

## ***Interactive comment on “Impact of a moderate volcanic eruption on chemistry in the lower stratosphere: balloon-borne observations and model calculations” by Gwenaël Berthet et al.***

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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 NO<sub>y</sub> 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 O<sub>3</sub> 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 hetero-

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geneous chemistry in NO<sub>y</sub> partitioning; this is not new science."

→ Our goal is not to discuss the general understanding of the role of heterogeneous chemistry on NO<sub>y</sub> 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<sub>2</sub> 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<sub>2</sub> hydrolysis through further production of OH when ClONO<sub>2</sub> 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.

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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<sub>2</sub>, HNO<sub>3</sub> 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<sub>2</sub> hydrolysis."

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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<sub>2</sub> 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

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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<sub>2</sub>O<sub>5</sub> 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 NO<sub>y</sub> 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 dy-

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namical 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<sub>2</sub>, 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: “How-

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ever, 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<sub>2</sub> 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 O<sub>3</sub> 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

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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<sub>2</sub>O and NO<sub>y</sub> 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 NO<sub>y</sub>\* 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 cam-

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paign (August-September) on which is based our study. The text in former section 3.2 (now section 3.1) has been changed to: "N<sub>2</sub>O<sub>5</sub> is produced mainly at night from the recombination of NO<sub>2</sub> with NO<sub>3</sub> and destroyed during the day by photolysis leading to the reformation of NO<sub>2</sub>. Polar summer is characterised by continuous solar illumination preventing the formation of N<sub>2</sub>O<sub>5</sub> (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<sub>y</sub> partitioning via elevated N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub>) and 3.5 (NO<sub>2</sub>/HNO<sub>3</sub> 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<sub>2</sub>). Discussion about the NO<sub>x</sub> saturation effect and the description of figure 8 have been simplified. All simulations are only shown for NO<sub>2</sub> (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<sub>3</sub>) 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

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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.

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