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

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Abstract

~~Continuous~~ The chemistry ~~measurements~~ of reactive gases ~~in the snowpack and above the snowpack surface~~ inside the snowpack and in the lower atmosphere was investigated~~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 station main infrastructure inside the station clean air sector and within the station electrical power grid boundary. Ambient air was sampled continuously from inlets mounted above the surface on a 10 m meteorological tower. In addition, snowpack air was collected at 30 cm intervals to 1.2 m depth from two manifolds that had both above and below surface sampling inlets.~~Ambient a~~Air ~~was sampled continuously from three 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, 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~~ 50 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 if and how snow-photochemical 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 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 (VOCs) 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~~ study yielded for the first time a year-long record of NO_x and O_3 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

Location: This experiment was conducted at the French/Italian Antarctic research station Concordia, located at the Dome Circe or Dome Charlie (Dome C, 75.10°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 to the 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

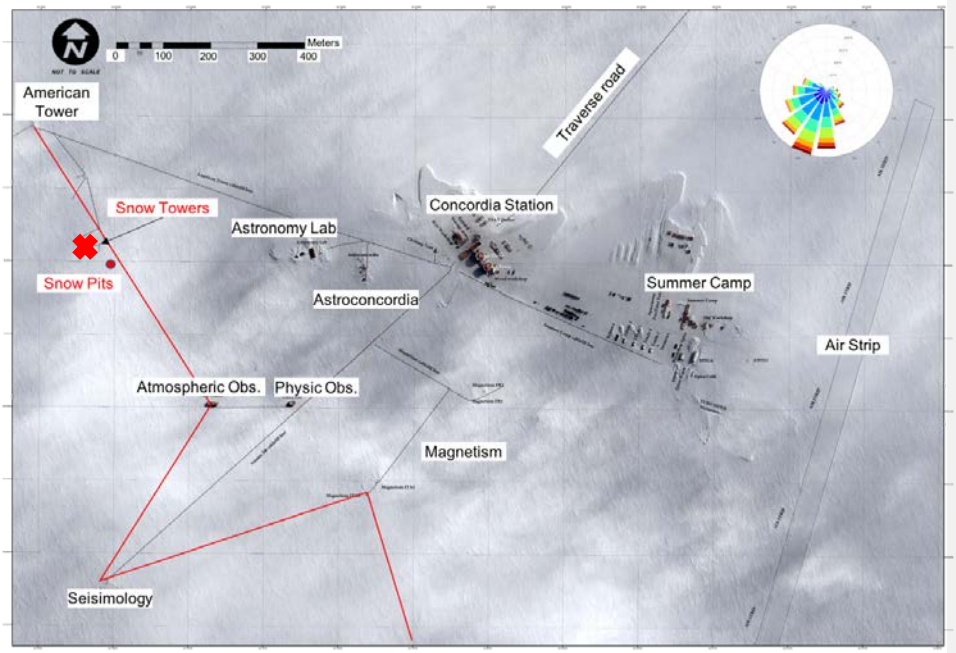

Figure 1: Satellite image of research station Concordia with location of the snow photochemistry experiment indicated by the red text and cross marker. Its location was ~1 km west of the station main buildings and power generation plant. The map also indicates the location where the snow pits were collected, the border of the clean air sector (which is west of the red line), and a wind rose for a full year of wind data collected from the met tower that was adjacent to the snow tower manifolds. ~~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.~~

positioned 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 until~~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

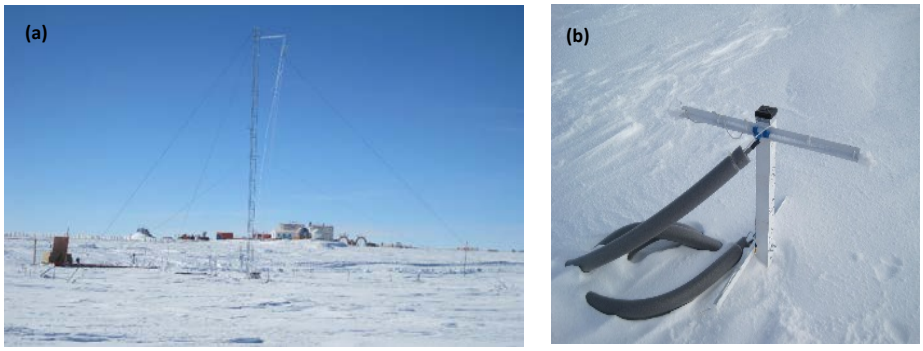

Figure 2: (a) Meteorological tower with the station infrastructure in the background. The wooden box to the left is the entry hatch to the underground laboratory. Air sampling inlets were located at 0.5 m, 2 m and 10 m above the surface on the tower. Two snowpack air sampling towers were located approximately 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. (see Figure 1 in *Van Dam et al.* [2015] for a schematic of a similar installation at Summit, Greenland).

to a manual pulley allowing the upperat 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 20 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 inlets were lines inserted horizontally into the clean untouched walls of the pit. 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 installation and subsequent changes in the snow morphology as the snowpack re-equilibrated.The hole was then loosely refilled with the excavated snow, respecting 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.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

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meteorological tower, which were of 0.78 cm o.d. because they were continuously pumped to maintain a flow of at least 2 l min^{-1}. Air was pulled through the snow tower sampling lines by the combined flow of the gas analyzers (ozone monitor at 1 l min^{-1}, a gaseous elemental mercury (GEM) analyzer at 1 l min^{-1}, NO_x monitor at 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 l min^{-1}. Each height was sampled for 10 min every 2 hours, resulting in an approximately volume of a sphere with a radius of 25 cm around each inlet every 2 hours. ~~Sampling from the two snow towers was alternated every 24 hr.~~ Sampling from the two snow towers was alternated every 24 hours. Each sampling inlet had a thermocouple wire attached for monitoring of the snowpack temperature gradient.

Ozone Measurements: Ozone was measured with a Thermo Environmental (TEI) 49i UV absorption monitor that was calibrated against a NOAA Global Monitoring Division reference standard before field shipment.

NO_x Measurements: Nitrogen oxides were monitored with a TEI chemiluminescence analyzer (TEI 42C-TL). The TEI 42C-TL has two channels. The first channel measures NO via NO + O_3 chemiluminescence. The second channel measures total nitrogen oxides (NO_x = NO + NO_2) by redirecting air through a heated (325°C) molybdenum converter, which causes NO_2—including other oxidized nitrogen compounds—to be converted to NO. NO_2 is then determined by subtracting NO, obtained from the first channel, from the resulting NO_x signal. There are a number of other oxidized nitrogen species that can contribute to the NO_2 measurement [*Steinbacher et al.*, 2007]. The error in the NO_2 measurement increases with rising levels of interfering gases such as nitrous acid (HONO), peroxyacetyl nitrate (PAN), and alkyl nitrates that contribute to the NO_2-mode signal. Consequently, NO_2 concentrations obtained with the TEI 42C-TL represent an estimate for the sum of these oxidized nitrogen species. Field calibrations were conducted with a NIST-traceable 1 ppm NO in N_2 gas standard (Scott-Marin, Inc., Riverside, CA, USA) that was dynamically diluted to low ppb mixing ratios ~~with NO_x scrubbed ambient air~~. We did not bring a zero air compressed gas cylinder to Concordia. Instead, a low NO_x dilution gas was prepared by pumping ambient air (which had significantly lower NO_x levels than snowpack air) through a cartridge filled with ≈ 1 dm^3 of granular Chemisorbent (Purafill, Doraville, GA). Calibration ranges were from 0.1-25 ppb, and the instrument response was linear within this range. Intercept values of the linear regression, and zero values from sampling of the scrubbed air, were below 0.1 ppb.

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Snow Sampling and NO_3^- Determination:

The snow pit NO_3^- 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 cleaned 50 ml centrifuge tubes inserted directly on a newly scraped wall of ~~the~~ a snow pit. Nitrate concentration in snow samples was~~ere~~ measured directly in the field, at the wet chemistry laboratory of Concordia station. Each sample was melted at room temperatures and NO_3^- concentrations were determined using a colorimetric method employed routinely at Concordia [*Frey et al.*, 2009].

Results and Discussion

Results of the year-round snowpack and ambient monitoring, including interpretations on photochemistry will be presented elsewhere [*Helmig et al.*, 2019]. Here, we primarily focus on occurrences of pollution transport to the sampling site and its penetration into the snowpack.

Figure 3 shows a photograph of the station main buildings. The power plant is adjacent to the two column structure. Approximately 300 m^3 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 of the atmosphere near the surface, the plume does not rise far above the stack height, but instead gets transported horizontally at a height of ~~≈~~ 5-10 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 hundred~~s of~~ meters before the stack emissions are encountered right at the surface.

Of the gases monitored in this experiment, NO_x were the most sensitive tracer for pollution impact. ~~,~~ We chose to concentrate on NO_x as the total of $NO+NO_2$, as this is a more representative indicator for the total amount of oxidized nitrogen, whereas NO would only indicate a fraction. Further, the fractionation between NO and NO_x is sensitive to other gases (such as ozone) and residence time and snowpack depth. Therefore, interpretation of NO data is more ambiguous. NO_x in ambient air at Concordia remained well below 1 ppb during background conditions year-round [*Helmig et al.*, 2019], in agreement with observations from prior shorter campaign NO_x measurement at Concordia

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Figure 3: Photograph of ~~Dome C~~Concordia S~~s~~tation illustrating the dispersion of the exhaust plume from the electrical power generating plant during conditions with a strong surface temperature inversion. The plume is dissipates~~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, the 1 ppb~~is~~ 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. We counted 15 events in total when there was a spike in the above surface NO_x measurements followed by an increase of at least 1 ppb of NO_x in snowpack air. It took up to in excess of 7 days for NO_x in the snowpack air to return to pre-event levels.~~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 overall largest share. NO_x levels were consistently well below 1 ppb when winds were from east to northeast. The sector with pollution transport is ~~rather~~ 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.

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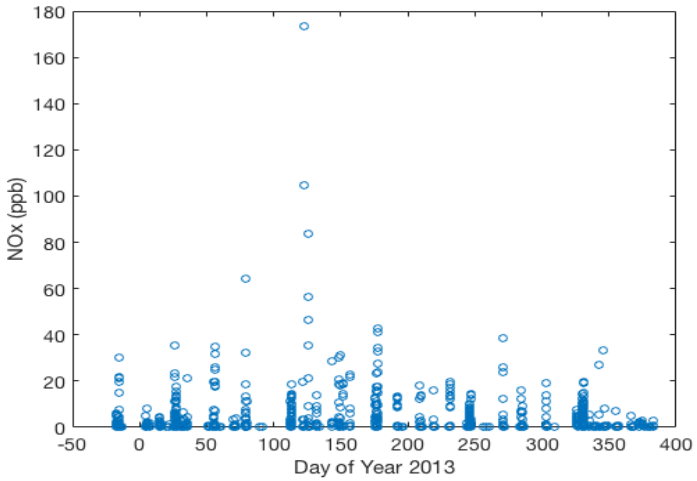

Figure 4: NO_x measured from the above surface inlets on the two snow towers, and from all inlets on the meteorological tower. Circles represent 10-min averaged data. Plotted are data that were extracted from occurrences when NO_x was above 1 ppb, well above the background mixing ratio, and any time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

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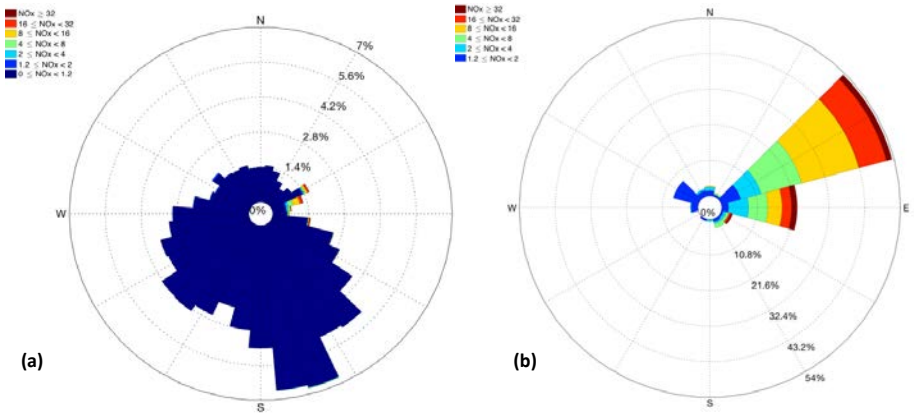

Figure 5: (a) Concentration wind rose with the relative frequency of NO_x mixing ratio data from the above surface inlets of the two snow towers segregated by 10° sectors for the full year of observation data. This panel shows all data. (b) The same analysis, with wind direction data binned in 20° sectors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

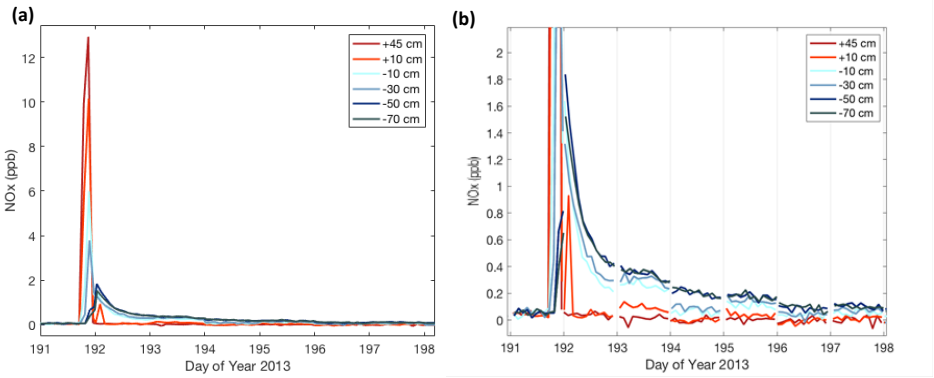

Figure 6. Combined mMeasurements froom the two snow towers capturing a pollution event at Concordia during the middle of the winter (Day of Year 191 = July 11). Plotted time series traces correspond to the sampling heights indicated in the legend, with positive numbers giving the height above the snow 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 two snow tower measurements removed to 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 the snowpack NO_x measurements from within the snowpack.

One of these elevated NO_x~~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.

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% of 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 ≈ one~~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~~ steadily 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 of ≥ 0.95.

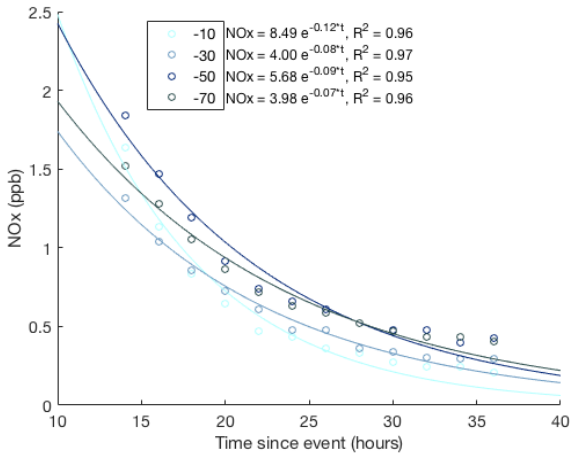

Figure 7. Exponential decay function fits to the NO_x snowpack measurements versus time at four depths for the event starting on Day of Year 191 shown in Figure 6. The start of the event was defined as the time when high NO_x was detected above the snowpack. Solutions for the best fit exponential decay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

Effects of the exhaust transport were also observed in the ozone signal. The ozone record, shown in Figure 8, shows a plethora of short positive and negative spikes superimposed on the annual cycle. The up to 15-20 ppb sudden ozone increases seen during the austral summer months are attributable to the photochemical ozone production events that occur in the surface layer of the Antarctic Plateau (see discussion in the introduction section). Occurrences of these elevated ozone events at Concordia Station have previously been investigated by *Legrand et al.* [2009] and *Cristofanelli et al.* [2018]. Besides these positive ozone spikes, this annual record also ~~Here, the signal~~ shows numerous~~was~~ sudden negative ozone changes that can be attributed to ~~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 8~~S 1~~).

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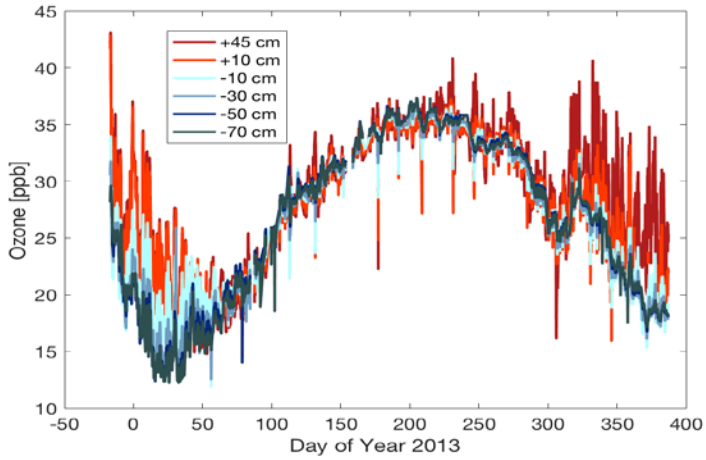

~~Supplement~~ **Figure ~~S~~ 8~~S-1~~.** Ozone measured from the snow tower inlets throughout the year. Negative spikes in the data coincide with elevated NO_x from exhaust infiltration in the snowpack.

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Enhancements in formaldehyde in ambient samples suspected to be influenced by station emissions have previously been noted in measurements taken during the OPALE campaign [*Preunkert et al., 2015*]. We therefore investigated if pollution signatures were present in formaldehyde measurements taken in the record from our study. Furthermore, we revisited the gaseous elemental mercury (GEM) measurements taken during the campaign [*Angot et al., 2016*]. Both of these measurements did not quite have the time resolution and sensitivity as the NO_x and ozone monitoring. Formaldehyde measurements overlapped with the ozone and NO_x monitoring only for a short period during the 2012/2013 austral summer, and this measurement period suffered from a number of instrument problems. The remaining data did not allow a conclusive evaluation on the behavior of formaldehyde in the snowpack during pollution events. Similarly, we did not identify a clear signature of GEM changes in snowpack air that correlated with the NO_x enhancements during pollution events.

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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 phase~~s~~. 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 and NO_2 with ~~oxidants, such as with~~ OH~~,~~ may be a source of HNO_2 and HNO_3 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_2^- or NO_3^- 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~~ term chemical signature in the snowpack (such as of NO_3^-).

We investigated this question by comparing NO_3^- results from snow pit sampling at different locations within the camp and at up to 25 km distance of ~~the Dome C~~Concordia Station. 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~~9; and Supplement Figure S-1 for a summary graph where data from both groups were combined and binned in 15 cm depth intervals). The results from the seven snow pits are consistent in the depth profile~~;~~.

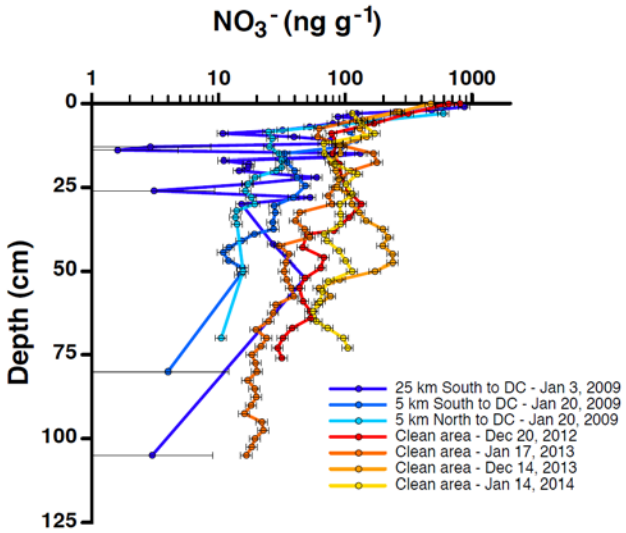

Figure ~~8~~9. Nitrate concentration in snow pits in proximity (~~≈~~≈ 20 m) to the snow towers ~~(warm colors)~~ at the border of the clean air sector (warm colors), and sampling locations up and downwind of Concordia (cold colors). ~~–~~Sampling dates are indicated in the figure legend. Horizontal 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}.

however, there appears to be a tendency that the four snow pits within the camp have somewhat higher, as well as more variable snow NO_3^- ~~at intermediate depths (around 50 cm)~~. Deeper into the snowpack the difference between the two groups of data becomes ~~weaker~~stronger. At 1 m depth, the snow age is approximately ten years, and therefore approximately corresponds to the start of permanent and year-round activities in 2005 (note that summer activities at ~~Dome~~ Concordia Station were established in 1996). ~~This behavior in the~~Similar vertical NO_3^- ~~vertical gradient~~concentration profiles in the Antarctic snowpack ~~has been~~have previously ~~investigated and~~been documented [*France et al.*, 2011]. Further, relatively higher NO_3^- concentrations (approximately 5 times) are observed in the upper layers of the snowpack ~~is observed~~ during the Antarctic summer (Supplement Figure S-2~~-2~~), ~~with average NO_3^- levels approximately 5 times higher~~ than during the winter. This NO_3^- enhancement in surface snow and the seasonal cycle

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have been linked to the production of HNO_3 in the photoactive summer months from reaction of OH with NO_2, with the NO_3^- enhancement being the result of HNO_3 deposition to the snow surface [*Erbland et al.*, 2013]. Elevated NO_3^- 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 NO_3^- to the seasonal cycle and ~~sampling strategy~~, the high variability of NO_3^- observed ~~at the~~in surface snow and vertical profiles, the currently available data do not allow ~~surface precludes~~ a conclusive quantitative assessment ~~interpretation to what~~of the degree to which the snowpack at Concordia is chemically impaired by ventilation of the snowpack with pollution-NO_x enriched air. Contamination of the snowpack around Concordia station has been noted in previous investigations. *Warren et al.* [2006] reported an > 3-fold increase in snowpack black carbon concentration after the station was established in 2003, with black carbon levels in pre-2003 snow (from deeper depths) also being in closer agreement with snow collected from further distance to the station. Black carbon is one of the contributing factors for a decrease in light penetration into the snowpack -[*Warren et al.*, 2006]-[*France et al.*, 2011]-[*Libois et al.*, 2013]. Consequently, the increased presence of black carbon causes a shallower e-folding depth compared to pristine, uncontaminated snow. ~~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 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 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 NO_x 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 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.~~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 potentially is linked to differences in the snow sampling locations and camp influences.~~

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Summary and Conclusions

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 enhancements in NO_x were~~as~~ observed at that depth from exhaust

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infiltration. While our experiment was no~~'~~t able to access air deeper (than 70 cm), the observed concentration gradients ~~observed~~ imapply that this transport and contamination extends well beyond the depth that was probed in these measurements.

~~Our~~ This 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 distance of our site.

Several other previous studies have noted challenges in sampling clean air at polar research sites that stem from pollution caused by camp exhaust. For atmospheric sampling, this interference can be mitigated by careful postprocessing/filtering of the monitoring data, or by interrupting the sampling during unfavorable wind conditions, which is particularly critical for integrated aerosol collection [*Wolff and Cachier*, 1998; *Wolff et al.*, 1998]. Our experiments ~~measurements~~ from Concordia Station emphasize the pronounced and longer-lasting influence that station exhaust can have on NO_x levels inside the snowpack air (compared to ambient air). ~~-~~A tendency of potentially enhanced snowpack 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 chemical oxidized nitrogen composition at the station may be compromised (i.e. contaminated) from the re-occurring ventilation of the snowpack with polluted, NO_x-enriched air. A similar conclusion was derived from $d^{15}N$ nitrate analyses of snow at Summit Samples collected in the predominant downwind direction of the station generator showed an isotopic signature that had a stronger association with engine exhaust than samples collected at further distance [*Fibiger et al.*, 2016]. Even in the Summit clean air sector elemental carbon in snow was 1.8 – 2.4 times higher than in snow collected at 10-20 km distance from the camp [*Hagler et al.*, 2008]. ~~A tendency of potentially enhanced snowpack 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 (NO_x-enriched) air, which adds to the previous findings on black carbon, and organic gases snowpack contamination from engine exhaust.A tendency of potentially enhanced snowpack 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 (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 NO_3^-, 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 NO_3^- signature.

These observations emphasize concerns about the representativeness of experimental snow chemistry data collected within a Polar research camp periphery. This raises the question 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 distance from the main camp

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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.

Author contribution:

DH oversaw the study, participated in field work, conducted data analyses and quality control, and prepared the manuscript.

DL conducted data analyses, quality control, prepared figures, and contributed to the manuscript preparation.

JH fabricated the instrumental equipment and data acquisition system, and participated in the field work.

JS contributed to the study design, participated in field work, conducted data analyses and interpretation, and contributed to the manuscript preparation.

Acknowledgements:

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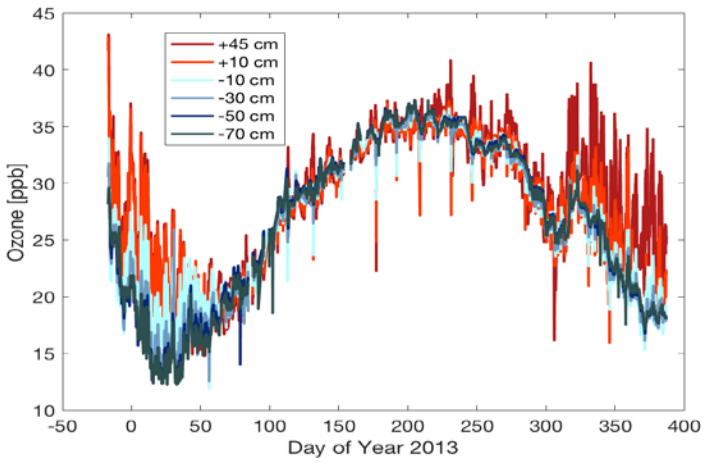
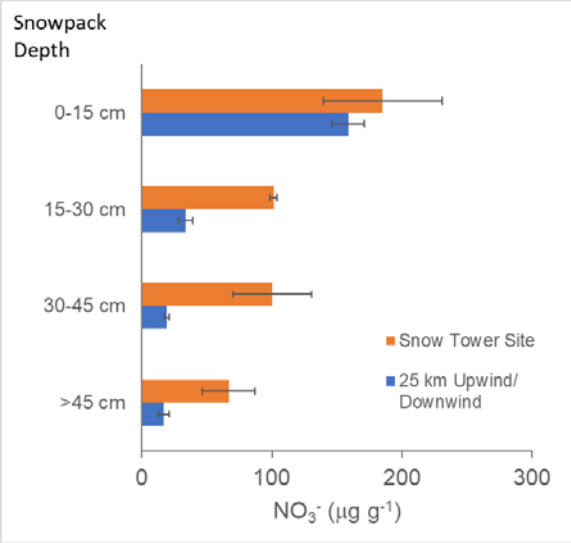
Supplemental Materials



Supplement Figure S-1. Ozone measured from the snow tower inlets throughout the year. Negative spikes in the data coincide with elevated NO_x from exhaust infiltration in the snowpack.



Supplement Figure S-12. ~~Seasonal cycle of nitrate in skin layer surface snow collected at Dome C three times per week during October 2012 – January 201~~ Data from manuscript Figure 9, with the two types of samples (snow pits in proximity (≈ 20 m) to the snow towers (orange), and sampling locations up and downwind of Concordia (blue)) combined and binned in 15 cm depth intervals. Error bars depict the 1-σ standard deviation of available data within each bin.~~4.~~

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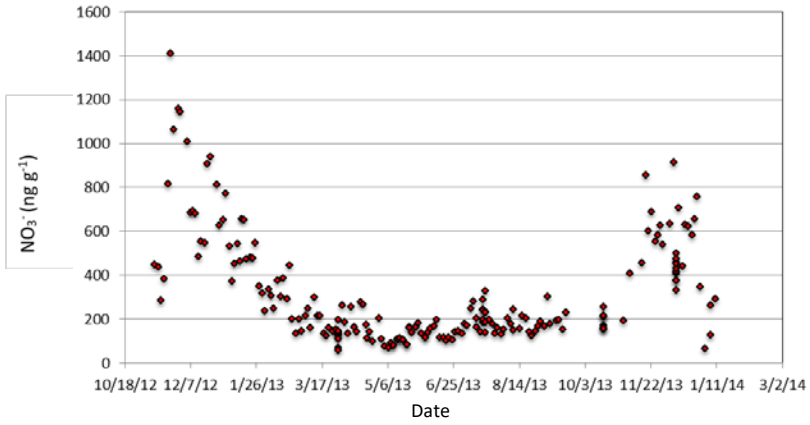

Supplement Figure S-22. Seasonal cycle of nitrate in skin layer surface snow collected at Dome C three times per week during October 2012 - January 2014.

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Response to Anonymous Referee #1 Comments

We thank this reviewer for the constructive feedback on our manuscript. Our responses and changes implemented in the manuscript are summarized below in blue bold font after each of the reviewer's comment points.

GENERAL COMMENTS

This study reports observations of air and snow chemistry from a 14 month measurement campaign at Dome C, East Antarctica with a focus on pollution episodes caused by the year-round operated Concordia station. Gasphase concentrations of nitrogen oxides (NOx) increased by several orders of magnitude during a total of 15 events of pollution transport from the station during the study period, with concurrent decreases in ozone indicating titration by nitric oxide. While near-surface air concentrations of NOx settled to background levels within hours, firn air concentrations remained elevated for days to up to a week. The snow chemical composition may be affected as indicated by nitrate concentrations in snow below the top layer being higher near the station than further away. The authors conclude that these observations provide insight to the discussion on how representative snow photo-chemistry studies near research stations are for the wider Antarctic ice sheet.

The detection of elevated NOx and associated O3 decrease when sampling station power generator exhaust, and of course also any kind of motorised traffic (air plane, ski doo, tractors etc) is not new, but a well-known limitation of studies of background atmospheric chemistry at most polar research stations. This is typically mitigated by careful filtering of atmospheric measurements.

A new insight from this study is the observation that pollution plumes diffuse into the upper snowpack and remain there for several days, with the potential to alter chemical composition of the upper snowpack near the station and therefore compromise local snow photochemistry being representative for the wider ice sheet. Understanding changes in air and snowpack chemistry near Concordia station would be potentially very useful for the design of future experiments at Dome C and elsewhere. Rather than just casting doubt on previous measurement campaigns I suggest the authors improve the manuscript by broadening the range of considered chemical species and by providing more quantitative detail in their discussion of pollution impacts on snow chemistry as promised by the title:

The abstract states that other reactive chemical species were also measured, notably formaldehyde and gaseous elemental mercury (GEM). Even though not as sensitive to pollution as NOx I urge the authors to present and discuss those data during pollution events to achieve a more general picture of pollution impacts near the station. For example formaldehyde has been discussed as a snowpack HOx radical precursor at Dome C (Preunkert et al., 2015), and it would be important to understand if and how station pollution changes also nearby CH2O profiles in snow.

We re-examined the available formaldehyde and GEM data from the campaign. Those measurements do not quite have the time resolution and sensitivity as the NOx and ozone monitoring. Enhancements in ambient samples suspected to be influenced by station emissions have previously been noted by in measurements taken during the OPALE campaign in 2011 [*Preunkert et al., 2015*]. Formaldehyde measurements overlapped with the ozone and NOx monitoring only for a

short period during the 2012/2013 austral summer, and this measurement period suffered from a number of instrument problems. The remaining data did not allow a conclusive evaluation on the behavior of formaldehyde in the snowpack during pollution events. We also revisited the gaseous elemental mercury (GEM) measurements taken during the campaign [*Angot et al., 2016*]. These data did not show a clear signature of GEM in snowpack air that correlated with the NOx enhancements during pollution events. This information has been added to the manuscript text. There are no other chemical gas measurements available from the campaign for a further investigation.

Snow nitrate profiles observed in the clean-air sector near the station show a less steep decline with depth and slightly higher concentrations than at sites further away (>5km). Please discuss the role of spatial variability in snow accumulation and stratigraphy. The presence of sastrugi as well as substantial snow drift around buildings/obstacles as seen on Fig.1 certainly have an impact on snow chemistry profiles. Accumulation rate determines exposure time of a given snow layer to actinic flux as well as stratigraphy/ snow optical properties.

Authors' response: The skin layer of the surface snow has been collected at Concordia every 3 days for more than 8 years. Furthermore, every three months surface snow is collected randomly in an area of ca. 100 m^2 at the same time. The standard deviation in the nitrate concentration is ca. 20-30%. Manuscript Figure 8, and the new Supplement Figure 3 provide the available data for evaluation of the variability in nitrate results in snow samples collected from snow pits at different locations.

Can the authors provide an estimate of at least the order of magnitude of how much snow nitrate could be produced from pollution episodes throughout a year, knowing O3 and NOx in firn air & assuming HOx levels in summer?

Authors' response: We agree that this is an interesting and compelling question, but we do not see a way to possibly develop a nitrate production estimate given the available data and analysis tools.

I'd suggest to double-check with co-author Savarino, who has measured the stable nitrogen isotope 15N in atmospheric and snow nitrate over several years now at Dome C. Assuming d15N in NOx from the station plume is different from other sources, did they ever detect any evidence from existing measurements of d15N in nitrate in snow (or in atmospheric particulate no3) that would indicate a contribution from local pollution?

Authors' response: Thus far there has been no indication of 15N signals from plume pollution. It needs to be realized that that the amount of nitrate in the snowpack is orders of magnitude larger than the sum of total oxidized nitrogen gases in the atmospheric boundary layer. Therefore, influences on the differences in the isotopic signature of atmospheric nitrogen would be very difficult to detect in snowpack samples.

SPECIFIC COMMENTS

Abstract & l162: in the text and Fig.4 a total of 50 pollution events are reported, whereas the abstract states 15 occasions of plume transport, how do the different numbers arise? Please explain.

Authors' response: In total there were about 50 pollution events. Of those, we counted 15 events in total when there was a spike in the above surface NOx measurements followed by an increase of at least 1 ppb of NOx within the snowpack. This detail has been added to the text.

l96-115 Please clarify the schedule of the firn air sampling. Apparently inlets were switched between the 2 snow towers every 24 hr (caption of Fig.6)?

Authors' response: Yes, the reviewer is correct. We added this information to the method description as well.

l235-239 This section requires further clarification: e-folding depth depends in a non- linear fashion on both, absorbing impurities (BC, HULIS etc) as well as on snow density & grain size/shape (scattering). Thus, the variability observed (Warren et al., 2006; France et al., 2011) is not only due to BC deposition but in part also due to the snow stratigraphy present at DC.

Authors' response: The sentence was reworded to: "Contamination of the snowpack around Concordia station has been noted in previous investigations. [*Warren et al.*, 2006] reported an > 3-fold increase in snowpack black carbon concentration after the station was established in 2003, with black carbon levels in pre-2003 snow (from deeper depths) also being in closer agreement with collected snow from further distance to the station. Black carbon is one of the contributing factors for a decrease in light penetration into the snowpack [*Warren et al.*, 2006; *France et al.*, 2011; *Libois et al.*, 2013]. Consequently, the black carbon snowpack contamination results in a shallower e-folding depth compared to pristine, uncontaminated snow.

Fig.1: To better illustrate the location of the Atmospheric Observatory add a wind rose and boundaries of the clean air sector.

Authors' response: A wind rose and lines that indicate the border of the clean air sector were added to the figure. The revised figure is shown below.

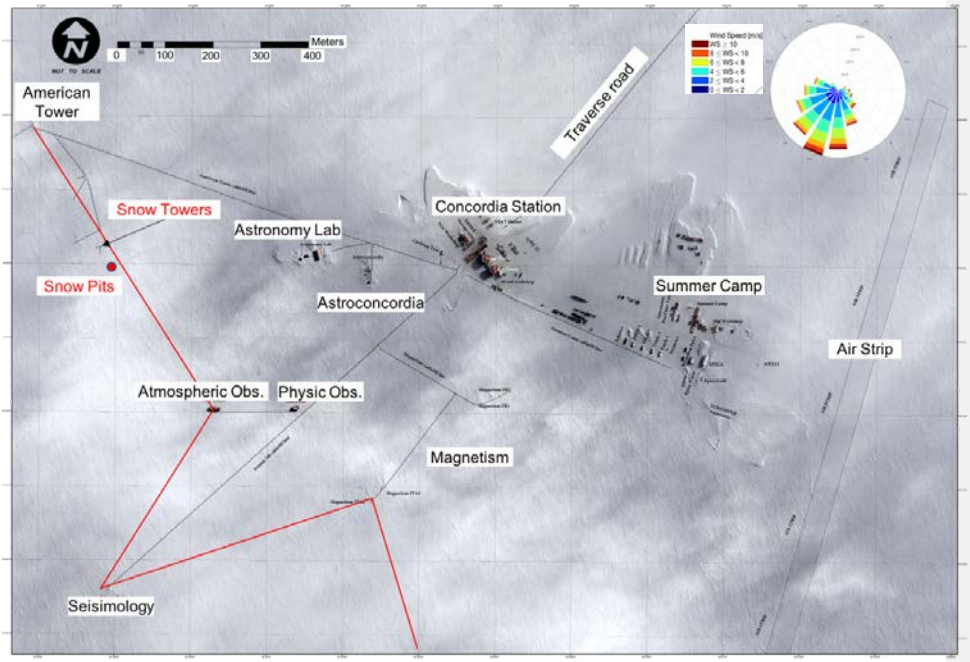

Figure 1: Satellite image of research station Concordia with location of the snow photochemistry experiment indicated by the red text. Its location was ~1 km west of the station main buildings and power generation plant. The map also indicates the location where the snow pits were collected, the border of the clean air sector (which is west of the red line), and a wind rose for a full year of wind data collected from the met tower that was adjacent to the snow tower manifolds.

Fig.2: Text only is hard to follow so please add a schematic indicating location and height/depth of all inlets and sensors, as well as of the snow pit profile.

Authors' response: We added this text to the figure caption: "(see Figure 1 in *van Dam et al.* (2015) for a schematic of a similar installation at Summit, Greenland)". Indication of the location of the snow pit sampling was added to Figure 1, and the snow pit profile data are shown in Figure 9.

Fig.6: caption "... measurements FROM the snow tower.." Supplement-Fig S-1 and S-2: in the online version no supplement was available. I suggest to show the O3 mixing ratios and the surface snow no3 also in the main manuscript.

Authors' response: The ozone graph was moved from the Supplement to the main manuscript. But we prefer keeping the surface nitrate graph in the Supplement as these data are purely ancillary supporting information.

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Response to Anonymous Reviewer #2 Comments

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 NOx above the snowpack correspond with winds from camp. They also show the lag in higher NOx 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 NOx from station power generation.

General comments:

The authors do not cite other work showing the impact of station exhaust on NOx in the air and nitrate in the snow. Fibiger et al. (2016) show the impact of station exhaust on NOx 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 NOx, which contains several other NOy species. Throughout the manuscript, however, the authors use the NOx measurement. Why has this been chosen over NO? The enhancements should still show up in NO, without the interference issues.

Authors' response: We chose NOx 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 NOx 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 NOx 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 NOx 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 NOx 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^3 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.

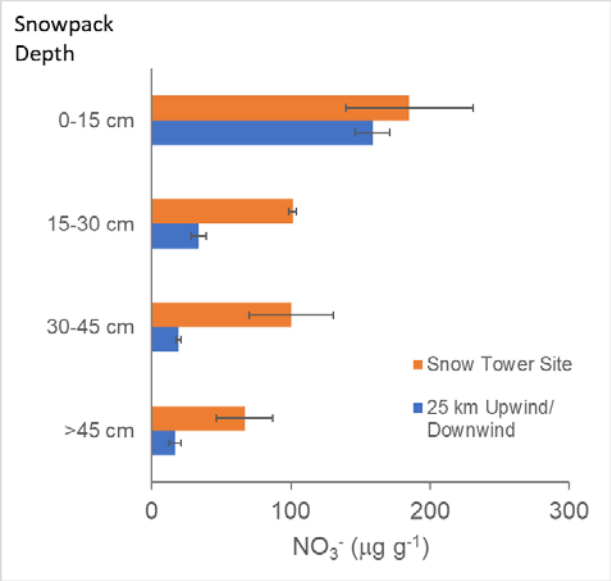
Line 192. Show this data in the supplement. It's hard to know what these qualitative and quantitative comparisons look like without showing the data.

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_x 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 NO_3^- contamination at the snow tower site in the upper snowpack layers. However, deeper in the snowpack, 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 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 (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."

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