

## ***Interactive comment on “Atmospheric nitric oxide and ozone at the WAIS Divide deep coring site: a discussion of local sources and transport in West Antarctica” by S. Masclin et al.***

**Anonymous Referee #2**

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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, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and MHP at the boundary layer of WAIS Divide, together with a set of measurements of snowpit nitrate, nitrite and H<sub>2</sub>O<sub>2</sub>. 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<sub>x</sub> is a significant boundary layer NO<sub>x</sub> source above the inner WAIS, and transport dominates the abundance of O<sub>3</sub> at WAIS. Although the conclusions sound, the interpretation of the

C1309

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.

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<sub>x</sub> emissions to the atmospheric boundary layer NO<sub>x</sub> abundance. The authors measured atmospheric NO, and calculated the NO<sub>2</sub> concentration ( $\sim 5$  pptv) assuming a steady state of NO<sub>x</sub> cycling. In addition, the authors calculated the emission rate (flux) of NO<sub>2</sub> ( $\sim 7$  pptv h<sup>-1</sup>) from snowpack nitrate photolysis. By comparison of these two results, the steady-state NO<sub>2</sub> concentration and the snowpack NO<sub>2</sub> emission rate, the authors conclude that snowpack emission contributes significantly to the NO<sub>x</sub> 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 NO<sub>2</sub> from snowpack is  $\sim 7$  pptv h<sup>-1</sup>, and the lifetime of NO<sub>x</sub> at WAIS Divide is 17 h, does that give the concentration of NO<sub>2</sub> originating from snowpack emission is  $7 \text{ pptv h}^{-1} \times 17 \text{ h} = 119 \text{ pptv}$  that is much more than the observed atmospheric NO<sub>x</sub> concentration?

A more convincing way to prove the conclusion is to calculate the concentration of NO<sub>x</sub> emitted from snowpack, and compared that to the measured NO<sub>x</sub> 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<sub>x</sub> 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.

C1310

Concern 2: The way, that the authors use to evaluate the relative importance of local source versus transport to O<sub>3</sub> concentration, has fault and is misleading at some points. For the local production of O<sub>3</sub> (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 O<sub>3</sub> production. However, that general scenario assumes that NO<sub>x</sub> emitted from the source(s) is mainly in the form of NO, which of course needs another radical (HO<sub>2</sub>) to produce NO<sub>2</sub> and then the photolysis of NO<sub>2</sub> leads to the production of O<sub>3</sub>. For snow covered areas, the emission of NO<sub>x</sub> from snowpack nitrate photolysis is mainly in the form of NO<sub>2</sub>, which doesn't need the presence of HO<sub>2</sub> to trigger the production of O<sub>3</sub>. Especially, considered the authors' first conclusion that snowpack photolysis at WAIS Divide is significant for local NO<sub>x</sub> concentration, the evaluation of local O<sub>3</sub> production performed by the authors makes little sense, and probably largely underestimate the local O<sub>3</sub> production rate.

The Thomas et al. paper also has the method to quantify the impact of local snow NO<sub>x</sub> emission on O<sub>3</sub> production. The authors should invoke a similar approach instead of using a rather simple and bold way.

In addition, there are clear temporal trends in the concentration of O<sub>3</sub> (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 O<sub>3</sub> is small compared to the transport, as deduced from the temporal trends of O<sub>3</sub> 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.

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

C1311

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.

Point2: page 6809, Line 12, the Thomas et al. 2012 paper shows snowpack photolysis doesn't affect boundary layer O<sub>3</sub> concentration.

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.

Point4: page 6817, the paragraph about O<sub>3</sub> variation. The author state that there is no diel cycle of O<sub>3</sub> concentration, but why don't show that data of O<sub>3</sub> concentration as the measurement of O<sub>3</sub> is at 1-min resolution?

Point5: page 6817, the paragraph about H<sub>2</sub>O<sub>2</sub> and MHP is an example of not carefully proofreading. In addition, how the effects of chemical loss procedures on the variations in H<sub>2</sub>O<sub>2</sub> and MHP?

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 H<sub>2</sub>O<sub>2</sub> in snowfall is above the average in surface snow. In addition, you need label the symbols in your figure (e.g., Figure 5).

Point7: page 6819, the paragraph about snowpit measurements of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and H<sub>2</sub>O<sub>2</sub> need more extensive interpretation, given the history of research and depth of

C1312

available information regarding the preservation of nitrate in snow and snowpack photochemical reactions. For example, the authors should at least discuss the decrease of H<sub>2</sub>O<sub>2</sub> profile.

Point8: page 6823, line 10. Does ignoring the production of NO<sub>2</sub> from NO<sub>2</sub><sup>-</sup> lead to underestimate the emission of snowpack NO<sub>2</sub>? So how this account for the “resulting emission fluxes may therefore be an upper limit”?

Point9: page 6824, line 15; the lifetime of HNO<sub>3</sub> is against photochemical reaction or against dry and wet deposition? Be specific.

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C1313