

We thank Referee #2 for a helpful and constructive review which helped to further improve this manuscript. Our responses follow each comment in bold type.

Overview

The manuscript titled, "atmospheric nitric oxide and ozone at the WAIS Divide deep coring site: a discussion of local sources and transport in West Antarctica", reports a set of measurements of atmospheric NO, O₃, H₂O₂ and MHP at the boundary layer of WAIS Divide, together with a set of measurements of snowpit nitrate, nitrite and H₂O₂. This is a relatively interesting, high quality and still unique data set. While the data set is interesting, the paper, which focuses almost entirely in its discussion and analysis on the relative importance of local source versus transport in nitric oxide and ozone at WAIS Divide, and ends up with conclusions that local snowpack emission of NO_x is a significant boundary layer NO_x source above the inner WAIS, and transport dominates the abundance of O₃ at WAIS. Although the conclusions sound, the interpretation of the data presented does not adequately support the author's main conclusions. I feel that more work could and should be done to make supportive and convincing conclusions, before the dataset is considered to be publishable.

Major comments

The main two concerns I have are related to the main conclusions the authors made. The methods that the authors used to draw their conclusion are not convincing:

Concern 1: evaluating the importance of local snowpack NO_x emissions to the atmospheric boundary layer NO_x abundance. The authors measured atmospheric NO, and calculated the NO₂ concentration (~ 5pptv) assuming a steady state of NO_x cycling. In addition, the authors calculated the emission rate (flux) of NO₂ (~ 7 pptv h⁻¹) from snowpack nitrate photolysis. By comparison of these two results, the steady-state NO₂ concentration and the snowpack NO₂ emission rate, the authors conclude that snowpack emission contributes significantly to the NO_x budget at WAIS Divide. This conclusion is rather bold and intriguing, and the way the authors draw this conclusion is problematic. The first problem is that it is not appropriate to compare a concentration to a flux, the units are different. The second problem is, based on the authors' calculation, the emission rate of NO₂ from snowpack is ~ 7 pptv h⁻¹, and the lifetime of NO_x at WAIS Divide is 17 h, does that give the concentration of NO₂ originating from snowpack emission is 7 pptv h⁻¹ x 17 h = 119 pptv that is much more than the observed atmospheric NO_x concentration?

A more convincing way to prove the conclusion is to calculate the concentration of NO_x emitted from snowpack, and compared that to the measured NO_x concentration. This work has been done by Thomas et al. 2012 in ACP (cited by this manuscript). In the Thomas et al. paper, a framework to calculate the

concentration of NO_x emitted from snowpack nitrate photolysis is built, making a quantitative comparison possible. Considered that similar work has been performed and published in the same journal, and for the review criteria, I feel the authors should do the same thing to valid their conclusion, because the current way they did is not necessarily supporting their conclusion.

This study is a semi-quantitative comparison that shows that snowpack NO_x emissions are a significant contributor to the atmospheric nitrogen budget at WAIS Divide. Using a detailed 1-D model to answer this question is beyond the scope of this manuscript, which mainly presents field observations and places them in a regional-transport and local context. A modeling approach will be developed in a future publication.

Based on the referee's comments, we changed several points of our calculations. We added the NO production from nitrite photolysis into the estimation of snowpack NO_x emissions.

We updated our calculations of the steady-state NO₂ concentration and of the NO_x lifetime with HO_x mixing ratios estimated for WAIS Divide (see comment from Jennie Thomas). Similar calculations were performed with reported HO_x from Halley and South Pole in order to give the possible range of our estimation.

The NO_x concentration calculated from the estimated NO_x production rate and its lifetime overestimate the sum of measured concentration NO and steady-state estimated NO₂. We therefore mention that our estimates are upper bounds and explain the possible uncertainties of our calculations (Sections 4.1.4, 4.1.5 and 4.1.6).

Concern 2: The way, that the authors use to evaluate the relative importance of local source versus transport to O₃ concentration, has fault and is misleading at some points. For the local production of O₃ (in section 4.1.5), the authors use the general scenario presented in the book chapter of John Seinfeld and Spyros Pandis to calculate the O₃ production. However, that general scenario assumes that NO_x emitted from the source(s) is mainly in the form of NO, which of course needs another radical (HO₂) to produce NO₂ and then the photolysis of NO₂ leads to the production of O₃. For snow covered areas, the emission of NO_x from snowpack nitrate photolysis is mainly in the form of NO₂, which doesn't need the presence of HO₂ to trigger the production of O₃. Especially, considered the authors' first conclusion that snowpack photolysis at WAIS Divide is significant for local NO_x concentration, the evaluation of local O₃ production performed by the authors makes little sense, and probably largely underestimate the local O₃ production rate.

The Thomas et al. paper also has the method to quantify the impact of local snow NO_x emission on O₃ production. The authors should invoke a similar approach instead of using a rather simple and bold way.

The analysis of the WAIS Divide photochemistry with a 1-D model will be developed in a future publication. In the current manuscript, we added

details in Section 4.1.7 to clarify that our pseudo steady-state estimate of local O₃ production rate accounts for the NO_x emitted from the snowpack (Section 4.1.7). The 1-m mixing ratios of O₃ may already reflect the contribution of NO_x, as Frey et al. (2013) demonstrated that a pseudo steady-state between NO₂ and NO is reached at 1-m above surface snow.

In addition, there are clear temporal trends in the concentration of O₃ (Figure 1, and Figure 9), but the authors have not tried to explain these trends. The trends exist even in the period when the air-mass originates from the same region (Figure 9), does that mean the strength of transport varies? If so, the authors have to state that and give at least a brief discussion (e.g., local daily wind speed should tell something about that). It is very likely the local production of O₃ is small compared to the transport, as deduced from the temporal trends of O₃ and NO concentration (one has trends well the other does not). However, this more supportive evidence than the authors have presented for their conclusion is ignored by the authors.

A better interpretation of the temporal trends in O₃ concentration has been developed. The possible seasonal trend and apparent small local production of O₃ are now discussed further in Section 4.1.1. Analysis of O₃ mixing ratios with local wind speeds suggests that local production of O₃ is not the main process controlling the O₃ cycle (Section 4.1.1). Further interpretation of transport differences around an unexplained high O₃ event was added to Section 4.2.2. We also mention now in the conclusion that local O₃ production is small in comparison to air-mass transport.

Minor comments

There are some detailed questions/comments regarding the entire manuscript listed below.

Point1: Page 6808, line 25, 'from east Antarctica plateau', please to specify which part it is, above 2500 m or below 2500 m? You may want to define the two layers (above and below 2500 m) with different names, as in the rest of the manuscript these two layers are mentioned a lot.

Changes were made. We are now classifying the different Antarctic regions on the basis of the slope and elevation. The East Antarctic Plateau refers to the East Antarctic region above 2500 masl with the slope less than 1 degree. The inner WAIS is the West Antarctic region above 1500 masl with the slope less than 1°. Finally we merged the two previously defined regions, Antarctic coast and East Antarctic regions below 2500 masl, into one: the Antarctic coastal slopes which is defined as the territory with a slope greater than 1 degree, below 1500 masl in West Antarctica or below 2500 masl in East Antarctica (Section 4.2).

Note that this classification changes the air-mass contributions modeled by HYSPLIT but does not affect the outcomes and conclusion.

Point2: page 6809, Line 12, the Thomas et al. 2012 paper shows snowpack photolysis doesn't affect boundary layer O₃ concentration.

Note that on page 6545 Section 4.2 of Thomas et al. 2012: "Influence of snow chemistry on ozone" the authors mentioned that "Ozone in the boundary layer is also impacted by snow photochemistry", "the comparison of the base and the noNit case shows that nitrate snow chemistry leads to the formation of an additional 2–3 ppb in the boundary layer" and "nitrate snow chemistry increases ozone formation rates at Summit approximately by a factor of four around noon".

Point3: page 6817, the discussion of NO diel cycle is fault. No attempt is made to involve the impact of boundary chemistry. Not only the boundary height altering the concentration of NO, but also the production and sink of NO. In the noon, the sink of NO is enhanced due to photochemical reaction, while in the morning and in the afternoon the production starts and sink is not that strong, which cause the diel cycle (high in the morning and evening, low at night and in the noon). This phenomenon has been observed for a lot of gaseous species at a lot of locations. Simply attributes that to boundary layer height change is too bold.

This part of the discussion was revised (see Section 4.1.1). From our dataset, we can conclude that the photochemistry in snow, the variations of boundary layer height and wind speed influence the NO diel cycle. The possible contribution of the NO_x photochemistry cannot be assessed since it requires more measurements or more assumptions that could be answered with the use of a 1-D model, which is beyond the scope of this publication.

Point4: page 6817, the paragraph about O₃ variation. The author state that there is no diel cycle of O₃ concentration, but why don't show that data of O₃ concentration as the measurement of O₃ is at 1-min resolution?

We thank the referee for this comment, as the data reanalysis revealed a small diel cycle of O₃, which is now presented in Figure 2b. Therefore we have rewritten the corresponding sections (Sections 3.1 and 4.1.1) and conclusion.

Point5: page 6817, the paragraph about H₂O₂ and MHP is an example of not carefully proofreading. In addition, how the effects of chemical loss procedures on the variations in H₂O₂ and MHP?

The section was reviewed and edited. The H₂O₂ is impacted by photochemistry, snow source and temperature-driven physical recycling between the snow and air whereas the MHP is not because of its reduced solubility. A more detailed discussion of this topic is developed by Frey et al. (2009). We refer to this article in the paragraph without more discussion since H₂O₂ and MHP do not represent the main scope of this manuscript.

Point6: page 6818, line 20. “low concentrations”, compared to which they are low? In Figure 5, the concentration of nitrate is normal (if the • represents snowfall concentration). And there is one measurement of H₂O₂ in snowfall is above the average in surface snow. In addition, you need label the symbols in your figure (e.g., Figure 5).

The text was modified as suggested and the figure is now labeled.

Point7: page 6819, the paragraph about snowpit measurements of NO₃⁻, NO₂⁻ and H₂O₂ need more extensive interpretation, given the history of research and depth of available information regarding the preservation of nitrate in snow and snowpack photochemical reactions. For example, the authors should at least discuss the decrease of H₂O₂ profile.

The discussion of the snow chemistry regarding nitrate has been extended significantly (see reply to comment by Dr. Joel Savarino and Section 4.1.2). A discussion on H₂O₂ is beyond the scope of this manuscript, and we refer to a previous discussion on this topic (Hutterli, 2003, and references therein).

Point8: page 6823, line 10. Does ignoring the production of NO₂ from NO₂⁻ lead to underestimate the emission of snowpack NO₂? So how this account for the “resulting emission fluxes may therefore be an upper limit”?

We revised our calculations and Sections 4.1.5 and 4.1.6, based on this comment.

Boxe and Saiz-Lopez (2008) demonstrated the significant contribution of the photolysis of NO₂⁻ in the NO_x production from snow. Therefore we calculated the potential emission fluxes of NO from NO₂⁻ photolysis in snow considering Reaction R9. With the previous estimate of NO₂ emission fluxes, we estimated fluxes of NO_x emitted from surface snow. This approach is similar to previous studies (France et al., 2012, and references therein). Adding this photolytic pathway increases considerably our potential estimate of NO_x emission fluxes.

Photolysis of both NO₃⁻ and NO₂⁻ is the main source of NO_x in regards to other pathways (France et al., 2012, and references therein). In addition, our calculations were made under the assumptions detailed in Sections 4.1.5 and 4.1.6. Therefore we are confident to present upper-limit NO_x emission fluxes from surface snow and NO_x production rates.

Point 9: page 6824, line 15; the lifetime of HNO₃ is against photochemical reaction or against dry and wet deposition? Be specific.

Change was made. The lifetime of HNO₃ is against dry deposition, as loss from photolysis and reaction with OH was found negligible (Slusher et al., 2002).

References

Boxe, C. S. and Saiz-Lopez, A.: Multiphase modeling of nitrate photochemistry in the quasi-liquid layer (QLL): implications for NO_x release from the Arctic and coastal Antarctic snowpack, *Atmos Chem Phys*, 8(16), 4855–4864, 2008.

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