wegner, personal communication, 2010).

Under realistic conditions in the polar stratosphere in winter, circumstances will be more complex. If rapid cooling to several degrees below $T_{ACL}$ occurs, the heterogeneous chlorine activation rate will rapidly exceed the activation rate prevailing at

$T_{ACL}$ by a large amount (Fig. 1). Further, there are conditions when the reformation of $ClONO_2$ will enhance chlorine activation. Namely, when temperatures remain below $T_{ACL}$ long enough for $ClONO_2$ to be completely depleted while the HCl reservoir is not entirely activated. Under these conditions, the reformation of $ClONO_2$ provides a reaction partner for HCl so that the heterogeneous activation can proceed further instead of being stopped by the lack of a reaction partner for HCl. In contrast, there may be conditions when the HCl reservoir is depleted strongly enough to suppress chlorine activation even though the heterogeneous reaction rates are large. Under such conditions chlorine deactivation would occur at temperatures below $T_{ACL}$.

Therefore, tests have been done using a full photochemical model (Drdla and Schoeberl, 2002) to determine the conditions under which chlorine deactivation is too slow to compete with heterogeneous activation, assuming no denitrification. The criteria used were the timescale for deactivation was more than 15 days (taking into account all possible chlorine deactivation pathways) and that the amount of available $NO_x$ ($NO + NO_2$) was less than 0.5 ppbv. Under a range of stratospheric conditions, these conditions were always met by air parcels in which the noon-time solar elevation was less than 20° (i.e., the solar zenith angle is greater than 70°). Thus, when solar elevation is less than 20°, deactivation is too slow to significantly influence $T_{ACL}$ which covers the region and time period of interest for the onset of polar chlorine activation (see Supplement for further discussion of this issue).

This definition of the threshold temperature $T_{ACL}$ yields 194.5 K at typical stratospheric conditions (Fig. 1a), consistent with observations of increased ClO at 195 K (Toohey et al., 1993; Webster et al., 1993; Kawa et al., 1997; Wegner et al., 2010). Using the model by Drdla et al. (2002), $T_{ACL}$ has been calculated for a wide range of stratospheric conditions and in all cases significant $HNO_3$ uptake from the gas-phase and STS PSC formation were not necessary for efficient liquid aerosol reactions. Based on the model results, a parameterization of $T_{ACL}$ is deduced, where $T_{ACL}$ depends only on $H_2O$, aerosol surface area and altitude, but has no dependence on $HNO_3$:

$$T_{ACL} = a + b \cdot v + c \cdot v^2 + d \cdot s + e \cdot s^2 + f \cdot s^3 + g \cdot v \cdot s + h \cdot v \cdot s^2 \quad (2)$$

with

$$v = \ln([\mathrm{H_2O}] \cdot z^{\alpha}) \quad (3)$$

$$s = \ln(\mathrm{SA}) \quad (4)$$

where $z$, the input vertical coordinate, can be either potential temperature ($\theta$) or pressure ($p$). Here, $[\mathrm{H_2O}]$ is $H_2O$ molar mixing ratio in ppmv (range 1 to 20 ppmv), SA is sulfate surface area at 210 K in $\mu m^2\,cm^{-3}$ (range 0.1 to 100 $\mu m^2 cm^{-3}$), $\theta$ is potential temperature in Kelvin (range 375 to 700 K) and $p$ is pressure in hPa. Equation (2) can be applied in regions where the maximum solar elevation is less than 20°; the coefficients used are listed in Table 1.

The most obvious difference between $T_{ACL}$ and $T_{NAT}$ is the sensitivity to sulfate surface area (Fig. 3). Large volcanic eruptions can increase stratospheric aerosol surface areas, causing enhanced chlorine activation (Toon et al., 1993) and ozone loss (e.g., Hofmann and Solomon, 1989; Hofmann and Oltmans, 1993; Portmann et al., 1996; Deshler et al., 1996; Solomon et al., 2005; Tilmes et al., 2008b). In contrast to $T_{NAT}$, $T_{ACL}$ provides a seamless transition from background to volcanic conditions, allowing a full range of sulfate loadings to be considered within the same framework.

$T_{ACL}$ and $T_{NAT}$ are both dependent upon $H_2O$ (Fig. 3c) and potential temperature (Fig. 3d), but $T_{ACL}$ shows greater sensitivity to both variables. The vertical sensitivity is further enhanced for $T_{ACL}$ by incorporating a gradient in aerosol surface area (Fig. 3d). Even moderate differences between $T_{ACL}$ and $T_{NAT}$ have consequences, for example, when comparing the areal extent of temperatures below each threshold for an Arctic winter (Fig. 4). For the example of the cold Arctic winter 2004–2005, the start of chlorine activation occurs two weeks earlier for $T_{NAT}$ than for $T_{ACL}$ and extends to higher altitudes throughout the winter. The total areal extent of chlorine activation is 50% smaller for $T_{ACL}$ than for $T_{NAT}$ at 22 km, even though $T_{ACL}$ is only 2 K lower than $T_{NAT}$. In regions with the most direct impact on column ozone, namely lower altitudes and late in the winter, $T_{ACL}$ yields considerably greater activation than $T_{NAT}$.

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Research has often focused on the 20 km region, but the similarity between $T_{ACL}$ and $T_{NAT}$ implies that 20 km is not the best region for distinguishing which particles cause chlorine activation. Although the role of liquid particles can be identified in individual case studies (Kawa et al., 1997; Engel et al., 2000; Hanisco et al., 2002; Wegner et al., 2010), evaluating the relative importance of different particle types becomes more ambiguous in large scales. Above 20 km, analyses of chlorine activation and ozone loss will be more sensitive to the differences between $T_{ACL}$ and $T_{NAT}$, as evident in Fig. 3 and 4. These differences could influence, for example, analyses examining the upper boundary of the Antarctic ozone hole (Hoppel et al., 2005), where the description of the vertical dependence of chlorine activation may impact results.

## 5 Discussion

Numerous models at many scales incorporate stratospheric chemistry, leading to a range of different assumptions about heterogeneous chemistry and about the onset of chlorine activation (e.g., Krämer et al., 2003; Eyring et al., 2010). Substantially different model results regarding the onset and the spatial and temporal extent of chlorine activation emerge depending on these assumptions. It is important whether PSC formation in the model is assumed at $T_{NAT}$, whether supercooling is required and whether a temperature dependence of the reaction probabilities $\gamma$ is implemented in the model (Krämer et al., 2003). Model simulations that assume the onset of chlorine activation at $T_{NAT}$ (i.e., at the NAT equilibrium temperature) tend to overestimate the magnitude, spatial extent and duration of chlorine activation in comparison to observations of halogen species in the stratosphere (Engel et al., 2000; Santee et al., 2008).

Furthermore, models with full PSC microphysics have introduced small NAT concentrations (Davies et al., 2005; Grooß et al., 2005), in order to produce realistic denitrification. As long as most particles remain liquid, the chemistry in these models is comparable to the liquid aerosol chemistry adopted here. The only implication comes when interpreting the model results, since even with aerosol-dominated chemistry, analyses have still attributed the chlorine activation to PSCs (Drdla and Schoeberl, 2002).

Other stratospheric models which cannot incorporate detailed particle chemistry, instead use simplified parameterizations that are often derived from NAT-based assumptions. Assumptions employed are: that NAT particles replace liquid particles below $T_{NAT}$; that NAT particles have large surface areas (i.e., concentrations of $1\,cm^{-3}$ or radii of 1 µm); and that reaction probabilities are constant on NAT (as recommended by the JPL evaluation of atmospheric chemistry, Sander et al., 2006). However, NAT particles require large supersaturations to form (Schlager et al., 1990; Dye et al., 1990, 1992; Peter, 1997; Wagner et al., 2005) and observational evidence for NAT concentrations of $\sim 1\,cm^{-3}$ is very limited. Furthermore, there is evidence from laboratory studies that reaction probabilities on solid particles are dependent on humidity and, thus, on temperature (Abbatt and Molina, 1992; Hanson and Ravishankara, 1993).

Even with aerosol chemistry incorporated into a model, these assumptions can result in NAT-controlled heterogeneous chemistry. For example, the well-established SLIMCAT chemical transport model (Chipperfield et al., 2005) introduced an improved denitrification scheme with large NAT particles, but still includes a second mode of numerous small NAT particles that determine the heterogeneous chemistry (Davies et al., 2002). Chemistry climate models used for assessments of stratospheric ozone loss (WMO, 2007; Eyring et al., 2007, 2010) frequently adopt even simpler heterogeneous chemistry schemes. Although the conditions at which various types of PSCs are condensed and evapourated vary between CCMs, the simplest assumption, namely that PSCs are formed at the saturation points of $HNO_3$ over NAT and $H_2O$ over water-ice is made in most CCMs participating in the current initiative to validate CCM models (Eyring et al., 2010). However, there are models that allow for NAT and ice supersaturation (Pitari et al., 2002; Garcia et al., 2007) or that allow NAT formation only on ice or preexisting NAT particles (Buchholz, 2005). For chemistry calculations, an assumption that possibly leads to a more realistic description of chlorine activation, would be to assume that NAT particles are never present, and instead rely solely upon liquid aerosol for chlorine activation. The latter approach has indeed been recently adopted for the

Canadian Middle Atmosphere Model (Hitchcock et al., 2009).

Some models, for example, numerical weather prediction models which assimilate ozone, have implemented simplified chemistry schemes that explicitly use $T_{NAT}$ to predict chlorine activation. These assimilation schemes treat chlorine activation considering a "cold tracer" that is turned on below $T_{NAT}$ (Hadjinicolaou et al., 1997; Eskes et al., 2003, 2005; Geer et al., 2006). The overly fast activation that, in this way, is assumed to occur immediately at $T_{NAT}$ may explain the overprediction of ozone loss that has been noted with these models (Eskes et al., 2005). If such simple parameterizations were based on $T_{ACL}$, they should provide more realistic chlorine activation without additional computational expense.

Moreover, the chlorine activation threshold $T_{NAT}$ has been used as a metric for examining interannual variability in ozone loss (Rex et al., 2004; Tilmes et al., 2004) and evaluating model performance (Chipperfield et al., 2005; Douglass et al., 2006). However, by using $T_{NAT}$ these analyses do not accurately represent the processes controlling chlorine activation. Since a few years ago, observational estimates of vortex-wide PSC coverage are available from the CALIPSO (Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations) experiment (Pitts et al., 2007, 2009, 2010). These measurements show that the area covered with PSC is significantly smaller than it would be if inferred from $T_{NAT}$.

Replacing $T_{NAT}$ with $T_{ACL}$ provides a more robust scientific basic for the definition of the activation transition temperature. First studies that use $T_{ACL}$ as the threshold for chlorine activation have recently been reported (Tilmes et al., 2007, 2008a; Feck et al., 2008; Tilmes et al., 2009). Tilmes et al. (2009) found that measures based on $T_{ACL}$ result in a better proxy for observed Arctic ozone loss than measures based on $T_{NAT}$.

PSC-based assumptions about chlorine activation alter the perceptions of how various factors influence polar ozone loss. One example is the inference that denitrification reduces ozone loss: if PSCs control chemistry, then the suppression of PSCs in springtime denitrified conditions would lead to less efficient chlorine activation (e.g., Grooß et al., 2005). However, liquid aerosol reactivities and, thus, $T_{ACL}$ are insensitive to

$HNO_3$, allowing chlorine activation to remain equally efficient even in denitrified conditions. Strong chlorine activation under cold, but strongly denitrified conditions (with NAT formation being unlikely) was observed in the Arctic vortex in March 2005 (Wegner et al., 2010). As a result, the only effect of denitrification on ozone loss is to increase loss, by delaying chlorine deactivation.

## 6 Conclusions

A temperature threshold for activation of chlorine in the polar stratosphere is a useful quantity to diagnose and to parameterize the onset of chlorine activation and subsequent polar ozone loss. It is a coincidence, however, that under typical stratospheric conditions at ~20 km a temperature of 195 K (or $T_{NAT}$) provides an approximate estimate for the threshold that describes both the onset of heterogeneous chlorine activation and PSC occurrence. This coincidence does not imply that the same processes control the microphysics of PSC formation and heterogeneous chemistry, nor does it imply that chlorine activation occurs at $T_{NAT}$ under different conditions. $T_{NAT}$ is a microphysical parameter that is essential for understanding where NAT PSCs may form or exist and where denitrification is likely. However, for chemical applications $T_{NAT}$ misrepresents the processes controlling the threshold for the onset of chlorine activation.

We suggest that as a metric for the onset of polar chlorine activation and the resulting chemical ozone loss, $T_{NAT}$ should no longer be used. It is important that in models including full heterogeneous chemistry, liquid phase reactions are included in detail and that NAT formation and NAT surface areas are realistically represented. Further, the temperature dependence of heterogeneous reaction probabilities $\gamma$ should be implemented in models in a realistic manner.

For many applications replacing $T_{NAT}$ with $T_{ACL}$ will provide a simple, practical way of achieving a more process-oriented basis for ozone loss metrics or parameterizations. This will allow improvements such as more accurate model-measurement intercomparisons (especially when accounting for $HNO_3$ variations) and an integrated treatment of volcanic aerosol effects. Assessments based on $T_{NAT}$ will, for example, underestimate the ramifications of artificially enhancing stratospheric aerosol, which has been proposed as a climate modification to mitigate global warming (Crutzen, 2006; Tilmes et al., 2008a; Rasch et al., 2008). Similarly, using $T_{ACL}$ in place of $T_{NAT}$ results in a stronger dependence of chlorine activation on stratospheric water vapour.

Although $T_{NAT}$ is inappropriate for describing chlorine activation, it remains a useful parameter for assessing where PSCs are likely to occur. $T_{NAT}$ is the highest temperature at which NAT PSCs could possibly form; other $HNO_3$ containing PSCs, for example STS, occur at relatively constant temperature offsets relative to $T_{NAT}$. $T_{NAT}$ may also be relevant for processes that are controlled by PSC microphysics. Denitrification, in particular, will be controlled by exposure to temperatures below $T_{NAT}$, introducing a connection between $T_{NAT}$ and ozone loss. However, denitrification can only supplement the ozone loss caused by chlorine activation and, therefore, is a secondary influence on ozone.

In summary, the onset of heterogeneous chlorine activation leading to polar ozone depletion is dominated by reactions on liquid, cold binary particles, which do not cause substantial uptake of $HNO_3$ from the gas-phase. As a metric for the onset of heterogeneous chlorine activation, $T_{ACL}$ is a more appropriate parameter than $T_{NAT}$ and will allow for a more accurate description of the response of the polar stratosphere to future climate change.

**Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/10/28687/2010/ acpd-10-28687-2010-supplement.pdf**.

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## References

Abbatt, J. P. D. and Molina, M. J.: Heterogeneous interactions of $ClONO_2$ and HCl on nitric acid trihydrate at 202 K, J. Phys. Chem., 96, 7674–7679, 1992. 28693, 28702, 28717

Bauman, J. J., Russel, P. B., Geller, M. A., and Hamill, P.: A stratospheric aerosol climatology from SAGE II and CLAES measurements: 2. Results and comparisons, 1884–1999, J. Geophys. Res., 108, 4383, doi:10.1029/2002JD002993, 2003. 28719

Buchholz, J.: Simulations of physics and chemistry of polar stratospheric clouds with a general circulation model, Ph.D. thesis, University of Mainz, Germany, http://ubm.opus.hbz-nrw.de/volltexte/2005/818/pdf/diss.pdf, 2005. 28702

Carslaw, K. S. and Peter, T.: Uncertainties in reactive uptake coefficients for solid stratospheric particles – 1. Surface chemistry, Geophys. Res. Lett., 24, 1743–1746, 1997. 28689, 28693, 28695, 28717

Carslaw, K. S., Luo, B. P., Clegg, S. L., Peter, T., Brimblecombe, P., and Crutzen, P. J.: Stratospheric aerosol growth and $HNO_3$ gas phase depletion from coupled $HNO_3$ and water uptake by liquid particles, Geophys. Res. Lett., 21, 2479–2482, doi:10.1029/94GL02799, 1994. 28690

Carslaw, K. S., Luo, B. P., and Peter, T.: An analytical expression for the composition of aqueous $HNO_3$-$H_2SO_4$-$H_2O$ stratospheric aerosols including gas phase removal of $HNO_3$, Geophys. Res. Lett., 22, 1877–1880, doi:10.1029/95GL01668, 1995. 28696

Carslaw, K. S., Peter, T., and Clegg, S. L.: Modeling the composition of liquid stratospheric aerosols, Rev. Geophys., 35, 125–154, 1997a. 28690, 28694, 28695

Carslaw, K. S., Peter, T., and Müller, R.: Uncertainties in Reactive Uptake Coefficients for Solid Stratospheric Particles – 2. Effect on Ozone Depletion, Geophys. Res. Lett., 24, 1747–1750, 1997b. 28693

Chipperfield, M. P., Cariolle, D., and Simon, P.: A 3D transport model study of chlorine activation during EASOE, Geophys. Res. Lett., 21, 1467–1470, doi:10.1029/93GL01679, 1994. 28690

Chipperfield, M. P., Feng, W., and Rex, M.: Arctic ozone loss and climate sensitivity: Updated three-dimensional model study, Geophys. Res. Lett., 32, L11813, doi:10.1029/2005GL022674, 2005. 28691, 28702, 28703

Cox, R. A., MacKenzie, A. R., Müller, R. H., Peter, T., and Crutzen, P. J.: Activation of stratospheric chlorine by reactions in liquid sulphuric acid, Geophys. Res. Lett., 21, 1439–1442, 1994. 28690

Crutzen, P. J.: Albedo enhancements by stratospheric sulfur injections: a contribution to resolve a policy dilemma? An Editorial Essay, Clim. Change, 77, 211–219, 2006. 28689, 28692, 28705

Crutzen, P. J., Müller, R., Brühl, C., and Peter, T.: On the potential importance of the gas phase reaction $CH_3O_2 + ClO \rightarrow ClOO + CH_3O$ and the heterogeneous reaction $HOCl + HCl \rightarrow H_2O + Cl_2$ in "ozone hole" chemistry, Geophys. Res. Lett., 19, 1113–1116, doi:10.1029/92GL01172, 1992. 28690

Davies, S., Chipperfield, M. P., Carslaw, K. S., Sinnhuber, B.-M., Anderson, J. G., Stimpfle, R. M., Wilmouth, D. M., Fahey, D. W., Popp, P. J., Richard, E. C., von der Gathen, P., Jost, H., and Webster, C. R.: Modeling the effect of denitrification on Arctic ozone depletion during winter 1999/2000, J. Geophys. Res., 107, 8322, doi:10.1029/2001JD000445, (printed 108(D5), 2003), 2002. 28702

Davies, S., Mann, G. W., Carslaw, K. S., Chipperfield, M. P., Kettleborough, J. A., Santee, M. L., Oelhaf, H., Wetzel, G., Sasano, Y., and Sugita, T.: 3-D microphysical model studies of Arctic denitrification: comparison with observations, Atmos. Chem. Phys., 5, 3093–3109, doi:10.5194/acp-5-3093-2005, 2005. 28701

Del Negro, L. A., Fahey, D. W., Donnelly, S. G., Gao, R. S., Keim, E. R., Wamsley, R. C., Woodbridge, E. L., Dye, J. E., Baumgardner, D., Gandrud, B. W., Wilson, J. C., Jonsson, H. H., Loewenstein, M., Podolske, J. R., Webster, C. R., May, R. D., Worsnop, D. R., Tabazadeh, A., Tolbert, M. A., Kelly, K. K., and Chan, K. R.: Evaluating the role of NAT, NAD, and liquid $H_2SO_4/H_2O/HNO_3$ solutions in Antarctic polar stratospheric cloud aerosol: Observations and implications, J. Geophys. Res., 102, 13255–13282, 1997. 28696

Deshler, T., Bryan, B. J., Hofmann, D. J., and Nardi, B.: Correlation between ozone loss and volcanic aerosol at altitudes below 14 km over McMurdo Station, Antarctica, Geophys. Res. Lett., 21, 2931–2934, 1996. 28700

Douglass, A. R., Schoeberl, M. R., Stolarski, R. S., Waters, J. W., Russell III, J. M., Roche, A. E., and Massie, S. T.: Interhemispheric differences in springtime production of HCl and $ClONO_2$ in the polar vortices, J. Geophys. Res., 100, 13967–13978, 1995. 28698

Douglass, A. R., Stolarski, R. S., Strahan, S. E., and Polansky, B. C.: Sensitivity of Arctic ozone loss to polar stratospheric cloud volume and chlorine and bromine loading in a chemistry and transport model, Geophys. Res. Lett., 33, L17809, doi:10.1029/2006GL026492, 2006. 28691, 28703

Drdla, K.: Temperature thresholds for polar stratospheric ozone, Eos Trans. AGU, 86, Fall Meet. Suppl., Abstract A31D–03, 2005. 28691

Drdla, K. and Schoeberl, M. R.: Microphysical modeling of the 1999–2000 Arctic winter 2. Chlorine activation and ozone depletion, J. Geophys. Res., 107, 8319, doi:10.1029/2001JD001159, (printed 108 (D5), 2003), 2002. 28692, 28696, 28699, 28702

Drdla, K., Schoeberl, M. R., and Browell, E. V.: Microphysical modeling of the 1999–2000 Arctic winter 1. Polar stratospheric clouds, denitrification, and dehydration, J. Geophys. Res., 107, 8312, doi:10.1029/2001JD000782, (printed 108 (D5), 2003), 2002. 28692, 28696, 28699, 28718

Dye, J., Gandrud, B., Baumgardner, D., Chan, K., Ferry, G., Loewenstein, M., Kelly, K., and Wilson, J.: Observed particle evolution in the polar stratospheric cloud of January 24, 1989, Geophys. Res. Lett., 17, 413–416, 1990. 28694, 28702

Dye, J. E., Baumgardner, D., Gandrud, B. W., Kawa, S. R., Kelly, K. K., Loewenstein, M., Ferry, G. V., Chan, K. R., and Gary, B. L.: Particle size distributions in Arctic polar stratospheric clouds, growth and freezing of sulfuric acid droplets and implications for cloud formation, J. Geophys. Res., 97, 8015–8034, 1992. 28702

Engel, A., Müller, R., Schmidt, U., Carslaw, K. S., and Stachnik, R. A.: Indications of heterogeneous chlorine activation on moderately cold aerosol based on chlorine observations in the Arctic stratosphere, Atmos. Environ., 34, 4283–4289, 2000. 28701

Eskes, H., van Velthoven, P., Valks, P., and Kelder, H.: Assimilation of GOME total ozone satellite observations in a three-dimensional tracer-transport model, Q. J. R. Meteorol. Soc., 129, 1663–1682, 2003. 28703

Eskes, H. J., Segers, A., and van Velthoven, P.: Ozone forecasts of the stratospheric polar vortex splitting event in September 2002, J. Atmos. Sci., 62, 812–821, 2005. 28703

Eyring, V., Waugh, D. W., Bodeker, G. E., Cordero, E., Akiyoshi, H., Austin, J., Beagley, S. R., Boville, B. A., Braesicke, P., Brühl, C., Butchart, N., Chipperfield, M. P., Dameris, M., Deckert, R., Deushi, M., Frith, S. M., Garcia, R. R., Gettelman, A., Giorgetta, M. A., Kinnison, D. E., Mancini, E., Manzini, E., Marsh, D. R., Matthes, S., Nagashima, T., Newman, P. A., Nielsen, J. E., Pawson, S., Pitari, G., Plummer, D. A., Rozanov, E., Schraner, M., Scinocca, J. F., Semeniuk, K., Shepherd, T. G., Shibata, K., Steil, B., Stolarski, R. S., Tian, W., and Yoshiki, M.: Multimodel projections of stratospheric ozone in the 21st century, J. Geophys. Res., 112, D16303, doi:10.1029/2006JD008332, 2007. 28702

Eyring, V., Sheperd, T. G., and Waugh, D. W., eds.: SPARC report on the evaluation of chemistry-climate models, SPARC Rep. No. 5, WRCP-132, WMO-TD No. 1526, World Meteorol. Organ., Geneva, 2010. 28701, 28702

Fahey, D. W., Gao, R. S., Carslaw, K. S., Kettleborough, J., Popp, P. J., Northway, M. J., Holecek, J. C., Ciciora, S. C., McLaughlin, R. J., Thompson, T. L., Winkler, R. H., Baumgardner, D. G., Gandrud, B., Wennberg, P. O., Dhaniyala, S., McKinley, K., Peter, T., Salawitch, R. J., Bui, T. P., Elkins, J. W., Webster, C. R., Atlas, E. L., Jost, H., Wilson, J. C., Herman, R. L., Kleinböhl, A., and von König, M.: The detection of large $HNO_3$-containing particles in the winter Arctic stratosphere, Science, 291, 1026–1031, 2001. 28694

Farman, J. C., Gardiner, B. G., and Shanklin, J. D.: Large losses of total ozone in Antarctica reveal seasonal $ClO_x/NO_x$ interaction, Nature, 315, 207–210, 1985. 28688

Feck, T., Grooß, J.-U., and Riese, M.: Sensitivity of Arctic ozone loss to stratospheric $H_2O$, Geophys. Res. Lett., 35, L01803, doi:10.1029/2007GL031334, 2008. 28692, 28703

Garcia, R. R., Marsh, D. R., Kinnison, D. E., Boville, B. A., and Sassi, F.: Simulation of secular trends in the middle atmosphere, 1950–2003, J. Geophys. Res., 112, D09301, doi:10.1029/2006JD007485, 2007. 28702

Geer, A. J., Lahoz, W. A., Bekki, S., Bormann, N., Errera, Q., Eskes, H. J., Fonteyn, D., Jackson, D. R., Juckes, M. N., Massart, S., Peuch, V.-H., Rharmili, S., and Segers, A.: The ASSET intercomparison of ozone analyses: method and first results, Atmos. Chem. Phys., 6, 5445–5474, doi:10.5194/acp-6-5445-2006, 2006. 28691, 28703

Grooß, J.-U., Pierce, R. B., Crutzen, P. J., Grose, W. L., and Russell III, J. M.: Re-formation of chlorine reservoirs in southern hemisphere polar spring, J. Geophys. Res., 102, 13141–13152, doi:10.1029/96JD03505, 1997. 28698

Grooß, J.-U., Günther, G., Müller, R., Konopka, P., Bausch, S., Schlager, H., Voigt, C., Volk, C. M., and Toon, G. C.: Simulation of denitrification and ozone loss for the Arctic winter 2002/2003, Atmos. Chem. Phys., 5, 1437–1448, doi:10.5194/acp-5-1437-2005, 2005. 28701, 28703

Hadjinicolaou, P., Pyle, J. A., Chipperfield, M. P., and Kettleborough, J. A.: Effect of interannual meteorological variability on mid-latitude $O_3$, Geophys. Res. Lett., 24, 2993–2996, 1997. 28703

Hanisco, T. F., Smith, J. B., Stimpfle, R. M., Wilmouth, D. M., Perkins, K. K., Spackman, J. R., Anderson, J. G., Baumgardner, D., Gandrud, B., Webster, C. R., Dhaniyala, S., McKinney, K. A., and Bui, T. P.: Quantifying the rate of heterogeneous processing in the Arctic polar vortex with in situ observations of OH, J. Geophys. Res., 107, 8278, doi:10.1029/2001JD000425, 2002. 28690, 28697, 28701

Hanson, D. R. and Mauersberger, K.: Laboratory studies of the nitric acid trihydrate: Implications for the south polar stratosphere, Geophys. Res. Lett., 15, 855–858, doi:10.1029/88GL00209, 1988. 28692

Hanson, D. R. and Ravishankara, A. R.: Reaction of $ClONO_2$ with HCl on NAT, NAD, and frozen sulfuric acid and hydrolysis of $N_2O_5$ and $ClONO_2$ on frozen sulfuric acid, J. Geophys. Res., 98, 22931–22936, 1993. 28693, 28702

Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions in sulfuric acid aerosols: A framework for model calculations, J. Geophys. Res., 99, 3615–3629, 1994. 28690, 28695

Hitchcock, P., Shepherd, T. G., and McLandress, C.: Past and future conditions for polar stratospheric cloud formation simulated by the Canadian Middle Atmosphere Model, Atmos. Chem. Phys., 9, 483–495, doi:10.5194/acp-9-483-2009, 2009. 28703

Hofmann, D. and Oltmans, S.: Anomalous Antarctic ozone during 1992: Evidence for Pinatubo volcanic aerosol effects, J. Geophys. Res., 98, 18555–18561, 1993. 28690, 28700

Hofmann, D. J. and Solomon, S.: Ozone destruction through heterogeneous chemistry following the eruption of El Chichón, J. Geophys. Res., 94, 5029–5041, 1989. 28690, 28692, 28700

Hoppel, K., Nedoluha, G., Fromm, M., Allen, D., Bevilacqua, R., Alfred, J., Johnson, B., and König-Langlo, G.: Reduced ozone loss at the upper edge of the Antarctic Ozone Hole during 2001–2004, Geophys. Res. Lett., 32, L20816, doi:10.1029/2005GL023968, 2005. 28701

IPCC/TEAP: Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues Related to Hydrofluorocarbons and Perfluorocarbons, edited by: Metz, B., Kuijpers, L., Solomon, S., Andersen, S. O., Davidson, O., Pons, J., de Jager, D., Kestin, T., Manning, M., and Meyer, L., Cambridge University Press, Cambridge, United Kingdom, and New York, NY, USA, 2005. 28689

Jones, A. E. and Shanklin, J. D.: Continued decline of total ozone over Halley, Antarctica, since 1985, Nature, 376, 409–411, 1995. 28688

Jones, R. L., McKenna, D. S., Poole, L. R., and Solomon, S.: On the influence of polar stratospheric cloud formation on chemical composition during the 1988/89 arctic winter, Geophys. Res. Lett., 17, 545–548, 1990. 28690

Kawa, S. R., Newman, P. A., Lait, L. R., Schoeberl, M. R., Stimpfle, R. M., Kohn, D. W., Webster, C. R., May, R. D., Baumgardner, D., Dye, J. E., Wilson, J. C., Chan, K. R., and Loewenstein, M.: Activation of chlorine in sulfate aerosol as inferred from aircraft observations, J. Geophys. Res., 102, 3921–3933, 1997. 28690, 28696, 28699, 28701

Kettleborough, J. A., Carver, G. D., Lary, D. J., Pyle, J. A., and Scott, P. A.: Three dimensional modelling of chlorine activation in the Arctic stratosphere, Geophys. Res. Lett., 21, 1471–1474, doi:10.1029/93GL03048, 1994. 28691

Kiesewetter, G., Sinnhuber, B.-M., Vountas, M., Weber, M., and Burrows, J. P.: A long term stratospheric ozone data set from assimilation of satellite observations: High latitude ozone anomalies, J. Geophys. Res., 115, D10307, doi:10.1029/2009JD013362, 2010. 28691

Knudsen, B. M., Harris, N. R. P., Andersen, S. B., Christiansen, B., Larsen, N., Rex, M., and Naujokat, B.: Extrapolating future Arctic ozone losses, Atmos. Chem. Phys., 4, 1849–1856, doi:10.5194/acp-4-1849-2004, 2004. 28691

Krämer, M., Müller, R. I., Bovensmann, H., Burrows, J., Brinkmann, J., Röth, E. P., Grooß, J. U., Müller, R. O., Woyke, T. H., Ruhnke, R., Günther, G., Hendricks, J., Lippert, E., Carslaw, K. S., Peter, T., Zieger, A., Brühl, C. H., Steil, B., Lehmann, R., and McKenna, D. S.: Intercomparison of stratospheric chemistry models under polar vortex conditions, J. Atmos. Chem., 45, 51–77, doi:10.1023/A:1024056026432, 2003. 28701

Kühl, S., Dörnbrack, A., Wilms-Grabe, W., Sinnhuber, B.-M., Platt, U., and Wagner, T.: Observational evidence of rapid chlorine activation by mountain waves above northern Scandinavia, J. Geophys. Res., 109, D22309, doi:10.1029/2004JD004797, 2004. 28691

Lowe, D. and MacKenzie, A. R.: Polar stratospheric cloud microphysics and chemistry, J. Atmos. Solar Terr. Phys., 70, 13–40, doi:10.1016/j.jastp.2007.09.011, 2008. 28689, 28690

Manney, G. L., Froidevaux, L., Santee, M. L., Livesey, N. J., Sabutis, J. L., and Waters, J. W.: Variability of ozone loss during Arctic winter (1991 to 2000) estimated from UARS Microwave Limb Sounder measurements, J. Geophys. Res., 108, 4149, doi:10.1029/2002JD002634, 2003. 28688

McElroy, M. B., Salawitch, R. J., Wofsy, S. C., and Logan, J. A.: Antarctic ozone: Reductions due to synergistic interactions of chlorine and bromine, Nature, 321, 759–762, 1986. 28688

Molina, L. T. and Molina, M. J.: Production of $Cl_2O_2$ from the selfreaction of the ClO radical, J. Phys. Chem., 91, 433–436, 1987. 28688

Müller, R., Crutzen, P. J., Oelhaf, H., Adrian, G. P., v. Clarmann, T., Wegner, A., Schmidt, U., and Lary, D.: Chlorine chemistry and the potential for ozone depletion in the Arctic stratosphere in the winter of 1991/92, Geophys. Res. Lett., 21, 1427–1430, 1994. 28690

Northway, M. J., Gao, R. S., Popp, P. J., Holecek, J. C., Fahey, D. W., Carslaw, K. S., Tolbert, M. A., Lait, L. R., Dhaniyala, S., Flagan, R. C., Wennberg, P. O., Mahoney, M. J., Herman, R. L., Toon, G. C., and Bui, T. P.: An analysis of large $HNO_3$-containing particles sampled in the Arctic stratosphere during the winter of 1999/2000, J. Geophys. Res., 107, 8298, doi: 10.1029/2001JD001079, 2002. 28694

Peter, T.: Microphysics and heterogeneous chemistry of polar stratospheric clouds, Ann. Rev. Phys. Chem., 48, 785–822, 1997. 28689, 28690, 28694, 28702

Pitari, G., Mancini, E., Rizi, V., and Shindell, D. T.: Impact of future climate and emission changes on stratospheric aerosols and ozone, J. Atmos. Sci., 59, 414–440, 2002. 28702

Pitts, M. C., Thomason, L. W., Poole, L. R., and Winker, D. M.: Characterization of Polar Stratospheric Clouds with spaceborne lidar: CALIPSO and the 2006 Antarctic season, Atmos. Chem. Phys., 7, 5207–5228, doi:10.5194/acp-7-5207-2007, 2007. 28703

Pitts, M. C., Poole, L. R., Dörnbrack, A., and Thomason, L. W.: The 2009–2010 Arctic polar stratospheric cloud season: A CALIPSO perspective, Atmos. Chem. Phys. Discuss., in press, 2010. 28689, 28703

Pitts, M. C., Poole, L. R., and Thomason, L. W.: CALIPSO polar stratospheric cloud observations: second-generation detection algorithm and composition discrimination, Atmos. Chem. Phys. Discuss., 9, 8121–8157, doi:10.5194/acpd-9-8121-2009, 2009. 28689, 28690, 28694, 28703

Portmann, R. W., Solomon, S., Garcia, R. R., Thomason, L. W., Poole, L. R., and McCormick, M. P.: Role of aerosol variations in anthropogenic ozone depletion in the polar regions, J. Geophys. Res., 101, 22991–23006, 1996. 28690, 28695, 28700

Prather, M. J.: More rapid ozone depletion through the reaction of HOCl with HCl on polar stratospheric clouds, Nature, 355, 534–537, 1992. 28690

Rasch, P. J., Tilmes, S., Turco, R. P., Robock, A., Oman, L., and Chen, C.-C.: An overview of geoengineering of climate using stratospheric sulphate aerosols, Proc. R. Soc. London A, 366, 4007–4037, doi:10.1098/rsta.2008.0131, 2008. 28689, 28692, 28705

Ravishankara, A. R. and Hanson, D. R.: Differences in the reactivity of Type I polar stratospheric clouds depending on their phase, J. Geophys. Res., 101, 3885–3890, 1996. 28689, 28690

Rex, M., Salawitch, R. J., von der Gathen, P., Harris, N. R. P., Chipperfield, M. P., and Naujokat, B.: Arctic ozone loss and climate change, Geophys. Res. Lett., 31, L04116, doi:10.1029/2003GL018844, 2004. 28688, 28691, 28703

Sander, S. P., Friedl, R. R., Golden, D. M., Kurylo, M. J., Huie, R. E., Orkin, V. L., Moortgat, G. K., Wine, P. H., Ravishankara, A. R., Kolb, C. E., Molina, M. J., and Finlayson-Pitts, B. J.: Evaluation number 15, Chemical kinetics and photochemical data for use in atmospheric studies, NASA Panel for Data Evaluation, JPL Publication 06–2, Jet Propulsion Laboratory, California Insitute of Technology, Pasadena, California, 2006. 28689, 28693, 28702

Santee, M. L., Manney, G. L., Froidevaux, L., Zurek, R. W., and Waters, J. W.: MLS observations of ClO and $HNO_3$ in the 1996-97 Arctic polar vortex, Geophys. Res. Lett., 24, 2713–2716, 1997. 28691

Santee, M. L., MacKenzie, I. A., Manney, G. L., Chipperfield, M. P., Bernath, P. F., Walker, K. A., Boone, C. D., Froidevaux, L., Livesey, N. J., and Waters, J. W.: A study of stratospheric chlorine partitioning based on new satellite measurements and modeling, J. Geophys. Res., 113, D12307, doi:10.1029/2007JD009057, 2008. 28701

Schlager, H., Arnold, F., Hofmann, D. J., and Deshler, T.: Balloon observations of nitric acid aerosol formation in the Arctic stratosphere: I Gaseous nitric acid, Geophys. Res. Lett., 17, 1275–1278, doi:10.1029/90GL01621, 1990. 28694, 28702

Shi, Q., Jayne, J. T., Kolb, C. E., Worsnop, D. R., and Davidovits, P.: Kinetic model for reaction of $ClONO_2$ with $H_2O$ and HCl and HOCl with HCl in sulfuric acid solutions, J. Geophys. Res., 106, 24259–24274, doi:10.1029/2000JD000181, 2001. 28690, 28695, 28696

Shindell, D. T. and de Zafra, R. L.: Limits on heterogeneous processing in the Antarctic spring vortex from a comparison of measured and modeled chlorine, J. Geophys. Res., 102, 1441–1449, 1997. 28697

Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, Rev. Geophys., 37, 275–316, doi:10.1029/1999RG900008, 1999. 28688, 28689, 28690, 28691, 28694, 28695, 28696

Solomon, S., Garcia, R. R., Rowland, F. S., and Wuebbles, D. J.: On the depletion of Antarctic ozone, Nature, 321, 755–758, 1986. 28689

Solomon, S., Portmann, R. W., Sasaki, T., Hofmann, D. J., and Thompson, D. W. J.: Four decades of ozonesonde measurements over Antarctica, J. Geophys. Res., 110, D21311, doi:10.1029/2005JD005917, 2005. 28700

Stolarski, R. S., Krueger, A. J., Schoeberl, M. R., McPeters, R. D., Newman, P. A., and Alpert, J. C.: Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease, Nature, 322, 808–811, 1986. 28688

Tilmes, S., Müller, R., Grooß, J.-U., and Russell, J. M.: Ozone loss and chlorine activation in the Arctic winters 1991–2003 derived with the tracer-tracer correlations, Atmos. Chem. Phys., 4, 2181–2213, 2004, http://www.atmos-chem-phys.net/4/2181/2004/. 28688, 28691, 28703

Tilmes, S., Kinnison, D., Müller, R., Sassi, F., Marsh, D., Boville, B., and Garcia, R.: Evaluation of heterogeneous processes in the polar lower stratosphere in the Whole Atmosphere Community Climate Model, J. Geophys. Res., 112, D24301, doi:10.1029/2006JD008334, 2007. 28692, 28703

Tilmes, S., Müller, R., and Salawitch, R. J.: The sensitivity of polar ozone depletion to proposed geoengineering schemes, Science, 320, 1201–1204, doi:10.1126/science.1153966, 2008a. 28689, 28692, 28703, 28705

Tilmes, S., Müller, R., Salawitch, R. J., Schmidt, U., Webster, C. R., Oelhaf, H., Russell III, J. M., and Camy-Peyret, C. C.: Chemical ozone loss in the Arctic winter 1991–1992, Atmos. Chem. Phys., 8, 1897–1910, 2008b. 28700

Tilmes, S., Garcia, R. R., Kinnison, D. E., Gettelman, A., and Rasch, P. J.: Impact of geoengineered aerosols on the troposphere and stratosphere, J. Geophys. Res., 114, D12305, doi:10.1029/2008JD011420, 2009. 28692, 28703

Toohey, D. W., Avallone, L. M., Lait, L. R., Newman, P. A., Schoeberl, M. R., Fahey, D. W., Woodbrige, E. L., and Anderson, J. G.: The seasonal evolution of reactive chlorine in the northern hemisphere stratosphere, Science, 261, 1134–1136, 1993. 28691, 28699

Toon, G. C., Blavier, J.-F., Sen, B., Margitan, J. J., Webster, C. R., May, R. D., Fahey, D., Gao, R., Del Negro, L., Proffitt, M., Elkins, J. W., Romashkin, P. A., Hurst, D. F., Oltmans, S., Atlas, E., Schauffler, S., Flocke, F., Bui, T. P., Stimpfle, R. M., Bonne, G. P., Voss, P. B., and Cohen, R. C.: Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric trace gases, J. Geophys. Res., 104, 26779–26790, 1999. 28720

Toon, O. B., Browell, E., Gary, B., Lait, L., Livingston, J., Newman, P., Pueschel, R., Russell, P., Schoeberl, M., Toon, G., Traub, W., Valero, F. P. J., Selkirk, H., and Jordan, J.: Heterogeneous reaction probabilities, solubilities, and the physical state of cold volcanic aerosols, Science, 261, 1136–1140, 1993. 28700

Voigt, C., Schlager, H., Luo, B. P., Dörnbrack, A., Roiger, A., Stock, P., Curtius, J., Vössing, H., Borrmann, S., Davies, S., Konopka, P., Schiller, C., Shur, G., and Peter, T.: Nitric Acid Trihydrate (NAT) formation at low NAT supersaturation in Polar Stratospheric Clouds (PSCs), Atmos. Chem. Phys., 5, 1371–1380, doi:10.5194/acp-5-1371-2005, 2005. 28695

Wagner, R., Möhler, O., Saathoff, H., Stetzer, O., and Schurath, U.: Infrared spectrum of Nitric Acid Dihydrate: Influence of particle shape, J. Phys. Chem. A, 109, 2572–2581, 2005. 28694, 28702

Webster, C. R., May, R., Toohey, D., Avallone, L., Anderson, J., Newman, P., Lait, L., Schoeberl, M., Elkins, J., and Chan, K.: Hydrochloric acid loss and chlorine chemistry on polar stratospheric cloud particles in the Arctic winter, Science, 261, 1130–1134, 1993. 28691, 28699

Wegner, T., Grooß, J.-U., von Hobe, M., Stroh, F., Volk, C. M., and Müller, R.: Chlorine activation on cold binary aerosol in Arctic spring 2004/05, Geophys. Res. Lett., to be submitted to ACP, 2010. 28690, 28697, 28699, 28701, 28704, 28717

WMO: Scientific assessment of ozone depletion: 1998, Global Ozone Research and Monitoring Project–Report No. 44, Geneva, Switzerland, 1999. 28693

WMO: Scientific assessment of ozone depletion: 2006, Global Ozone Research and Monitoring Project–Report No. 50, Geneva, Switzerland, 2007. 28689, 28702

Wolff, E. W. and Mulvaney, R.: Reactions on sulphuric acid aerosol and on polar stratospheric clouds in the Antarctic stratosphere, Geophys. Res. Lett., 18, 1007–1010, 1991. 28690

Worsnop, D. R., Fox, L. E., Zahniser, M. S., and Wofsy, S. C.: Vapor Pressures of Solid Hydrates of Nitric Acid: Implications for Polar Stratospheric Clouds, Science, 259, 71–74, 1993. 28692

**Table 1.** Coefficients for the parameterization of $T_{ACL}$ in Eq. (2). Parameters are valid for potential temperature $\theta$ in Kelvin and for pressure $p$ in hPa.

| | $z=\theta$ | $z=p$ |
|---|---|---|
| $\alpha$ | −4.0628 | 1.1612 |
| $a$ | 480.781 | 170.216 |
| $b$ | 18.569 | 2.8625 |
| $c$ | 0.2711 | 0.197 |
| $d$ | 6.4481 | 0.1587 |
| $e$ | 1.9915 | −0.2457 |
| $f$ | 0.05857 | 0.04705 |
| $g$ | 0.2201 | 0.1665 |
| $h$ | 0.07958 | 0.05914 |

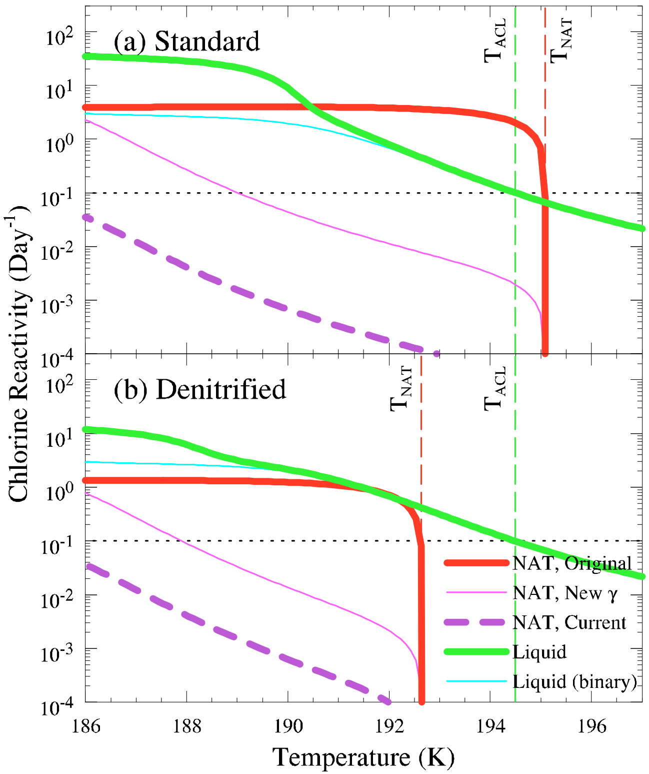

**Fig. 1.** Chlorine reactivity from heterogeneous reactions as a function of temperature, for several particulate compositions and reaction probabilities. **(a)** Typical stratospheric conditions (10 ppbv $HNO_3$). **(b)** Denitrified conditions (2 ppbv $HNO_3$). "NAT, Current" demonstrates the decrease in NAT reactivity relative to the most simple assumption on NAT PSCs ("NAT, Original") caused by updated assumptions about surface area and reaction probability. "NAT, New $\gamma$" combines the high surface areas from "NAT, Original" with the updated reaction probabilities (from Carslaw and Peter (1997), lower limit based on the measurements by Abbatt and Molina, 1992) of "NAT Current". Each NAT case shows the reactivity due to NAT particles alone. "Liquid" shows the reactivity on liquid sulfate aerosols, incorporating $HNO_3$ uptake to form STS. "Liquid (binary)" shows the reactivity on liquid aerosols for binary $H_2SO_4$/$H_2O$ solutions, i.e. without $HNO_3$ uptake. The reactivities shown here are in agreement with those reported recently by Wegner et al. (2010).

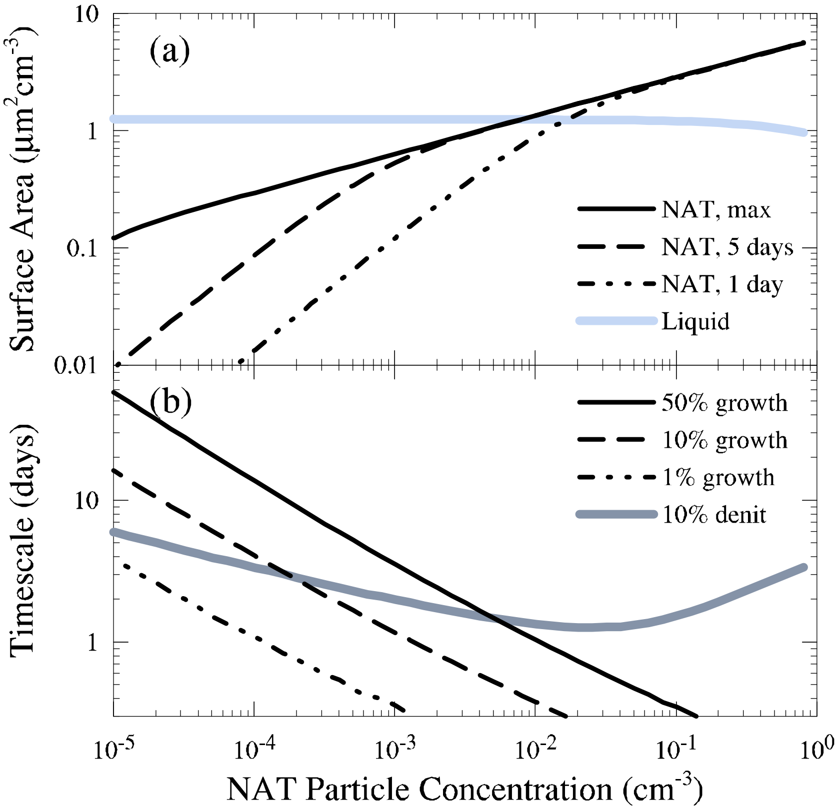

**Fig. 2.** Surface area and growth for low NAT particle concentrations. **(a)** Surface area. "NAT, max" shows the maximum (equilibrium) surface area. "NAT, 1 day" and "NAT, 5 days" show microphysical model calculations (Drdla et al., 2002) after one and five days (see Supplement for more details). The coexistent liquid surface area is also shown. **(b)** Timescales for growth and denitrification. The growth curves show the time necessary for 50%, 10% and 1% of the $HNO_3$ to condense. The denitrification curve shows the time necessary for 10% of the $HNO_3$ to sediment 1 km.

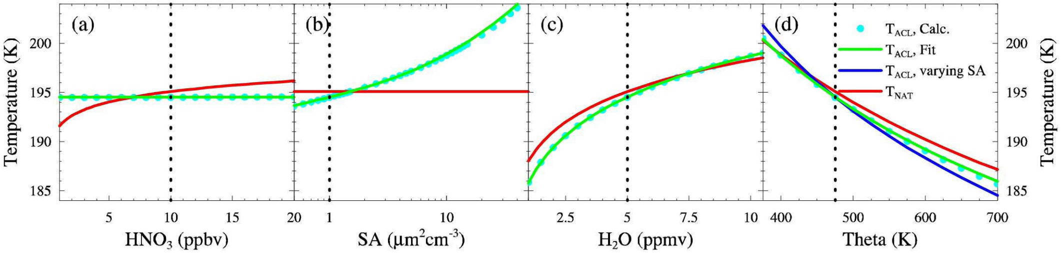

**Fig. 3.** Comparison of the chlorine activation temperature, $T_{ACL}$ (calculated values: green dots; equation 2: green line), with $T_{NAT}$ (red line). The vertical dashed lines mark the standard conditions of 10 ppbv HNO$_3$, 1 μm$^2$cm$^{-3}$ surface area, 5 ppmv H$_2$O, and 475 K; one parameter is varied in each panel. **(a)** HNO$_3$. **(b)** Sulfate aerosol surface area. **(c)** H$_2$O. **(d)** Potential temperature. For (d), the green dots and solid green line assume a constant 1 μm$^2$cm$^{-3}$ surface area; the dashed line incorporates a simplified aerosol surface area profile. The simplified surface area profile is constructed by assuming that the surface area varies according to the air density (i.e., the surface area in units of μm$^2$/mg-air is fixed); in this profile, the surface area at 475 K remains 1 μm$^2$cm$^{-3}$. The resulting profile is comparable to measured values at background conditions (Bauman et al., 2003).

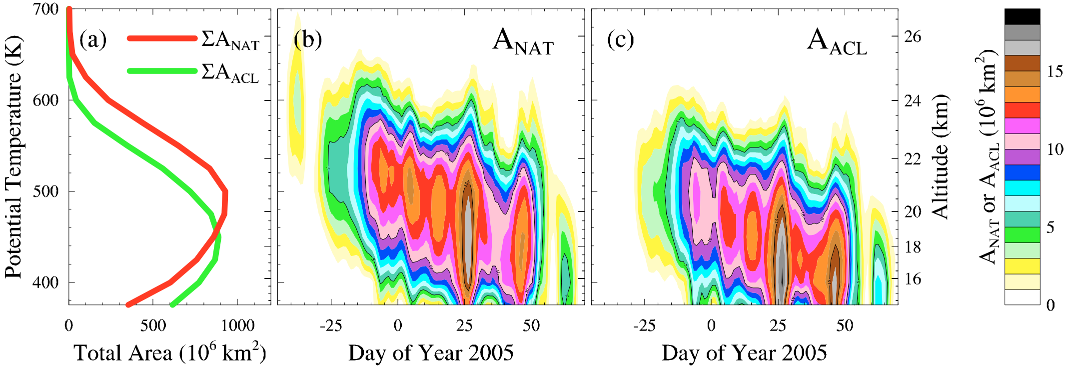

**Fig. 4.** Comparison for the 2004–2005 Arctic winter of the areal extent of temperatures below $T_{NAT}$ and $T_{ACL}$, labelled $A_{NAT}$ and $A_{ACL}$, respectively. **(a)** Winter-long integrals of $A_{ACL}$ and $A_{NAT}$. **(b)** Daily values of $A_{NAT}$. **(c)** Daily values of $A_{ACL}$. The calculations are based on daily UK Met Office analysis temperatures, interpolated onto potential temperature surfaces. Both $A_{ACL}$ and $A_{NAT}$ calculations assume 5 ppmv $H_2O$. For $A_{NAT}$, $HNO_3$ is initialized from a MkIV balloon profile (Toon et al., 1999) measured on 3 December 1999; denitrification is not incorporated into the calculation. For $A_{ACL}$, the "varying SA" sulfate surface area profile was used, similar to Fig. 3d.