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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 ClONO₂. 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:



In each case, reservoir species (ClONO₂, HCl) are converted into less stable species (Cl₂, 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 H₂SO₄/H₂O 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 HNO₃, either the more stable

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solid-phase compound nitric acid trihydrate (NAT), or liquid supercooled ternary solutions (STS) of $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$. The transition from binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ particles to STS particles, in principle, is continuous; however, the uptake of HNO_3 and the resulting growth in particle volume increases rapidly below $\sim 193\text{ K}$ 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 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ 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; Köhl 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-order 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

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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

$$k = \frac{1}{4} \gamma \cdot SA \cdot v \quad (1)$$

(Hofmann and Solomon, 1989), where γ 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 cm^{-3} . This yields a large surface area ($\sim 7 \mu\text{m}^2 \text{ cm}^{-3}$).

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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 ClONO₂ and HCl due to Reactions (R1)–(R3) have been summed, and divided by the concentration of ClONO₂ 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 ClONO₂ 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 γ ”). 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 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, $<10^{-2} \text{ cm}^{-3}$ (Northway et al., 2002; Pitts et al., 2009).

The discovery of very large NAT particles ($>5 \mu\text{m}$ 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 ($<10^{-3} \text{ cm}^{-3}$). 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} cm^{-3} , the liquid surface area density always exceeds the NAT surface area

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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 $\sim 10^{-4} \text{ cm}^{-3}$, 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 $\sim 0.005 \mu\text{m}^2 \text{ cm}^{-3}$ 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 $0.1 \mu\text{m}^2 \text{ cm}^{-3}$, 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 γ ” 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 ($\sim 1 \mu\text{m}^2 \text{ cm}^{-3}$) 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 $\sim 195 \text{ K}$, the reactivity exceeds 0.1 day^{-1} . For the “Liquid” simulation in Fig. 1, the

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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 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ 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

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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 $\sim 3 \text{ K}$ 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.

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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 day^{-1} , which is the point at which detectable levels of active chlorine ($\sim 10\%$) 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 ($p = 50 \text{ hPa}$, $\text{H}_2\text{O} = 0.5 \text{ ppmv}$, $\text{HCl} = 1.0 \text{ ppbv}$, $\text{ClONO}_2 = 0.5 \text{ ppbv}$, $\text{HNO}_3 = 10 \text{ ppbv}$, $\text{H}_2\text{SO}_4 = 0.15 \text{ ppbv}$) 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

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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

$$v = \ln([\text{H}_2\text{O}] \cdot z^\alpha) \quad (3)$$

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

where z , the input vertical coordinate, can be either potential temperature (θ) or pressure (p). Here, $[\text{H}_2\text{O}]$ is H_2O molar mixing ratio in ppmv (range 1 to 20 ppmv), SA is sulfate surface area at 210 K in $\mu\text{m}^2 \text{cm}^{-3}$ (range 0.1 to $100 \mu\text{m}^2 \text{cm}^{-3}$), θ 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 γ 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

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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 $1 \mu\text{m}$); 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 $\sim 1 \text{ cm}^{-3}$ 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 evaporated 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

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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 basis 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 spring-time 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

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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 $\sim 20\text{km}$ a temperature of 195K (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 γ 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

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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](http://www.atmos-chem-phys-discuss.net/10/28687/2010/acpd-10-28687-2010-supplement.pdf).

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

	$z = \theta$	$z = p$
α	-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

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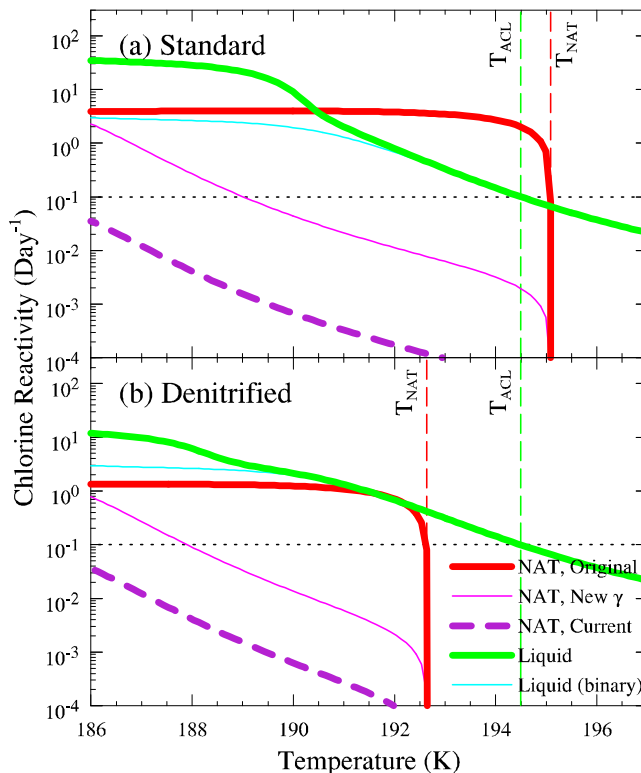


Fig. 1. Chlorine reactivity from heterogeneous reactions as a function of temperature, for several particulate compositions and reaction probabilities. **(a)** Typical stratospheric conditions (10 ppbv HNO₃). **(b)** Denitrified conditions (2 ppbv HNO₃). “NAT, Current” demonstrates the decrease in NAT reactivity relative to the most simple assumption on NAT PSCs (“NAT, Original”) caused by updated assumptions about surface area and reaction probability. “NAT, New γ ” 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 HNO₃ uptake to form STS. “Liquid (binary)” shows the reactivity on liquid aerosols for binary H₂SO₄/H₂O solutions, i.e. without HNO₃ uptake. The reactivities shown here are in agreement with those reported recently by Wegner et al. (2010).

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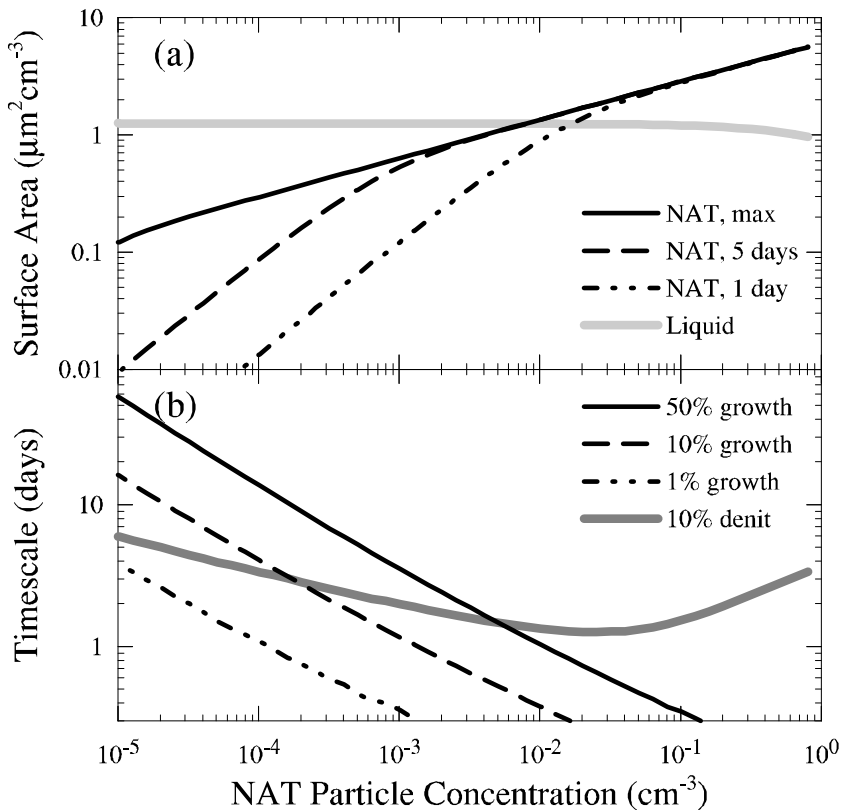


Fig. 2. Surface area and growth for low NAT particle concentrations. **(a)** Surface area. “NAT, max” shows the maximum (equilibrium) surface area. “NAT, 1 day” and “NAT, 5 days” show microphysical model calculations (Drdla et al., 2002) after one and five days (see Supplement for more details). The 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.

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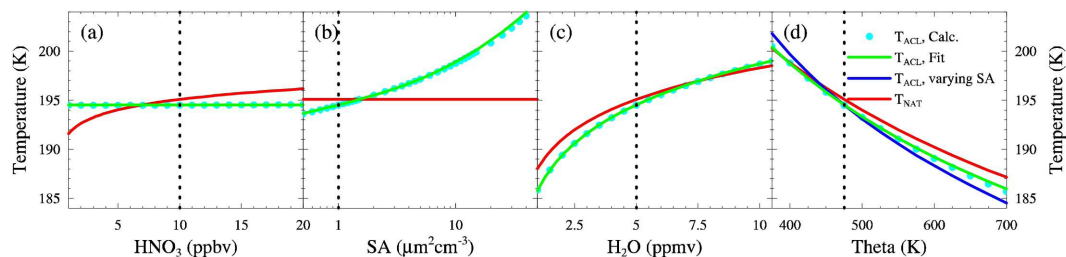


Fig. 3. Comparison of the chlorine activation temperature, T_{ACL} (calculated values: green dots; equation 2: green line), with T_{NAT} (red line). The vertical dashed lines mark the standard conditions of 10 ppbv HNO_3 , $1 \mu\text{m}^2\text{cm}^{-3}$ surface area, 5 ppmv H_2O , and 475 K; one parameter is varied in each panel. **(a)** HNO_3 . **(b)** Sulfate aerosol surface area. **(c)** H_2O . **(d)** Potential temperature. For (d), the green dots and solid green line assume a constant $1 \mu\text{m}^2\text{cm}^{-3}$ 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 $\mu\text{m}^2/\text{mg-air}$ is fixed); in this profile, the surface area at 475 K remains $1 \mu\text{m}^2\text{cm}^{-3}$. The resulting profile is comparable to measured values at background conditions (Bauman et al., 2003).

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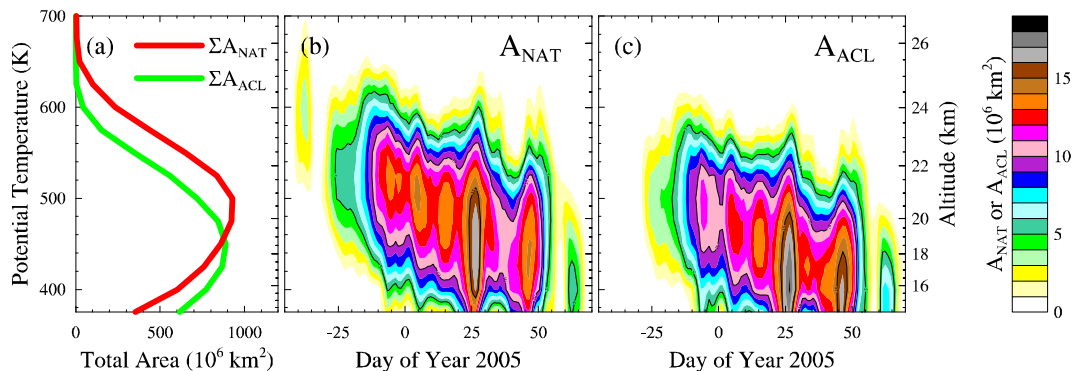


Fig. 4. Comparison for the 2004–2005 Arctic winter of the areal extent of temperatures below T_{NAT} and T_{ACL} , labelled A_{NAT} and A_{ACL} , respectively. **(a)** Winter-long integrals of A_{ACL} and A_{NAT} . **(b)** Daily values of A_{NAT} . **(c)** Daily values of A_{ACL} . The calculations are 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.

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