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Impact of a moderate volcanic eruption on chemistry in the lower stratosphere: balloon-borne observations and model calculations

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Abstract.

The major volcanic eruption of Mount Pinatubo in 1991 has been shown to have significant effects on stratospheric chemistry and ozone depletion even at mid-latitudes. Since then, only "moderate" but recurrent volcanic eruptions have modulated the stratospheric aerosol loading such as the eruption of the mid-latitude Sarychev volcano which injected 0.9 Tg of sulfur dioxide (about 20 times less than Pinatubo) in June 2009. In this study, we investigate the chemical impacts of the enhanced liquid sulfate aerosol loading resulting from this moderate eruption using data from a balloon campaign conducted in northern Sweden (Kiruna-Esrange, 67.5°N, 21.0°E) in August-September 2009. Balloon-borne observations of NO_2, HNO_3 and BrO from infrared and UV-visible spectrometers are compared with the outputs of a three-dimensional (3D) Chemistry-Transport Model (CTM). It is shown that differences between observations and model outputs are not due to transport calculation issues but rather reflect the chemical impact of the volcanic plume below 19 km in altitude. Good measurement-model agreement is obtained when the CTM is driven by volcanic aerosol loadings derived from in situ or space-borne data. As a result of enhanced N_2O_5 hydrolysis in the Sarychev volcanic aerosol conditions, the model calculates reductions of ~45% and increases of ~11% in NO_2 and HNO_3 amounts respectively over the summer 2009 period. The decrease in NO_x abundances is limited due to the expected saturation effect for high aerosol loadings. The links between the various chemical catalytic cycles involving chlorine, bromine, nitrogen and HO_x compounds in the lower stratosphere are discussed. The increased BrO amounts (~22%) compare rather well with the balloon-borne observations when volcanic aerosol levels are accounted for in the CTM and appear to be mainly controlled by the coupling with nitrogen chemistry rather than by enhanced $BrONO_2$ hydrolysis. Simulated effects of the Sarychev eruption on chlorine activation and partitioning are very limited in the high temperature conditions in the stratosphere at the period considered, inhibiting the effect of $ClONO_2$ hydrolysis. As a consequence, the simulated ozone loss due to the Sarychev aerosols is low with a reduction of 1.1% of the ozone budget at 16.5 km. Some comparisons with the reported Pinatubo chemical impacts are also provided and overall the Sarychev aerosols have led to less chemical effects than the Pinatubo event.

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1. Introduction

In the stratosphere, the photo-oxidation of N_2O is the main source of the total nitrogen species (NO_y). About 97% of the stratospheric NO_y budget can be explained by the NO, NO_2, HNO_3, $ClONO_2$, and N_2O_5 compounds and the partitioning between reactive and reservoir nitrogen species is an important issue in stratospheric ozone chemistry (e.g. Wetzel et al., 2002; Brohede et al., 2008). Nitrogen oxides (NO_x = NO + NO_2) are major catalysts responsible for significant ozone destruction in the middle stratosphere. In the gas phase, NO_x interacts with the hydrogen and halogen species in catalytic cycles affecting ozone loss rates in the lower stratosphere (e.g. Portmann et al., 1999; Salawitch et al., 2005). Therefore NO_x can also buffer the ozone destruction by halogenated compounds through the formation reaction of $ClONO_2$ and $BrONO_2$ (e.g. Rivière et al., 2004). The HNO_3 reservoir is formed from NO_x indirectly via the hydrolysis of N_2O_5 on liquid sulfate aerosols:

$$N_2O_5 + H_2O_{(aq)} \rightarrow 2\ HNO_3 \quad (1)$$

It has been shown that models need to include reaction (1) to better reproduce observations of NO_y partitioning at mid-latitude for background aerosol conditions (i.e. in volcanically quiescent periods) in the lower stratosphere (Rodriguez et al., 1991; Granier and Brasseur, 1992; Fahey et al., 1993; Webster et al., 1994; Salawitch et al., 1994b; Sen et al., 1998). This reaction tends to decrease NO_x amounts and reduces the ozone loss efficiency associated with the NO_x catalytic cycle as the less reactive nitrogen reservoir HNO_3 is formed (e.g. Rodriguez et al., 1991; Weisenstein, 1991; McElroy et al., 1992). Reaction (1) is fairly insensitive to temperature and has the potential to greatly reduce reactive nitrogen globally, even under background aerosol conditions.

The hydrolysis of $ClONO_2$ can be expressed by:

$$ClONO_2 + H_2O_{(aq)} \rightarrow\ HNO_3 + HOCl \quad (2)$$

It results in additional formation of HNO_3 on sulfate aerosols and to the formation of reactive chlorine in the sunlight where HOCl is rapidly photolyzed releasing Cl radicals (e.g. Hofmann and Solomon, 1989; Prather, 1992; McElroy et al., 1992). This heterogeneous reaction is highly dependent on the water content in the aerosols and has been shown to be of considerable importance in determining the abundance of active chlorine available to destroy ozone under some conditions, i.e. for temperatures typically below 210-215 K and where HNO_3 photolysis rates are slow (typically in winter at high latitudes), (e.g. Hanson et al., 1994; Tie et al., 1994; Borrmann et al., 1997). However, for higher temperatures the $ClONO_2$ hydrolysis is not expected to be significant enough to compete with reaction (1) on the NO_y partitioning under these conditions (Fahey et al., 1993; Cox et al., 1994; Sen et al., 1998). Also, the reaction,

$$ClONO_2 + HCl_{(aq)} \rightarrow\ HNO_3 + Cl_2 \quad (3)$$

of $ClONO_2$ with dissolved HCl in sulfuric acid droplets have negligible effects on chlorine activation at such temperatures (Hanson et al., 1994; Borrmann et al., 1997).
Some works also suggest that the hydrolysis of $BrONO_2$,

$$BrONO_2 + H_2O_{(aq)} \rightarrow\ HNO_3 + HOBr \quad (4)$$

on background sulfate aerosols also plays a significant role in ozone depletion in the lower stratosphere with rates almost independent of temperature making this reaction efficient at all latitudes and for all seasons (Hanson and Ravishankara, 1995; Hanson et al., 1996; Lary et al., 1996; Randeniya et al., 1997; Erle et al., 1998).

After large volcanic eruptions, the aerosol loading in the stratosphere and the surface area densities (hereafter SAD) available for reaction (1) to occur are dramatically enhanced (e.g. Deshler et al., 2003). As a result, the amount of ozone-depleting NO_x is strongly reduced (e.g. Prather, 1992; Johnston et al., 1992; Fahey, 1993; Mills et al., 1993; Solomon et al., 1994; Kondo et al., 1997; Sen et al., 1998) whereas HNO_3 amounts increase (Koike et al., 1993; Webster et al., 1994; Koike et al., 1994; Rinsland et al.,

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2003) as shown for the Pinatubo aerosols. Different impacts on stratospheric ozone are expected depending on the altitude. In the middle stratosphere (above ~30 hPa) where ozone loss is dominated by NO_x, the presence of volcanic aerosols can result in layers of increased net production of ozone due to the suppression of the NO_x cycle by the N_2O_5 hydrolysis (Hofmann et al., 1994; Bekki and Pyle, 1994; Tie and Brasseur, 1995). In the lower stratosphere, halogen (ClO_x and BrO_x) and hydrogen (HO_x) radicals play a dominant role in ozone depletion and their abundances, which depend on NO_x levels, are increased (in particular for halogen species, as the rate of gas-phase conversion of ClO into the $ClONO_2$ reservoir is reduced), resulting in an enhanced catalyzed ozone loss (McElroy et al., 1992; Granier and Brasseur, 1992; Brasseur and Granier, 1992; Hofmann et al., 1994; McGee et al., 1994; Bekki and Pyle, 1994; Salawitch et al., 1994a; 2005; Tie et al., 1994; Solomon et al., 1996; Solomon, 1999).

However, the NO_x-to-HNO_3 conversion by reaction (1) shows saturation as the aerosol SAD increases because the amount of N_2O_5 present in the stratosphere is limited by its production rate by the gaseous reaction $NO_2 + NO_3$ (Fahey, 1993; Prather, 1992; Mills et al., 1993; Tie et al., 1994; Solomon et al., 1996; Kondo et al., 1997; Sen et al., 1998). Consequently, ozone loss rates are expected to be limited because the saturation of the NO_x/NO_y response to the aerosol increase dampens the increase in ClO/Cl_y (Fahey et al., 1993; Tie et al., 1994). Reaction (2) does not show such a rapid saturation resulting in enhanced ozone depletion by chlorine catalytic cycles in cold air masses as the aerosol loading increases (Fahey et al., 1993). The $BrONO_2$ hydrolysis through reaction (3) is primarily dependent on the aerosol loading and is enhanced in periods of high volcanic aerosol loading. The resulting increase of BrO_x and HO_x radical concentrations and decrease in HCl (due to enhanced OH) accompanied by an increase in ClO_x radicals is expected to give further ozone loss in the lower stratosphere at all latitudes and seasons (Lary et al., 1996).

The year-to-year variability of ozone at northern mid-latitudes appears closely linked to changes in chlorine partitioning driven by volcanic aerosols from major eruptions, with stronger effects than solar cycle contributions on the mid-latitude ozone depletion (Solomon et al., 1999 and references therein). This is expected in periods with a stratosphere perturbed by elevated chlorine levels from anthropogenic activities (Tie and Brasseur, 1995; Solomon et al., 1996). In the past decade no event comparable to the Pinatubo or El Chichon eruptions was observed. However, several volcanic eruptions, though of much lesser amplitude, impacted the aerosol burden in the lower stratosphere over periods of months (Vernier et al., 2011). These "moderate" eruptions have occurred in a period of still high chlorine loading with potential impact on stratospheric ozone chemistry.

In this paper, we study the chemical impact of a short-term change in the amount of stratospheric sulfate aerosols resulting from one of these "moderate" volcanic eruptions on some key aspects of stratospheric chemistry and on ozone loss. The eruption of the Sarychev volcano on 15 and 16 June 2009 provides a very good opportunity to conduct such an investigation because 0.9 Tg of sulfur dioxide were injected in the lower stratosphere (Clarisse et al., 2012) resulting in enhanced sulfate aerosol loading and surface area densities up to 19 km for a period of about 8 months (Jégou et al., 2013). The approach consists in analyzing the effect of the heterogeneous chemical reactions associated with enhanced sulfate aerosol amounts on the lower stratospheric composition from balloon-borne observations conducted in August-September 2009 from Kiruna in Northern Sweden (67.5°N, 21.0°E) and aerosol-constrained simulations using a 3D Chemistry Transport Model (CTM). We show that at the period of the measurements N_2O_5 has reformed and the role of its hydrolysis becomes important again after the sunlit summer period. Here we estimate the ozone loss and discuss its amplitude in comparison with the effect of the Pinatubo eruption.

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2. Methodology

2.1 Balloon-borne observations

Our study is based on in situ and remote-sensing balloon-borne observations obtained during summer 2009 in Northern Sweden. More details about the instrument descriptions and retrieval techniques are given in the Appendix and in the references.

2.1.1 In situ observations

Aerosol in situ measurements have been performed by the STAC (Stratospheric and Tropospheric Aerosol Counter) instrument which is an optical particle counter providing aerosol size distributions (Ovarlez and Ovarlez, 1995; Renard et al., 2008). This instrument has been used in a number of studies dedicated to the quantification of the aerosol content in the stratosphere at various locations and seasons (e.g. Renard et al., 2002; Renard et al., 2010). Eight vertical aerosol concentration profiles have been observed between August and September 2009 as reported by Jégou et al. (2013).

We focus here on the in situ vertical profiles of N_2O, NO_2 and HNO_3 provided by the SPIRALE (French acronym for SPectroscopie InfraRouge d'Absorption par Lasers Embarqués) infrared absorption spectrometer (Moreau et al., 2005) from two balloon flights. Firstly, the measurements during the 7 August 2009 flight (further on called SPIRALE-07082009) were conducted between 02:00 UT (04:00 local time) and 03:20 UT (05:20 local time) corresponding to altitudes of 14 km and 34 km respectively. The position of the balloon varied from 67.72°N-21.40°E to 67.63°N-20.92°E during the ascent. Secondly, the SPIRALE balloon flight on 24 August 2009 (furtheron SPIRALE-24082009, the measurements started at 21:00 UT (23:00 local time) at an altitude of 14 km and the maximum altitude of 34 km was reached at 22:30 UT (00:30 local time). The measurement position remained rather constant during the ascent with a displacement of the balloon from 67.91°N-21.09°E to 67.86°N-20.94°E. The data used in this study are averaged over a vertical range of 250 m (corresponding to ~1 minute of measurements).

2.1.2 Remote-sensing observations

Since 1996 stratospheric NO_2 and BrO have been measured by solar occultation by the DOAS balloon-borne instrument using the so-called Differential Optical Absorption Spectroscopy (DOAS) technique (e.g. Platt, 1994; Stutz and Platt, 1996; Ferlemann et al., 2000). The details of the vertical profile retrieval can be found in Butz et al. (2006) for NO_2 and in Harder et al. (1998), Aliwell et al. (2002), Dorf et al. (2006b) and Kreycy et al. (2013) for BrO. In our study we use the DOAS profile recorded in the stratosphere during the balloon ascent on 7 September 2009 between 15:15 UT (17:15 local time) and 16:35 UT (18:35 local time), corresponding to altitudes of 10 km and 30 km respectively.

The SALOMON (French acronym for "Spectroscopie d'Absorption Lunaire pour l'Observation des Minoritaires Ozone et NO_x") balloon-borne UV-visible spectrometer also uses the DOAS method to derive the mixing ratio profile of NO_2 (Renard et al., 2000; Berthet et al., 2002). SALOMON was initially based on the lunar occultation technique but on 25 August 2009, we flew a new version also able to use the Sun as direct light source to derive BrO amounts. The profiles used in this study have been obtained on 25 August 2009 during solar occultation between 18:50 UT (20:50 local time) and 19:30 UT (21:30 local time). The float altitude was of 33 km and the position of the tangent point varied from 71.0°N-13.3°E to 71.4°N-12.6°E for altitudes below 19 km which are the main focus of our study as a result of the presence of the volcanic aerosols.

Variations of solar zenith angle (SZA) along solar occultation lines of sight and associated concentration variations are likely to impact the retrieved vertical profiles near sunrise and sunset especially below 20 km (Newchurch et al., 1996; Ferlemann et al., 1998). This effect can be corrected using a photochemical model (e.g. Payan et al., 1999; Harder et al., 2000; Butz et al., 2006). However, some retrievals from occultation measurements do not include corrections for diurnal variations in

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concentrations because such corrections are strongly dependent on the photochemical model used in the retrieval algorithm and are likely to result in additional errors (Randall et al., 2002).

In our study, the NO_2 profile from SALOMON instrument was recorded on 25 August 2009 from a typical solar occultation at constant float altitude. Applying a photochemical correction to convert the NO_2 concentrations to values expected at 90° SZA results in differences of only 3%. This calculation is in agreement with the work of Payan et al. (1999) who have reported differences of less than 6% between photo-chemically corrected and non-corrected profiles of NO_2. We note that Bracher et al. (2005) have estimated larger diurnal variation effects, i.e. of about 10%. In the following the SALOMON uncorrected profile is used for comparisons with model outputs. The vertical profile observed by the DOAS instrument was recorded on 7 September 2009 with a different observation geometry, i.e. during the balloon ascent. In this case applying a photochemical correction gives differences of 24% and the model-measurement comparison must be done for an SZA = 90°. Photochemical effects on the BrO profile obtained by the SALOMON instrument from solar occultation measurements are estimated to be of 10% and are taken into account in the error estimation in accordance with the study of Ferlemann et al. (1998). Photochemical changes in the BrO SCDs recorded during balloon ascent are small and the DOAS BrO profile has not been corrected to 90°SZA (Ferlemann et al., 1998; Harder et al., 2000; Dorf et al., 2006b).

2.2 Model calculations

The REPROBUS 3D CTM has been used in a number of studies of stratospheric chemistry involving nitrogen and halogen compounds in particular through comparisons with space-borne and balloon-borne observations (e.g. Krecl et al., 2006; Berthet et al., 2005; Brohede et al., 2007). It is designed to perform annual simulations as well as detailed process studies. A description of the model is given in Lefèvre et al. (1994) and Lefèvre et al. (1998), as well as in the Appendix.

In this study, REPROBUS was integrated from 1 October 2008 to 1 October 2009 with a horizontal resolution of 2° latitude by 2° longitude. The ozone field was initialized on 1 April 2009 from the ECMWF ozone analysis. We have conducted a REPROBUS simulation (hereafter called Ref-sim) constrained with typical background aerosol levels inferred from the 2D model and used as reference, namely without presence of volcanic aerosols. A simulation (hereafter called Sat-sim) has been set up by prescribing time-dependent variations of the stratospheric sulfate aerosol content from 1-km vertical resolution extinction measurements by the Optical Spectrograph and Infrared Imaging System (OSIRIS) instrument onboard the Odin satellite. OSIRIS aerosol extinction data used in this study are the validated version 5 retrieved at 750 nm (Bourassa et al., 2012). They compare well with the profiles inferred from the STAC balloon-borne aerosol counter (Jégou et al., 2013) thus providing confidence in the use of the data as a basis for consideration of time dependent changes of aerosol content. OSIRIS data have been averaged daily and zonally over 10° latitude bins. A standard Mie scattering model (Van de Hulst, 1957; Wiscombe, 1980; Steele and Turco, 1997) has been run to convert extinction values to H_2SO_4 mixing ratios from parameters of log-normal unimodal size distributions provided by the STAC instrument and used in the work of Jégou et al. (2013) in the Sarychev aerosol conditions. The derived 3D H_2SO_4 mixing ratios have been then incorporated into the model over the period of presence of the Sarychev aerosols in the northern hemisphere lower stratosphere, i.e. from the beginning of July 2009 onwards. The simulation has been conducted until October 2009 because OSIRIS data at high latitudes are lacking beyond this period due to decreasing solar illumination.

We have conducted another simulation (hereafter called Bal-sim) driven by aerosol observations with a slightly different approach. The method here consists in adjusting the H_2SO_4 mixing ratios in the model to reproduce the range of SADs observed by the STAC aerosol counter in summer (Jégou et al., 2013). These observed SAD values are used as reference from the beginning of August until the end of the model run and are homogeneously distributed for latitudes above 40°N. This simplification is supported by the similar aerosol SAD values observed by Kravitz et al. (2011) at a different mid-latitude location in November 2009, i.e. ~2 months after the STAC measurements as mentioned by Jégou et al. (2013). Also, the SO_2 plume rapidly converts into aerosol sulfate, spreads out over the hemisphere and appears rather uniformly distributed from about the end of July (Haywood et al., 2010). Our computed uniformity of enhanced levels of SAD from August to September 2009 is representative, at least to some

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extent, of the geographical distribution of the optical depth signal observed by the CALIOP/CALIPSO space-borne lidar over the northern hemisphere for this period (O'Neill et al., 2012). Note that in Balsim, H_2SO_4 mixing ratios in July are taken from the Sat-sim simulation.

The simulation presented hereafter accounts for the standard deviations of aerosol SADs observed from the balloon-borne STAC instrument and shown in **Figure 1**.

3. Impact of the volcanic aerosols on stratospheric nitrogen compounds: comparisons between balloon-borne observations and model simulations

3.1 Impact of transport on simulated N_2O and NO_y

It has been shown that wind fields from meteorological analysis produce an excessively strong Brewer-Dobson circulation (BDC) in the stratosphere (e.g. Legras et al., 2005; Monge-Sanz et al., 2007) which affects the ability of CTMs to represent the global distribution of long-lived tracers. Past model calculations used to significantly underestimate NO_x and NO_y concentrations (e.g. Sen et al., 1998; Gao et al., 1999; Wetzel et al., 2002; Stowasser et al., 2003) and Berthet et al., (2006) mainly attributed this problem to transport calculation issues for N_2O. Following the work of Legras et al. (2005), REPROBUS has been driven by 3-hourly ECMWF wind fields obtained by interleaving operational analysis and forecasts. Using these more timely resolved and less noisy ECMWF wind fields reduced the ascent velocities of the upward branch of the Brewer-Dobson circulation in the tropics, largely reduced the model-measurement discrepancies by increasing the simulated global NO_y and NO_x amounts from increased N_2O photo-oxidation (Berthet et al., 2006). In this configuration, the summer 2009 REPROBUS simulations are in agreement with the SPIRALE in situ observations, especially at the altitudes of the Sarychev aerosols (**Figure 2**).

The effect on simulated total NO_y can be investigated by converting the vertical profile of N_2O, following the strategy of Berthet et al. (2006) based on N_2O-NO_y correlation curves. Since the study of Michelsen et al. (1998) global emissions of N_2O have increased and therefore the N_2O-NO_y correlation curve reported therein needs some revision. As a consequence, we have constructed updated high-latitude N_2O-NO_y correlation curves from the IMK/IAA V5R_220 MIPAS-Envisat data for the high-latitude in summer stratosphere (Fischer et al., 2008; data available at http://www.imk-asf.kit.edu/english/308.php) as shown in **Figure 3** in which the Michelsen et al.'s former results are also represented for comparison. The estimated vertical profile of NO_y (hereafter NO_y*) derived from the conversion of the in-situ profile of N_2O using the MIPAS correlation curve is presented in **Figure 2**. Above 25 km, the NO_y* profile presents a non-monotonous trend in comparison with the NO_y profile computed by the 3D version of REPROBUS, since in the model the vertical structures on the observed N_2O profile are amplified by the conversion to NO_y* through the N_2O-NO_y correlation. Above about 20 km NO_y* is almost systematically lower than the 3D REPROBUS NO_y profile whereas better overall agreement is observed for the volcanic aerosol loaded lower stratosphere.

3.2 Photochemical conditions

N_2O_5 is produced mainly at night from the recombination of NO_2 with NO_3 and destroyed during the day by photolysis leading to the reformation of NO_2. NO_3 is formed mainly at night by the reaction of NO_2 with O_3. The summer season provides particular conditions for stratospheric NO_y chemistry. In this period, some regions of the polar stratosphere receive continuous solar illumination for many weeks which results in permanent photolysis reactions and enhances conversion of nitrogen reservoirs (N_2O_5 and HNO_3) to NO_x. Decreases of HNO_3, the major NO_y species at mid- and high latitudes are manifest

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in observations (Santee et al., 2004; Lindenmaier et al., 2011) and models (Chipperfield, 1999). With the onset of continuous photolysis in high-latitude air masses, N_2O_5 production (occurring significantly at night) stops abruptly because NO_3 amounts are kept low due to rapid photolysis, thereby preventing N_2O_5 formation as shown on **Figure 4** above the Esrange/Kiruna balloon launching base. N_2O_5 hydrolysis ceases as well and the NO_x/NO_y ratio becomes primarily controlled by gas-phase reactions, NO_x being principally destroyed by NO_2 + OH reaction and produced by HNO_3 + OH reaction and photolysis of HNO_3 (Osterman et al., 1999; Dufour et al., 2005). A period of enhanced conversion of NO_y to NO_x occurs until about beginning of August (Brühl et al., 1998) as reflected in **Figure 4**. Consequently, NO_x becomes the principal catalyst for ozone loss with local destruction rates which can exceed 0.3% per day in summer air masses (Fahey and Ravishankara, 1999).

Figure 4 shows the recovery of N_2O_5 on the return of sunset at high latitude (around day 213 at the beginning of August for the considered location) around 17.5 km. When NO_3 reforms at the beginning of August, significant conversion of NO_2 to N_2O_5 occurs during the night. The associated decrease in NO_x is reflected in **Figure 4**. The conversion of N_2O_5 to HNO_3 through reaction (1) occurs almost exclusively at night. As the season progresses, the increase in the conversion rate caused by the increase in night duration is moderated by the decrease in NO_2 amounts at the beginning of the night. As expected, increasing SAD values in the model to reproduce the volcanic aerosol levels has no effect on N_2O_5 (and on the production of HNO_3) and on NO_x during the period of continuous solar illumination. However, from the onset of N_2O_5 recovery a significant decrease in the N_2O_5 and NO_x levels in comparison with the background aerosol simulation is calculated as the lifetime of N_2O_5 in reaction (1) is reduced (e.g. Kinnison et al., 1994) and as further nitrogen oxides are converted to the more stable HNO_3 reservoir.

This situation implies that the balloon flights performed from August 7, 2009 match the photochemical conditions for which volcanic aerosols likely had an impact on NO_y partitioning via elevated N_2O_5 hydrolysis. Some variability in modelled N_2O_5 (**Figure 4)** is due to the effect of meridional transport to high latitudes which can be an important factor setting the stage of the chemical conditions at the measurements location.

3.3 NO_2

3.3.1 Model comparisons with observations

In a stratosphere impacted by enhanced aerosol loadings after major volcanic eruptions, NO_x amounts are expected to be linked to aerosol concentrations. Observations of the NO_2 column has shown strong anti-correlation with increasing aerosol amounts in mid-latitude conditions in spring (Mills et al., 1993). In polar summer, strong reductions of NO_x amounts have been observed in the presence of the Pinatubo aerosols as a result of enhanced N_2O_5 hydrolysis (e.g. Solomon et al., 1994). For the Sarychev situation, minima in NO_2 concentrations appear closely correlated with enhancements in aerosol amounts in the lower stratosphere (**Figure 5)**. Thus the empirical evidence supports the view that NO_x chemistry is largely driven by heterogeneous processes even in the case of a moderate volcanic eruption. Here reductions in expected NO_2 of up to a factor of ~2 is seen for aerosol increases of ~3 (with respect to the mean profiles). Conversely, layers with lower aerosol amounts, i.e. not affected by transport of the volcanic aerosols, show maximums in NO_2 concentrations.

Model simulations have been conducted to provide further insight into the chemical impact of the volcanic aerosols on NO_x and NO_y partitioning and to compare with several balloon-borne observations. **Figure 6** presents the measured in-situ profiles of NO_2 obtained for two different cases of photochemical conditions, i.e. for SPIRALE-07082009 around 02:15 UT, at ~87° SZA, and SPIRALE-242009, around 21:15 UT at a SZA of ~100°, together with REPROBUS model outputs for altitudes below 20 km where the Sarychev aerosols were present. The reference simulations (i.e. without volcanic aerosols) significantly overestimate the NO_2 observations with differences as large 56-57% (values with respect to the measured profile) between 14 and 19 km for SPIRALE-07082009 and SPIRALE-24082009 (**Table 1)**. The model results have also been assessed by the remote sensing observations from the SALOMON and DOAS instruments flown on 25 August and 7 September 2009 respectively. Non-volcanic model calculations show also discrepancies with solar occultation measurements in the lower

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stratosphere (**Figure 7**), where the model overestimates measured NO_2 by 51% and 75% for the SALOMON flight on 25 August 2009 and the DOAS flight on 7 September 2009, respectively (**Table 1**).

The embedded plots in **Figure 6 and Figure 7** show the comparison above the Sarychev aerosol layer, i.e. for the whole range of altitudes observed by the instruments (up to ~35 km). Calculated NO_2 amounts overestimate the observations by 23% and 15% on average above 20 km for the SPIRALE-07082009 and SPIRALE-07082009 simulations, respectively. These values suggest that the model-measurement differences in the lower stratosphere may be only partly attributed to remaining uncertainties in calculations of transport. This issue is further investigated in section 3.6. Above 20 km the simulated profiles show good agreement with SALOMON and DOAS observations, except above 30 km for the flight on 25 August 2009.

The Sat-sim simulations driven by the aerosol content inferred from OSIRIS satellite data show significant improvement in comparison with the non-volcanic calculations, the model outputs matching well the NO_2 observations with model-measurement differences of 5-7% (in absolute values) for all dates (**Table 1**). Likewise, the measured NO_2 profiles and the model results obtained from the Bal-sim constrained by a range of aerosol SADs observed by the STAC aerosol counter show good agreement with for instance average differences of 3±20% and -16±20% for the SPIRALE-07082009 and SPIRALE-24082009, respectively. It can be noted that the REPROBUS calculations do not reproduce some of the vertical structures detected by the SPIRALE instrument, i.e. between 17.5 and 19.5 km for SPIRALE-07082009 and at 17 km and 20.5 km for SPIRALE-24082009. This is likely due to vertical resolution of the model or inaccurate simulation of mixing effects in the CTM as already mentioned in previous studies showing this kind of comparisons (e.g. Berthet et al., 2006). We note also that all simulation results deviate from the lower altitude points in the SALOMON and DOAS profiles. Part of this discrepancy might be due to effects of possible concentration inhomogeneities along the lines of sight which are likely to induce biases in the retrieved profiles from remote sensing instruments especially in the lower stratosphere (Berthet et al., 2007).

Calculated differences between the volcanic-aerosol-constrained and the reference simulations provide an estimation of the chemical perturbation induced by the Sarychev aerosols. Considering together the results from OSIRIS and balloon-driven simulations, reductions in NO_2 mixing ratios between 31 and 47 % are simulated on average below 19 km (**Table 2**). The similar NO_2 reduction for SPIRALE-07082009 and SPIRALE-24082009 once again indicates that enhanced hydrolysis of N_2O_5 onto volcanic aerosols is efficient even for conditions of incomplete recovery of N_2O_5. For a stratosphere affected by the Pinatubo aerosols, decreases ranging from 30 to 45% have been reported both in model calculations of NO_2 concentrations (Kinnison et al., 1994; Webster et al., 1994) and in the NO_2 columns (Johnston et al., 1992; Koike et al., 1993; Koike et al., 1994; Solomon et al., 1994). At a glance, the amplitude in the NO_2 reduction is therefore similar for both eruptions but it should be noted that results from these above-mentioned studies were provided for different latitudes, various seasons and correspond to wider altitude ranges as a result of the larger vertical extent of the Pinatubo aerosol cloud.

3.3.2 Saturation effect of NO_x reduction

The reduction of NO_x from the results described above is significant but also indicates some saturation through reaction 1 for the range of SAD observed for the Sarychev aerosols. The partitioning between NO_x and NO_y is expected to become insensitive to increases in aerosol SAD beyond a certain value when N_2O_5 hydrolysis is the dominant sink for NO_x because the nighttime formation of N_2O_5 by reaction of NO_2 and NO_3 is quadratically dependent on NO_x. This effect is reflected in **Figure 8** presenting the NO_2 amounts versus aerosol SAD as observed by the SPIRALE instrument and simulated by the REPROBUS CTM. NO_2 reduction shows a kind of asymptotic behaviour as the heterogeneous rate of reaction 1 becomes large with increasing aerosol SAD. In this case 82-88% of NO_y are stored in HNO_3. We must keep in mind that Figure 8 does not accurately demonstrate the saturation effect because our NOx-SAD curve has been constructed for a wide range of altitudes (i.e. with different NOy amounts and photochemistry) and not for a constant level. Observations obtained separately for different aerosol loadings but similar in terms of altitude levels and SZA would have been necessary to point out a clear asymptotic value, as a proof of the saturation effect. Nevertheless, our results indicate saturation for SAD values larger than about 4 $\mu m^2.cm^{-3}$ which is reached on average for altitudes around 18 km. The

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net reduction of NO_x reported for the Pinatubo aerosols tends to saturate at similar SAD values in the 18-22 km range, as shown in the works of Fahey et al. (1993), Kondo et al. (1997) and Sen et al. (1998).

3.4 HNO_3

Figure 9 compares the HNO_3 profiles observed by the SPIRALE instrument and the simulations by the REPROBUS CTM for SPIRALE-07082009 and SPIRALE-24082009. We show here model outputs for total HNO_3 (i.e. both in the gas phase and condensed), but note that because HNO_3 is rapidly released into the gas phase, gaseous HNO_3 would give the same results.

In the lower stratosphere, the simulated reference profiles for HNO_3 are mostly within the errors bars of the measurements (calculated model-measurement differences are of -3% and -4% below 19 km for SPIRALE-07082009 and SPIRALE-24082009, respectively as shown in **Table 1**) though some specific vertical structures are not reproduced by the model. The agreement is even good up to 35 km confirming that transport may not be a major issue in the comparisons.

Results from the volcanic-aerosol simulations appear also within the measurement error bars (calculated model-measurement differences are between 6 and 8% for the Sat-sim results for SPIRALE-07082009 and SPIRALE-24082009, respectively as shown in **Table 1**). The production of HNO_3 by heterogeneous chemistry generally appears less effective in the lower stratosphere than above 20 km when volcanic aerosols are present (see figure 3 of Webster, 1994; Plate 3 of Danilin et al., 1999). However, the production of HNO_3 in the lower stratosphere is considered as significant for the Sarychev derived aerosols because the simulations including volcanic aerosols increase simulated HNO_3 amounts by 9-11% below 19 km as indicated by the Sat-sim results (**Table 2**). Simulated reduced levels of NO_x correspond to the produced additional amounts of HNO_3. For instance, the simulated NO_x decrease of -0.21 ppbv matches the +0.22 pbbv increase of HNO_3 at 16 km for SPIRALE-07082009. Note that in this context, the role of the NO_2 + OH reaction with respect to NO_x conversion by enhanced N_2O_5 hydrolysis on the detailed partitioning between NO_x and HNO_3 is not so clear (Coffey and Mankin, 1993).

After the Pinatubo eruption, maximum HNO_3 column increases of 30-40% were measured at mid-latitudes (Koike et al., 1994). When Pinatubo aerosol SADs had decreased to values comparable to the summer 2009 SADs around 16 km, i.e. 7.5-9 $\mu m^2.cm^{-3}$ in fall 1993 (Berthet et al., 2002), the percent change in the HNO_3 column had dropped below 20% (Koike et al., 1994; Rinsland et al., 2003). Overall, this reported effect is larger than in our observations indicating a more limited production of stratospheric HNO_3 after the Sarychev eruption. However, quantifying the difference between both eruptions in term of chemical effects remains difficult as mentioned for NO_2. In particular, the observed signature of the Pinatubo-induced HNO_3 enhancement was not limited to the lower stratosphere and was prevailing above the 420-465 K (~16-18 km) vertical range (Webster et al., 1994; Santee et al., 2004).

3.5 NO_2/HNO_3 ratio

The uncertainty in the simulated NO_y is expected to be minimized by considering the ratios of individual components of NO_y to total NO_y as shown by Wetzel et al. (2002) for summer mid-latitude conditions. When no measurements of total NO_y are available, the NO_2/HNO_3 ratio can be used as a good approximation to reduce the uncertainty in the model estimate of NO_y (e.g. Webster et al., 1994; Berthet et al., 2006). This is especially useful for SPIRALE-07082009 and SPIRALE-24082009 for which modelled NO_2 and HNO_3 amounts account for more than 92% of total NO_y.

Figure 10 presents the NO_2/HNO_3 ratios observed by SPIRALE in comparison with the REPROBUS model simulations. The NO_2/HNO_3 ratio in the lower stratosphere is typically 0.2 but the measurements indicate a smaller ratio. Under background aerosol loadings the observed low NO_2/HNO_3 ratios are not matched by the reference simulation with the differences below 19 km being 62-63% for both flights (**Table 1**). A good agreement is obtained between both measurements and the model by including the Sarychev aerosols with absolute differences decreasing to 3±20% and 1% for the Balloon-aero-sim and Satellite-aero-sim simulations, respectively, for SPIRALE-07082009. No clear improvement can be noticed from the model-measurement comparisons of the NO_2/HNO_3 ratio and the both species (**Figures**

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4 and **7)**. Again this indicate that uncertainties in transport calculation are not the main explanation for the model-measurement discrepancy observed for the lower stratosphere.

The Sat-sim aerosol constrained simulations of the reduction in the NO_2/HNO_3 ratio are 36% and 44% for SPIRALE-07082009 and SPIRALE-24082009, respectively (**Table 2**). These ratios are similar to the Bal-sim outputs. For the Pinatubo aerosol loaded stratosphere, comparable reductions ranging from 20 to 45% have been reported both in the observed NO_2/HNO_3 column ratios (Koike et al., 1994) and in model calculations (Webster et al. (1994).

3.6 One-dimensional model calculations

The measurement-model comparisons still show some discrepancies above 20 km. A way to discard a possible remaining effect of transport and further improve the modelling of total NO_y is to use constrained one-dimensional (1D) calculations (Dufour et al., 2005; Berthet et al., 2006). These may allow us to refine the quantification of the enhanced heterogeneous processes resulting from the Sarychev eruption. Following the strategy of Berthet et al. (2006), the 1D-REPROBUS initialization is constrained by available N_2O observations (here the profile measured by SPIRALE) and by the corresponding NO_y* profile as illustrated in **Figure 2**.

The 1D reference simulation (Ref-sim 1D) is computed with background aerosol levels, while the Sarychev aerosol affected simulation is constrained with the mean aerosol profile measured during the balloon-borne observations (Bal-sim 1D). As a result of the NO_y* input in the calculations, the Ref-sim 1D simulations show very good agreement for NO_2 and HNO_3 (and consequently for NO_2/HNO_3) with the SPIRALE measurements above 20 km, thus mostly leading to better results than the 3D reference simulation **(Figures 6, 9 and 10**) especially for NO_2 and NO_2/HNO_3. At the altitudes affected by the Sarychev aerosols, the model results deviate from the observed profile. Here differences are 48-60% (absolute values) for the NO_2/HNO_3 ratio for SPIRALE-07082009 and SPIRALE-24082009 (**Table 1**). We note that fine structures in the measured profile are not reproduced by the 1D model as a matter of height resolution and interpolation (Berthet et al., 2006). As for the 3D model profiles, the 1D simulations constrained by observed aerosol quantities (Bal-sim 1D) are in good agreement with the in situ measurements with the calculated model-observation differences being 12-16% (absolute values) for the NO_2/HNO_3 ratio (**Table 1**). Overall the 1D simulations including volcanic aerosol loadings do not show evidence of significant improvement in the comparisons. These results confirm that the model-observations differences in the lower stratosphere can be mostly attributed to heterogeneous processes and not to spurious calculations of transport.

The calculated chemical impact of the Sarychev aerosols on NO_2 and HNO_3 gives percentage values comparable to the 3D simulation results, with for instance a reduction by 22 and 34% in NO_2 amounts for SPIRALE-07082009 and SPIRALE-24082009, respectively (**Table 2**).

4. Impact of the volcanic aerosols on the coupled catalytic cycles involving halogen, nitrogen and HO_x compounds

4.1 Chlorine partitioning

Several studies have revealed the impact of the Pinatubo eruption on the stratospheric halogen chemistry. This has been shown to be of particular importance regarding ozone destruction processes through the partitioning of chlorine reservoir species and activation of chlorine radicals on volcanic aerosols (e.g. Solomon, 1999 and references therein). Some volcanic eruptions are likely to inject halogenated compounds within the stratosphere therefore impacting directly the halogen content and

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bypassing (or adding to) in situ heterogeneous processes. For the Sarychev volcano eruption, an injection of several ppbv of HCl in the stratosphere has been reported by Carn et al. (2016) using Microwave Limb Sounder (MLS) data, mainly below the 140 hPa level (see their Figure 4). However the exact altitude of injection is inaccurate because of the low vertical resolution of MLS data, i.e. ~3 km. In addition, MLS HCl measurements are known to be biased high below the 100 hPa level and are not recommended for scientific use (Livesey et al., 2011) making difficult to infer a robust injection amount. HCl amounts in the lower stratosphere has returned to background levels within about two weeks (Carn et al., 2016). No difference with respect to background HCl levels is apparent above Kiruna and over the Northern hemisphere in July and at the period of the balloon campaign, indicating fast dilution of the HCl plume after the eruption (MLS data available at http://giovanni.gsfc.nasa.gov/giovanni/ and http://disc.sci.gsfc.nasa.gov/). Thus no effect is expected on the total inorganic chlorine in our model calculations.

We therefore examine the direct impact of the Sarychev sulfate aerosols on the chlorine partitioning in connection with NO_x and HO_x in the lower stratosphere. Heterogeneous reactions on volcanic aerosols involving the $ClONO_2$ and HCl chlorine reservoirs (especially reaction 2) have been shown to play a major role in determining the abundance of active chlorine and therefore they are likely to compete with reaction 1 as a sink of NO_x depending on ambient temperature values (e.g. Hanson et al., 1994). Significant decreases of HCl and corresponding increases in $ClONO_2$ have been reported for temperatures below 210 K in the lower stratosphere with a strong temperature sensitivity when volcanic aerosol amounts are large (Michelsen et al., 1999; Webster et al., 1998; Webster et al., 2000). **Table 3** presents the calculated effects of the Sarychev aerosols on the partitioning of the halogen species at 16.5 km. Simulated levels of HCl decrease by 3% (~20 pptv) which is much smaller than the change observed by Webster et al. (2000) for the Pinatubo aerosols (about -31% at 21 km). Higher levels of $ClONO_2$ are simulated post the Sarychev eruption with respect to background conditions with increases of about 16% (~20 pptv). ClO and HOCl increase by 106% (~6 pptv) and 217% (~2 pptv) respectively at daytime. It is interesting to notice that these results for ClO are comparable to the calculations of Tie et al. (1994) who show ClO increases by at least 5 pptv in the lower stratosphere for summer 1992 at a time when Pinatubo related aerosol SADs were similar to August 2009 values.

The impact of the volcanic aerosols on the chlorine partitioning appears somewhat small since it is primarily the consequence of the increasing losses of HCl by enhanced OH through reaction $HCl + OH \rightarrow Cl + H_2O$ (McElroy et al., 1992; Webster et al., 2000) rather than by reaction 2 for which the efficiency is low in the ~215-225 K range of temperatures mostly encountered in the lower stratosphere over the August-September 2009 period (see Figure 9 in Jégou et al., 2013). In fact, in the model HO_x is increased by 51% (~1.4 pptv) (**Table 3**) and destruction of HCl by OH is faster than the HCl formation reaction $Cl + CH_4 \rightarrow HCl + CH_3$. An additional source of OH may be due to photolysis of HNO_3 (Rodriguez et al., 1991; Webster et al., 2000). Also the decreased reaction rate of reaction $NO_2 + OH + M \rightarrow HNO_3 + M$ in reduced NO_x conditions (Kinnison et al., 1994) may increase OH. As also described by Bekki and Pyle (1994), subsequent production of reactive chlorine and increase in ClO is accompanied by an increase in $ClONO_2$ amounts through increased rate of reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$, for which ClO is the limiting reactant. To a lesser extent, decreased rate of reaction 3 for the observed temperature range contributes to this increase. Overall, the $ClONO_2$ increase compensates for the HCl decrease in reaction 3 (Kinnison et al., 1994; Michelsen et al., 1999; Webster et al., 2000). HOCl amounts rise as a result of slightly enhanced $ClONO_2$ hydrolysis and production by enhanced HO_x through reaction $HO_2 + ClO \rightarrow HOCl + O_2$.

4.2 Bromine compounds

4.2.1 Effect on BrO

Coupling between chlorine and bromine compounds is of particular importance in the lower stratosphere and the role of bromine chemistry in regulating chlorine partitioning must be considered (e.g. Lary et al., 1996; Erle et al., 1998; Salawitch et al., 2005). Heterogeneous bromine reactions are

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expected to increase the coupled gas phase ClO/BrO catalytic ozone destruction cycles. Because $BrONO_2$ hydrolysis (reaction 4) is not temperature dependent, its effects on the chemistry of the lower stratosphere are primarily dependent on the aerosol loading and not on latitude or SZA (Lary et al., 1996; Kondo et al., 1997; Erle et al., 1998).

Some incidents of a direct injection of bromine into the stratosphere by volcanic eruptions have been reported. The study of Hormann et al. (2013) based on space-borne observations of BrO however indicate that stratospheric injection of bromine was insignificant after the Sarychev eruption. We therefore expect that stratospheric bromine chemistry was only modified by the enhanced aerosol loading (e.g., Lary et al., 1996). BrO was the only key halogenated radical detected during the summer 2009 balloon campaign. Vertical profiles were provided by the SALOMON and DOAS instruments on 25 August 2009 and 7 September 2009 respectively (**Figure 11**). They were simultaneously measured with the NO_2 profiles presented in section 3.2.2. When volcanic aerosol SAD are included BrO amounts are increased in the lower stratosphere, matching the observations within the error bars (**Figure 11**). Differences between the model and the observations and between the various simulations are summarized in **Table 1** and **Table 2** respectively.

Simulated results related to the bromine chemistry at 16.5 km are presented in **Table 3** for the August-September 2009 period. At daytime part of the BrO enhancement is linked to the decreased loss by the three body reaction with decreased NO_2. The other part is expected to be controlled by $BrONO_2$ hydrolysis which is by far the most efficient bromine heterogeneous reaction in the temperature range observed in our study (Hanson and Ravishankara, 1995; 1996). Under high aerosol loading the rate of the $BrONO_2$ hydrolysis is likely to compete with the $BrONO_2$ photolysis and with other gas phase reactions which normally control the bromine partitioning at daytime (Lary et al., 1996). Here note that the conclusion of Kreycy et al., (2013) on a possibly larger ratio of the photolysis and the three body formation reaction for $BrONO_2$ (J(k) than compiled by Sander et al., (2011) is not by affected by the presence of the Sarychev aerosols in the lower stratosphere, since they addressed solar occultation observations for solar zenith angles $< 92.5^o$ at 31 km (i.e., tangent heights > 24 km). After sunset $BrONO_2$ production is ceasing and its enhanced hydrolysis on volcanic aerosols leads to strongly increased formation of HOBr (+3.9 pptv or +141%) at an early stage of the night so that little $BrONO_2$ remains before dawn. This conversion at nighttime results in further release of OH and Br atoms in the morning through photolysis of HOBr.

However, it is not clear if $BrONO_2$ hydrolysis is mainly responsible for the increase in BrO within the lowermost stratosphere. Dedicated simulations to estimate the respective contribution of gas-phase chemistry and heterogeneous processes on the control of BrO production under volcanic conditions have thus been performed. The effects of the Sarychev aerosols on each chemical compound are calculated by switching off reaction 4 and compared in terms of percentage differences with the simulations including all chemistry. Results are summarized in **Table 3**. It particularly shows that under the Sarychev aerosol loading, 18% of the daytime BrO production (+0.9 pptv or +22% at 16.5 km during the August-September 2009 period when volcanic aerosols were present) is due to $BrONO_2$ hydrolysis. This results implies that bromine chemistry in the gas phase coupled to processes controlling the NO_y partitioning mainly govern BrO amounts (e.g., Lary et al., 1996).

4.2.2 Role of $BrONO_2$ hydrolysis on other compounds

As shown in **Table 3** for an altitude of 16.5 km, at night $BrONO_2$ amounts are mainly affected by reaction 4 which controls 98% of its decrease under volcanic aerosol influence. Nearly 100% of the night-time HOBr production is due to $BrONO_2$ hydrolysis which accounts for 44% of the increase in OH radical amounts from the subsequent photolysis of HOBr at dawn. Therefore, under volcanic conditions enhanced $BrONO_2$ hydrolysis nearly matches the contribution of nitrogen chemistry (see section 4.1) as a source of OH (e.g., Hanisco et al., 2001).

This additional release of OH radicals has significant consequences in the chemistry of the lower stratosphere. In our study the reduction in NO_x from $BrONO_2$ hydrolysis are small (less than 2%) as well as the overall effects on nitrogen partitioning confirming the conclusions of Lary et al. (1996) and Kondo et al. (1997). In contrast, there is substantial repartitioning of the active chlorine families. The catalytic increase in OH due to the hydrolysis of $BrONO_2$ leads to a reduction in the HCl lifetime which is primarily dependent on the aerosol loading (Tie and Brasseur, 1996). The additionally produced OH

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converts further HCl to ClO and, ultimately, to $ClONO_2$. As shown in **Table 3**, ~60% of the HCl decrease, 39% of the ClO increase and 66% of the $ClONO_2$ increase are due to reaction 4 under the Sarychev aerosol loading, thus illustrating a significant enhancement of the coupling between the stratospheric chlorine and bromine photo-chemistry.

5. Stratospheric ozone

5.1 Chemical ozone change

Several studies have demonstrated that the effect of the Pinatubo aerosols on stratospheric ozone depletion at mid-latitudes is particularly significant in winter and spring. For instance, maximum ozone losses of 20-30% were reported for the 12 and 22 km altitude range monitored at some mid-latitude locations during 1993 winter and spring (Hofmann et al., 1994) whereas O_3 decreases of 10-15% occurred for the total ozone column (McGee et al., 1994; Randel et al., 1995). For the mid-latitude total ozone column Tie and Brasseur (1995) calculated reductions of the order of 6% in late winter/early spring. Similar decreases of total ozone were simulated for the summer northern hemisphere by Brasseur and Granier (1992).

It is interesting to estimate the stratospheric ozone depletion induced by the Sarychev eruption which differs from the Pinatubo eruption in terms of aerosol loading, season and latitude of injection, and aerosol residence time. As said above, the model does not directly calculate possible effects of aerosols on stratospheric temperature and circulation. All our simulations use the same transport calculations, whereas ozone loss from Pinatubo in the northern mid-latitudes can be both attributed to chemical and transport (such as increased tropical upwelling) effects (e.g. Telford et al., 2009). In the following, we therefore solely calculate the change in ozone due to photochemistry.

We then compare model simulations with enhanced and background aerosol levels (**Figure 12**). Results indicate chemical reductions in ozone of a few percent following the eruption when aerosol levels are computed from the OSIRIS space-borne data. Accumulated ozone depletion reaches its maximum above Kiruna around mid-September with changes of -1.5% (-20 ppbv) and -2.5% (-25 ppbv) at 16.5 km and 14 km, respectively. Similar ozone changes are simulated when the model is driven by the lower values of aerosol loading taken from STAC in-situ observations whereas when maximum aerosol values from the STAC instrument are used ozone depletion is -2.8% (-25 ppbv) and -4% (-35 ppbv) at 16.5 km and 14 km, respectively (not shown). We clearly see that the reduction increases with decreasing altitude. Ozone depletion values close to the tropopause appear larger than in the lower stratosphere. This conclusion must be taken cautiously because the model does not include detailed influence of various other chemicals (especially organic compounds) entrained from the troposphere into lower stratosphere.

5.2 Chemical mechanisms for the ozone change in the lower stratosphere

In the lower stratosphere ozone removal rates are mainly controlled by the HO_x and halogen catalytic cycles which have been found to typically account for 30-50% and 30% of the total ozone loss respectively, in non-volcanic conditions (Portmann et al., 1999; Salawitch et al., 2005). The NO_x cycles play a relatively minor role in the direct removal of ozone in the lower stratosphere but, as a result of the coupling among the NO_x, HO_x and halogen cycles, the rate of ozone removal is still very sensitive to the concentration of NO_x (Wennberg et al., 1994; Gao et al., 1999; Portmann et al., 1999; Salawitch et al., 2005). Through the reaction of HO_2 with NO ($HO_2 + NO \rightarrow NO_2 + OH$), the decreased NO_x concentrations after the Sarychev eruption result in a larger HO_2/OH ratio (as shown in **Table 3**) than for background conditions (HO_2/OH ratios typically ranging from 4 to 7). Because the photochemical

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removal of ozone in the lower stratosphere is dominated by processes involving HO_2, catalytic ozone destruction by HO_x cycles is likely to be amplified after volcanic eruptions (Wennberg et al., 1994; 1995) though ozone loss rates are limited due to the saturation of the NO_x/NO_y response. After the eruption of Sarychev the effectiveness of halogen cycles is enhanced due to increased ClO_x resulting from OH increase (**Table 3**) (as explained in section 4.1). As said above, heterogeneous reactions activating chlorine are strongly and non-linearly dependent on temperature, implying slow rates at the average mid-latitude temperature conditions (minimum values of 215 K) (Hanson et al., 1994; Webster et al., 1998; Michelsen et al., 1999). Under these conditions the simulated depletion in ozone is restrained similarly to the finding of Tie et al. (1994). Note that in their study ozone reduction was about 5% in the lower summer stratosphere when Pinatubo aerosol SADs were comparable to our observations.

Part of the ozone depletion can be related to the coupled BrO_x/ClO_x cycle which is expected to be responsible for 20-25% of the halogen-controlled loss under non-volcanic aerosol conditions (Portmann et al., 1999; Salawitch et al., 2005). **Table 3** shows that the hydrolysis of $BrONO_2$ accounts for more than 22% of the ozone loss at 16.5 km after the Sarychev eruption. Reaction 4 acts as a source of OH and accordingly reduces the HCl lifetime. This reduction in HCl lifetime is accompanied by an increase in the ClO_x concentration and thereby indirectly couples the atmospheric chemistry of chlorine and bromine to amplify the chlorine-mediated ozone depletion. Because the sticking coefficient for hydrolysis of $BrONO_2$ on sulfate aerosols is not temperature dependent, this effect occurs at all latitudes and seasons in the lower stratosphere during high aerosol loading periods (Lary et al., 1996; Tie and Brasseur, 1996).

6. Summary and conclusions

Our study provides key observations of the chemical perturbation in the lower stratosphere by the moderate Sarychev volcano eruption in June 2009. 3D and 1D CTM simulations are performed to interpret balloon-borne observations of some key chemical species made in the summer high-latitude lower stratosphere. The modelled chemical response to the volcanic aerosols is treated by comparing simulations using background aerosol levels and simulations driven by volcanic aerosol amounts inferred from balloon-borne and space-borne observations.

Quantifying the impact of volcanic aerosols on stratospheric ozone chemistry is difficult as chemical and dynamical (radiative) effects simultaneously occur (Pitari and Rizi, 1993; Robock, 2000). The model is a CTM driven by ECMWF off-line meteorological data and does not describe radiative processes. In other words, volcanic aerosol radiative effects are not directly interactive with the circulation computed by the model. Radiative processes from the injection of volcanic aerosols in the tropics have been shown to have an impact on mean meridional circulation and ozone transport (Brasseur and Granier, 1992; Pitari et Rizi, 1993). In our study, effects of the Sarychev aerosols on mid-latitude stratospheric dynamics, if any, are at least at the first order intrinsically taken into account in the ECMWF analyses used for all simulations. REPROBUS does not take into account the aerosol impact on calculated photolysis rates which is likely to result in some differences between models when this process is computed or ignored (Pitari et Rizi, 1993; Pitari et al., 2014). However because the Sarychev eruption has impacted only mid-latitude lower stratosphere the effect on the photolysis frequency of molecular oxygen and ozone due to absorption and backscattering of solar radiation by the volcanic aerosols is expected to be very small in this region (Tie et al., 1994). Therefore, since all our simulations have been driven with the same wind and temperature fields our approach only estimates the chemical effects of the Sarychev aerosols.

The NO_y chemistry appears to be very sensitive to the increase in SAD within the lower stratosphere resulting from the Sarychev eruption. A decrease in the NO_x abundances is evident but shows some saturation as emphasized in a number of studies referring to cases of high sulfate aerosol loadings (e.g. Fahey et al., 1993). The effect of volcanic aerosols on nitrogen partitioning is also reflected in the

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calculated production of HNO_3 as a result of the decrease of the N_2O_5 nitrogen reservoir from its enhanced hydrolysis and NO_x reduction.

Although direct comparisons in terms of solar illumination, latitude, injection altitudes and temperature are not possible for distinct volcanic eruptions such as Pinatubo and Sarychev, it is interesting to compare the effect of both eruptions on the photochemistry of the lower stratosphere. Overall, although different in magnitude, the eruptions of Pinatubo and Sarychev show similar observed and simulated depletion of NO_2, probably due to the saturation effect of the enhanced N_2O_5 hydrolysis. In comparison with the Pinatubo period, the Sarychev aerosols led to less overall HNO_3 production in the stratosphere possibly because the related HNO_3 enhancement has been shown to be considerably weaker in the lowermost stratosphere (below ~18 km) than for sulfur injection into higher altitudes (Webster et al., 1994; Santee et al., 2004). However, one must notice that previously reported modelling studies on the Pinatubo aerosols were conducted with former chemical kinetic rate constants and photolysis rates which have been largely updated ever since, somewhat adding complexity for comparisons discussed within the present study.

For the Pinatubo aerosols, ozone destruction was not observed throughout the volcanic aerosol layer because N_2O_5 hydrolysis reduced NO_x related ozone loss, which even resulted in small increases of ozone in the middle stratosphere (Bekki and Pyle, 1994; Tie and Brasseur, 1995). For the Sarychev eruption, the volcanic aerosol layer is restrained to altitude levels below 19 km where the ozone destruction processes by HO_x and halogen catalytic cycles are expected to play a major role (e.g. Salawitch et al., 2005) with some sensitivity towards NO_x levels. To summarize, the increased production of HNO_3 via N_2O_5 hydrolysis enhances the photolytic production of OH from HNO_3. As a result, the gas-phase sink for HCl by reaction with OH is slightly enhanced and is associated with an increase of ClO amounts. An important result from the heterogeneous hydrolysis of $BrONO_2$ is the formation and subsequent photolysis of additional HOBr. The OH so produced additionally converts HCl to ClO (and ultimately to $ClONO_2$). Accordingly, there is substantial repartitioning of the active chlorine but effects of the $BrONO_2$ hydrolysis on nitrogen partitioning are insignificant. In this chemical context, the magnitude of the ozone response to the Sarychev volcanic perturbation appears limited (i.e. between -2.5 and -4% at 14 km considering the whole range of observed SADs) because the saturation of the NO_x/NO_y response limits the increase in HO_x and in active chlorine (ClO) by enhanced HO_x, precluding important ozone loss rates. Moreover, stratospheric temperatures remained too high (i.e. mainly above 215 K) for efficient heterogeneous conversion of $ClONO_2$ to active chlorine, which could have led to significant ozone depletion. For these temperature conditions, reaction 2 is not expected to compete with N_2O_5 hydrolysis in the NO_y partitioning (Fahey et al., 1993; Cox et al., 1994). Eventually, the largest ozone destruction is restricted to the lowermost stratosphere (the bottom of the volcanic aerosol layer close to the tropopause) where catalytic cycles are primarily controlled by HO_x and where the NO_x photochemistry plays a very minor role.

However limitations in our model simulations also contribute to some model-measurement discrepancies. A first major difficulty is to drive the model simulations with representative and consistent inputs in term of volcanic aerosol loading. To address this issue, two different model runs for aerosol forcing have been performed, one using OSIRIS satellite data converted to aerosol SAD fields and the other one from in-situ balloon-borne observations. The OSIRIS satellite data represent zonally and daily averaged values of SAD which may vary from a 3D construction based on the local surface areas. The possible presence of aerosol streamers (geographical variations of the aerosol content) resulting from the transport of the volcanic aerosols over the northern hemisphere present from mid-July to September 2009 is likely to affect locally and regionally the N_2O_5 abundances and, to a lesser extent, NO_2 and HNO_3 (Küll et al., 2002; Jucks et al. 1999). If our aerosol SAD dataset had been obtained when the local concentrations were higher than the zonal mean values, then the calculated rate of the heterogeneous reactions would be biased low and calculated NO_x and HNO_3 abundances would be systematically biased high and low respectively. This is not however evident in all our comparisons from simulations based on OSIRIS aerosols. We also note that former studies mostly used 2D simulations to investigate the chemical effects of the enhanced aerosol burden following the Pinatubo eruption with some limitations in terms of meridional transport simulations. The second type of aerosol-constrained simulation uses SADs from balloon-borne observed profiles. By definition, such in situ observations deal with a particular location. Extrapolating in situ derived SADs to drive a 3D model at a large scale may induce inaccurate simulations of the chemical impact of the aerosols (Kondo et al.,

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2000). To account for this SAD-related uncertainty, our simulations based on in-situ data encompass the range of SADs derived from the STAC balloon-borne observations over the August-September 2009 period. Both satellite- and balloon-driven simulations give similar results in terms of NO_2 and HNO_3 amounts possibly because the in-situ observations represent well the aerosol loading at the northern mid-latitudes. Another explanation is that the saturation effect (roughly when SADs become larger than 3 $\mu m^2.cm^{-3}$) of the NO_x/NO_y ratio is more relevant for the range of observed SADs than spatiotemporal inhomogeneities.

Secondly, adequate modelling of transport is also crucial for the partitioning of NO_y. Processes that control the vertical profiles of NO_2 and HNO_3 in the stratosphere are based on a complex interplay between dynamics and chemistry with the key issue to accurately simulate total NO_y which may be not systematically achieved with 3D CTM calculations. Improved simulations of transport can be obtained by combing operational analyses with forecasts to construct 3-hourly meteorological data to drive the CTM (Berthet et al., 2006). We have applied this strategy in the present study. Using 1D modelling driven by in-situ observations or calculating NO_2/HNO_3 ratios to reduce transport effects does not clearly improve the model-measurement comparisons for the lower stratosphere. Although some features in the vertical profiles are not systematically captured by the model, this tends to indicate that the error in calculated transport is not large enough to account for the overall difference between measured and modelled NO_2 and HNO_3 when no volcanic aerosol loading is included in the model. Rather, these results show some evidence of the role of heterogeneous reactions at the surface of volcanic aerosols.

Thirdly, part of the discrepancies between model and observations might be attributed to spatial resolution issues. It may be tricky to compare model calculations with high resolution in-situ profiles and with remote sensing observations integrating over tens of kilometers (Berthet et al., 2007). For instance, discrepancies between remote sensing observations and model calculations have been reported for stratospheric NO_3 in case of localized temperature inhomogeneities as a result of the strong dependence of NO_3 cross sections and kinetics on temperature (Renard et al., 2001). N_2O_5 and NO_2 may be subsequently impacted because NO_3, together with NO_2, plays a central role in the equilibrium reaction controlling N_2O_5 in the gas phase.

In our study, no comprehensive sulfur chemistry is included in the model. We have also excluded dynamical and radiative effects on the ozone response which have been shown to be of primary importance when dense volcanic clouds are present (e.g. Pitari and Rizi, 1993; Kinnison et al., 1994; Tie et al., 1994). In a forthcoming study it would be interesting to compare dynamical/radiative and chemical effects of moderate volcanic eruptions on stratospheric ozone using Chemistry-Climate models with full sulfur chemistry and aerosol-dynamics interactive calculations.

Finally, it might interesting to investigate the effects of other volcanic plumes coming from moderate volcanic eruptions which are then transported to high-latitude regions when stratospheric temperatures are more favourable for chlorine activation and enhanced ozone loss (e.g. in winter). Activation of chlorine from volcanic sulfate aerosols and associated ozone depletion is arguably more significant in the cold temperature conditions of winter/spring, even above the formation threshold of Polar Stratospheric Clouds (Hanson et al., 1994). The eruption of the Calbuco volcano in the southern hemisphere in April 2015 could be a good candidate for the study of this process.

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Appendix A: Technical description

A.1 The STAC aerosol counter

Aerosol size distributions are provided in the 0.4–5 µm diameter size range (Ovarlez and Ovarlez, 1995; Renard et al., 2008). Since 2008, the number of available size classes has been increased from 7 to 14 within this size range (Renard et al., 2010). The counting uncertainty is obtained from the statistical probability given by Poisson counting statistics (Willeke and Liu, 1976). This uncertainty, defined as the relative standard deviation, is 60% for aerosol concentrations of 10^{-3} cm^{-3}, 20% for 10^{-2} cm^{-3}, and 6% for concentrations higher than 10^{-1} cm^{-3}. Laboratory comparisons between two copies of the STAC aerosol counter using identical aerosol samples have shown differences of ±10% for concentrations higher than 10^{-2} cm^{-3}. From these results, we define a measurement precision limited to ±10%. It should be noted that comparisons with the aerosol concentrations measured by the University of Wyoming optical particle counter (Deshler et al., 2003) have shown consistent results between both instruments (Renard et al., 2002). STAC is calibrated in order to provide size distributions of non-absorbing liquid aerosols which have been unambiguously observed in the 8–19 km altitude range in the case of the Sarychev eruption (Jégou et al., 2013). Aerosol distribution moments are derived using well-known analytical expressions. Using a statistical approach as described in Deshler et al. (2003), STAC counting uncertainties (Poisson statistics and the ±10% precision) translate into uncertainties on distribution moments, with estimated values of 40% for SAD. Profiles are typically averaged over a vertical range of 250 m (corresponding to ~1 minute of measurements).

A.2 The SPIRALE in-situ infrared spectrometer

A detailed description of the instrumental characteristics of SPIRALE and of its operating mode can be found in Moreau et al. (2005). Six tunable laser diodes emitting in spectral micro-windows (< 1 cm^{-1}) in the mid-infrared domain (1250 to 3000 cm^{-1}) are used for in situ measurements of trace gas species from the upper troposphere to the stratosphere. The six laser beams are injected into a multipass Heriott cell, comprising two mirrors spaced 3.50 m apart by a telescopic mast, allowing for 434.0 m optical path. This cell is deployed under the gondola during the flight, above ~9 km altitude, i.e. when pressure is below ~300 hPa and thus absorption lines are significantly narrower than the scanned micro-windows. Species concentrations are retrieved from direct absorption, by fitting experimental spectra with spectra calculated using HITRAN 2012 database (Rothman et al., 2013) and the temperature and pressure measured on board the gondola. Measurements of pressure (by two calibrated and temperature-regulated capacitance manometers) and temperature (by two probes made of resistive platinum wire) allow for conversion of the species concentrations to volume mixing ratios. Uncertainties on these parameters are negligible regarding the other uncertainties discussed below. The instrument provides measurements each 1.1 s, thus with a vertical resolution of a few meters depending on the vertical velocity of the balloon (2 to 5 m s^{-1}). Absorption lines in the micro-windows 1260.95-1261.25 cm^{-1}, 1598.45-1598.85 cm^{-1} and 1701.50-1701.80 cm^{-1} were selected for N_2O, NO_2 and HNO_3, respectively. The overall uncertainties for the volume mixing ratios have been assessed by taking into account the random errors and the systematic errors, and combining them as the square root of their quadratic sum (Moreau et al., 2005). There are two important sources of random errors: (1) the fluctuations of the laser background emission signal and (2) the signal-to-noise ratio. These error sources are the main contributions for NO_2 giving a total uncertainty of 30% at the lower altitudes (around 15 km), gradually reduced to 20% around 20 km, and decreasing to 5% at higher altitudes (above 30 km). For HNO_3 these random errors are less significant but two sources of systematic errors have to be considered: the laser line width (an intrinsic characteristic of the laser diode) and the non-linearity of the detectors resulting in an uncertainty of 20% on the whole profile. Concerning N_2O and ozone, which are abundant and measured using detection systems with proper linearity of the photovoltaic conversion, the overall uncertainties are 3% over the whole vertical profile, and decrease from 10% at 14 km (i.e. for mixing ratios below 1 ppmv) to 5% above 17 km, respectively. With respect to the above errors, systematic errors on spectroscopic data (essentially molecular line strength and pressure broadening coefficients) are considered to be negligible for these well studied species (Rothman et al., 2013). SPIRALE has been used routinely during the

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2000's, in particular as part of European projects and satellite validation campaigns (Grossel et al., 2010; Mébarki et al., 2010; Krysztofiak et al., 2012 and 2015, and references therein).

A.3 The DOAS remote-sensing UV-visible spectrometer

Direct solar spectra from two UV/visible DOAS spectrometers are collected onboard the azimuth-controlled LPMA/DOAS (Limb Profile Monitor of the Atmosphere/Differential Optical Absorption Spectroscopy) balloon payload which carries a sun-tracker (Hawat et al., 1995). The solar reference spectrum is usually the spectrum for which the air mass along the line-of-sight and the residual trace gas absorption are minimal. The residual absorption in the solar reference is determined using Langley's extrapolation to zero air mass. Rayleigh and Mie scattering are accounted for by including a third order polynomial in the fitting procedure. The relative wavelength alignment of the absorption cross sections and the solar reference spectrum is fixed and only the measured spectrum is allowed to shift and stretch. O_3 Slant Column Densities (SCDs) are retrieved from the differential structures in the Chappuis absorption band between 545 nm and 615 nm. The line-of-sight absorptions of NO_2 are inferred from the 435 nm to 485 nm wavelength range. Two O_3 absorption cross sections recorded in the laboratory at 230K and 244 K, aligned to cross sections from Voigt et al. (2001), are orthogonalized and fitted simultaneously. Broad band spectral features are represented by a fourth order polynomial. Additional complications arise from the temperature dependence of the NO_2 absorption cross section (Pfeilsticker et al., 1999). The NO_2 analysis is performed using absorption cross sections recorded in the laboratory, scaled and aligned to convolved and orthogonalized cross sections from Harder et al. (1997) taken at 217 K, and 230 K. The error bars of the retrieved SCDs are estimated via Gaussian error propagation mainly from the statistical error given by the fitting routine, the error in determining the residual absorber amount in the solar reference spectrum and the errors of the absorption cross sections. In total, typical accuracies of the DOAS O_3 and NO_2 measurements are better than 5% and 10%, respectively. The retrieval process for NO_2 is described in Butz et al. (2006).

Bromine monoxide (BrO) is detected in the UV wavelength range from 346 nm to 360 nm as recommended by Aliwell et al. (2002). This wavelength range contains the UV vibration absorption bands (4−0 at 354.7 nm, and 5−0 at 348.8 nm) of the $A(^2\pi) \leftarrow X(^2\pi)$ electronic transition of BrO. Typical optical densities are 10^{-4}–10^{-3} for UV vibration absorption bands. The set of reference spectra used contains a NO_2 reference spectrum for T=233 K, and two O_3 spectra at T=197 K and T=253 K, in order to account for temperature effects. All NO_2 and O_3 spectra were recorded with the balloon spectrograph in the laboratory. The BrO reference is the absolute cross-section measured by Wahner et al. (1988), with the wavelength calibration taken from our own laboratory measurements. Profile information was obtained by a least-squares profile inversion technique (Maximum A Posteriori) (Rodgers, 2000). Further details on the BrO DOAS-retrieval and the profile inversion can be found in Harder et al. (1998) and (2000), Aliwell et al. (2002), Dorf et al. (2006b) and Kreycy et al. (2013).

In our study we use the DOAS profile recorded in the stratosphere during the balloon ascent on 7 September 2009 between 15:15 UT (17:15 local time) and 16:35 UT (18:35 local time), corresponding to altitudes of 10 km and 30 km respectively.

A.4 The SALOMON remote-sensing UV-visible spectrometer

The data presented in this study were obtained using a SAOZ-type UV-visible spectrometer (Pommereau and Piquard, 1994) connected to a sun/moon tracker for the detection of ozone and NO_2 amounts. The one-band spectral window of SALOMON between 400 and 950 nm is adequate for the retrieval of absorption features over large spectral ranges, i.e. roughly from 400 to 680 nm for ozone and from 400 to 550 nm for NO_2. The spectrum recorded at float altitude (more than 36.5 km) corresponds to a minimum air mass and is considered as a reference spectrum. Occultation spectra recorded for elevation angles between 0° and -5° below the gondola horizon are taken into account for the retrieval of the SCDs. Owing to the thermal insulation of the spectrometer, no spectral drift of the Fraunhofer lines and no instrumental resolution changes have been observed between the reference and the occultation spectra. The Rayleigh scattering contribution is calculated and removed from the spectra using these profiles and the spectral cross-sections given by Bucholtz (1995). Then, O_3 and NO_2 SCDs are determined by least-squares fits using the University of Bremen high resolution absorption cross-

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sections convolved to the spectral resolution of the instrument (data available from http://www.iup.uni-bremen.de/gruppen/molspec/databases/index.html). Aerosols are a major low frequency spectral contribution which is removed by a high-pass filter to derive the NO_2 SCDs. All lines of sight are not used to derive SCDs since the retrieval is performed only when signal-to-noise ratios (computed in our case by the ratio of the fit maximum amplitude to the standard deviation between the measurement and the fit) are greater than 1. NO_2 fitting errors are typically of 5-9% for SCDs crossing the altitude levels of the volcanic aerosol layer (i.e. below ~19 km). Vertical concentration profiles have been derived using an a posteriori least-squares inversion technique (Rodgers et al., 2000) taking into account the fitting error and the uncertainties of the cross sections. Note that the data reduction method used in this study is described by Renard et al. (2000) and Berthet et al. (2002).

For the flight presented in this study we have added a HR4000 UV spectrometer from Ocean Optics to detect BrO absorption lines in the 346-360 nm range as done for the DOAS instrument. The spectrometer is thermally insulated and regulated using Peltier devices to avoid spectral shifts. It has its own connection to the sun tracker but collects the sunlight simultaneously with a Jobin-Yvon UV-visible spectrometer. We use the same data reduction method as for DOAS as described in details by Dorf et al. (2006b) to retrieve SCDs and the vertical profile of BrO. In our case the Wahner et al. BrO and Bremen ozone and NO_2 cross sections are convolved to the resolution of the instrument determined in the laboratory using a UV lamp. SCD data are smoothed to increase the signal-to-noise ratio. The altitude grid for profile inversion is 2 km. Associated random errors are those provided by the spectral fit. The major systematic error comes from the uncertain estimation of the residual BrO column above float altitude.

Appendix B: Model description

The REPROBUS 3D CTM computes the evolution of 55 species by means of about 160 photolytic gas-phase and heterogeneous reactions, with a time step of 15 minutes in this study. A semi-Lagrangian code transports 40 species or chemical families, typically long-lived tracers but also more unstable compounds (Lefèvre et al., 1994; Lefèvre et al., 1998).

Temperature, winds and surface pressure are specified from the 3D European Centre for Medium-Range Weather Forecast (ECMWF) meteorological data from the surface up to 0.01 hPa (i.e. about 80 km in altitude) on 91 levels. This results in a vertical resolution of about 0.45 km in the lower stratosphere. REPROBUS is driven by 3-hourly ECMWF wind fields obtained by interleaving operational analysis and forecasts because in this way spurious calculation of transport is reduced in comparison with simulations based on 6-hourly analysis (Legras et al., 2005; Berthet et al., 2006).

Gas-phase kinetics parameters used in the present study are based on the recommendation by the Jet-Propulsion-Laboratory (JPL) described in Sander et al. (2011). In particular for nitrogen gas-phase chemistry, revised kinetic data were recommended because, following a number of studies (e.g. Brown et al., 1999; Gao et al., 1999; Jucks et al., 1999; Osterman et al., 1999; Kondo et al., 2000; Prasad, 2003), a lower rate for the reaction of NO_2 with OH and a higher rate for HNO_3 with OH significantly reduced model-measurement discrepancies highlighted in former published work (e.g. Fahey et al., 1993; Kondo et al., 1997; Sen et al., 1998).

The heterogeneous chemistry module includes reactions on liquid aerosols. An analytical expression is used to calculate the equilibrium composition and volume of the H_2SO_4-H_2O droplets as a function of temperature and the total amounts of H_2O and H_2SO_4 (Carslaw et al., 1995). The routine calculates the aqueous phase concentrations for the soluble species HCl, HBr, HOCl, and HOBr to calculate the rates of the heterogeneous reactions involving these compounds on stratospheric liquid aerosols. Reactions of N_2O_5, $ClONO_2$, and $BrONO_2$ on/in sulfuric acid are usually dependent on the species' Henry's law solubility and liquid phase diffusion coefficient in the liquid as well as the surface and/or liquid phase reaction rates (Hanson et al., 1994; Shi et al., 2001; Sander et al., 2011). N_2O_5 hydrolysis takes place at the surface of the particles (Hanson et al., 1994). As in a number of previous studies (e.g. Mills et al., 1993; Gao et al., 1999; Bracher et al., 2005) REPROBUS computes a γ reaction efficiency of 0.1 as default value (0.05-0.2 in Sander et al., 2011) and which is independent of temperature and acid composition. The reaction rate is proportional to γ and increases with aerosol SAD. For heterogeneous

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reactions involving $ClONO_2$, kinetics are taken from the well-detailed uptake model of Shi et al. (2001) which uses the parameterization of H_2SO_4/H_2O composition of Tabazadeh et al. (1997). These processes are strongly functions of the acid composition and temperature. Note that the γ reaction efficiency for $ClONO_2$ described in the JPL recommendation of Sander et al. (2011) is taken from Shi et al. (2001). The $BrONO_2$ reactivity on sulfuric acid particles is computed from the JPL parameterization which is based on the work of Hanson (2003) and shows a rather limited dependence on acid composition and temperature.

Initialized amounts of species are taken from a 2D model long-term simulation (Bekki and Pyle, 1994). Initialization of stratospheric chlorine precursors is based on scenarios defined by the World Meteorological Organization (WMO, 2014). Total inorganic chlorine ($Cl_y = HCl + ClONO_2 + HOCl + ClO + Cl_2O_2$) is calculated by the model, and approaches 3.3 ppbv in the upper stratosphere in 2009, in accordance with the WMO (2014). Note that as expected this value is reduced compared to the study (3.7 ppbv) by Berthet et al. (2005). Total stratospheric inorganic bromine takes into account the contributions from Halons, methyl bromide and very-short-lived bromine compounds to reach 19.5 pptv, matching the scenario given by WMO (2010) updated from Dorf et al. (2006a). The 2D model climatology (Bekki and Pyle, 1994) also provides the initialization of H_2SO_4 mixing ratios for the background aerosols. Liquid particles are formed in equilibrium and are assumed to have a predefined number density. Mean particle radii and SADs of the liquid aerosols are calculated from the number density and the amount of H_2SO_4 and H_2O assuming a lognormal unimodal distribution with a fixed distribution width.

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Table 1: Averaged percentage differences between model calculations and balloon-borne observations (with respect to the measured profile) below 19 km. The model outputs from the one-dimensional version are provided for the SPIRALE flights (see text).

Balloon flight	Observed species	Ref-sim 3D version (no volcanic aerosols)	Bal-sim 3D version (aerosols from balloon data)	Sat-sim 3D version (aerosols from satellite data)	sim 1D version (no volcanic aerosols)	Bal-sim 1D version (aerosols from balloon data)
SPIRALE 7 August 2009 around 02H15 UT	NO_2	+57%	+3±20%	+7%	+54%	+20%
	HNO_3	-3%	+8±4%	+8%	-5%	+3%
	NO_2/HNO_3	+62%	-3±19%	-1%	+60%	+16%
SPIRALE 24 August 2009 around 21H15 UT	NO_2	+56%	-16±20%	-5%	+42%	-7%
	HNO_3	-4%	+8±3%	+6%	-4%	+6%
	NO_2/HNO_3	+63%	-22±20%	-10%	+48%	-12%
SALOMON 25 August 2009 around 19H30 UT	NO_2	+51%	-16±17%	-5%	-	-
	BrO	-66%	-34±12%	-47%	-	-
DOAS 7 September 2009 around 15H45 UT	NO_2	+75%	-12±16%	-7%	-	-
	BrO	-20%	12±6%	+9%	-	-

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Table 2: Averaged percentage differences between the aerosol-constrained and the reference simulations (with respect to the reference) at the dates of the various balloon flights. Differences are provided for 3D and 1D REPROBUS simulations. Calculations are done below 19 km where observations are available, i.e. for the same levels as in **Table 1**.

Date	Species	Bal-sim (3D) - Ref-sim (3D)	Sat-sim (3D) - Ref-sim (3D)	Ref-sim (1D) - Ref-sim (3D)	Bal-sim (1D) - Ref-sim (3D)	Bal-sim (1D) - Ref-sim (1D)
7 August 2009 around 02H15 UT	NO_2	-34±13%	-31%	-3%	-24%	-22%
	HNO_3	+10±4%	+9%	+7%	+15%	+8%
	NO_2/HNO_3	-40±13%	-36%	-9%	-34%	-27%
24 August 2009 around 21H15 UT	NO_2	-46±12%	-39%	-9%	-41%	-34%
	HNO_3	+13±3%	+11%	+2%	+13%	+11%
	NO_2/HNO_3	-52±12%	-44%	-10%	-47%	-41%
25 August 2009 around 19H30 UT	NO_2	-47±10%	-40%	-	-	-
	BrO	181±74%	128%	-	-	-
7 September 2009 around 15H45 UT	NO_2	-50±8%	-47%	-	-	-
	BrO	38±8%	34%	-	-	-

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Table 3: Simulated changes on various stratospheric key species due to the Sarychev volcanic aerosols over the August-September 2009 period at 16.5 km. Calculations are done from the Sat-sim simulation. Effects for daytime and nighttime conditions are provided depending on statistically significant amounts in the diurnal cycle of a given compound. The contribution of $BrONO_2$ hydrolysis to changes on the various species is also shown (see text).

Species	All chemistry				$BrONO_2$ hydrolysis effect	
	12H UT		00H UT		12H UT	00H UT
NO_x	-0.23 ppbv	-44%	-0.19 ppbv	-48%	1.8%	1.1%
NO_2	-0.12 ppbv	-43%	-0.19 ppbv	-48%	1.8%	1.1%
NO	-0.11 ppbv	-45%	---	---	2.0%	---
HNO_3	+0.31 ppbv	+11%	+0.31 ppbv	+11%	-2.3%	-0.9%
N_2O_5	-0.08 ppbv	-80%	-0.12 ppbv	-66%	-3.6%	-3.1%
$ClONO_2$	+0.02 ppbv	+16%	+0.02 ppbv	+22%	66.2%	60.6%
HCl	-0.02 ppbv	-3%	-0.02 ppbv	-3%	58.8%	58.9%
ClO_x	+5.77 pptv	+106%	---	---	39.3%	---
ClO	+5.77 pptv	+106%	---	---	39.3%	---
HOCl	+2.17 pptv	+217%	+1.16 pptv	+346%	47.4%	50.1%
$BrONO_2$	-1.37 pptv	-33%	-4.15 pptv	-70%	18.3%	98%
BrO	+0.94 pptv	+22%	---	---	16.2%	---
HOBr	---	---	+3.89 pptv	+141%	---	98.8%
HO_x	+1.41 pptv	+51%	---	---	24.1%	---
OH	+0.05 pptv	+16%	---	---	44.1%	---
HO_2	+1.36 pptv	+56%	---	---	23.1%	---
O_3	-13.1 ppbv	-1.1%	-12.6 ppbv	-1.1%	22.5%	26.3%

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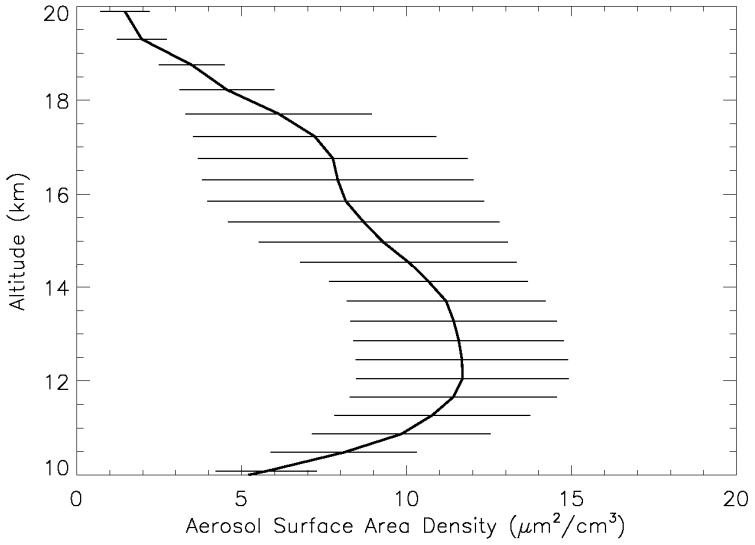

Figure 1: Range of aerosol SAD values derived from several balloon-borne observations in the lower stratosphere in summer 2009. Based on Table 1 in the work of Jégou et al. (2013) this average profile excludes data supposed to be spoiled by balloon outgassing as revealed from simultaneous in situ water vapour observations.

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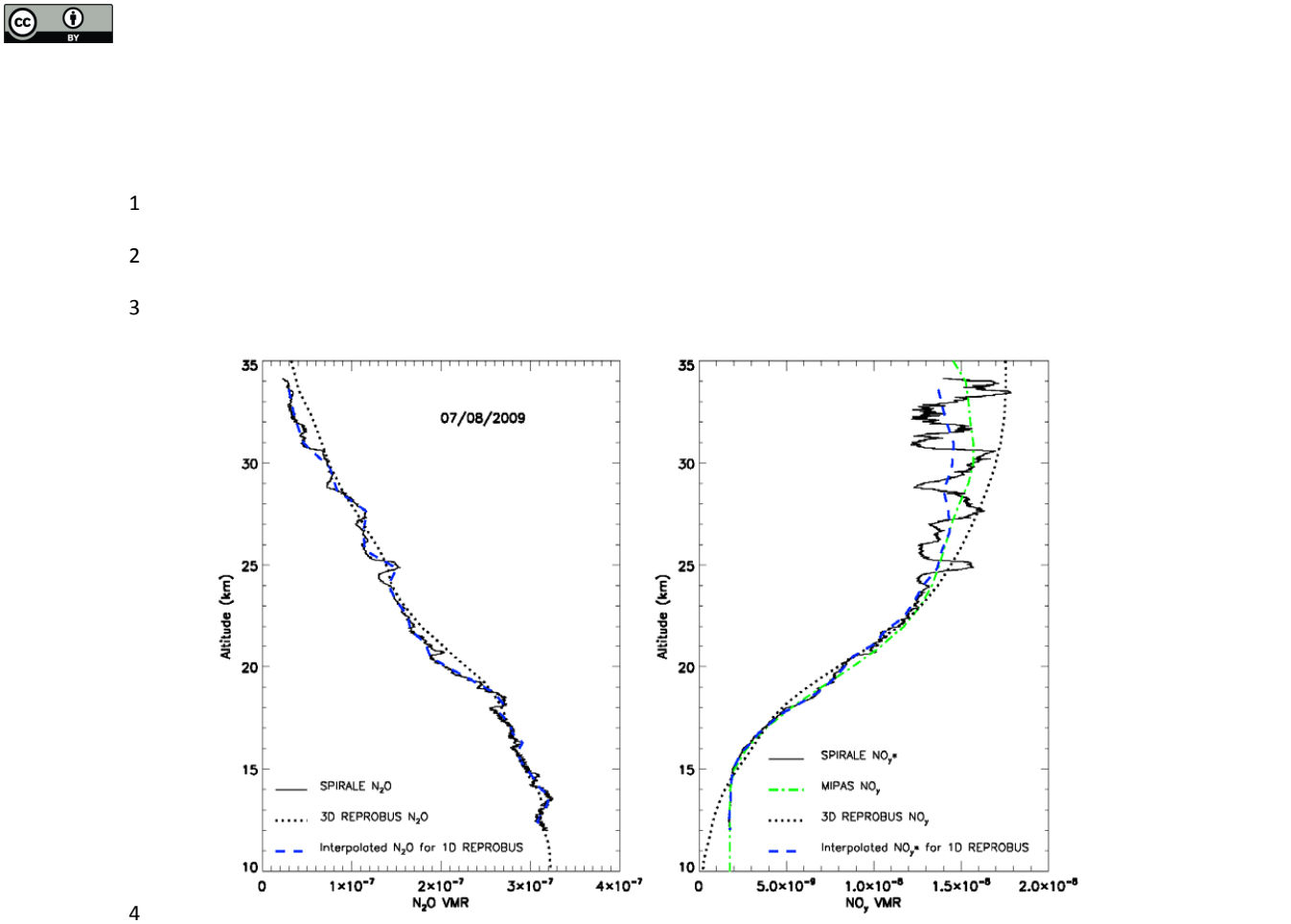

Figure 2: In situ vertical profiles recorded by the SPIRALE instrument used to constrain 1D simulations of the REPROBUS model. Left: profile of N_2O recorded on 7 August 2009 (black line) compared to the results from the 3D version of REPROBUS (dotted line). Right: profile of NO_y inferred from N_2O observations converted using the N_2O-NO_y correlation curve presented in **Figure 3** (referred to as NO_y*). Also shown are the NO_y profiles from the 3D version of REPROBUS (dotted line) and the MIPAS averaged data (green line). The 1D version of REPROBUS is computed with the profiles interpolated to the model resolution (blue lines).

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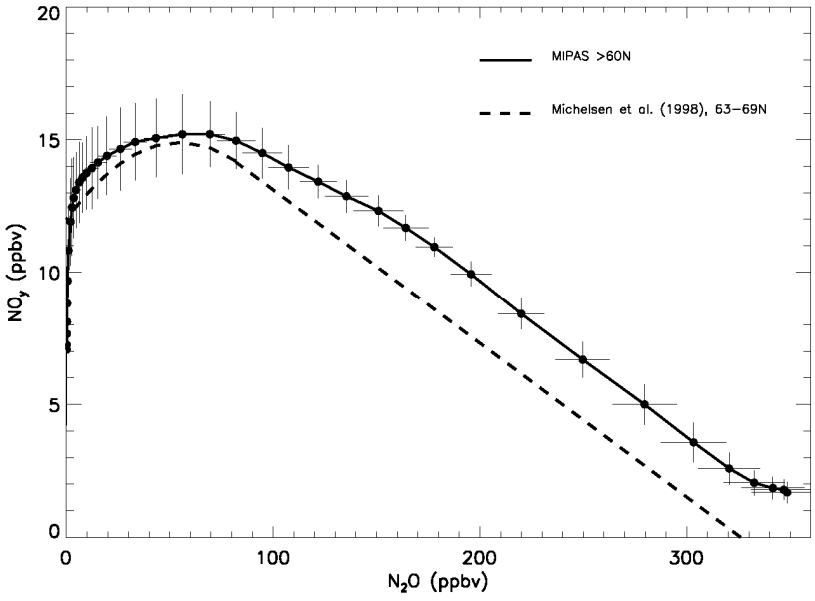

Figure 3: N_2O-NO_y correlation curve inferred from IMK/IAA V5R_220 MIPAS-Envisat data at high latitudes (> 60°N) in July-August 2009 (full line). Error bars reflect the spread of the data. The former Michelsen et al. (1998) correlation is also shown for comparison (dashed line).

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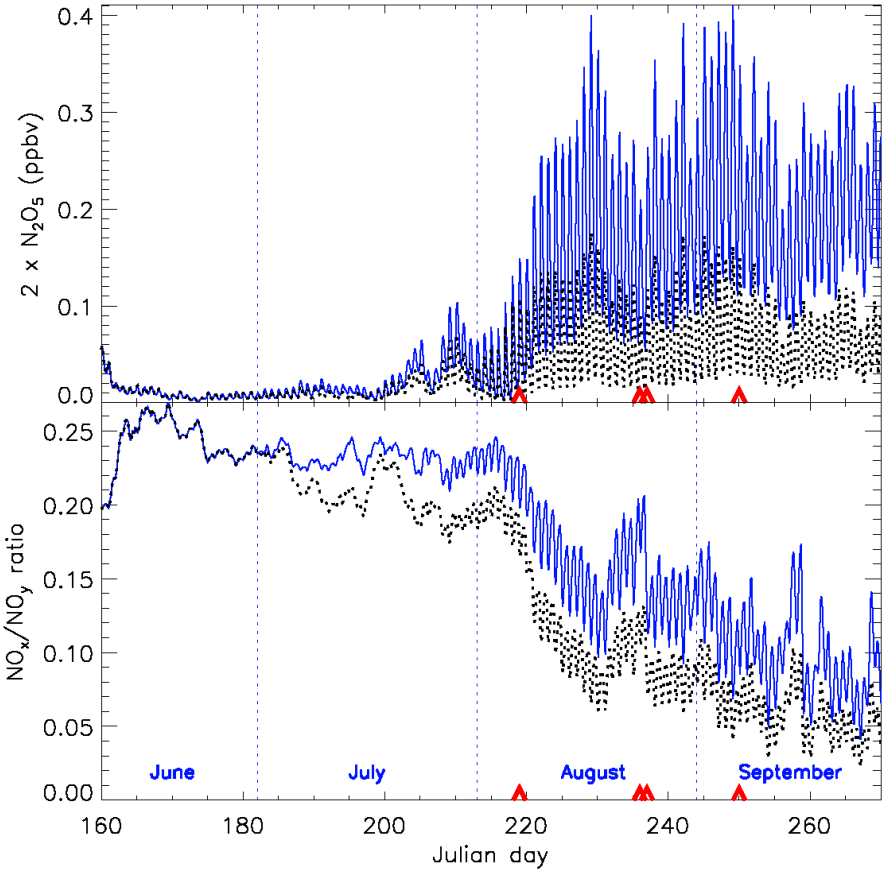

Figure 4: Seasonal variation of N_2O_5 (a) and of the NO_x/NO_y ratio (b) simulated by the REPROBUS CTM above Kiruna in Northern Sweden (67.5°N, 21.0°E) around 17.5 km. The simulation driven by non-volcanic aerosol contents (Ref-sim) is shown in blue. The black dotted line is the REPROBUS simulation driven by volcanic aerosol levels from STAC balloon-borne observations (Bal-sim). Red triangles represent the dates of the balloon flights. N_2O_5 recovery is onset at the beginning of August (day 213 is August 1, 2009) i.e. when SZA become >90°.

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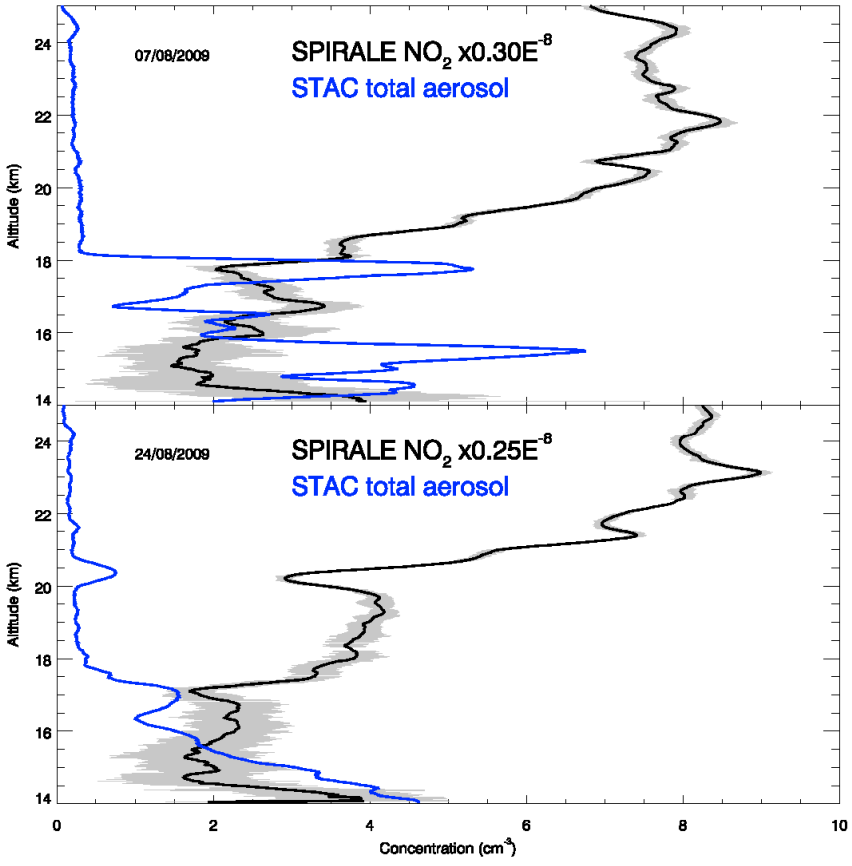

Figure 5: Vertical profiles of NO_2 observed by the SPIRALE balloon-borne instrument (black line) on 7 and 24 August 2009 compared to the total aerosol concentration profiles simultaneously recorded by the STAC aerosol counter (blue line) above Kiruna during balloon ascent. SPIRALE data have been averaged over 250 m (corresponding to ~1 minute of measurements).

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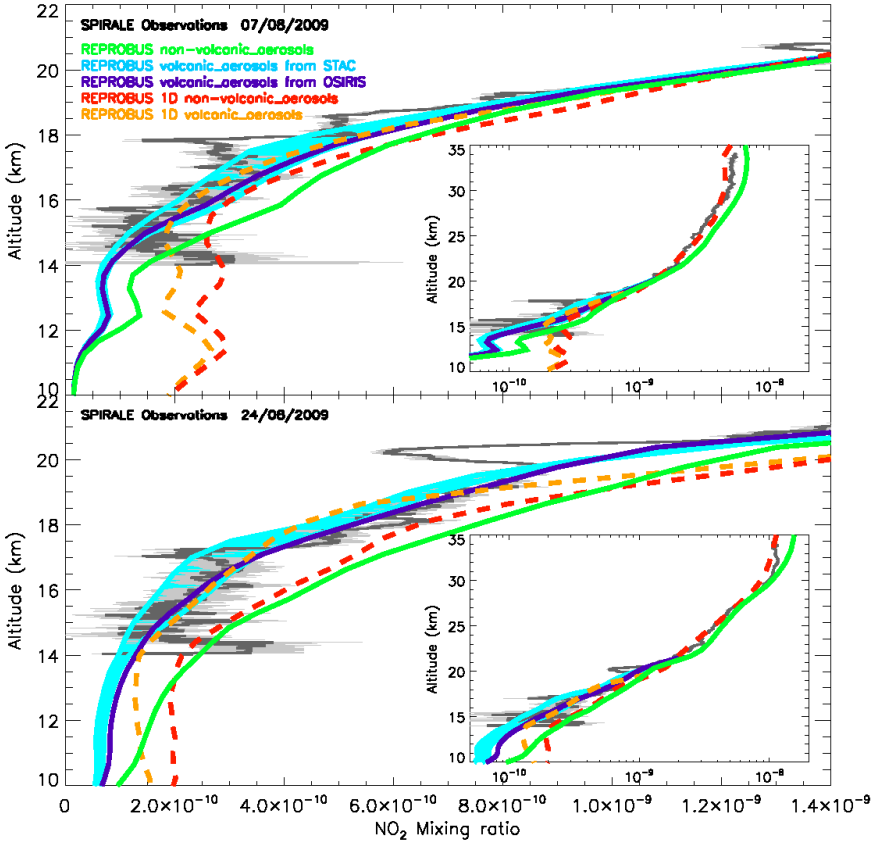

Figure 6: Vertical profile of NO_2 observed by the SPIRALE balloon-borne instrument (black line) above Kiruna during balloon ascent between 02:00 and 02:30 UT for the 7 August 2009 flight (top) and between 21:00 and 21:30 UT for the 24 August 2009 flight (bottom). Model outputs (available every 15 minutes) are provided for the closest location of the instrument and interpolated to the time of observations. Three-dimensional simulations have been driven without volcanic aerosols (green), with volcanic aerosols from balloon-borne observations (blue shaded area) and with volcanic aerosols from satellite data (dark blue line). Results from a one-dimensional (1D) version of the REPROBUS model (dashed lines) computed using hybrid NO_y profiles (NO_y*) derived from the observed profiles of N_2O are also provided (see text), with in red the non-volcanic reference simulations and in orange the calculations driven with volcanic aerosols from the mean observed balloon-borne profile presented in **Figure 1**.

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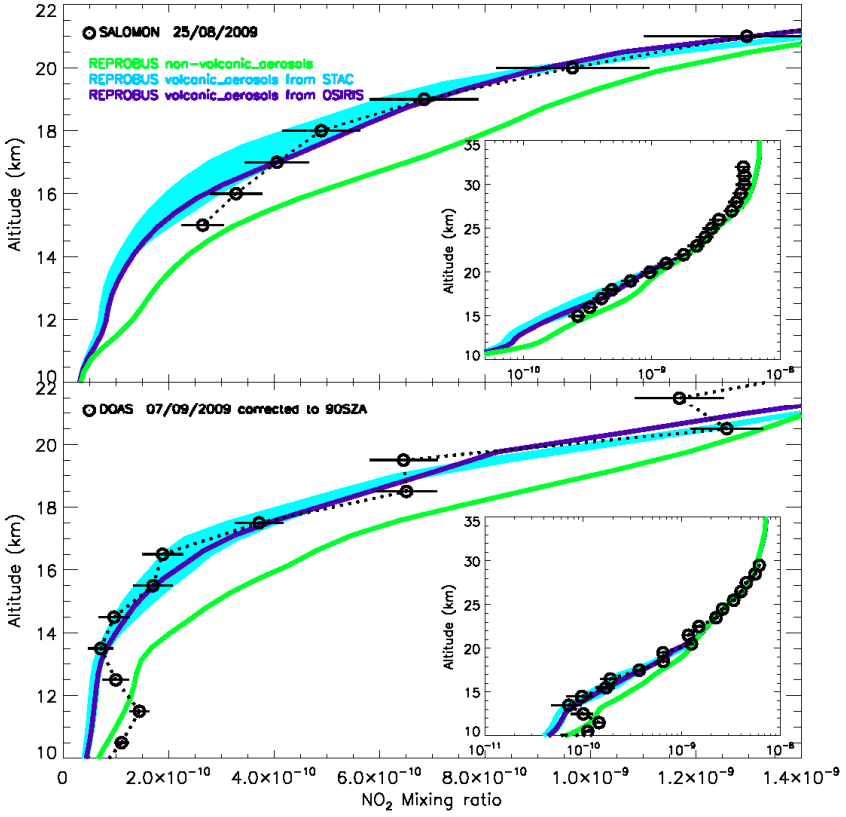

Figure 7: (top) Vertical profile of NO_2 recorded by the SALOMON instrument (black lines) obtained during solar occultation between 18:50 and 19:30 UT on 25 August 2009 above Kiruna. Chemistry-transport model simulations computed with no volcanic aerosols (green line), with volcanic aerosols from balloon-borne observations (blue shaded area) and with volcanic aerosols from satellite data (dark blue line) are shown. The model output is provided for the closest location of the tangent points. (bottom) Vertical profile of NO_2 recorded by the DOAS instrument (black lines) on 7 September 2009 above Kiruna. The DOAS profile has been recorded during the balloon ascent and has been converted to 90°SZA (~17:30 UT) as well as the simulated profile.

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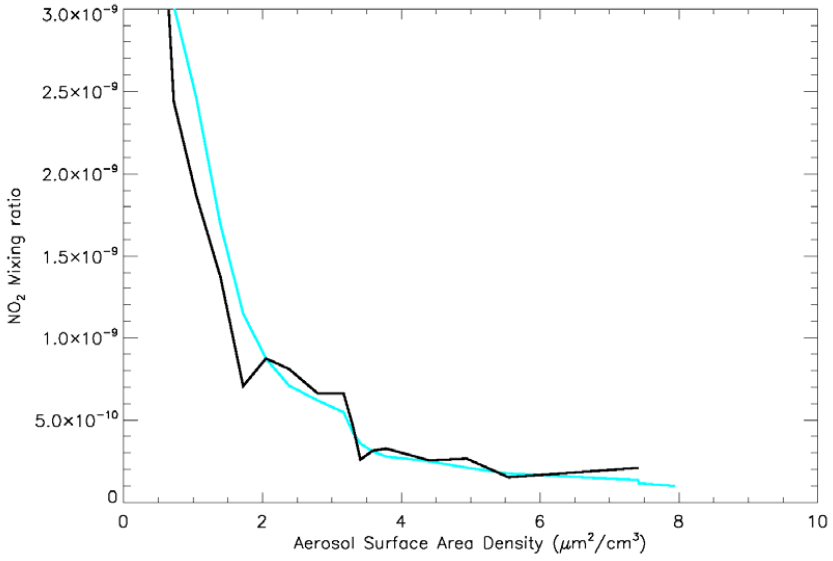

Figure 8: NO_2 mixing ratio as a function of aerosol SAD as simultaneously observed in the lower stratosphere by the SPIRALE and STAC instruments on 24 August 2009 (black curve). The result from the REPROBUS Bal-sim simulation is also plotted (blue curve).

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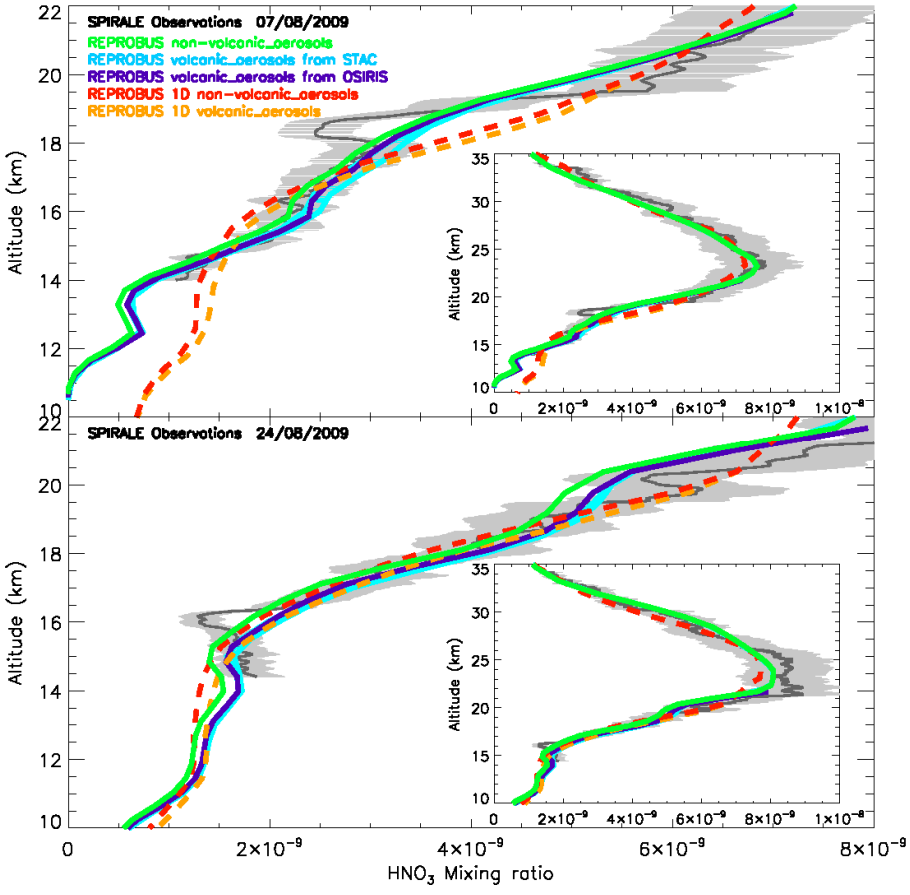

Figure 9: same as **Figure 6** but for HNO_3.

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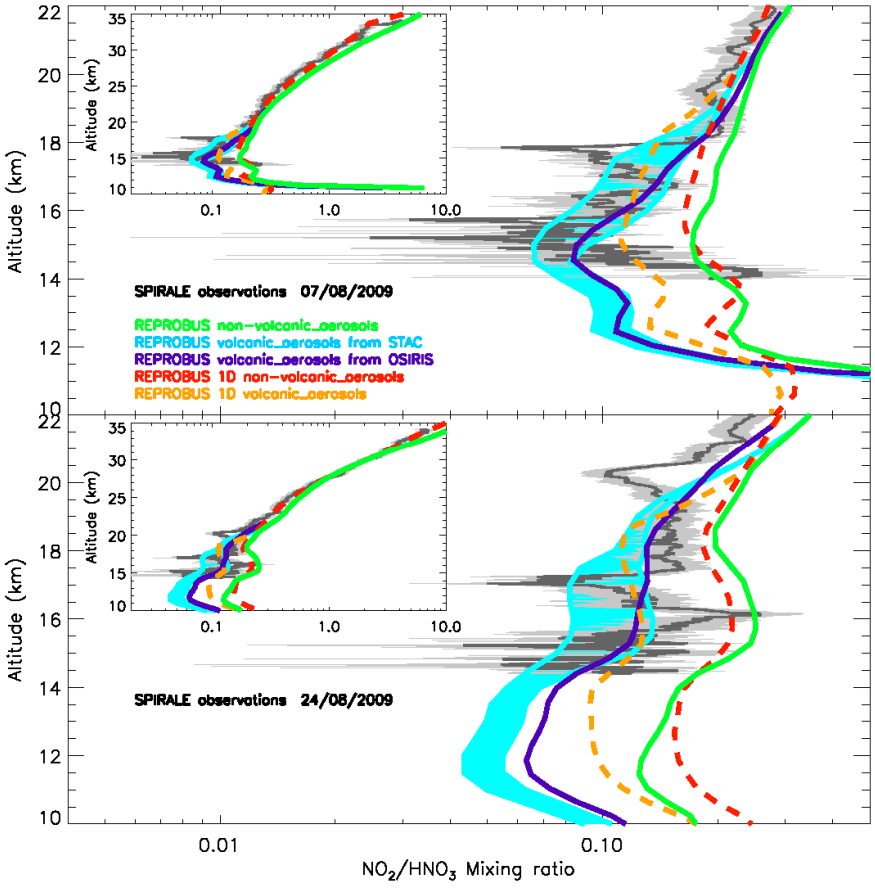

Figure 10: same as **Figure 8** but for the NO_2/HNO_3 ratio.

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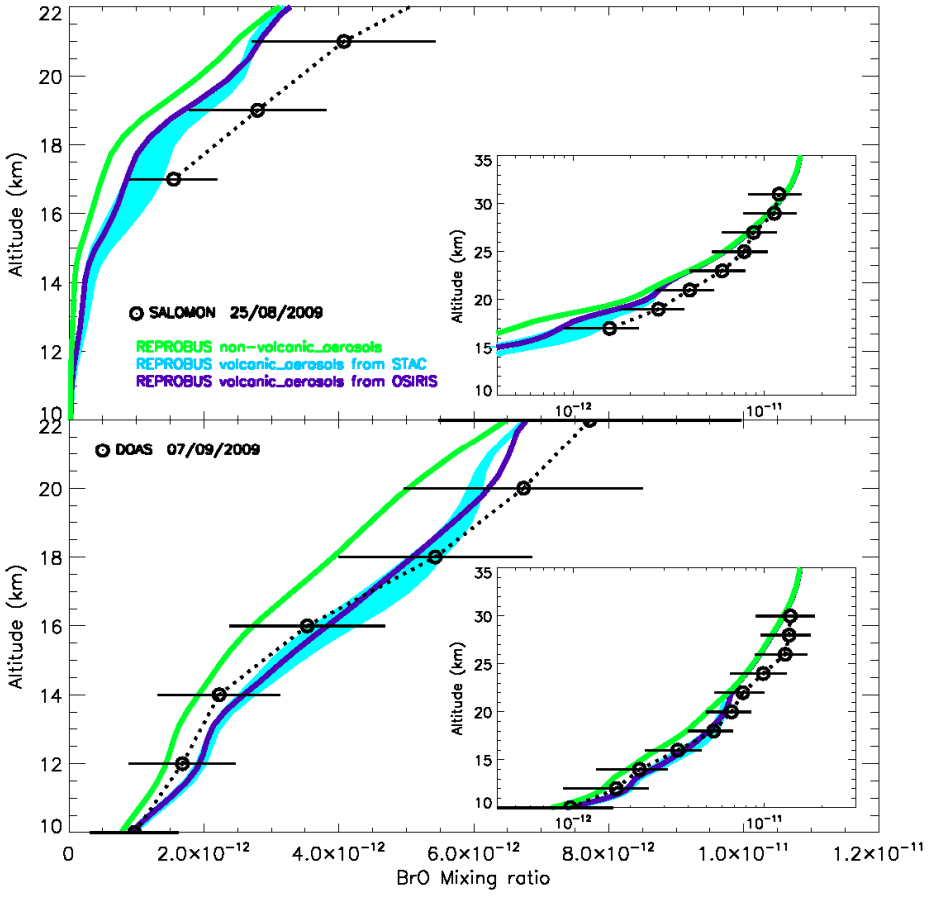

Figure 11: same as **Figure 7** but for BrO. The BrO profile from DOAS in the lower stratosphere has been obtained between 15:15 and 15:55 UT.

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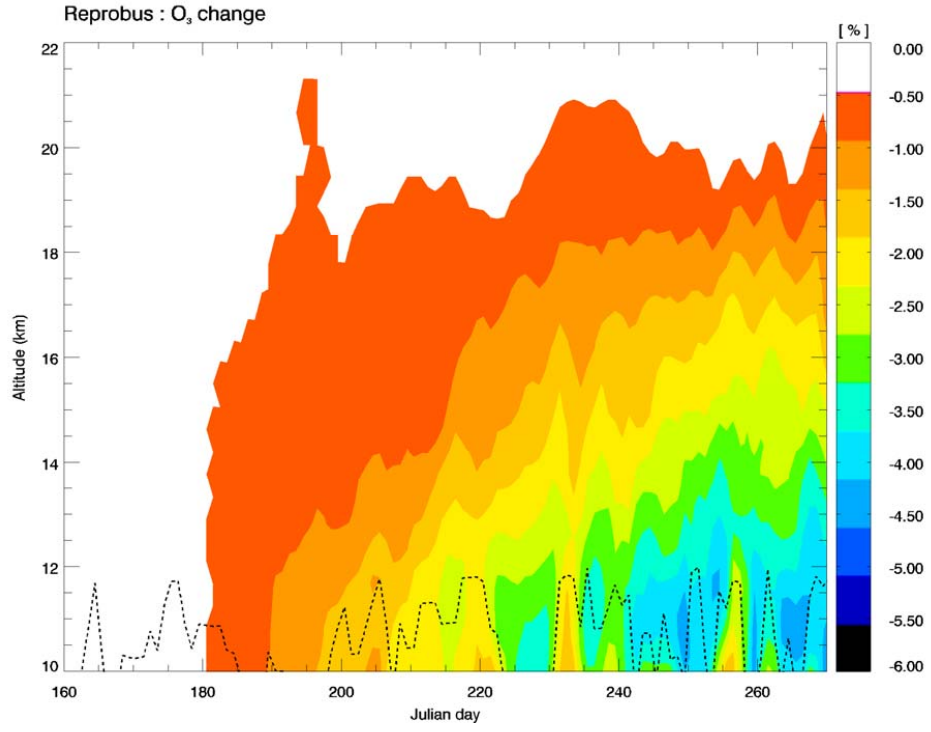

Figure 12: Percentage changes in ozone over Kiruna (67.5°N, 21.0°E) as a function of altitude and time between 1 July and 1 October 2009. Calculations are done by subtracting outputs from the volcanic simulation driven by OSIRIS observations with the background simulation. The position of the tropopause is given by the black dotted line.