Answers to Reviewer#1

We thank the reviewer for his/her comments on the manuscript. Hereafter, please find point-by-point answers.

Reviewer's comment: "The main purpose of this paper is to present measurements of various NOy family species from several balloon flights through a region of volcanically enhanced aerosol surface area density, then show that the observations are consistent with chemical perturbations calculated by a 3D chemistry transport model driven with reanalysis meteorology. The paper also presents estimates of O3 depletion caused by the volcanic aerosols and discusses chemical perturbations to the inorganic Br and Cl families. The measurements confirm our existing understanding of the role of heterogeneous chemistry in NOy partitioning; this is not new science."

→ Our goal is not to discuss the general understanding of the role of heterogeneous chemistry on NO_y partitioning which, we agree with the reviewer, has been widely investigated. We aim at quantifying for one of the first times (if we consider the work of Adams et al. 2016 in ACPD) the chemical impact of "moderate" volcanic eruptions (focusing here on the Sarychev eruption because high-resolution data are available, see below) which are supposed to be the main explanation (possibly together with the increasing SO_2 emissions in Asia) for the increase in the stratospheric aerosol content over the past 15 years (Vernier et al., GRL, 2011). We specifically investigate this eruption because stratospheric chemistry is impacted from August to November, i.e. in extra-vortex and high temperature conditions, precluding polar winter processes.

The manuscript is not only focused on effects on nitrogen chemistry but also on bromine through measurements of stratospheric BrO which are made by a very limited number of teams in the world, and rarely obtained in high aerosol loading conditions. An interesting result is that chlorine partitioning is significantly controlled by enhanced $BrONO_2$ hydrolysis through further production of OH when $ClONO_2$ hydrolysis is not efficient.

An interest is to try provide some comparisons with the Pinatubo effects though both events are not easily comparable as a result of various features (e.g. altitude/latitude of injection) as said in the manuscript.

Also, we provide for the first time high-resolution data obtained within the volcanic plume from a moderate eruption to investigate locally the chemical effects. The limited vertical extent of the aerosol plume produced by this kind of eruption in comparison with the Pinatubo event requires (rare) observations well resolving the lower stratosphere. This is not easily achieved by space-borne instruments.

To summarize, we are convinced that it is new and of interest to investigate stratospheric chemistry and effects on ozone using valuable tools in a "background" aerosol loading context which is different from the very low aerosol content situation in the late 90's and early 2000 years, especially when almost no one has done it and considering that the scientific community has been using the Pinatubo major eruption as the only reference so far.

Reviewer's comment: "The paper is quite long for the content. The abstract describes what is in the paper, but it is unclear whether the results are new or significant. The Intro describes the study as "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", but the authors' have not shown how this advances the state of knowledge in this field, which is already well studied."

→ Following our answer to the previous reviewer's comment, we have modified the abstract and introduction accordingly. We better describe the rationale of our study, i.e. focus on a mid-latitude eruption in a high-temperature stratospheric context. Finally, we can argue that our investigation of a specific moderate volcanic event initiates future quantification of the possible chemical impacts resulting from the series of eruptions since the beginning of the 21st century, especially those occurring in the tropics (with longer aerosol residence times) and/or in winter (low temperature conditions enhancing chlorine catalytic cycles).

In the abstract, we have modified the text:
"…only "moderate" but recurrent volcanic eruptions have modulated the stratospheric aerosol loading and are assumed to be one cause for the reported increase in the global aerosol content over the past 15 years. This particular enhanced aerosol context raises questions about the effects on stratospheric chemistry which depend on the latitude, altitude and season of injection. In this study, we focus on the mid-latitude Sarychev volcano eruption in June 2009 which injected 0.9 Tg of sulfur dioxide (about 20 times less than Pinatubo) in a lower stratosphere mainly governed by high stratospheric temperatures. Together with in situ measurements of aerosol amounts, we analyse high-resolution in situ and/or remote-sensing observations of NO_2, HNO_3 and BrO from balloon-borne infrared and UV-visible spectrometers launched in Sweden in August-September 2009."

We have also added: "We show that the chlorine partitioning is significantly controlled by enhanced $BrONO_2$ hydrolysis."

And added at the end of the abstract: "…the simulated chemical ozone loss due to the Sarychev aerosols is low with a reduction of -22 ppbv (-1.5%) of the ozone budget around 16 km. This is at least 10 times lower than the maximum ozone depletion from chemical processes (up to -20%) reported in the northern hemisphere lower stratosphere over the first year following the Pinatubo eruption. This study suggests that moderate volcanic eruptions have limited chemical effects when occurring at mid-latitudes (restricting residence times) and outside winter periods (high temperature conditions). However, among the other reported moderate eruptions it would be of interest to investigate longer lasting tropical volcanic plumes or sulfur injections in the wintertime low temperature conditions."

The end of the introduction has been changed to:
"…In periods following major eruptions, the year-to-year variability in stratospheric ozone at northern mid-latitudes appears closely linked to dynamical changes induced by the volcanic aerosol radiative perturbation (e.g. Telford et al., 2009; Aquila et al., 2013) and to changes in chlorine partitioning (e.g. Solomon et al., 1999; Chipperfield, 1999). Effects on stratospheric chemistry are expected in periods of elevated chlorine levels from anthropogenic activities (Tie and Brasseur, 1995; Solomon et al., 1996)... Their effects depend on the amount of released SO_2 and on latitudes and altitudes of injection which directly influence aerosol residence times. The season of the eruption is also important for photochemical processes which are directly connected to temperatures and solar illuminations.
The goal of this paper is to show how such moderate eruptions are likely to modify the chemical balance of the northern hemisphere lower stratosphere at periods excluding wintertime/springtime halogen-activating photochemistry. We specifically focus on the eruption of the Sarychev volcano on 15 and 16 June 2009 which injected 0.9 Tg of sulfur dioxide in the lower stratosphere (Clarisse et al., 2012) resulting in enhanced sulfate aerosol loading up to 19 km, for a period of about 8 months ending before winter (Haywood et al., 2010; Kravitz et al., 2011; O'Neill et al., 2012; Jégou et al., 2013).
The approach consists in analysing some key aspects of lower stratospheric chemistry and ozone loss in a context of high aerosol surface area densities and high stratospheric temperatures using balloon-borne observations conducted in August-September 2009 from Kiruna/Esrange in Sweden (67.5°N, 21.0°E) within the frame of the STRAPOLETE project. To our knowledge we show here the first high-resolution in situ observations of chemical compounds obtained within the volcanic aerosol plume of a moderate eruption. We show that at the period on which the study is focused N_2O_5 has reformed and the role of its hydrolysis becomes important again after the sunlit summer period justifying the use of these balloon data for the investigation of heterogeneous processes. Aerosol-constrained simulations using a 3D Chemistry Transport Model (CTM) are compared to the observations. These model calculations ignore possible dynamical effects induced by the volcanic aerosols but are used to estimate the amplitude of the chemical impacts and ozone loss with some comparisons with the post-Pinatubo eruption period."

Reviewer's comment: "Just how well studied this is, is indicated by the 136 references given and that the majority of them are dated before 2000. The authors may not be aware of relevant recent results. For example, they state that most models used to estimate chemical effects of aerosols are 2D models (p. 15, line 50) but this was true 10 years ago. Recent results using 3D models are overlooked (e.g., a CCM study by Aquila et al, JAS 2013, and a CTM study by Dhomse et al., GRL 2015). These recent papers also confirm our understanding of the role of volcanic aerosols in NOy partitioning by showing good model agreement with observations. This underscores my concern that there is not new science in this manuscript."

→ The reviewer is right, 3D modelling studies of the Pinatubo eruption and its impact on stratospheric ozone have been available since the years 2000. We have removed the following sentence highlighted by the reviewer (p. 15, line 50 in the ACPD version): "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".

However, most of these recent studies mentioned by the reviewer focus on the dynamical mechanisms influencing ozone variability and hemispheric asymmetries in a volcanically perturbed stratosphere (and all cases, the post-Pinatubo eruption period). Though both papers cited by the reviewer present responses of NO_2, and not only of ozone, to the Pinatubo aerosols they deal with a different issue than our work which is centred on detailed stratospheric chemistry allowing to estimate the halogen effect on ozone loss, specifically in the northern hemisphere.

Anyway, we have added some references dealing with 3D model calculations in the introduction, section 5.1 (together with the Telford et al. (2009) paper which is already cited) and/or in the final discussion: Al-Saadi et al. (2001), Aquila et al. (2013) and Dhomse et al. (2015).

Reviewer's comment: "The style is verbose and the writing can be confusing. Here is an example (starting line 47, p. 4). We are told that solar zenith angle impacts the retrieved profile so it needs correction with a photochemical model, but then we are told that using such a model would introduce larger errors in the retrieval (so it's a bad idea to correct?). In the next paragraph they estimate the correction anyway, saying it is only 3%. But then they cite the correction as being a 24% effect on a particular balloon flight. I don't know what to conclude here, there is no clear message."

→ We mean that a photochemical correction is not systematically used for remote sensing observations. The applicability of this correction procedure has been widely discussed in the literature as reported in the former works provided in our manuscript and might vary from one study to another because: 1) the need to apply this procedure depends on a combination of different parameters such as the considered chemical compound, the observation geometry (i.e. balloon ascent or occultation) and daytime (SZA variation) and 2) using theoretical (model) calculations to correct measurements requires good knowledge of the diurnal variation of the retrieved species and is likely to depend on the model used.

To avoid confusion in this part of the manuscript we have removed the sentence: "However, some retrievals from occultation measurements do not include corrections for diurnal variations in 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)."

We now write:
"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). Some works propose to use a photochemical model to correct for this effect (e.g. Harder et al., 2000; Butz et al., 2006) depending on

the considered chemical compound, the observation geometry (i.e. balloon ascent or occultation) and daytime (SZA variation). Typically concentrations are converted to values expected at 90° SZA.

In our study, the NO_2 profile from the SALOMON instrument recorded on 25 August 2009 from a typical solar occultation at constant float altitude is not photochemically corrected since conversion to 90° SZA conditions results in differences of less than 6%, in agreement with the work of Payan et al. (1999). 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 is done for SZA = 90°."

Reviewer's comment: "A paragraph on p. 13 gives a quantitative estimate of the impact of aerosols on O3 depletion using a simulation with varying amounts of aerosols. At the end of the paragraph we are told not to take the results too seriously because the model is missing (presumably) relevant chemical reactions. These two examples illustrate a common problem with the manuscript: a meandering discussion without a clear message."

→ About the last sentence of paragraph 5.1 (p13 line 37 in the ACPD version), we are specifically referring here to model calculations at (or very close to) the tropopause. We were mentioning that the model is driven with stratospheric chemistry and does not account for the detailed chemistry of tropospheric organic compounds (e.g. PAN, etc.) possibly impacting the ozone budget (production in the case of PAN) at (or very close to) the tropopause level.

However, we agree that the writing might be confusing and we have removed the sentence since it becomes obsolete when absolute ozone destruction values (in ppbv) are shown as suggested by reviewer 2.

Reviewer's comment: "The manuscript, not counting tables, figures, and captions, is more than 10,000 words. This is too long for the presentation of a few balloon profiles and model simulations that show aerosol impacts. The information in Tables 1 and 2 shows percentage disagreements between simulations and observations. This is unnecessary and corresponding figures that show model/data comparisons are sufficient."

→ We agree that some parts of the manuscript can be shortened as suggested by the reviewer. Some sections have been reorganized. However note that some details have been added at some specific locations in the manuscript as required by reviewer 2.

Firstly, the information provided in (now former) section 3.1 about the robustness of the transport calculation before investigating photochemical issues and heterogeneous processes has been reduced: the 2 first sentences and some associated references (dealing with simulation of N_2O and NO_y as a test for correct simulation of transport) have been removed. For consistency, part of the discussion about transport issues has been moved to section 2.2 because it actually deals with the model description. Also as a matter of consistency, the second half of (now former) section 3.1 and explaining how the in situ profile of NOy* is obtained has been moved to the discussion about 1D calculations.

Secondly, the general description of the photochemical polar summer conditions (first paragraph in former section 3.2 which is now section 3.1) is not very useful and has been removed since it focuses on the period (~May-July) prior to the balloon campaign (August-September) on which is based our study. The text in former section 3.2 (now section 3.1) has been changed to:

"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. Polar summer is characterised by continuous solar illumination preventing the formation of N_2O_5 (Fahey and Ravishankara, 1999) until about the beginning of August (Brühl et al., 1998), i.e. around day 213 for the considered Esrange/Kiruna location as illustrated in **Figure 3** at 17.5 km…

This situation implies that the balloon flights performed from August 7, 2009 in the Kiruna region match the photochemical conditions for which volcanic aerosols likely have an impact on NO_y partitioning via elevated N_2O_5 hydrolysis and can be suitably used to investigate heterogeneous processes."

Thirdly, the description of the model-measurement comparisons (Section 3) has been shortened from ~5 to less than 3 pages. Former sections 3.4 (HNO_3) and 3.5 (NO_2/HNO_3 ratio) have been merged and reduced. The description and discussion of one-dimensional model calculations have been transferred to the new section 3.2 (NO_2). Discussion about the NO_x saturation effect and the description of figure 8 have been simplified.
All simulations are only shown for NO_2 (now figure 5). As a result, the following figures have been simplified for better clarity and to lighten the associated discussions. Former figure 9 (HNO_3) has been removed.

Table 1 and Table 2 have been removed.

Section 4 about impacts on halogen chemistry has been reduced too: HCl injection discussion in section 4.1 has been shortened. Some sentences have been simplified.

Some sentences have been shortened (in particular references about Pinatubo effects on ozone) in section 5.1.

→ New figures' numbering:

Former figure 1 is now figure 2
Former figure 2 is now figure 1
Former figure 3 is now figure 7
Former figure 4 is now figure 3
Former figure 5 is now figure 4
Former figure 6 is now figure 5
Former figure 7 is now figure 6

→ Some grammatical/typo (e.g. 'in situ' instead of 'in-situ') and other minor writing errors have been corrected throughout the text.

Answers to Reviewer#2

We thank the reviewer for his/her constructive comments which help us to improve the manuscript. Please find below our point-by-point answers.

Reviewer's comment: "However, the reasoning for exploring the effect of a moderate eruption on chemical composition at Arctic latitudes in summer must be better rationalized in the introduction. Why is this important? Currently only the relevant chemical, aerosol and some dynamical processes are explained."

→ We agree with the reviewer that our introduction and the abstract can be misleading. We better explain the rationale of our study in the abstract and in the introduction.

Our main point is to study the enhanced aerosol effects in mid-latitude and high temperature conditions, not to specifically focus on impacts on polar summer chemistry which typically correspond to the late spring-July period (see POLARIS campaigns and Fahey and Ravishankara, Science, 1999). Here we pay attention on the August-September period for which we explain in new section 3.1 (formerly section 3.2 in the ACPD version) that photochemical conditions closely reflect mid-latitude conditions even at 68°N. Note that is why the title does not mention "polar summer" and remains rather general.

Because these recurrent moderate eruptions span different characteristics in terms of latitude and altitude of injection (directly connected to aerosol residence times), and season (temperature effects, solar illumination for photochemical issues), different associated potential impacts on stratospheric chemistry and ozone are expected. The goal of the paper is to focus on the specific extra-vortex situation outside the wintertime low temperature conditions (i.e. comparable to mid-latitude conditions). A next step would be to investigate tropical eruptions (situation for the Kelud eruption) or injections in winter with some volcanic aerosols trapped in the polar vortex (situation for the Calbuco eruption).

We have therefore modified the end of the introduction:

"…In periods following major eruptions, the year-to-year variability in stratospheric ozone at northern mid-latitudes appears closely linked to dynamical changes induced by the volcanic aerosol radiative perturbation (e.g. Telford et al., 2009; Aquila et al., 2013) and to changes in chlorine partitioning (e.g. Solomon et al., 1999; Chipperfield, 1999). Effects on stratospheric chemistry are expected in periods of elevated chlorine levels from anthropogenic activities (Tie and Brasseur, 1995; Solomon et al., 1996)... Their effects depend on the amount of released SO_2 and on latitudes and altitudes of injection which directly influence aerosol residence times. The season of the eruption is also important for photochemical processes which are directly connected to temperatures and solar illuminations.

The goal of this paper is to show how such moderate eruptions are likely to modify the chemical balance of the northern hemisphere lower stratosphere at periods excluding wintertime/springtime halogen-activating photochemistry. We specifically focus on the eruption of the Sarychev volcano on 15 and 16 June 2009 which injected 0.9 Tg of sulfur dioxide in the lower stratosphere (Clarisse et al., 2012) resulting in enhanced sulfate aerosol loading up to 19 km, for a period of about 8 months ending before winter (Haywood et al., 2010; Kravitz et al., 2011; O'Neill et al., 2012; Jégou et al., 2013).

The approach consists in analysing some key aspects of lower stratospheric chemistry and ozone loss in a context of high aerosol surface area densities and high stratospheric temperatures using balloon-borne observations conducted in August-September 2009 from Kiruna/Esrange in Sweden (67.5°N, 21.0°E) within the frame of the STRAPOLETE project. To our knowledge we show here the first high-resolution in situ observations of chemical compounds obtained within the volcanic aerosol plume of a moderate eruption. We show that at the period on which the study is focused N_2O_5 has reformed and the role of its hydrolysis becomes important again after the sunlit summer period justifying the use of these balloon data for the investigation of heterogeneous processes. Aerosol-constrained simulations using a 3D Chemistry Transport Model (CTM) are compared to the observations. These model calculations ignore possible dynamical effects induced by the volcanic aerosols but are used to estimate the amplitude of the chemical impacts and ozone loss with some comparisons with the post-Pinatubo eruption period."

We have also added in the last paragraph in new section 3.1 (formerly section 3.2 in the ACPD version): “This situation implies that the balloon flights performed from August 7, 2009 in the Kiruna region match the photochemical conditions for which volcanic aerosols likely have an impact on NO_y partitioning via elevated N_2O_5 hydrolysis and can be suitably used to investigate heterogeneous processes.”

Reviewer’s comment: “From the satellite data presented in Haywood (2010) and Jegou (2013) and also Fig.5 it seems obvious that the plume is not homogeneously mixed over the Arctic region by August/September 2009. Therefore the expected horizontal and vertical structure has to be discussed in some more detail.
The STAC balloon data from different flights needs to be introduced in Fig. 1 (e.g. grey underlayed traces?), not just ranges of the observations so the reader gets a better impression of the vertical structure of the plume and its variability. Horiz. and vertical variability should be discussed at least. Currently no filtering for high/low or even background aerosol regions is done for the interpretation of the data which may well be warranted but must be better supported.”

→ If we have well understood the reviewer’s point, our description about the mixing state of the Sarychev plume in section 2.2 (model calculations) is not consistent with results reported in the literature. It is true that space-borne data shown by Haywood et al. (2010) and Jégou et al. (2013) reflect still unmixed conditions throughout August-September 2009. In this case our discussion about the Sarychev aerosol spatial distribution in section 2.2 is not convincing and even contradictory with respect to the results presented in Figure 5 (now Figure 4 in the revised version; the new figure numbering is provided at the end of this reply). Actually, the two simulations driven by the STAC balloon-borne aerosol observations have been performed to account for the aerosol spatial inhomogeneity. In other words the two cases correspond to the 1-sigma spread of the in situ SAD observations by the STAC instrument reflecting the range of variability of the aerosol content over the northern hemisphere.

Figure 1 (which is now figure 2) has been modified accordingly. It now includes the various STAC data (average between balloon ascent and descent) and the two profiles inferred from the 1-sigma of the mean used for the Bal-sim simulation. The STAC profiles have been interpolated to a fixed 500-m vertical scale and smoothed (over 3 points, i.e. less than the plot presented on the first version of the manuscript). We have excluded data from two flights (2nd and 26th August) for which balloon outgassing is suspected as deduced from joint water vapour measurements. Also, flights revealing the sporadic presence of clouds are not considered to derive the range of SAD below 12 km.

As a result, the text in section 2.2 has been changed to:

“We have conducted another type of simulation (hereafter called Bal-sim) consisting in adjusting the input H_2SO_4 mixing ratios so that the model output matches SADs observed by the STAC aerosol counter. Although similar aerosol SAD values were observed by Kravitz et al. (2011) in November 2009, i.e. ~2 months after the STAC measurements as mentioned by Jégou et al. (2013), a single vertical profile may be not representative of the geographical distribution of the still unmixed volcanic plume throughout summer 2009. To account for the range of aerosol variability as observed by STAC over the Arctic region for the August-September period (**Figure 2**) we have performed two simulations based on the spread (1σ standard deviation) of observed SADs. We have excluded data suspected to be spoiled by balloon outgassing as deduced from joint water vapour measurements. Also, flights revealing the sporadic presence of clouds are not considered to derive the range of SADs below 12 km. Each Bal-sim simulation is respectively driven by the lower and the upper bound of observed SAD values below 20 km (**Figure 2**) from the beginning of August until the end of the model run for latitudes above 40°N. Note that in Bal-sim, H_2SO_4 mixing ratios in July are taken from the Sat-sim simulation.”

We have added some discussion about the non-homogeneity of the plume when describing Figure 5 (now figure 4):

“For the Sarychev situation, minima in NO_2 concentrations appear closely correlated with enhancements in aerosol amounts in the lower stratosphere (**Figure 4)**. 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. The vertical structures depicted in **figure 4**confirm that the plume is not homogeneously mixed over the Arctic region ~2 months after the eruption. Minimum concentration values of 1 to 2 particles.cm^{-3} (for sizes > 0.4 µm) correspond to unperturbed background extra-vortex conditions (Renard et al., 2010) and therefore indicate air masses unaffected by the volcanic aerosols. Conversely, layers with aerosol concentration increases by more than a factor of 3 (with respect to the mean profiles) can be assigned to the presence of the volcanic plume and show associated reductions in NO_2 by up to a factor of ~2.”

Reviewer’s comment: “In order to explore the sensitivities of the model study to different parameters such as differences in aerosol surface area or dynamical effects a number of differently constrained simulations have been carried out and are intercompared in the figures and tables presented. Therefore partly the figures and tables and consequently the discussion gets quite busy and confusing. The results for the runs termed sat-sim and bal-sim generally don’t differ by more than 10%, mostly much less. Therefore this just needs to be shown in one plot (Fig. 6) but then can be neglected just stating that differences for other species are also minor. The same is true for the 1D simulations which are meant to check on dynamical influences. Once the results of these model experiments have been stated the following discussions can be simplified a lot by leaving all the other simulations out. Especially Table2 should be considerably simplified, I’m not aware that all the various differences presented there are even discussed in the text.”

→ We have simplified the figures and shortened the text accordingly. Figure 9 of the ACPD version presenting the HNO_3 profiles has been removed since it is difficult to distinguish between the various simulations which appear very close to the observation. We have written in the new section 3.3:

“All the REPROBUS simulated profiles for HNO_3 are mostly within the errors bars of the SPIRALE measurements and only differ by less than 10% on average (not shown). Calculated amounts from Bal-sim are increased by 10-13% when including volcanic aerosols below 19 km, highlighting limited effects on HNO_3”

All the simulations, i.e. Bal-sim, Sat-sim and 1D calculations, are shown only for NO_2 (now figure 5). For the NO_2/HNO_3 ratio we show only the Bal-sim results. The Sat-sim profile is maintained for the remote-sensing profiles of NO_2 and BrO because both figures are still understandable.

The description of the model-measurement comparisons have been shortened. Sections 3.2 to (previously) 3.6 have been reduced from 3 to 2 pages. Section 3.4 (HNO_3) and 3.5 (NO_2/HNO_3 ratio) have been merged and reduced. The description and discussion of one-dimensional model calculations have been transferred to the new section 3.2 (NO_2).
Tables 1 and 2 have been removed.

Reviewer’s comment: “The balloon-borne measurements aquired during the Strapolete experiment represents a data set that nicely covers an interesting episode of aerosol enhancement in this atmospheric domain and therefore publication is of it’s own value. Possibly a link or links to the appropriate data base(s) should be also given in order to enable use of the data for other studies.”

→ We thank the reviewer for his/her comment. Data can be found at http://www.pole-ether.fr. This address has been added in section 2.1 of the manuscript.

Answers to detailed and minor Comments:

Reviewer's comment: "p4:l16 Is the wording "We focus here on ..." meant to discriminate against the aerosol measurements or does it just refer to gas-phase data?"

→ It refers to gas-phase data. We now write: "Our study presents in situ vertical profiles of the N_2O, NO_2 and HNO_3 gases as observed by the SPIRALE…"

Reviewer's comment: "p4:l16ff Why are there only ascent data used for the SPIRALE measurements? It would be interesting to see also descent data to get a feeling on variability and possible contamination issues on ascent since the cell extends below the payload."

→ We would agree with the reviewer but firstly we have been advised to shorten the manuscript and secondly conclusions through model-SPIRALE comparisons are the same when focusing on the descent data. Thirdly, though it is always tricky to derive definitive conclusions (i.e. discriminating between contamination and fine scale variability), we have of course compared ascent/descent profiles and no obvious contamination effect, at least on a scale of 1 to a few km on the vertical axis, resulting from gondola/balloon outgassing has been pointed out. Note that independent water vapour observations were not available during the SPIRALE flights, which could have been an interesting way to infer possible fine scale contamination effects. To summarize, contamination effects, unlikely in this case, would not change our conclusions.

Reviewer's comment: "p5:l3ff This paragraph is somewhat chaotic and hard to understand and should be polished. Before switching to the BrO profiles a new paragraph might be started."

→ We have modified the text accordingly:

"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). Some works propose to use a photochemical model to correct for this effect (e.g. Harder et al., 2000; Butz et al., 2006) depending on the considered chemical compound, the observation geometry (i.e. balloon ascent or occultation) and daytime (SZA variation). Typically concentrations are converted to values expected at 90° SZA.

In our study, the NO_2 profile from the SALOMON instrument recorded on 25 August 2009 from a typical solar occultation at constant float altitude is not photochemically corrected since conversion to 90° SZA conditions results in differences of less than 6%, in agreement with the work of Payan et al. (1999). 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 is done for SZA = 90°."

The BrO paragraph is now separated.

Reviewer's comment: "p5:l21ff The fact that REPROBUS is used without any detailed sulfur chemistry should be clearly stated right away then referring in which different ways the aerosol plume is prescribed."

→ The REPROBUS CTM does not compute gaseous sulfur chemistry at all. Aerosols in the model are produced from H_2SO_4 mixing ratios provided by the UPMC 2D model (see Weisenstein and Bekki, SPARC aerosol report, chapter 6, 2006). This now specified in the Appendix and in section 2.2 (Model description).

We have added in the Appendix: "Gaseous sulfur chemistry is not included in the REPROBUS CTM. The UPMC 2D model climatology (Bekki and Pyle, 1994) provides the initialization of H_2SO_4 mixing ratios for the background aerosols."

And in section 2.2: “As sulfur chemistry is not included in REPROBUS we have conducted a simulation (hereafter called Ref-sim) constrained with typical background aerosol levels inferred from H_2SO_4 mixing ratios provided by the UPMC 2D model (Bekki and Pyle, 1994).”

Reviewer’s comment: “p5:l53 The Haywood (2010) reference is missing.”

→ Reference added.

Reviewer’s comment: “p6:l33 The analytical expression for the derived correlation in Fig.3 should be given.”

→ We have only plotted N_2O vs NO_y from MIPAS/Envisat observations in figure 3 (now figure 7 in the revised version). Conversely to the Michelsen et al.’s work we did not calculate an analytical expression for the N_2O-NO_y correlation since we have found unnecessary to do so in our case. The method is very simple. We have inferred the MIPAS N_2O/NO_y ratios for a range of (mean) stratospheric pressures, then we have interpolated these ratios to the pressure range observed during the SPIRALE flight and we have finally deduced SPIRALE “pseudo-NO_y“ (called here NO_y*) by multiplying SPIRALE observed N_2O by the interpolated ratio.
We have written in the new section 3.2.2: “…An example of the estimated vertical profile of NO_y (hereafter NO_y*) derived from the conversion of the SPIRALE N_2O profile (**Figure 1a**) using the N_2O-NO_y ratios derived from MIPAS data is presented in **Figure 1b**…”

Reviewer’s comment: “p6:l37 Better leave out the phrase in the model.”

→ The sentence has been removed.

Reviewer’s comment: “p9:Sect.3.4 can be considerably shortened since it doesn’t add new results (see Fig.9).”

→ As said above, former section 3.4 dealing with HNO_3 has been merged with section 3.5 (NO_2/HNO_3 ratio) and the associated discussion substantially shortened.

Reviewer’s comment: “p9:l53 Why is the nomenclature changed here to Balloonaero-sim instead of Bal-sim etc.?”

→ Sorry, this was a mistake now corrected.

Reviewer’s comment: “p10:Sect.3.6 The stated improvements of the 1D simulations above 20km are not at all obvious to me and are certainly not significant improvements that can be employed for the conclusion drawn in this section.”

→ We agree that our initial discussion about the effect of 1D calculations was overstated.

We now write:

“As a result of the NO_y* input in the calculations, the 1D reference simulations show very good agreement for NO_2 (in red in **Figure 5**) with the SPIRALE measurements above 20 km. The 1D simulations constrained by observed volcanic aerosol quantities (in yellow in **Figure 5**) match well with the in situ measurements. The calculated chemical impact on NO_2 gives percentage values similar to the 3D simulation results certainly because both NO_y* and 3D NO_y profiles agree well in the lower stratosphere (**Figure 1b**). 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).

Overall the 1D NO_y-constrained simulations do not significantly improve the comparisons. This result confirms that the model-observations differences in the lower stratosphere can be mostly attributed to heterogeneous processes and not to spurious calculations of transport."

Note that we now include in this new section 3.2.2 (dealing with 1D simulations) the description of the method to derive NOy* in situ profile use to drive the 1D simulation. This is more consistent than splitting the discussion about transport calculation issues in former 'Impact of transport on simulated N2O and NOy' section 3.1.

Reviewer's comment: "p12:l10ff With the introduction of Fig. 11 the dramatic difference of the two BrO profiles should be explained (sza?). Also what is the tropopause height for the DOAS measurement? More than 1 ppt of BrO below the tropopause seems quite suspicious to me."

→ We now mention in section 4.2.1: "Differences between both profiles in terms of BrO amounts are mainly due to differences in SZA."

Firstly, measured BrO at the local tropopause (here 10 km on Sept. 7, 2009 based on PTU sounding) is in agreement with previous measurements at high latitudes (Harder et al.., 1998; Dorf et al., 2006). The 2-km vertical segmentation in the BrO profile retrieval encompasses layers scanned below (upper troposphere) and above (lower stratosphere) the 10 km altitude level at which the BrO mixing ratio is provided. As a result the value at 10 km does not correspond to be purely tropospheric conditions. Secondly, the error bar at 10 km is almost compatible with 0 pptv and largely encompasses the modelled BrO. Finally, we must keep in mind that we are dealing with a lower stratosphere impacted by volcanic aerosols which are likely to enhance BrO amounts.

Reviewer's comment: "p12:l35 The meaning of the percentage changes for switching off the BrONO2 hydrolysis must be more clearly explained. For the example given it should be 16% of the daytime BrO production not 18%."

→ Sorry, this was a mistake. It is indeed 16% of BrO production due to $BrONO_2$ hydrolysis.
We have rewritten the sentence: "It particularly shows that under the Sarychev aerosol loading, only 16% of the 22% (0.9 pptv) increase in daytime BrO at 16.5 km for the August-September 2009 period is produced from $BrONO_2$ hydrolysis."

Reviewer's comment: "p12:l39 This result implies ..."

→ corrected

Reviewer's comment: "p12:l52 ... the active chlorine family species ..."

→ corrected

Reviewer's comment: "p13:l30ff I propose to use absolute values for the ozone loss discusion (see the comment on Fig.12)."

Reviewer's comment: "p13:l39 ... into the lower stratosphere."

→ This sentence has been changed following reviewer1‘s remark.

Reviewer’s comment: “p15:l33 When switching to absolute values for the accumulated ozone losses the discussion why “largest” losses occur just above the tropopause will become obsolete, I guess.”

→ Indeed, the sentence has been removed.

Reviewer’s comment: “p16:l35 It might be interesting ...”

→ corrected

Reviewer’s comment: “p18:l19 Does the uncertainty represent accuracy? Since several balloon-borne measurements are used along with each other and are compared to other aerosol SAD data it is not sufficient to just state the precision of the measurements.”

→ We are not sure to understand the reviewer’s point. Here (p18 l19) we focus on aerosol counting observations with 3 copies of the STAC instrument which have shown ±10% differences (random error or precision) using identical aerosol at high concentrations in the laboratory. Poisson statistics provide an estimate of the random error for lower aerosol concentration conditions (i.e. 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}). This calculation of aerosol counting uncertainties (precision) is detailed in Deshler et al. (2003). This reference is provided in this part of the manuscript. The accuracy (or measure of the bias if the reviewer is dealing with this other definition) of this type of instrument is very difficult to derive because one would need reference concentration values (true value from another aerosol counter) which are extremely difficult to obtain. In other words, no absolute reference aerosol counter is available. That is why, as in Deshler et al. (2003) we provide here precision.
We have then changed the text to:
“Using a statistical approach as described in Deshler et al. (2003), STAC counting precision (Poisson statistics and the ±10% measurement reproducibility) translate into uncertainties on distribution moments, with estimated values of 40% for SAD.”

Reviewer’s comment: “p18:l41 I guess overall uncertainty represents accuracy?
Rename or otherwise state the accuracy.”

→ This is total error combining precision and accuracy. “Overall uncertainties” has been replaced by “total error”.

Reviewer’s comment: “p19:l17 The Voigt et al. reference is missing. Also the Pfeilsticker et al. reference (l20). Please check over completely!”

→ We have checked all the references and added the missing ones.

Reviewer’s comment: “p21:l3 ... strong functions ...”

→ corrected

Reviewer's comment: "p22 All citations should be thoroughly rechecked since several citations have been missing from the references list."

→ We have checked all the references and added the missing ones.

Reviewer's comment: "Table 2 Several of the tabulated differences are not used at all in the text. The table can be reduced considerably or even removed completely."

→ Table 1 and 2 have been removed.

Reviewer's comment: "Table 3 In the caption it should better read: Numbers are taken from the Sat-sim simulation. Also ... BrONO2 hydrolysis (Reaction 4) to changes ... would help."

→ Changes done in the caption.

Reviewer's comment: "Fig.1 I propose to show the traces of the individual measurements on the plot to give the reader an impression on the variability. Also the altitudes shown should be extended somewhat to 25km and possibly below 10km to give a better impression on the vertical extend of the plume."

→ As stated above Figure 1 (now ranked as figure 2) has been modified (almost) accordingly. We have added the individual profiles (excluding suspected balloon/gondola outgassing cases) of Surface Area Densities (SAD) inferred from STAC size distributions (using a log-normal fitting procedure as described in Jégou et al., 2013) but this calculation was not done for altitudes above ~20 km (model outputs are used). The altitude range of the plume is still visible on the 10-20 km range. Below 10 km the presence of tropospheric clouds (depending on the varying tropopause height) is likely to spoil the interpretation of the SAD profiles. That is why some profiles have been truncated on the new figure 2. Note that the whole aerosol concentration profiles can be found in Renard et al. (2010).

Reviewer's comment: "Fig.2 For my taste in the right panel SPIRALE HNO3 should be included."

→ The idea of the reviewer is interesting but the figure (now figure 1b) would become very busy (this is already the case here) when including HNO_3 and therefore rather confusing for the reader. That is why we have decided to keep the figure as is.

Reviewer's comment: "Fig.5 The grey shaded (error bars?) on the NO2 profile should be explained in the caption."

→ These are indeed error bars. This is now indicated in the caption.

Reviewer's comment: "Fig.9 Due to the high partitioning into HNO3 this species is not sensitive for the aerosol effect. This plot therefore can be left out."

→ The plot has been removed as said above.

Reviewer's comment: "Fig.11 The solar zenith angles of the profiles have to be given in the caption due to the diurnal variation of BrO."

→ The following information is now provided in the caption: "The SALOMON data in the lower stratosphere were obtained between 19:15 UT (SZA=93.8° at 22 km tangent height) and 19:25 UT (SZA=94.5° at 17 km tangent height). The DOAS profile was measured between 15:15 UT (SZA=77.5° at 10 km) and 15:55 UT (SZA=81.3° at 22 km) during balloon ascent."

Reviewer's comment: "Fig.12 Showing the percentage changes in ozone is somewhat misleading. In order to point out the altitude regime of highest impact in terms of ozone loss an absolute scale should be used like loss rates of ppb/day. A percentage change of 5% doesn't have any major effect if ozone levels are negligible at the TP."

→ The point highlighted by the reviewer is relevant. Most papers referring to the Pinatubo aerosol-induced ozone loss provide plots with % values when the loss is expressed vs altitude levels (e.g. Brasseur and Granier, 1992; Pitari and Rizi, 1993; McGee et al., GRL, 1994; Kinnison et al., 1994; Tie et al., 1994; Solomon et al., 1996). That is the reason why chose to plot percentage values.

To address the reviewer's comment, we now plot (cumulated) ozone loss in pbbv (as is widely expressed in the literature regarding polar ozone depletion, not really in ppbv/day which in the case of the Sarychev will give too low numbers). We still provide in the text associated percentage values for comparison with the literature dealing with Pinatubo effects.

This is provided in section 5.1:

"Accumulated ozone depletion reaches its maximum above Kiruna near 16 km from around mid-September with changes of -22 ppbv corresponding to -1.5%. Below this level changes range from -10 ppbv to -18 ppbv, i.e. -2.5% to -3.5%. From the upper bound of the Bal-sim outputs calculated ozone depletion reaches -25 ppbv (-2.8%) and -35 ppbv (-4%) at 16.5 km and 14 km, respectively (not shown). It should be noted that at the tropopause level the possible detailed influence of various organic compounds originating from the upper troposphere is not taken into account in our simulations.

We note that for the post-Pinatubo eruption period, ozone reductions as large as -30% were measured for the 12 and 22 km altitude range monitored at some mid-latitude locations in winter and spring (Hofmann et al., 1994) but these losses are both due dynamical and chemical perturbations. Through 2D modelling, ozone losses of up to -20% directly resulting from heterogeneous chemical processes were calculated in the northern hemisphere lower stratosphere over the first year following the Pinatubo eruption (Pitari and Rizi, 1993; Tie et al., 1994). The calculated chemical loss had reduced to values much closer to those simulated for the Sarychev aerosols, i.e. ~-5%, at 60°N in the autumn 1992 extra-polar vortex conditions (Tie et al., 1994)."

And added in the abstract: "As a consequence, the simulated ozone loss due to the Sarychev aerosols is low with a reduction of -22 ppbv (-1.5%) of the ozone budget around 16 km".

And added in the conclusion: "…the magnitude of the ozone response to the Sarychev volcanic perturbation appears restricted for instance -22 ppbv or -1.5% at 16 km)..."

And we have to remove the following sentence in the conclusion (p15 line 34 in the ACPD version): "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."

→ It is important to note the new figures' numbering:

Former figure 1 is now figure 2
Former figure 2 is now figure 1
Former figure 3 is now figure 7

Former figure 4 is now figure 3
Former figure 5 is now figure 4
Former figure 6 is now figure 5
Former figure 7 is now figure 6

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 and are assumed to be one cause for the reported increase in the global aerosol content over the past 15 years. This particular enhanced aerosol context raises questions about the effects on stratospheric chemistry which depend on the latitude, altitude and season of injection. In this study, we focus on the mid-latitude Sarychev volcano eruption in June 2009 which injected 0.9 Tg of sulfur dioxide (about 20 times less than Pinatubo) in a lower stratosphere mainly governed by high stratospheric temperatures. Together with in situ measurements of aerosol amounts, we analyse high-resolution in situ and/or remote-sensing observations of NO_2, HNO_3 and BrO from balloon-borne infrared and UV-visible spectrometers launched in Sweden in August-September 2009. It is shown that differences between observations and three-dimensional (3D) Chemistry-Transport Model (CTM) outputs are not due to transport calculation issues but rather reflect the chemical impact of the volcanic plume below 19 km altitude~~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 August-September ~~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. We show that the chlorine partitioning is significantly controlled by enhanced $BrONO_2$ hydrolysis. However simulated ~~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 chemical ozone loss due to the Sarychev aerosols is low with a reduction of 22 ppbv (-1.5%) of the ozone budget around 16 km.~~1.1% of the ozone budget at 16.5 km.~~ This is at least 10 times lower than the maximum ozone depletion from chemical processes (up to -20%) reported in the northern hemisphere lower stratosphere over the first year following the Pinatubo eruption.~~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.~~ This study suggests that moderate volcanic eruptions have limited chemical effects when occurring at mid-latitudes (restricted residence times) and outside winter periods (high temperature conditions). However, among the other reported moderate eruptions it would be of interest to investigate longer lasting tropical volcanic plumes or sulfur injections in the wintertime low temperature conditions.

Commenté [g1]: In this new version of the abstract we better explain the rationale of the paper and new results provided, as as suggested by both reviewers.

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:

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

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:

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

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,

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

of $ClONO_2$ with dissolved HCl in sulfuric acid droplets ~~have~~ has negligible effects on chlorine activation at such temperatures (Hanson et al., 1994; Borrmann et al., 1997).

Some works also suggest that the hydrolysis of $BrONO_2$,

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

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; Dhomse et al., 2015) whereas HNO_3 amounts increase (Koike et al., 1993; Webster et al., 1994; Koike et al., 1994; Rinsland et al., 2003) as shown for the Pinatubo aerosols. Different chemical 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$_2$O$_5$ 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$_2$O$_5$ 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~~4) 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).

In periods following major eruptions, the year-to-year variability in stratospheric ozone at northern mid-latitudes appears closely linked to dynamical changes induced by the volcanic aerosol radiative perturbation (e.g. Telford et al., 2009; Aquila et al., 2013) and to changes in chlorine partitioning (e.g. Solomon et al., 1999; Chipperfield, 1999). Effects on stratospheric chemistry are expected in periods of elevated chlorine levels from anthropogenic activities (Tie and Brasseur, 1995; Solomon 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 1991 Pinatubo or 1982 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. Their effects depend on the amount of released SO$_2$ and on latitudes and altitudes of injection which directly influence aerosol residence times. The season of the eruption is also important for photochemical processes which are directly connected to temperatures and solar illumination.

The goal of this paper is to show how such moderate eruptions are likely to modify the chemical balance of the northern hemisphere lower stratosphere at periods excluding wintertime/springtime halogen-activating photochemistry. We specifically focus on the eruption of the Sarychev volcano on 15 and 16 June 2009 which injected 0.9 Tg of sulfur dioxide in the lower stratosphere (Clarisse et al., 2012) resulting in enhanced sulfate aerosol loading up to 19 km, for a period of about 8 months ending before winter (Haywood et al., 2010; Kravitz et al., 2011; O'Neill et al., 2012; Jégou et al., 2013).

~~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 analysing some key aspects of lower stratospheric chemistry and ozone loss in a context of high aerosol surface area densities and high stratospheric temperatures using ~~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/Esrange in ~~Northern~~ Sweden (67.5°N, 21.0°E) within the frame of the STRAPOLETE project. ~~and aerosol-constrained simulations using a 3D Chemistry Transport Model (CTM).~~ To our knowledge we show here the first high-resolution in situ observations of chemical compounds obtained within the volcanic aerosol plume of a moderate eruption. We show that at the period on which the study is focused ~~of the measurements~~ N_2O_5 has reformed and the role of its hydrolysis becomes important again after the sunlit summer period justifying the use of these balloon data for the investigation of heterogeneous processes. Aerosol-constrained simulations using a 3D Chemistry Transport Model (CTM) are compared to the observations. These model calculations ignore possible dynamical effects induced by the volcanic aerosols but are used to estimate the amplitude of the chemical impacts and ozone loss with some comparisons with the post-Pinatubo eruption period. ~~Here we estimate the ozone loss and discuss its amplitude in comparison with the effect of the Pinatubo eruption.~~

Commenté [g2]: As in the abstract we better explain the reasoning of the paper

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. Data can be found at http://www.pole-ether.fr.

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 obtained ~~observed~~ between August and September 2009 as reported by Jégou et al. (2013).

Our study presents in situ vertical profiles of the N_2O, NO_2 and HNO_3 gases as observed by the SPIRALE ~~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, for the SPIRALE balloon flight on 24 August 2009 (further on called 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). Some works propose to use a photochemical model to correct for this effect (e.g. Harder et al., 2000; Butz et al., 2006) depending on the considered chemical compound, the observation geometry (i.e. balloon ascent or occultation) and daytime (SZA variation). Typically, concentrations are converted to values expected at 90° SZA.~~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 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 is not photochemically corrected since conversion to 90° SZA conditions results in differences of less than 6%, in agreement with the work of Payan et al. (1999).~~. 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 NO_2 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~~is 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 slant column densities (SCD)~~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. 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 (**Figure 1a**).

As sulfur chemistry is not included in REPROBUS ~~We~~ we have conducted a ~~REPROBUS~~ simulation (hereafter called Ref-sim) constrained with typical background aerosol levels inferred from H_2SO_4 mixing ratios provided by the UPMC 2D model (Bekki and Pyle, 1994)~~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 type of simulation (hereafter called Bal-sim) consisting in adjusting the input H_2SO_4 mixing ratios so that the model output matches SADs observed by the STAC aerosol counter. Although similar aerosol SAD values were observed by Kravitz et al. (2011) in November 2009, i.e. ~2 months after the STAC measurements as mentioned by Jégou et al. (2013), a single vertical profile may be not representative of the geographical distribution of the still unmixed volcanic plume throughout summer 2009. To account for the range of aerosol variability as observed by STAC over the Arctic region for the August-September period (**Figure 2**) we have performed two simulations based on the spread (1σ standard deviation) of observed SADs. We have excluded data suspected to be spoiled by balloon outgassing as deduced from joint water vapour measurements. Also, flights revealing the sporadic presence of clouds are not considered to derive the range of SADs below 12 km. Each Bal-sim simulation is respectively driven by the lower and the upper bound of observed SAD values below 20 km (**Figure 2**) from the beginning of August until the end of the model run for latitudes above 40°N. Note that in Bal-sim, H_2SO_4 mixing ratios in July are taken from the Sat-sim simulation.~~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 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 Bal-sim, 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**.~~

Commenté [g3]: Elements taken from former section 3.1. This better fits in this model description part.

Commenté [g4]: We better explain the issue about the horizontal and vertical variability of the volcanic aerosol plume as required by reviewer 2.

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~~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~~ 1 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. Polar summer is characterised by continuous solar illumination preventing the formation of N_2O_5 (Fahey and Ravishankara, 1999) until about the beginning of August (Brühl et al., 1998), i.e. around day 213 for the considered Esrange/Kiruna location as illustrated in **Figure 3** at 17.5 km. ~~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 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~~

Commenté [g5]: This first paragraph has been shortened following reviewer 1's comment recommending to reduce the length of the manuscript. It has moved to section 2.2 which is more consistent

Commenté [g6]: To gather the discussion about possible remaining transport calculations issues, this paragraph has been moved to (new) section 3.2.2 dedicated to 1D simulations

Mis en forme : Centré

~~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~~3**. 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.

Mis en forme : Retrait : Première ligne : 0 cm

Commenté [g7]: Paragraph shortened as suggested by reviewer1

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 in the Kiruna region match the photochemical conditions for which volcanic aerosols likely ~~had~~ have an impact on NO_y partitioning via elevated N_2O_5 hydrolysis and can be suitably used to investigate heterogeneous processes. ~~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~~ 2 NO_2

3.~~3~~2.1 Model comparisons with observations

For the Sarychev situation, minima in NO_2 concentrations appear closely correlated with enhancements in aerosol amounts in the lower stratosphere (**Figure 4**). 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. The vertical structures depicted in **figure 4** confirm that the plume is not homogeneously mixed over the Arctic region ~2 months after the eruption. Minimum concentration values of 1 to 2 particles.cm^{-3} (for sizes > 0.4 µm) correspond to unperturbed background extra-vortex conditions (Renard et al., 2010) and therefore indicate air masses unaffected by the volcanic aerosols. Conversely, layers with aerosol concentration increases by more than a factor of 3 (with respect to the mean profiles) can be assigned to the presence of the volcanic plume and show associated reductions in NO_2 by up to a factor of ~2.

Figure 5 and **Figure 6** present the measured profiles of NO_2 obtained by the SPIRALE, SALOMON and DOAS instruments, together with REPROBUS model outputs for altitudes below 20 km where the Sarychev aerosols were present. In contrast to the reference simulations, the Bal-sim simulations constrained by the range of aerosol SADs observed by STAC show significant improvement in comparison with the non-volcanic calculations with for instance average differences of 3±20% for SPIRALE-07082009. Results from the Sat-sim simulations driven by OSIRIS satellite data are very close to the Bal-sim results and are only shown for the SPIRALE flights.

Commenté [g8]: The text in this section 3.2.1 has been significantly reduced as suggested by reviewer 1.

~~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~~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 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 the 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. Reductions in NO_2 mixing ratios between 34 and 50 % are simulated on average below 19 km. ~~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.

3.2.2 One-dimensional model calculations

Commenté [g9]: Former section 3.6

Some small model-measurement discrepancies in the 20-35 km altitude range as shown in the embedded plots in **Figure 5 and Figure 6** suggest that the model-measurement differences in the lower stratosphere may be only partly attributed to remaining uncertainties in calculations of transport. A way to discard a possible remaining effect of transport and improve the modelling of total NO_y is to use one-dimensional (1D) calculations constrained by observations (Dufour et al., 2005; Berthet et al., 2006).

Total NO_y from SPIRALE measurements can be derived from established N_2O-NO_y correlation curves. Since the study of Michelsen et al. (1998), global emissions of N_2O have increased and the N_2O-NO_y correlations reported therein need some revision. As a consequence, we have constructed updated 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 7** in which the Michelsen et al.'s former results are also represented for comparison. An example of the estimated vertical profile of NO_y (hereafter NO_y*) derived from the conversion of the SPIRALE N_2O profile (**Figure 1a**) using the N_2O-NO_y ratios derived from MIPAS data is presented in **Figure 1b**. Then, following the strategy of Berthet et al. (2006) the N_2O and the derived NO_y* profiles for SPIRALE-07082009 and SPIRALE-24082009 are used to initialise the REPROBUS 1D version.

The 1D-REPROBUS reference simulation is computed with background aerosol levels, whereas the Sarychev aerosol affected simulation is constrained with the mean observed aerosol profile presented in **Figure 2**. As a result of the NO_y* input in the calculations, the 1D reference simulations show very good agreement for NO_2 (in red in **Figure 5**) with the SPIRALE measurements above 20 km. The 1D simulations constrained by observed volcanic aerosol quantities (in yellow in **Figure 5**) match well with the in situ measurements. The calculated chemical impact on NO_2 gives percentage values similar to the 3D simulation results certainly because both NO_y* and 3D NO_y profiles agree well in the lower stratosphere (**Figure 1b**). 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).

Overall the 1D NO_y-constrained simulations do not significantly improve the comparisons. This result confirms that the model-observations differences in the lower stratosphere can be mostly attributed to heterogeneous processes and not to spurious calculations of transport.

3.3.~~2~~ 3 Saturation effect of NO_x reduction

The reduction of NO_x from the results described above (section 3.2.1) is significant but also indicates some saturation through reaction 1 for the range of SADs 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 night-time 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-SAD curve constructed for the range of altitudes spanned by the volcanic plume (i.e. with different NO_y amounts and photochemistry). ~~NO_2 amounts versus aerosol SAD as observed by the SPIRALE instrument and simulated by the REPROBUS CTM.~~ Although the asymptotic behaviour in the NO_2 reduction would be more evident if shown for a given altitude level with constant SZA and varying SADs, our results indicate saturation for SAD values larger than about 4 µm².cm^{-3} which is reached on average for altitudes around 18 km. ~~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 µm².cm^{-3} which is reached on average for altitudes around 18 km.~~ The net reduction of NO_x reported for the Pinatubo aerosols tends to saturate at similar SADs 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).

Commenté [g10]: Text reduced

~~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~~3 HNO_3 and NO2/HNO_3 ratio

Commenté [g11]: Former sections 3.4 (HNO3) and 3.5 (NO2/HNO3) have been merged and reduced in length.

We consider here total HNO_3, i.e. both in the gas phase and condensed. All the REPROBUS simulated profiles for HNO_3 are mostly within the errors bars of the SPIRALE measurements and only differ by less than 10% on average (not shown). Calculated amounts from Bal-sim are increased by 10-13% when including volcanic aerosols below 19 km, highlighting limited effects on HNO_3.

The NO_2/HNO_3 ratio can be used as a good approximation of the NO_x/NO_y ratio to reduce the uncertainty in a model estimate of NO_y (e.g. Webster et al., 1994; Berthet et al., 2006). This is especially useful for the SPIRALE flights for which modelled NO_2 and HNO_3 amounts account for more than 92% of total NO_y. Good agreement is obtained between the observed NO_2/HNO_3 ratio and the model outputs by including the Sarychev aerosols, with for instance absolute differences decreasing to 3±20% for the Bal-sim simulation for SPIRALE-07082009 (**Figure 9**). However no clear improvement can be noticed with respect to the model-measurement comparisons presented in **Figure 5** for NO_2 both at and above the altitudes of the plume. 1D calculations do not show improvement as well (not shown). Again this indicates that transport calculation is not a major issue in the comparisons. Reductions in the NO_2/HNO_3 ratios between 36 and 44% are simulated on average below 19 km for SPIRALE-07082009 and SPIRALE-24082009, respectively, when volcanic aerosols are included.

For the Pinatubo aerosol loaded stratosphere, maximum HNO_3 column increases of 30-40% have been measured at mid-latitudes (e.g. Koike et al., 1994). 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). However, quantifying the difference between both eruptions through comparisons of local concentrations versus columns remains challenging because the production efficiency of HNO_3 by heterogeneous processes generally depends on the altitude level where volcanic aerosols are present (Webster et al., 1994; Danilin et al., 1999). 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).

~~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 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~~

Commenté [g12]: Now section 3.2.2

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 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 because of the low vertical resolution of MLS data, i.e. ~3 km, the exact altitude of injection is unclear and requires further investigation. In addition, MLS HCl measurements are known to be biased high below the 100 hPa level (Livesey et al., 2011) making difficult to infer a robust injection amount. As a consequence, the possible effect of the HCl injection on the stratospheric chlorine chemistry is not investigated in our study. ~~However the exact altitude of injection is inaccurate because~~

Commenté [g13]: Sentences clarified and shortened

~~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~~ 1** 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~~1**) 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~~is 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 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~~ Since direct injection of bromine into the stratosphere was insignificant after the Sarychev eruption (Hormann et al., 2013) we expect that stratospheric bromine chemistry was only modified by the enhanced aerosol loading.~~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~~10**). They were simultaneously measured with the NO_2 profiles presented in section 3.2~~.2~~. Differences between both profiles in terms of BrO amounts are mainly due to differences in SZA. When volcanic aerosol SADs are included BrO amounts are increased in the lower stratosphere, matching the observations within the error bars (**Figure ~~11~~10**).~~ 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~~ 1** 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; Hanson et al., 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 $BrONO_2$ ($J(BrONO_2)/k_{BrO+NO_2}$) ~~(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 have addressed ~~solar occultation~~ observations ~~for solar zenith angles~~with SZA <92.5° 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 night-time 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~~1**. It particularly shows that under the Sarychev aerosol loading, only 16% of the 22% (0.9 pptv) increase in daytime BrO at 16.5 km for the August-September 2009 period is produced from $BrONO_2$ hydrolysis~~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 result~~s~~ 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~~ 1** 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 family~~ies~~ species. 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 converts further HCl to ClO and, ultimately, to $ClONO_2$. As shown in **Table ~~3~~1**, ~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).~~

Commenté [g14]: This paragraph has been moved to the end of section 5.1 and modified to provide information comparable to our results.

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; Dhomse et al., 2015). 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~~11**). 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 near 16 km from around mid-September with changes of -22 ppbv corresponding to -1.5%.~~-5% (-20 ppbv) and -2.5% (-25 ppbv) at 16.5 km and 14 km, respectively~~. Below this level changes range from -10 ppbv to -18 ppbv, i.e. -2.5% to -3.5%. From the upper bound of the Bal-sim outputs calculated ozone depletion reaches -25 ppbv (-2.8%) and -35 ppbv (-4%) at 16.5 km and 14 km, respectively (not shown).~~Similar ozone changes are simulated when the model is driven by the lower values of aerosol loading taken from STAC in-situ~~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.~~

Commenté [g15]: Following reviewer1's comment this sentence is misleading and has been removed.

We note that for the post-Pinatubo eruption period, ozone reductions as large as -30% were measured for the 12 and 22 km altitude range monitored at some mid-latitude locations in winter and spring (Hofmann et al., 1994) but these losses are both due dynamical and chemical perturbations. Through 2D modelling, ozone losses of up to -20% directly resulting from heterogeneous chemical processes were calculated in the northern hemisphere lower stratosphere over the first year following the Pinatubo eruption (Pitari and Rizi, 1993; Tie et al., 1994). The calculated chemical loss had reduced to values much closer to those simulated for the Sarychev aerosols, i.e. ~-5%, at 60°N in the autumn 1992 extra-polar vortex conditions (Tie et al., 1994).

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~~1**) than for background conditions (HO_2/OH ratios typically ranging from 4 to 7). Because the photochemical 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~~1**) (as explained in section 4.1). However as~~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) for the post-Pinatubo eruption period. ~~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~~ 1** shows that the hydrolysis of $BrONO_2$ accounts for more than 22% of the ozone loss at 16.5 km after the Sarychev eruption. As described in section 4.2.2, this is due to reaction 4 acting as a source of OH, reducing the HCl lifetime and thereby indirectly amplifying the chlorine-mediated ozone depletion. ~~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; Al-Saadi et al., 2001; Aquila et al., 2013). 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 the lower stratosphere at mid- and high latitudes ~~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~~ these regions (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 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 restricted (for instance -22 ppbv or -1.5% around 16 km)~~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 (Jucks et al. 1999; 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., 2000). To account for this SAD-related uncertainty, our simulations based on ~~in-situ~~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~~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 µm^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~~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~~in situ profiles and with remote sensing observations integrating over tens of kilometre~~er~~s (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; Al-Saadi et al., 2001). 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 be 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 (Solomon et al., 2016).

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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 precision ~~uncertainties~~ (Poisson statistics and the ±10% measurement reproducibility~~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~~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 Herriott 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 total error ~~overall uncertainties~~ for the volume mixing ratios ~~have~~ has 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 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-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 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 strong~~ly~~ 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 long-term simulation from the UPMC 2D model ~~2D model long-term simulation~~ (Bekki and Pyle, 1994; Weisenstein and Bekki; 2006). 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).

Gaseous sulfur chemistry is not included in the REPROBUS CTM. ~~-~~The UPMC 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 ~~3~~1: Simulated changes on various stratospheric key species due to the Sarychev volcanic aerosols over the August-September 2009 period at 16.5 km. Numbers are taken from ~~Calculations are done from~~ the Sat-sim simulation. Effects for daytime and night-time conditions are provided depending on statistically significant amounts in the diurnal cycle of a given compound. Also ~~The~~ the contribution of $BrONO_2$ hydrolysis (reaction 4) 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%

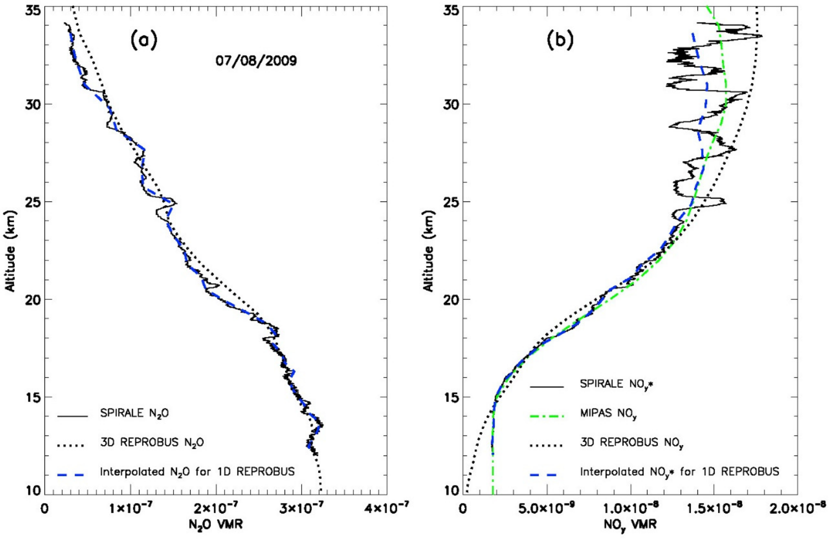

Figure 1: (a) Vertical profile of N_2O recorded on 7 August 2009 (black line) compared to the results from the 3D version of REPROBUS (dotted line). (b) Vertical profile of NO_y inferred from the SPIRALE N_2O profile converted using the N_2O-NO_y correlation curve presented in **Figure 7** (referred 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).

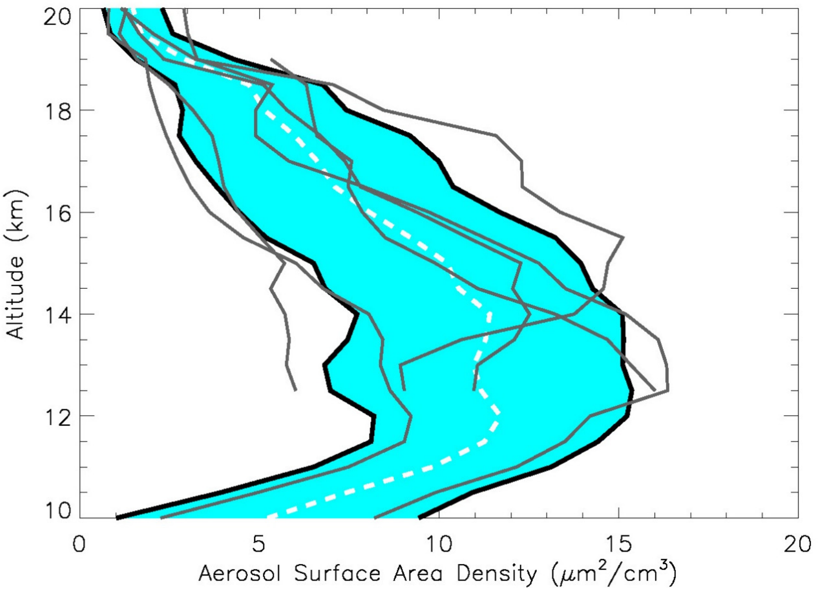

Figure 2: Range of aerosol SAD values (black lines) as derived from several balloon-borne observations in the lower stratosphere in summer 2009 (1σ standard deviation of the mean). The individual profiles (grey lines) and their average (white dashed line) are also presented. Data supposed to be spoiled by balloon outgassing as revealed from simultaneous in situ water vapour observations and data revealing the sporadic presence of clouds below 12 km have been excluded.

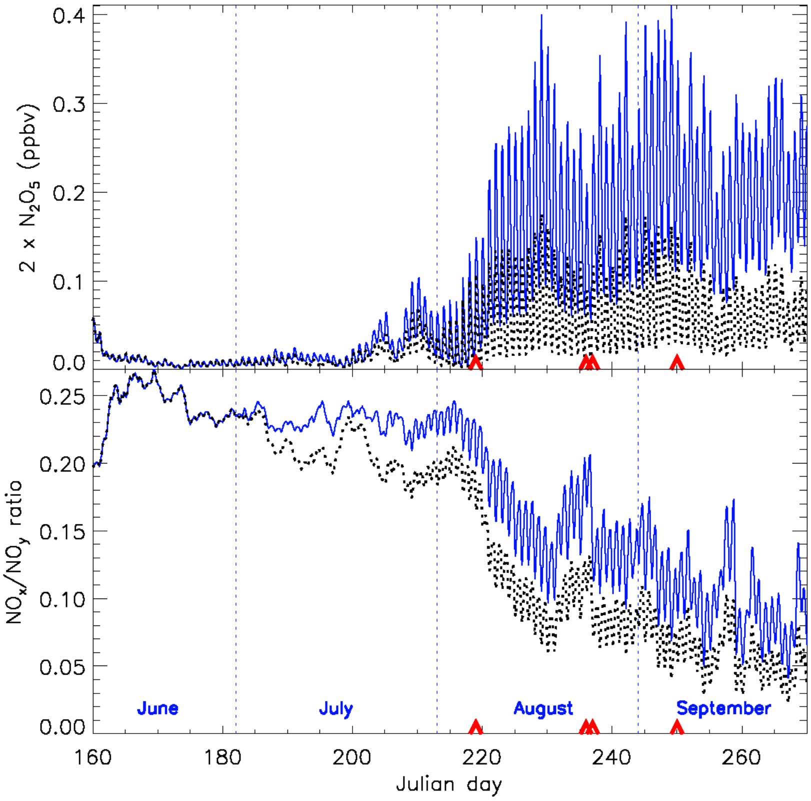

Figure 3: Seasonal variation of N_2O_5 (a) and of the NO_x/NO_y ratio (b) simulated by the REPROBUS CTM above Kiruna in Northern Sweden (67.5°N, 21.0°E) around 17.5 km. The simulation driven by non-volcanic aerosol contents (Ref-sim) is shown in blue. The black dotted line is the REPROBUS simulation 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°.

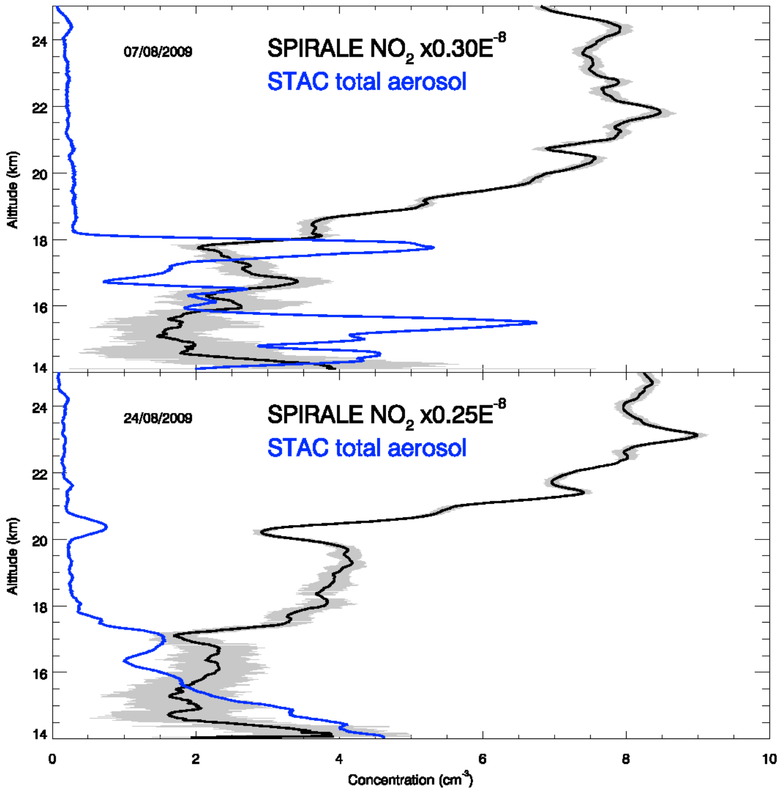

Figure 4: Vertical profiles of NO_2 observed by the SPIRALE balloon-borne instrument (black line with grey shaded error bars) on 7 and 24 August 2009 compared to the total aerosol concentration profiles (for sizes > 0.4 µm) simultaneously recorded by the STAC aerosol counter (blue line) above Kiruna during balloon ascent. SPIRALE data have been averaged over 250 m (corresponding to ~1 minute of measurements).

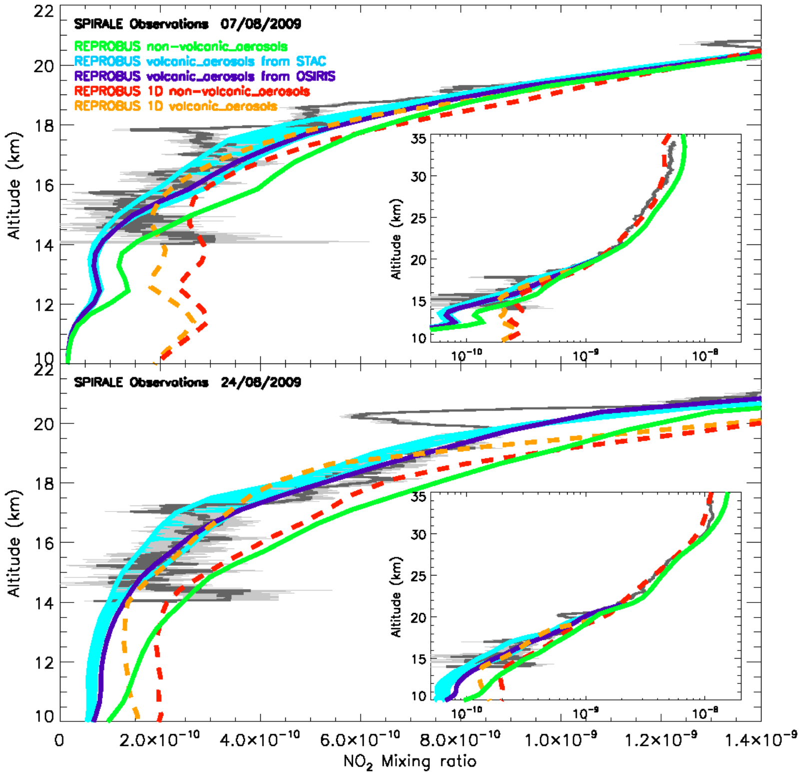

Figure 5: Vertical profile of NO_2 observed by the SPIRALE balloon-borne instrument (black line) above Kiruna during balloon ascent between 02:00 and 02:30 UT (~87° SZA at 02:15 UT) for the 7 August 2009 flight (top) and between 21:00 and 21:30 UT (~100° SZA at 21:15 UT) for the 24 August 2009 flight (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 yellow the calculations driven with volcanic aerosols from the mean observed balloon-borne profile presented in **Figure 2**.

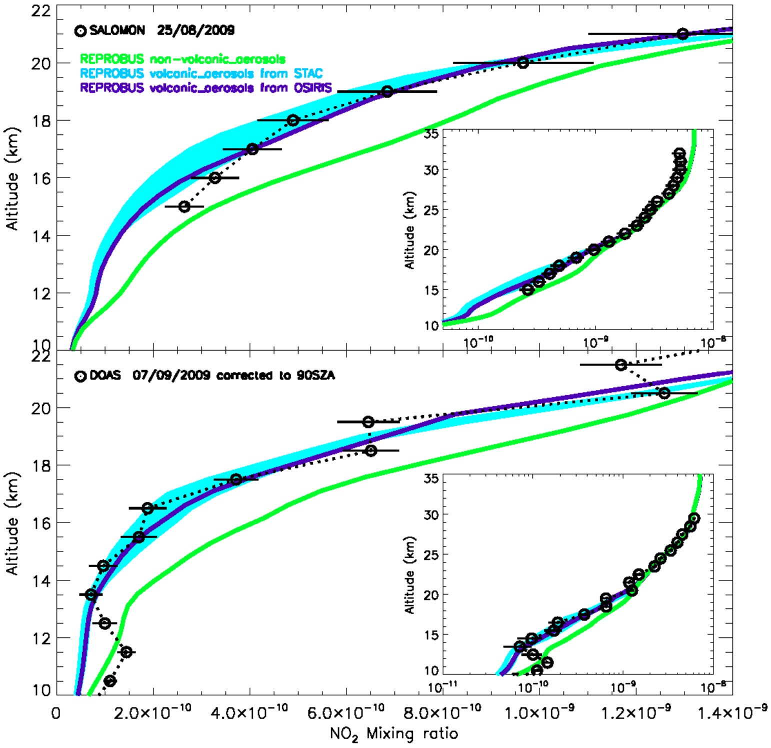

Figure 6: (top) Vertical profile of NO_2 recorded by the SALOMON instrument (black lines) obtained during solar occultation between 18:50 (32 km tangent height) and 19:30 UT (15 km tangent height) on 25 August 2009 above Kiruna. Chemistry-transport model simulations computed with no volcanic aerosols (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.

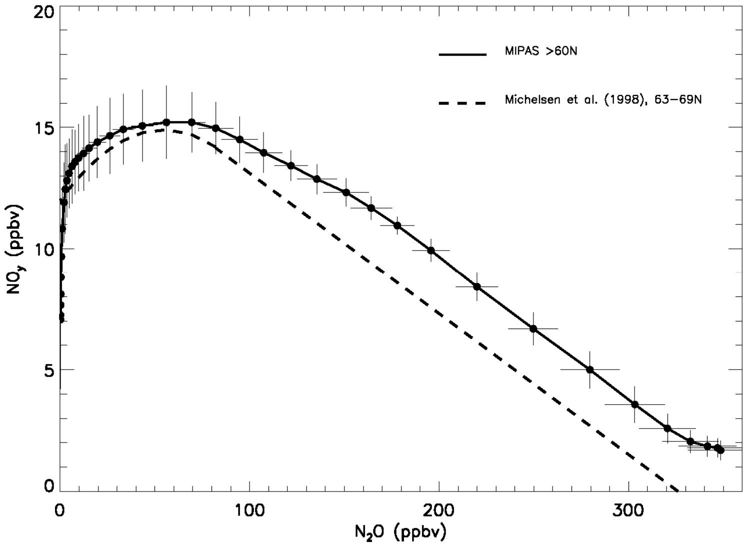

Figure 7: N_2O-NO_y correlation curve inferred from IMK/IAA V5R_220 MIPAS-Envisat data at high latitudes (> 60°N) in July-August 2009 (full line). Error bars reflect the spread of the data. The former Michelsen et al. (1998) correlation is also shown for comparison (dashed line).

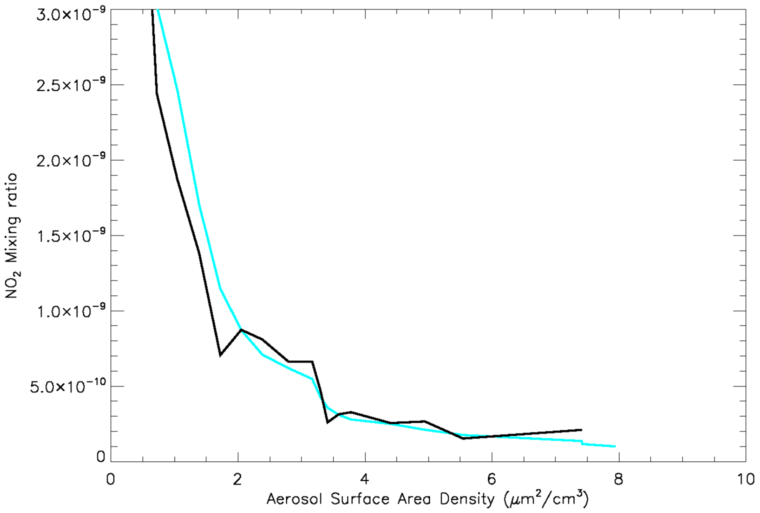

Figure 8: NO_2 mixing ratio as a function of aerosol SAD as simultaneously observed in the lower stratosphere by the SPIRALE and STAC instruments on 24 August 2009 (black curve). The result from the REPROBUS Bal-sim simulation is also plotted (blue curve).

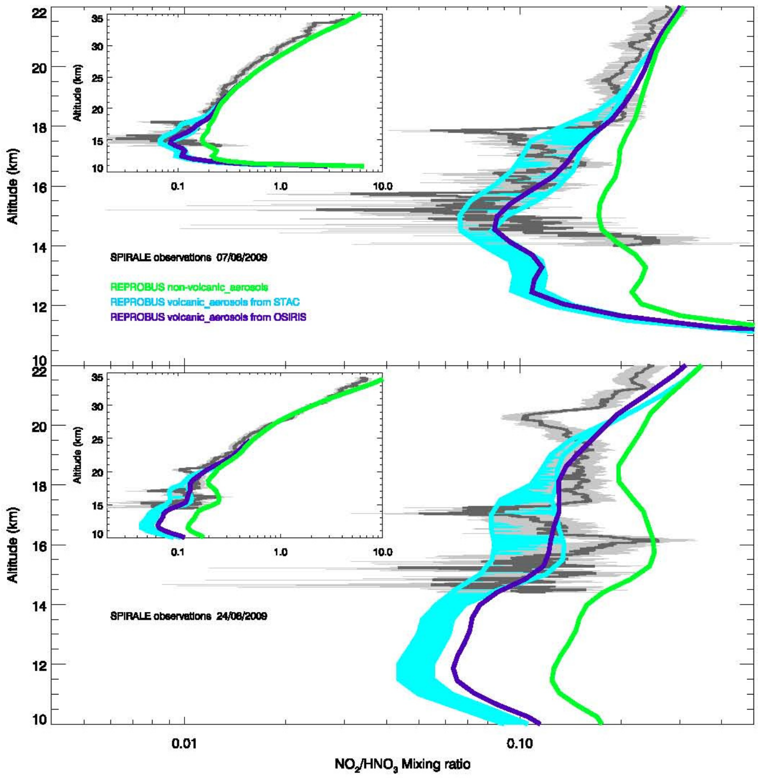

Figure 9: Same as **Figure 5** but for the NO$_2$/HNO$_3$ ratio observed by the SPIRALE instrument. Provided are the three-dimensional simulations driven without volcanic aerosols (green), with volcanic aerosols from balloon-borne observations (blue shaded area) and with volcanic aerosols from satellite data (dark blue line).

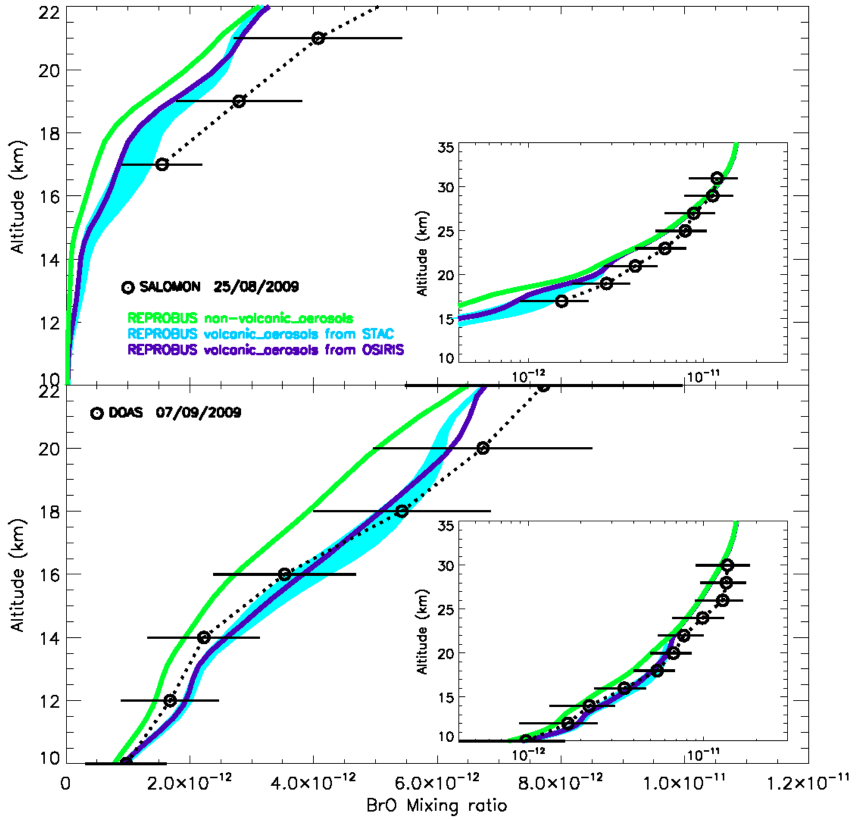

Figure 10: same as **Figure 6** but for BrO. The SALOMON data in the lower stratosphere were obtained between 19:15 UT (SZA=93.8° at 22 km tangent height) and 19:25 UT (SZA=94.5° at 17 km tangent height). The DOAS profile was measured between 15:15 UT (SZA=77.5° at 10 km) and 15:55 UT (SZA=81.3° at 22 km) during balloon ascent.

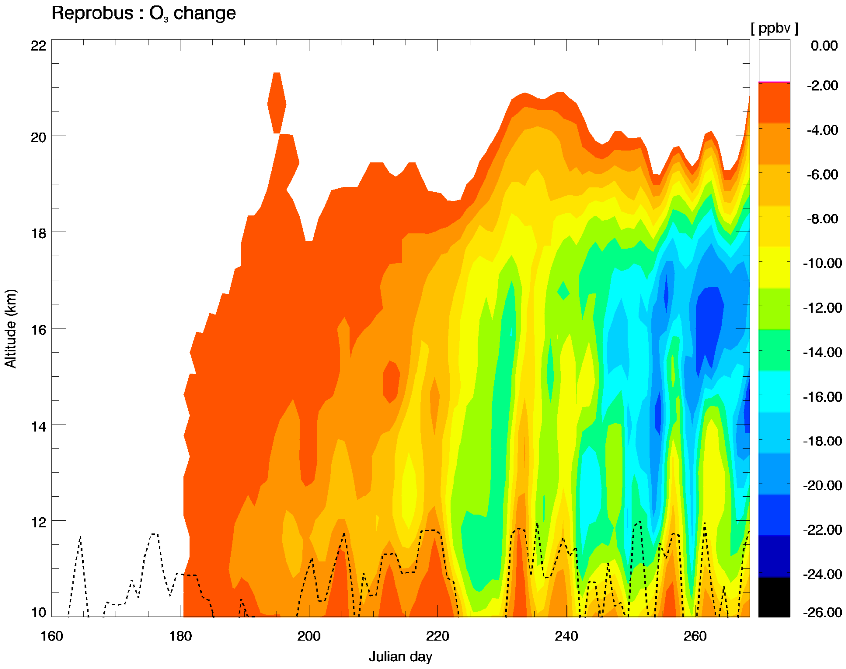

Figure 11: Changes in ozone over Kiruna (67.5°N, 21.0°E) as a function of altitude and time between 1 July and 1 October 2009. Calculations are done by subtracting outputs from the volcanic simulation driven by OSIRIS observations with the background simulation. The position of the tropopause is given by the black dotted line.