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Intrusion, retention, and snowpack chemical effects from exhaust emissions at Concordia Station, Antarctica

Detlev Helmig^{1.*}, Daniel Liptzin¹, Jacques Hueber¹, and Joel Savarino²

Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO 80305, USA

Univ. Grenoble Alpes, CNRS, IRD, Grenoble INP, IGE, F-38000 Grenoble, France

*corresponding author: detlev.helmig@colorado.edu

detlev.helmig@colorado.edu

Abstract

Continuous measurements of reactive gases in the snowpack and above the snowpack surface were conducted at Concordia Station (Dome C), Antarctica, from December 2012 - January 2014. Measured species included ozone, nitrogen oxides, gaseous elemental mercury, and formaldehyde, for study of photochemical reactions, surface exchange, and the seasonal cycles and atmospheric chemistry of these gases. The experiment was installed ~1 km from the main station infrastructure inside the station clean air sector and within the station electrical power grid boundary. Air was sampled continuously from three inlets on a 10 m meteorological tower, as well as from two above and four below the surface sampling inlets from within the snowpack. Despite being in the clean air sector, over the course of the 1.2-year study, we observed on the order of 15 occasions when exhaust plumes from the camp, most notably from the power generation system, were transported to the study site. Continuous monitoring of nitrogen oxides (NO_x) provided a measurement of a chemical tracer for exhaust plumes. Highly elevated levels of NO_x (up to 1000 x background) and lowered ozone (down to ~50%), most likely from titration with nitric oxide, were measured in air from above and within the snowpack. Within 5-15 minutes from observing elevated pollutant levels above the snow, rapidly increasing and long-lasting concentration enhancements were measured in snowpack air. While pollution events typically lasted only a few minutes to an hour above the snow surface, elevated NO_x levels were observed in the snowpack lasting from a few days to one week. These observations add important new insight to the discussion of if and how snowphotochemical experiments within reach of the power grid of polar research sites are possibly compromised by the snowpack being chemically influenced (contaminated) by gaseous and particulate emissions from the research camp activities. This question is critical for evaluating if snowpack trace chemical measurements from within the camp boundaries are representative for the vast polar ice sheets.

Introduction

Research conducted during the past ~15 years has revealed an active and remarkable spatial diversity of atmospheric oxidation chemistry in the polar lower atmosphere [*Grannas et al.*, 2007]. Ozone plays a

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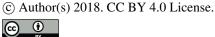




fundamental role in controlling the lifetime of many atmospheric trace gases directly and indirectly by modulating atmospheric OH. Unlike the episodic ozone depletion events observed at coastal sites, the opposite effect (i.e. ozone production) has been observed in the Antarctic interior [*Crawford et al.*, 2001; *Helmig et al.*, 2007b; *Helmig et al.*, 2008a; *Legrand et al.*, 2009; *Legrand et al.*, 2016]. The discovery of ozone production chemistry in the remote and pristine Antarctic environment was rather surprising because hitherto photochemical production in the lower atmosphere had exclusively been associated with polluted urban environments [*Molina and Molina*, 2004]. Photochemical production and snowpack emissions of nitric oxides (NO_x) have been identified as underlying processes driving this chemistry. NO_x has been shown to be formed from photochemical reactions in the snowpack [*Honrath et al.*, 1999; *Jones et al.*, 2000], with deposited nitrate constituting the reservoir of this chemistry. NO_x play a crucial role in snow photochemical reactivity [*Murray et al.*, 2015]. NO_x mixing ratios in interstitial air resulting from photochemical reactions can exceed those in the air above the snowpack by a factor of ~50 [*Van Dam et al.*, 2015].

This concentration gradient is driving NO_x emission fluxes out of the snowpack into the overlying atmosphere [Jones et al., 2001; Honrath et al., 2002], which, under stable atmospheric conditions, can cause large NO_x enhancements in the atmospheric surface layer [Helmig et al., 2008b; Neff et al., 2008; Frey et al., 2011; Frey et al., 2013], and in the presence of solar irradiance trigger photochemical ozone production, with resulting peak ozone levels that can be double those in the boundary layer [Crawford et al., 2001; Helmig et al., 2008a; Legrand et al., 2016]. Experiments on reactive nitrogen chemistry investigating this rather unexpected ozone production chemistry have built on a variety of atmospheric research strategies, including snowpack air sampling [Dibb et al., 2002; Jacobi et al., 2004; Helmig et al., 2007a; Van Dam et al., 2015], snow chambers [Dibb et al., 2002], snow chemical analyses [Dassau et al., 2002; Dibb et al., 2007b; France et al., 2011; Erbland et al., 2013], atmospheric monitoring [Frey et al., 2011; Kramer et al., 2015; Legrand et al., 2016], surface fluxes [Jones et al., 2001; Honrath et al., 2002; Frey et al., 2011; Frey et al., 2015], and boundary layer vertical profiling [Helmig et al., 2008a; Frey et al., 2015].

Most of these studies rely on observations from dedicated campaigns at research stations, including photochemistry campaigns at Summit, Greenland [$Dibb\ et\ al.$, 2007a], the Antarctic Tropospheric Chemistry Investigation [ANTCI; $Eisele\ and\ Davis$, 2008] at the South Pole, the Chemistry of the Antarctic Boundary Layer and the Interface with Snow (CHABLIS) experiment at Halley [$Jones\ et\ al.$, 2008], and the Oxidant Production over Antarctic Land and its Export (OPALE) campaign at Concordia Station [$Preunkert\ et\ al.$, 2012]. A common limitation of these studies is that experiments were conducted in proximity to large research stations, where use of fuel-powered engines in generators and vehicles cause exhaust emissions with highly elevated concentrations of particulates and gases, particularly of volatile organic compounds (VOC) and NO_x. A critical question is if and how this pollution, and possibly secondary products formed during the atmospheric transport and deposition, impact the snow chemical position and reactivity, and potentially the findings from this aforementioned literature. This is of particular importance for oxidized nitrogen species. This experiment yielded for the first time a year-long record of NO_x and O₃ in an Antarctic snowpack at Concordia and the atmosphere above it. This experiment also gave us the opportunity to study and evaluate occurrences of pollution episodes, using the NO_x monitoring as a sensitive chemical tracer for identification of exhaust plumes.



Methods

<u>Location</u>: This experiment was conducted at the French/Italian Antarctic research station Concordia, located at the Dome Circe or Dome Charlie (Dome C, 75.1°S/123.35°E3233 m asl, mean temperature -55°C). An experimental site was established at the border of the clean air sector, approximately ~1 km west of the station common buildings (Figure 1). The clean air sector is located in the opposite direction of the prevailing wind direction. The site consisted of a 8 m x 2 m x 2.5 m underground laboratory posit-

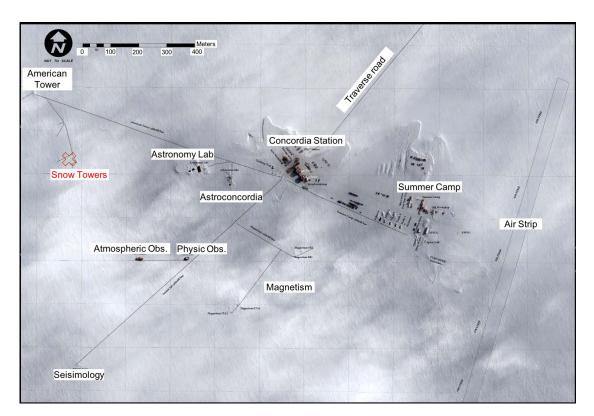


Figure 1: Satellite image of research station Concordia with location of the snow photochemistry experiment indicated by the red cross and text. Its location was ~1 km west of the station main buildings and power generation plant.

ioned at the border of the clean air area, a 10 m tall meteorological tower, and two snow air sampling manifolds placed 15 m into clean snow ('snow tower') for sampling the atmosphere and the snow interstitial air (Figure 2). The installation was in late November 2012 with continuous monitoring conducted to January 2014 (14 months).

Meteorological Tower: A 10 m meteorological tower (Figure 2a) was equipped with two sonic anemometers for atmospheric turbulence measurements, and three gas sampling inlets (0.5 m, 2 m, 10 m) with sampling lines inside a heated conduit running to the laboratory. The upper inlet was attached

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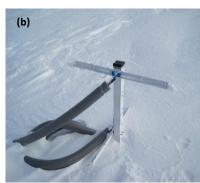


Figure 2: (a) Meteorological tower with the station infrastructure in the background. The wooden box to the left is the entry hatch to the underground laboratory. Air sampling inlets were located at 0.5 m, 2 m and 10 m above the surface on the tower. Two snowpack air sampling towers were located approximately 7 m to the left and 10 m to the right of the base of the meteorological tower. (b) One of the two snow pack air sampling manifold (snow tower), with one pair of inlets right on the snow surface, and one inlet pair at ~30 cm height. Four more equivalent sampling inlet pairs are below the snow surface at 30 cm depth intervals extending to a maximum depth of 1.2 m.

to a manual pulley allowing that inlet to be lowered for side by side sampling of both inlets for tracking and correcting sampling inlet/lines biases.

Snowpack Air Sampling: Two identical multi-inlet snow sampling manifolds ('snow tower') for collection of interstitial and ambient air at six ~20 cm vertical intervals were constructed, with a similar design to that described by [Seok et al., 2009] (Figure 2b). The snow tower consisted of a vertical post of square aluminum alloy (3.8 x 3.8 cm) with eight 60 cm long cross arms spaced vertically every 30 cm. Each of the cross bars supported a pair of sampling inlets. The inlets were fitted with 25 mm Acrodisc hydrophobic polytetrafluoroethylene (PTFE) syringe filters (Pall Life Sciences, Ann Arbor, Michigan, USA) to prevent snow and ice crystals from being pulled into the sampling line. For the installation, a snow pit was dug and the lines inserted into the clean untouched walls of the pit. The hole was then refilled with the excavated snow, respecting the stratigraphy as much as possible. Insulated and heated sampling lines connected the sampling inlets to the chemical analyzers in the underground laboratory. All sampling lines were of 0.64 cm o.d. x 30 m long pre-conditioned PFA tubing, except the lines to the gradient inlets on the meteorological tower, which were of 0.78 cm o.d. because they were continuously pumped to maintain a flow of 2 I min⁻¹. Air was pulled through the snow tower sampling lines by the combined flow of the gas analyzers (ozone monitor 1 l min⁻¹, a gaseous elemental mercury (GEM) analyzer 1 l min⁻¹, NO_x monitor 1 l min⁻¹). A maximum of two monitors sampled from the snow tower inlets together at a given time to limit the maximum snow air sampling. Since each line connected to a pair of inlets at equal height, the effective flow through each inlet was a maximum of ~1 I min⁻¹. Each height was sampled for 10 min every 2 hours, resulting in an approximate volume of a sphere with a radius of 25 cm around each inlet every 2 hours. Each sampling inlet had a thermocouple wire attached for monitoring the snowpack temperature gradient.

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- 116 Ozone Measurements: Ozone was measured with a Thermo Environmental (TEI) 49i UV absorption
- 117 monitor that was calibrated against a NOAA Global Monitoring Division reference standard before field
- 118 shipment.
- 119 NO_x Measurements: Nitrogen oxides were monitored with a TEI chemiluminescence analyzer (TEI 42C-
- 120 TL). The TEI 42C-TL has two channels. The first channel measures NO via NO + O_3 chemiluminescence.
- 121 The second channel measures total nitrogen oxides (NO_x = NO + NO₂) by redirecting air through a heated
- 122 (325°C) molybdenum converter, which causes NO₂—including other oxidized nitrogen compounds—to be
- 123 converted to NO. NO2 is then determined by subtracting NO, obtained from the first channel, from the
- 124 resulting NO_x signal. There are a number of other oxidized nitrogen species that can contribute to the
- 125 NO₂ measurement [Steinbacher et al., 2007]. The error in the NO₂ measurement increases with rising
- levels of interfering gases such as nitrous acid (HONO), peroxyacetyl nitrate (PAN), and alkyl nitrates that
- 127 contribute to the NO₂-mode signal. Consequently, NO₂ concentrations obtained with the TEI 42C-TL
- 227 contribute to the No₂ mode signal consequently, No₂ concentrations obtained with the 121 120 12
- represent an estimate for the sum of these oxidized nitrogen species. Field calibrations were conducted
- 129 with a NIST-traceable 1 ppm NO in N₂ gas standard (Scott-Marin, Inc., Riverside, CA, USA) that was
- dynamically diluted to low ppb mixing ratios with NO_x-scrubbed ambient air.
- 131 Snow Sampling and NO₃ Determination:
- 132 The snow pit NO₃⁻ data stem from sampling that was done at and near Concordia between January 2009
- and December 2010, and at ~3 m distance from snow tower 2 in January 2014. Snow was collected in pre
- 134 cleaned 50 ml centrifuge tubes inserted directly on a newly scraped wall of the snow pit. Nitrate
- 135 concentration in snow samples were measured directly in the field, at the wet chemistry laboratory of
- 136 Concordia station. Each sample was melted at room temperature and NO₃ concentrations were
- determined using a colorimetric method employed routinely at Concordia [Frey et al., 2009].

Results and Discussion

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- 139 Results of the year-round snowpack and ambient monitoring, including interpretations of photochemistry
- will be presented elsewhere [Helmig et al., 2018]. Here, we primarily focus on occurrences of pollution
- transport to the site and its penetration into the snowpack.
- 142 Figure 3 shows a photograph of the station main buildings. The power plant is adjacent to the two column
- 143 structure. Approximately 300 m³ of Special Antarctic Blend (SAB) diesel fuel are burned in the plant for
- electricity and heat generation per year. The exhaust plume from the 5-m high stack of the power plant
- can be seen in the picture, blowing towards the west. Due to the typical strong stratification and stability
- 143 can be seen in the picture, blowing towards the west. Due to the typical strong structure and stability
- of the atmosphere near the surface, the plume does not rise far above the stack height, but instead gets
- 147 transported horizontally at a height of \sim 5 m above the snow surface. This is a typical exhaust plume
- dispersion behavior for a cold regions environment, seen at many other polar research stations. The
- plume typically does not hit the surface within the immediate distance of the stack location. Depending
- on the actual turbulent mixing conditions it may take several hundreds of meters before the stack
- emissions are encountered right at the surface.
- 152 Of the gases monitored in this experiment, NO_x were the most sensitive tracer for pollution impact. NO_x
- in ambient air at Concordia remained well below 1 ppb during background conditions year-round [Helmig
- 154 et al., 2018], in agreement with observations from prior shorter campaign NO_x measurement at Concordia

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Figure 3: Photograph of Dome C station illustrating the dispersion of the exhaust plume from the electrical power generating plant during conditions with a strong surface temperature inversion. The plume is blown towards the west in the direction of the experimental site. This is a typical situation for a contamination event.

[Frey et al., 2011; Frey et al., 2013; Frey et al., 2015]. We did not observe highly elevated NO levels in the surface layer outside of pollution events, as what has been observed at South Pole [Helmig et al., 2008b; Neff et al., 2008]. During pollution events, this threshold was exceeded very quickly in measurements taken from the meteorological tower and from above-surface snow tower inlets, with resulting NO_x mixing ratios rising to as high as close to 200 ppb, representing an up to 1000-fold enhancement over background conditions (Figure 4).

During the course of the ~14 month study, a total of ~50 pollution events were observed, although some events overlapped (Figure 4). Most of these occurrences were relatively short, with elevated mixing ratios above the snowpack lasting from minutes to a few hours. Within the snowpack, NO_x mixing ratios remained elevated for 1-5 days after the event. Integrated over the entire campaign, pollution episodes constituted < 2.0 % of the measurements above the snowpack, and <10% of the measurements within the snowpack. The correlation analyses of pollution occurrences with wind direction clearly defines the direction of the transport. The predominant wind direction sector at Concordia is southeast to northwest (Figure 5a), with southeasterly winds having the largest share. NO_x levels were consistently well below 1 ppb when winds were from east to northeast. The sector with pollution transport is well defined, with wind directions covering approximately 45-120° (Figure 5b). These sectors perfectly line up with the upwind direction of the station power plant (Figure 1), clearly identifying the plant as the source of these pollution occurrences.





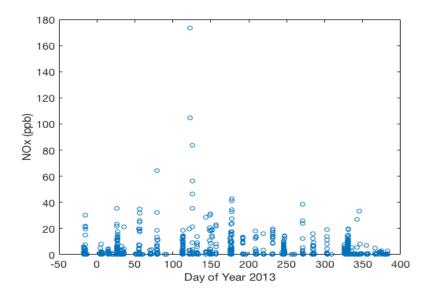


Figure 4: NO_x measured from the above surface inlets on the two snow towers, and from all inlets on the meteorological tower. Circles represent 10-min averaged data. Plotted are data that were extracted from occurrences when NO_x was above 1 ppb, well above the background mixing ratio, and any time when the wind direction was from the polluted wind sector.



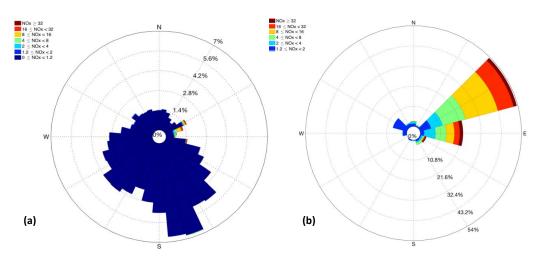
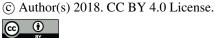


Figure 5: (a) Concentration wind rose with the relative frequency of NO_x mixing ratio data from the above surface inlets of the two snow towers segregated by 10° sectors for the full year of observation data. This panel shows all data. (b) The same analysis, with wind direction data binned in 20° sectors for events when NO_x in ambient air exceeded 1.2 ppb.





One of these elevated NO_x events is further investigated in Figure 6. Here, we show the measurements from six inlets on the snow tower over a one-week period. The sampling of a polluted plume is first observed in the two above surface inlets (orange/red colored data; +10 and +45 cm), by the sudden increase of NO_x from well below 1 ppb to a mixing ratio of ~13 ppb. This spike in NO_x lasted for ~3 hours. After that time, NO_x in air sampled above the surface dropped very quickly and equilibrated to prior mixing ratios within less than 0.5 hours.

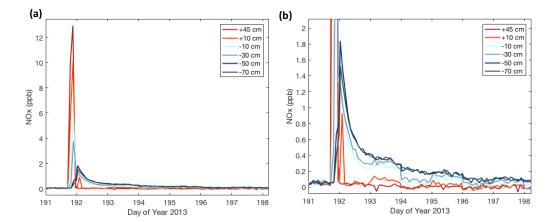


Figure 6. Measurements form the snow tower capturing a pollution event at Concordia during the middle of the winter (Day of Year 191 = July 11). Plotted time series traces correspond to the sampling heights indicated in the legend, with positive numbers giving the height above the snow surface, and negative numbers the depth below the snow surface. The right graph (b) is an enlargement of the data shown in the left (a). The sampling switched between the two snow towers every 24 hours leading to some abrupt shifts in NO_x measurements from within the snowpack.

A much different behavior was found in the air sampled from within the snowpack, indicated by the data in the blueish colors. The onset of the pollution signal is delayed, by 1-3 hours, with progressively later times towards deeper in the snowpack. Maximum mixing ratios that are reached in the snowpack are lower, i.e. 10-50% those that were measured above the surface, with mixing ratio maxima becoming progressively smaller with increasing depth. The most remarkable difference between the above and below surface measurements is the longer residence time of the pollution signal in the snowpack. NO_x mixing ratios in air withdrawn from all sampling inlets in the snowpack dropped steadily, but remained elevated in comparison to levels seen before the pollution event for a week. The behavior seen in the measurements from snow tower 1 were in full qualitative, and within ~30% quantitative agreement with the concurrent observations from the second snow tower. After the pollution event, NO_x in the snowpack air gradually declined over several days (Figure 6). Fitting of the data to an exponential decay function yields similar results for all snowpack depths (Figure 7), with exponential regression fit R^2 results ≥ 0.95 .

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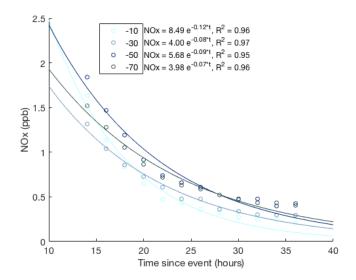


Figure 7. Exponential decay function fits to the NO_x snowpack measurements versus time at four depths for the event starting on Day of Year 191 shown in Figure 6. The start of the event was defined as the time when high NO_x was detected above the snowpack. Solutions for the best fit exponential decay functions are given in the legend.

Effects of the exhaust transport were also observed in the ozone signal. Here, the signal was negative from destruction of ozone by titration of NO in the exhaust plume. Up to 50% of the ambient ozone was destroyed in air sampled from the above surface inlets. Similar to NO_x, this signal, albeit weaker and attenuated in time, was also seen in the air sampled from within the snowpack (Supplement Figure S-1).

Nitrogen oxides undergo reaction with atmospheric oxidants, primarily the OH radical (summer only) and ozone, yielding higher oxidized nitrogen species (including NO_3 , N_2O_5 , HNO_3 , HNO_4) that can further react and partition into the snowpack aqueous and solid phases. The frequency, large enhancement, and long duration (in the snowpack) of NO_x pollution events constitute an apparent unnatural source of NO_x to the snowpack. One can hypothesize that further reaction of NO_x and NO_y with oxidants, such as with OH, may be a source of HNO_y and HNO_y in the snowpack, which would add acidity to the snow. This then also poses the question if and to what degree photochemical processes, building for instance on NO_y or NO_y as a substrate, may be altered from natural conditions. Further, the transformations of NO_x into these higher oxidized species may potentially leave a long-lasting signature in the snowpack (such as of NO_y).

We investigated this question by comparing NO₃⁻ results from snow pit sampling at different locations within the camp and at up to 25 km distance of the Dome C. Nitrate in the snowpack shows a steep vertical gradient, with highest levels observed right at the surface, and progressively lower concentrations with increasing depth (Figure 8). The results from the seven snow pits are consistent in the depth profile;

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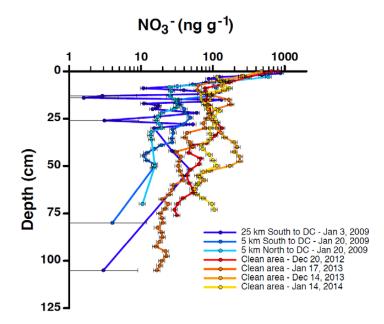


Figure 8. Nitrate concentration in snow pits in proximity (~ 20 m) to the snow towers (warm colors) at the border of the clean air sector, and sampling locations up and downwind of Concordia (cold colors). Sampling dates are indicated in the figure legend. Horizontal error bars depict the estimated uncertainty of the chemical analysis, i.e. 10% at > 10 ng g⁻¹, 50% between 5-10 ng g⁻¹, and 100% at < 5 ng g⁻¹.

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however, there appears to be a tendency that the four snow pits within the camp have somewhat higher, as well as more variable snow NO₃ at intermediate depths (around 50 cm). Deeper into the snowpack the difference between the two groups of data becomes weaker. At 1 m depth, the snow age is approximately ten years, and therefore approximately corresponds to the start of permanent and yearround activities in 2005 (note that summer activities at Dome C were established in 1996). This behavior in the NO₃ vertical gradient in the Antarctic snowpack has been previously investigated and documented [France et al., 2011]. Further, relatively higher NO₃ in the upper layers of the snowpack is observed during the Antarctic summer (Supplement Figure S-2), with average NO₃⁻ levels approximately 5 times higher than during the winter. This NO₃ enhancement in surface snow and the seasonal cycle have been linked to the production of HNO3 in the photoactive summer months from reaction of OH with NO2, with the NO₃ enhancement being the result of HNO₃ deposition to the snow surface [Erbland et al., 2013]. Elevated NO₃ concentrations observed at the surface of the snowpack are a common feature at low accumulation regions, with the concentration values depending strongly on the strategy for collection of the first few cm of the snow pack [Erbland et al., 2013; Shi et al., 2018]. With the sensitivity of surface snow NO₃ to the seasonal cycle and sampling strategy, the high variability of NO₃ observed at the surface precludes conclusive interpretation to what degree the snowpack at Concordia is impaired by ventilation of the snowpack with pollution-NO_x enriched air. Contamination of the snow pack around the Concordia station has been noted in previous investigation of black carbon, with a > 3-fold increase in concentration

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between pre- and post-2003 [Warren et al., 2006]. This increase in black carbon was shown to result in a significant decrease in light penetration into the snowpack [Warren et al., 2006; France et al., 2011; Libois et al., 2013]. In addition to the experiments described thus far, during the 2014 campaign a number of dynamic flow through snow chamber photochemistry experiments were conducted comparing snow from near the snow tower site to snow sampled 25 km away from camp. These experiments showed on the order of 15% differences in ozone loss in the chambers (unpublished results). We did not conduct a high enough number of repeats for evaluating the repeatability of these experiments 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 chemical behavior that is potentially linked to differences in the snow sampling locations and camp influences.

Summary and Conclusions

249 With our snowpack sampling manifold we were able to sample snowpack air to a maximum depth of 70 cm below the surface. Up to ~2 ppb enhancement was observed at that depth from exhaust infiltration.
251 While our experiment wasn't able to access air deeper (than 70 cm), the concentration gradients observed
252 apply that this transport and contamination extends well beyond the depth that was probed in these
253 measurements.

Our experiment was a one spot measurement, at ~1 km distance from the camp main facilities. We have no data that would allow us to assess to what distance from the camp the snowpack pollution from exhaust infiltration would be of noticeable and of importance, but it likely extends well beyond the

257 distance of our site.

Our measurements from Concordia Station emphasize the pronounced and long-lasting influence that station exhaust can have on NO_x levels in snowpack air. A tendency of potentially enhanced snowpack NO₃⁻ 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 (NO_x-enriched) air. Chemical signatures of other trace species that have enhanced concentration levels in engine exhaust, such as black carbon, organic gases are left behind in the snowpack is already demonstrated, resulting in a decrease of the e-folding depth of the light penetration. The associations shown in our study argue for further investigation, for instance by a high resolution spatial survey of surface snow composition within and beyond camp boundaries. Given the strong seasonality of NO₃⁻, this survey should be done with as close as possible concurrently conducted snow sampling at selected locations to minimize the influence of temporal changes on the NO₃⁻ signature.

These observations emphasize concerns about the representativeness of experimental snow chemistry data collected within a Polar research camp periphery. This raises the question of how interpretations from such experiments reflect conditions in the remote Polar environment. Furthermore, our findings should motivate comparison studies with sampling along transects to further distances from the main camp facilities. Comparison of these observations will likely yield new insights for evaluating prior polar research site observations and interpretation of snow photochemistry in the glacial snowpack.

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277 Author contribution:

- 278 DH oversaw the study, participated in field work, conducted data analyses and quality control, and
- prepared the manuscript.
- 280 DL conducted data analyses, quality control, prepared figures, and contributed to the manuscript
- 281 preparation.
- JH fabricated the instrumental equipment and data acquisition system, and participated in the field work.
- 283 JS contributed to the study design, participated in field work, conducted data analyses and interpretation,
- and contributed to the manuscript preparation.

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