

## Response to Anonymous Reviewer #2

**We thank reviewer #2 for the constructive comments and suggestions for improving our manuscripts. Our responses are inserted below and highlighted in dark blue font for easier identification.**

In “Intrusion, retention, and snowpack chemical effects from exhaust emissions at Concordia Station, Antarctica,” Helmig, et al. show the impact station exhaust can have on even the clear air sector, at a remote, high-latitude, research station. The show incidents of high NO<sub>x</sub> above the snowpack correspond with winds from camp. They also show the lag in higher NO<sub>x</sub> concentrations in the snowpack and that the higher concentrations at depth persist for longer than those over the snowpack.

This work is important, but not unique. It reemphasizes that more researchers need to look at the potential impacts of station activities on snow and air chemistry, even in the designated “clean air sector” at these stations. Others have shown the impact of station emissions on snow and air chemistry at remote stations, including the impact of NO<sub>x</sub> from station power generation.

General comments:

The authors do not cite other work showing the impact of station exhaust on NO<sub>x</sub> in the air and nitrate in the snow. Fibiger et al. (2016) show the impact of station exhaust on NO<sub>x</sub> concentrations above the snowpack and on nitrate in snow at Summit, Greenland. They use d15N to quantify this influence on snow nitrate. More discussion of how the influence at Dome C compares with these findings would greatly strengthen this analysis.

**Authors' response: We have included discussion and a reference to this publication in the section on our results of the snow pit data in our revised manuscript.**

Wolff et al. (1998), also show this issue with filter collections at various stations, including Durmont d'Urville, which could result in deposited nitrate.

**Authors' response: We have also added reference to two articles published by this group of authors in the discussion and conclusion sections (Wolff et al., 1998a,b).**

The authors state in the methods section that the NO measurement is more accurate than NO<sub>x</sub>, which contains several other NO<sub>y</sub> species. Throughout the manuscript, however, the authors use the NO<sub>x</sub> measurement. Why has this been chosen over NO? The enhancements should still show up in NO, without the interference issues.

**Authors' response: We chose NO<sub>x</sub> as it is a more representative indicator for the total of the oxidized nitrogen, whereas NO would only indicate a fraction. Further, the fractionation between NO and NO<sub>x</sub> is sensitive to other gases (such as ozone) and residence time and snowpack depth. Therefore, interpretation of NO data is more ambiguous.**

In figure 6 the authors show the impact on firn NO<sub>x</sub> continues past day 198, which is 6 days after event onset. Separately, the authors state there are 15 (abstract) or 50 (text) occurrences of plumes over the sampling site. They conclude that less than 10% of the measurements were contaminated by the plume, but this is difficult to reconcile. The authors should provide more detail on how many events there are, how long they last.

**Authors' response: We counted 15 events in total when there was a spike in the above air NO<sub>x</sub> measurements followed by an increase of at least 1 ppb within the snowpack. This detail has been added to the text.**

Also, the abstract states the NO<sub>x</sub> levels last “a few days to one week,” but in the text it says “1-5

days." These statements need to be verified and data needs to be presented more consistently and clearly.

**Authors' response:** As can be seen in Figure 6, even after 7 days NOx in the snowpack still hadn't completely returned to the pre-event levels. We have corrected the text accordingly, and now state that "..... it took up to in excess of 7 days for NOx in the snowpack air to return to pre-event levels."

Specific comments:

Lines 18-20. This sentence needs to be reworded. It is not clear how many inlets there are or how many are above or below the snowpack.

**Authors' response:** Sentence was reworded to: "Ambient air was sampled continuously from inlets mounted above the surface on a 10 m meteorological tower. In addition, snowpack air was collected in 30 cm intervals to 1.2 m depth from two manifolds that had both above and below surface sampling inlets."

Line 102. The authors explain how they set inlets in the snow for sampling firn air.

They do not explain how confident they are that digging a pit and refilling it does not change the porosity of the snow or the dynamics of air flow. This could influence how applicable the firn results are.

**Authors' response:** We added some more explanation. The text now reads: "The hole was then loosely refilled with the excavated snow, re-establishing the stratigraphy as much as possible. Blowing snow then refilled any remaining gaps within the following 2-3 days. The snow tower was kept in place after the campaign, so we have no data on the potential changes in porosity and air flow dynamics that resulted from the snow tower installation and subsequent changes in the snow morphology as the snowpack re-equilibrated."

Line 130. The authors say their calibration gas was diluted with NOx scrubbed air. Was this tested against dilution with true zero air? Most NOx scrubbers emit a low, constant, level of NOx, which must be accounted for in calibrations. This tends not to be important in polluted areas, but is for 1 ppb NOx measurements.

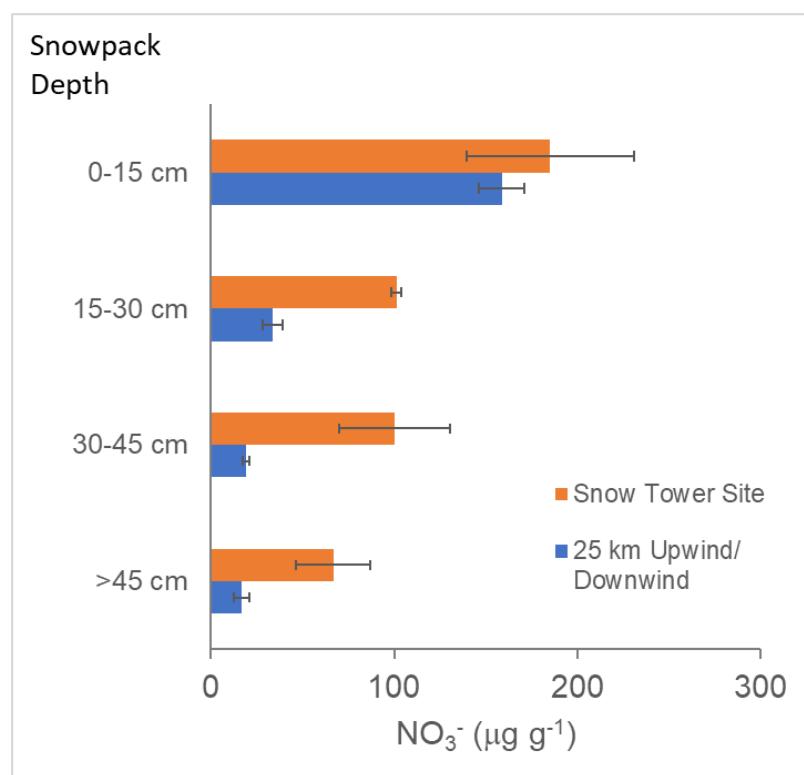
**Authors' response:** We did not bring zero air compressed gas cylinder to Concordia. Instead, we prepared a low NOx dilution gas by pumping ambient air (which had significantly lower NOx levels than snowpack air) through a cartridge filled with ~ 1 dm<sup>3</sup> of granular Chemisorbent (Purafill, <https://www.purafil.com/products/chemical-filtration/chemical-media/#chemisorbant>). Calibration ranges were from 0.1-25 ppb and the instrument response was linear within this range. Intercepts of the linear regression, and zero values from sampling of the scrubbed air were below 0.1 ppb.

Line 192. Show this data in the supplement. It's hard to know what these qualitative and quantitative comparisons look like without showing the data.

**Authors' response:** The results shown in Figure 6 are actually the combined data from both snow towers. Wording has been added to the figure caption to make this clearer: "Combined measurements from the two snow towers capturing a pollution event at Concordia during the middle of the winter (Day of Year 191 = July 11). Plotted time series traces correspond to the sampling heights indicated in the legend, with positive numbers giving the height above the snow surface, and negative numbers the depth below the snow surface. The right graph (b) is an enlargement of the data shown in the left (a), with the transitions between the connecting lines between the two snow tower measurements removed to better show the level of agreement in the data from the two sampling manifolds. The sampling switched between the two snow towers every 24 hours leading to some abrupt shifts in NO<sub>x</sub> measurements from within the snowpack."

Line 220. The authors say the difference becomes weaker at depth, but only one point seems to have a smaller difference. Support this statement with statistics. What are the differences at the surface and at depth? Is that difference significant?

**Authors' response:** Motivated by this reviewer comment we did some further analysis of these data. The within camp and 25 km distance data sets were combined and binned in 15 cm-depth increments. Results shown below indicate that the difference between the two data sets actually becomes larger with depth, and not weaker as we had mistakenly stated in the manuscript. This analysis does not show clear evidence for  $\text{NO}_3^-$  contamination at the snow tower site in the upper snowpack layers. However, deeper in the snowpack,  $\text{NO}_3^-$  levels appear to be higher at the snow tower site. A hypothesis explaining this behavior may be that the photolysis and loss of nitrate is weaker in the more contaminated snow, possibly due to the fact that the snowpack contains more chromophores than the unspoiled snow. Certainly, more snow pit sampling and chemical analyses are needed to investigate this stipulation. The figure was added to the Supplement, and this data discussion was added to the manuscript text.



Line 242. Do not cite unpublished results. Either publish them here, or do not include them. Also, which way is the 15% difference in ozone loss? Using data that others cannot see is bad scientific practice.

**Authors' response:** The section was changed to: "In addition to the experiments described above, during the 2014 campaign a number of dynamic flow-through snow chamber photochemistry experiments were conducted to investigate if there were differences in the reactive chemistry in the snow from near the snow tower site compared to snow sampled 25 km away from camp. These measurements showed on the order of 10-20% higher NOx and less ozone in the outflow of chambers filled with the snow from further away from the camp. We did not conduct a high enough number of repeats for evaluating the repeatability and statistical significance of these results to gauge if and how much of this signal was due to the experimental

setup or the due to differences in the snowpack chemical composition. Nonetheless, these preliminary findings point towards possible differences in the chemical behavior that potentially are linked to differences in the snow sampling locations and contaminant levels resulting from camp influences that warrant further investigation.

Line 264. Something is wrong in this sentence. You need to delete “organic gases” or reword.

**Authors' response:** Sentence was shortened and connected to the previous sentence. It now reads: “A tendency of potentially enhanced snowpack  $\text{NO}_3^-$  levels in two snow pits collected at the camp, compared to data from three sites at further distance, supports the suspicion that the snowpack composition at the station may be compromised (i.e. contaminated) from the re-occurring ventilation of the snowpack with polluted ( $\text{NO}_x$ -enriched) air, which adds to the previous findings on black carbon, and organic gases snowpack contamination from engine exhaust at polar research stations.”

## References

Fibiger, D. L., J. E. Dibb, D. Chen, J. L. Thomas, J. F. Burkhart, L. G. Huey, and M. G. Hastings (2016), Analysis of nitrate in the snow and atmosphere at Summit, Greenland: Chemistry and transport, *J. Geophys. Res. Atmos.*, 121, 5010–5030.

Wolff, E. W., M. R. Legrand, and D. Wagenbach (1998a), Coastal Antarctic aerosol and snowfall chemistry, *J. Geophys. Res.*, 103(D9), 10927–10934.

Wolff, E. W., and H. Cachier (1998b), Concentrations and seasonal cycle of black carbon in aerosol at a coastal Antarctic station, *J. Geophys. Res.*, 103(D9), 11,033–11,041.

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