Impact of exhaust emissions on chemical snowpack composition at Concordia Station, Antarctica

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Abstract

The chemistry of reactive gases inside the snowpack and in the lower atmosphere was investigated at Concordia Station (Dome C), Antarctica, from December 2012 - January 2014. Measured species included ozone, nitrogen oxides, gaseous elemental mercury (GEM), 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. Despite being in the clean air sector, over the course of the 1.2-year study, we observed on the order of 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. GEM and formaldehyde measurements were less sensitive and covered a shorter measurement period; neither of these species' data showed noticeable concentration changes during these events that were above the normal variability seen in the data. Nonetheless, the clarity of the NO_x and ozone 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 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 study yielded for the first time a year-long record of NO_x and O_3 in an Antarctic

78 snowpack at Concordia and the atmosphere above it. This experiment also gave us the opportunity to
79 study and evaluate occurrences of pollution episodes, using the NO_x monitoring as a sensitive chemical
80 tracer for identification of exhaust plumes.

81 **Methods**

82 Location: This experiment was conducted at the French/Italian Antarctic research station Concordia,
83 located at the Dome Circe or Dome Charlie (Dome C, 75.10°S/123.35°E3233 m asl, mean temperature –
84 55°C). An experimental site was established at the border of the clean air sector, approximately 1 km to
85 the west of the station common buildings (Figure 1). The clean air sector is located in the opposite
86 direction of the prevailing wind direction. The site consisted of a 8 m x 2 m x 2.5 m underground laboratory

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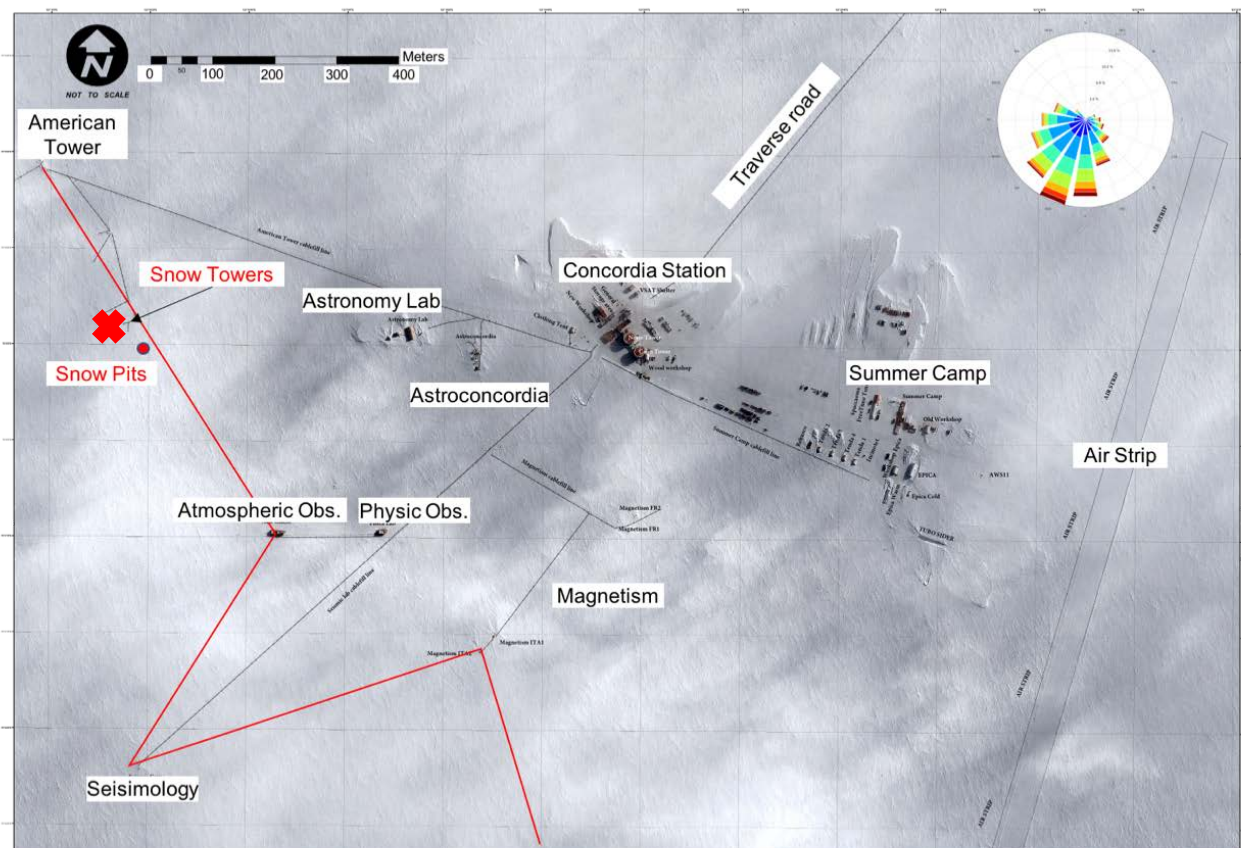
Figure 1: Satellite image of research station Concordia with location of the snow photochemistry experiment
indicated by the red text and cross marker. Its location was ≈1 km west of the station main buildings and power
generation plant. The map also indicates the location where the snow pits were collected, 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.

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89   positioned at the border of the clean air area, a 10 m tall meteorological tower, and two snow air sampling
90   manifolds for sampling the atmosphere and the snow interstitial air (Figure 2). The installation was in late
91   November 2012 with continuous monitoring conducted until January 2014 (14 months).

92   Meteorological Tower: A 10 m meteorological tower (Figure 2a) was equipped with two sonic
93   anemometers for atmospheric turbulence measurements, and three gas sampling inlets (0.5 m, 2 m, 10
94   m) with sampling lines inside a heated conduit running to the laboratory. The upper inlet was attached
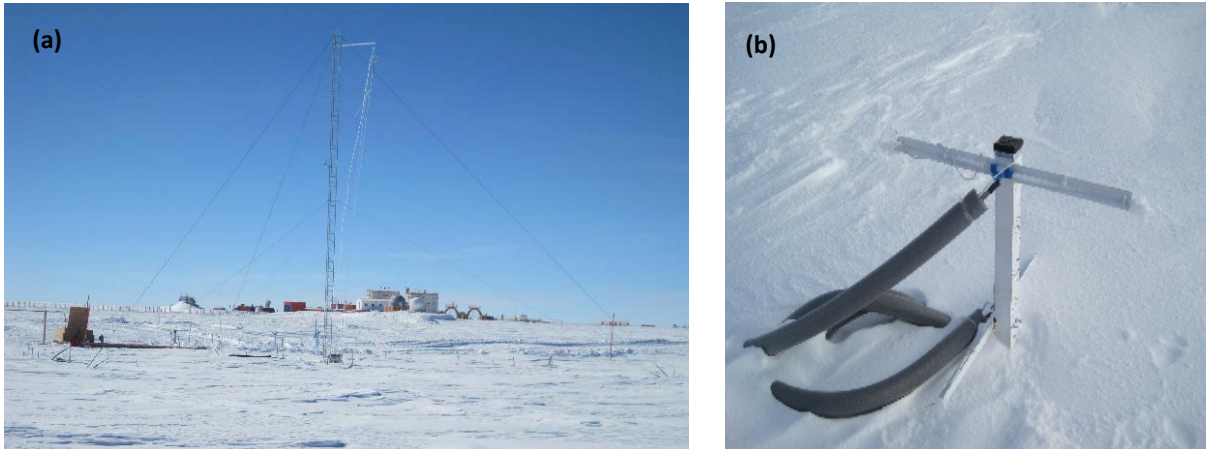
Figure 2: (a) Meteorological tower with the station infrastructure in the background. The wooden box to the left is the entry hatch to the underground laboratory. Air sampling inlets were located at 0.5 m, 2 m and 10 m above the surface on the tower. Two snowpack air sampling towers were located approximately 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).

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

98   Snowpack Air Sampling: Two identical multi-inlet snow sampling manifolds ('snow tower') for collection
99   of interstitial and ambient air were constructed, with a similar design to that described by [*Seok et al.*,
100 2009] (Figure 2b). The snow tower consisted of a vertical post of square aluminum alloy (3.8 x 3.8 cm)
101 with eight 60 cm long cross arms spaced vertically every 20 cm. Each of the cross bars supported a pair
102 of sampling inlets. The inlets were fitted with 25 mm Acrodisc hydrophobic polytetrafluoroethylene (PTFE)
103 syringe filters (Pall Life Sciences, Ann Arbor, Michigan, USA) to prevent snow and ice crystals from being
104 pulled into the sampling line. For the installation, a snow pit was dug and the inlets were inserted
105 horizontally into the clean untouched walls of the pit. The hole was then loosely refilled with the
106 excavated snow, re-establishing the stratigraphy as much as possible. Blowing snow then refilled any
107 remaining gaps within the following 2-3 days. The snow tower was kept in place after the campaign, so
108 we have no data on the potential changes in porosity and air flow dynamics that resulted from the
109 installation and subsequent changes in the snow morphology as the snowpack re-equilibrated. Insulated
110 and heated sampling lines connected the sampling inlets to the chemical analyzers in the underground

111 laboratory. All sampling lines were of 0.64 cm o.d. x 30 m long pre-conditioned PFA tubing, except the
112 lines to the gradient inlets on the meteorological tower, which were of 0.78 cm o.d. because they were
113 continuously pumped to maintain a flow of at least 2 l min^{-1}. Air was pulled through the snow tower
114 sampling lines by the combined flow of the gas analyzers (ozone monitor at 1 l min^{-1}, a gaseous elemental
115 mercury (GEM) analyzer at 1 l min^{-1}, NO$_x$ monitor at 1 l min^{-1}). A maximum of two monitors sampled from
116 the snow tower inlets together at a given time to limit the maximum snow air sampling. Since each line
117 connected to a pair of inlets at equal height, the effective flow through each inlet was a maximum of ≈1 l
118 min^{-1}. Each height was sampled for 10 min every 2 hours, resulting in an approximately volume of a sphere
119 with a radius of 25 cm around each inlet every 2 hours. Sampling from the two snow towers was
120 alternated every 24 hours. Each sampling inlet had a thermocouple wire attached for monitoring of the
121 snowpack temperature gradient.

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

125 NO$_x$ Measurements: Nitrogen oxides were monitored with a TEI chemiluminescence analyzer (TEI 42C-
126 TL). The TEI 42C-TL has two channels. The first channel measures NO via NO + O$_3$ chemiluminescence.
127 The second channel measures total nitrogen oxides (NO$_x$ = NO + NO$_2$) by redirecting air through a heated
128 (325°C) molybdenum converter, which causes NO$_2$—including other oxidized nitrogen compounds—to be
129 converted to NO. NO$_2$ is then determined by subtracting NO, obtained from the first channel, from the
130 resulting NO$_x$ signal. There are a number of other oxidized nitrogen species that can contribute to the
131 NO$_2$ measurement [*Steinbacher et al.*, 2007]. The error in the NO$_2$ measurement increases with rising
132 levels of interfering gases such as nitrous acid (HONO), peroxyacetyl nitrate (PAN), and alkyl nitrates that
133 contribute to the NO$_2$-mode signal. Consequently, NO$_2$ concentrations obtained with the TEI 42C-TL
134 represent an estimate for the sum of these oxidized nitrogen species. Field calibrations were conducted
135 with a NIST-traceable 1 ppm NO in N$_2$ gas standard (Scott-Marin, Inc., Riverside, CA, USA) that was
136 dynamically diluted to low ppb mixing ratios. We did not bring a zero air compressed gas cylinder to
137 Concordia. Instead, a low NO$_x$ dilution gas was prepared by pumping ambient air (which had significantly
138 lower NO$_x$ levels than snowpack air) through a cartridge filled with ≈ 1 dm^3 of granular Chemisorbent
139 (Purafill, Doraville, GA). Calibration ranges were from 0.1-25 ppb, and the instrument response was linear
140 within this range. Intercept values of the linear regression, and zero values from sampling of the scrubbed
141 air, were below 0.1 ppb.

142 Formaldehyde Measurements: Formaldehyde was monitored with a commercial analyzer by liquid
143 fluorimetry. Details of the measurement, instrument characterization, and deployment at Concordia
144 Station have been provided by [*Preunkert et al.*, 2015].

145 Gaseous Elemental Mercury Measurements: GEM was measured with a commercial Tekran Model 2537
146 instrument. The analytical protocol, and calibration and instrument characterization details are available
147 in [*Angot et al.*, 2016].

148 Snow Sampling and NO$_3^-$ Determination: The snow pit NO$_3^-$ data stem from sampling that was done at and
149 near Concordia between January 2009 and December 2010, and at ≈3 m distance from snow tower 2 in
150 January 2014. Snow was collected in pre cleaned 50 ml centrifuge tubes inserted directly on a newly

151 scraped wall of a snow pit. Nitrate concentration in snow samples was measured directly in the field, at
152 the wet chemistry laboratory of Concordia station. Each sample was melted at room temperatures and
153 NO_3^- concentrations were determined using a colorimetric method employed routinely at Concordia [*Frey*
154 *et al.*, 2009].

Results and Discussion

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

159 Figure 3 shows a photograph of the station main buildings. The power plant is adjacent to the two column
160 structure. Approximately 300 m^3 of Special Antarctic Blend (SAB) diesel fuel are burned in the plant for
161 electricity and heat generation per year. The exhaust plume from the 5-m high stack of the power plant
162 can be seen in the picture, blowing towards the west. Due to the typical strong stratification and stability
163 of the atmosphere near the surface, the plume does not rise far above the stack height, but instead gets
164 transported horizontally at a height of ≈5-10 m above the snow surface. This is a typical exhaust plume
165 dispersion behavior for a cold regions environment, seen at many other polar research stations. The
166 plume typically does not hit the surface within the immediate distance of the stack location. Depending
167 on the actual turbulent mixing conditions, it may take several hundred meters before the stack emissions
168 are encountered right at the surface.

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

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

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177 [*Frey et al.*, 2011; *Frey et al.*, 2013; *Frey et al.*, 2015]. We did not observe highly elevated NO levels in the
178 surface layer outside of pollution events, as what has been observed at South Pole [*Helmig et al.*, 2008b;
179 *Neff et al.*, 2008]. During pollution events, the 1 ppb threshold was exceeded very quickly in
180 measurements taken from the meteorological tower and from above-surface snow tower inlets, with
181 resulting NO_x mixing ratios rising to as high as close to 200 ppb, representing an up to 1000-fold
182 enhancement over background conditions (Figure 4).

183 During the course of the ≈≈14 month study, a total of ≈50 pollution events were observed, although some
184 events overlapped (Figure 4). Most of these occurrences were relatively short, with elevated mixing ratios
185 above the snowpack lasting from minutes to a few hours. We counted 15 events in total when there was
186 a spike in the above surface NO_x measurements followed by an increase of at least 1 ppb of NO_x in
187 snowpack air. It took up to in excess of 7 days for NO_x in the snowpack air to return to pre-event levels.
188 Integrated over the entire campaign, pollution episodes constituted < 2.0 % of the measurements above
189 the snowpack, and <10% of the measurements within the snowpack. The correlation analyses of pollution
190 occurrences with wind direction clearly defines the direction of the transport. The predominant wind
191 direction sector at Concordia is southeast to northwest (Figure 5a), with southeasterly winds having the
192 overall largest share. NO_x levels were consistently well below 1 ppb when winds were from east to
193 northeast. The sector with pollution transport is well defined, with wind directions covering
194 approximately 45-120° (Figure 5b). These sectors perfectly line up with the upwind direction of the station
195 power plant (Figure 1), clearly identifying the plant as the source of these pollution occurrences.

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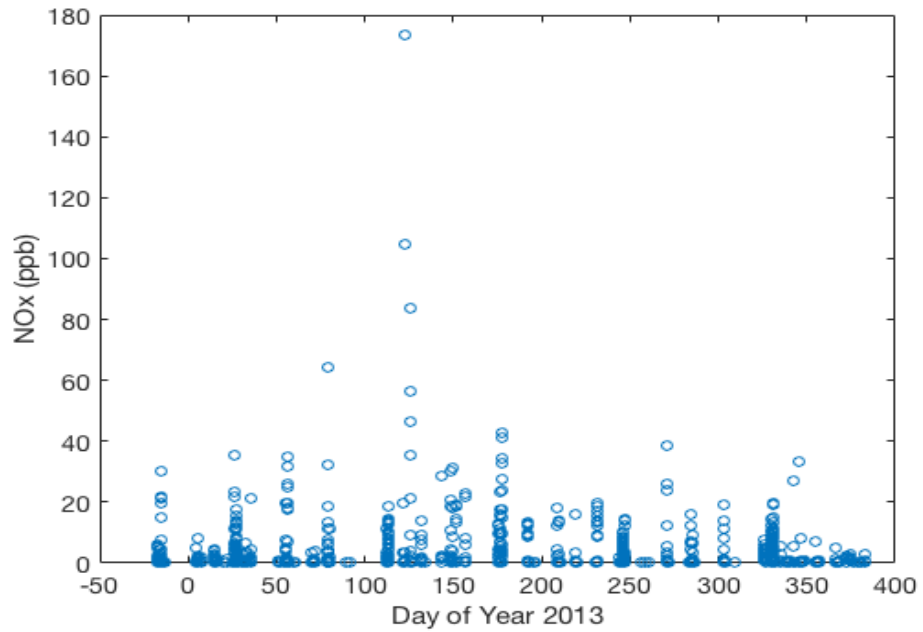
Figure 4: NOₓ measured from the above surface inlets on the two snow towers, and from all inlets on the meteorological tower. Circles represent 10-min averaged data. Plotted are data that were extracted from occurrences when NOₓ was above 1 ppb, well above the background mixing ratio, and any time when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

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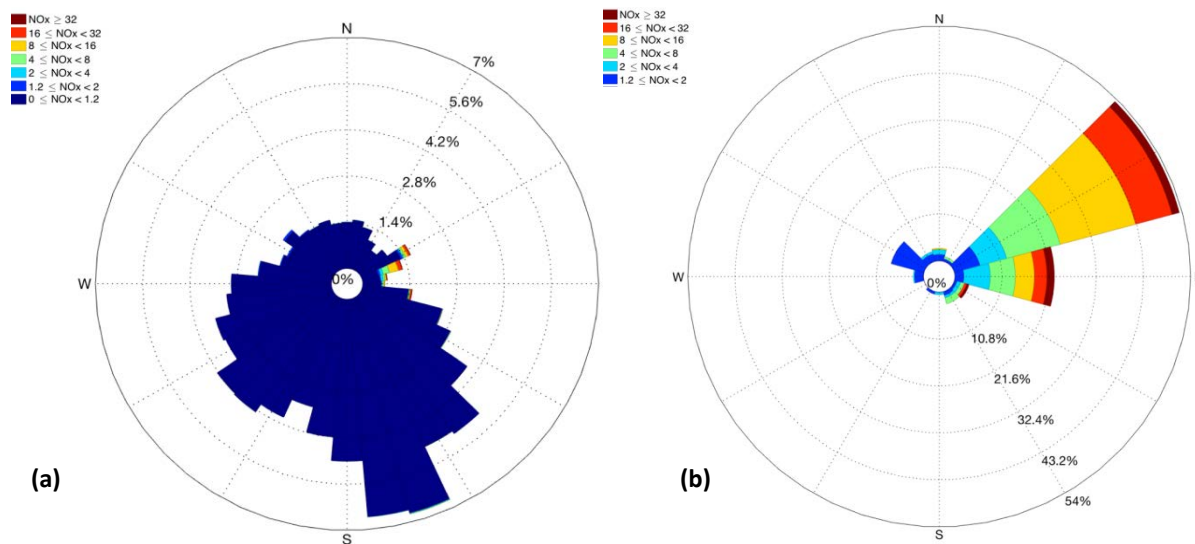
Figure 5: (a) Concentration wind rose with the relative frequency of NO_x mixing ratio data from the above surface inlets of the two snow towers segregated by $10°$ sectors for the full year of observation data. This panel shows all data. (b) The same analysis, with wind direction data binned in $20°$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

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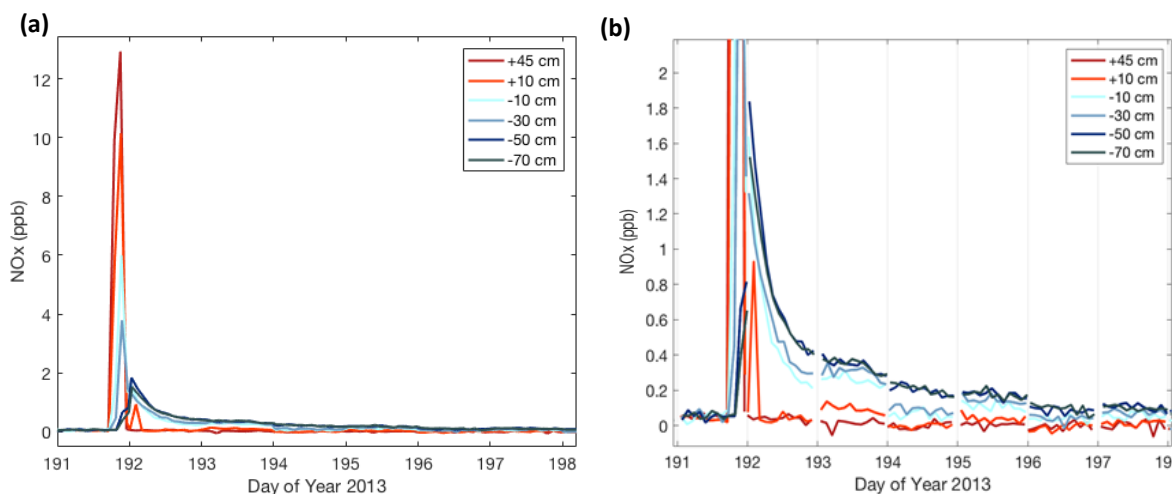
Figure 6. Combined measurements from the two snow towers capturing a pollution event at Concordia during the middle of the winter (Day of Year 191 = July 11). Plotted time series traces correspond to the sampling heights indicated in the legend, with positive numbers giving the height above the snow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

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

206 A much different behavior was found in the air sampled from within the snowpack, indicated by the data
207 in the blueish colors. The onset of the pollution signal is delayed, by 1-3 hours, with progressively later
208 times towards deeper in the snowpack. Maximum mixing ratios that are reached in the snowpack are
209 lower, i.e. 10-50% of those that were measured above the surface, with mixing ratio maxima becoming
210 progressively smaller with increasing depth. The most remarkable difference between the above and
211 below surface measurements is the longer residence time of the pollution signal in the snowpack. NOx
212 mixing ratios in air withdrawn from all sampling inlets in the snowpack dropped steadily, but remained
213 elevated in comparison to levels seen before the pollution event for ≈ one week. The behavior seen in the
214 measurements from snow tower 1 were in full qualitative, and within ≈ 30% quantitative agreement with
215 the concurrent observations from the second snow tower. After the pollution event, NOx in the snowpack
216 air steadily declined over several days (Figure 6). Fitting of the data to an exponential decay function
217 yields similar results for all snowpack depths (Figure 7), with exponential regression fit R^2 results of ≥ 0.95.
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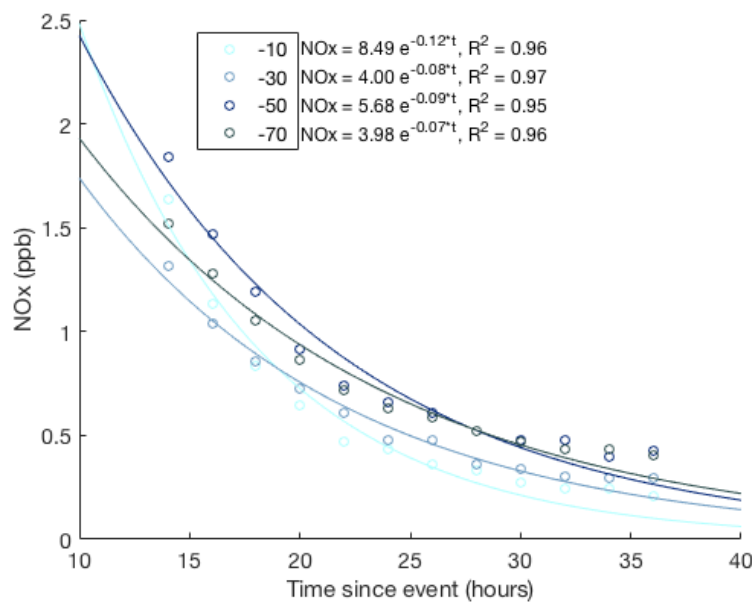
Figure 7. Exponential decay function fits to the NOx snowpack measurements versus time at four depths
for the event starting on Day of Year 191 shown in Figure 6. The start of the event was defined as the
time when high NOx was detected above the snowpack. Solutions for the best fit exponential decay
functions are given in the legend.

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221 Effects of the exhaust transport were also observed in the ozone signal. The ozone record, shown in Figure
222 8, shows a plethora of short positive and negative spikes superimposed on the annual cycle.   The up to
223 15-20 ppb sudden ozone increases seen during the austral summer months are attributable to the
224 photochemical ozone production events that occur in the surface layer of the Antarctic Plateau (see
225 discussion in the introduction section). Occurrences of these elevated ozone events at Concordia Station
226 have previously been investigated by *Legrand et al.* [2009] and *Cristofanelli et al.* [2018].   Besides these
227 positive ozone spikes, this annual record also shows numerous sudden negative ozone changes that can
228 be attributed to destruction of ozone by titration of NO in the exhaust plume. Up to 50% of the ambient
229 ozone was destroyed in air sampled from the above surface inlets. Similar to NO_x, this signal, albeit weaker
230 and attenuated in time, was also seen in the air sampled from within the snowpack (Figure 8).
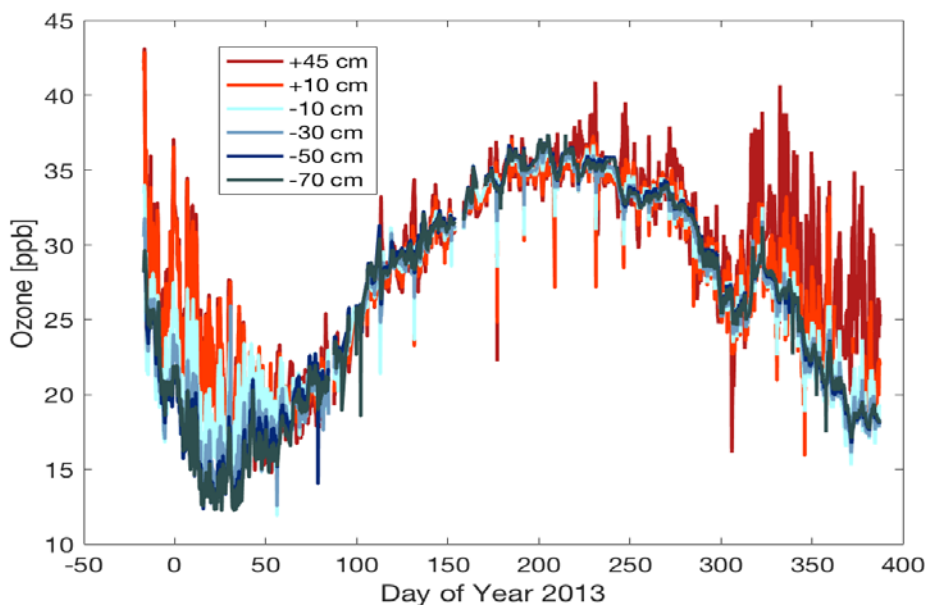
Figure 8. Ozone measured from the snow tower inlets throughout the year. Negative spikes in
the data coincide with elevated NO_x from exhaust infiltration in the snowpack.

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

242   not identify a clear signature of GEM changes in snowpack air that correlated with the NO_x enhancements
243   during pollution events.

244   Nitrogen oxides undergo reaction with atmospheric oxidants, primarily the OH radical (summer only) and
245   ozone, yielding higher oxidized nitrogen species that can partition into the snowpack aqueous and solid
246   phase. The frequency, large enhancement, and long duration (in the snowpack) of NO_x pollution events
247   constitute an apparent unnatural source of NO_x to the snowpack. One can hypothesize that reaction of
248   NO and NO_2 with OH may be a source of HNO_2 and HNO_3 in the snowpack, which would add acidity to the
249   snow. This then also poses the question if and to what degree photochemical processes, building for
250   instance on NO_2^- or NO_3^- as a substrate, may be altered from natural conditions. However, the overall
251   quantitative effect is likely relatively minor given the large overall NO_3^- reservoir in the solid phase of the
252   snowpack.).

253   We investigated this question by comparing NO_3^- results from snow pit sampling at different locations
254   within the camp and at up to 25 km distance of Concordia Station. Nitrate in the snowpack shows a steep
255   vertical gradient, with highest levels observed right at the surface, and progressively lower concentrations
256   with increasing depth (Figure 9; and Supplement Figure S-1 for a summary graph where data from both
257   groups were combined and binned in 15 cm depth intervals). The results from the seven snow pits are
258   consistent in the depth profile;

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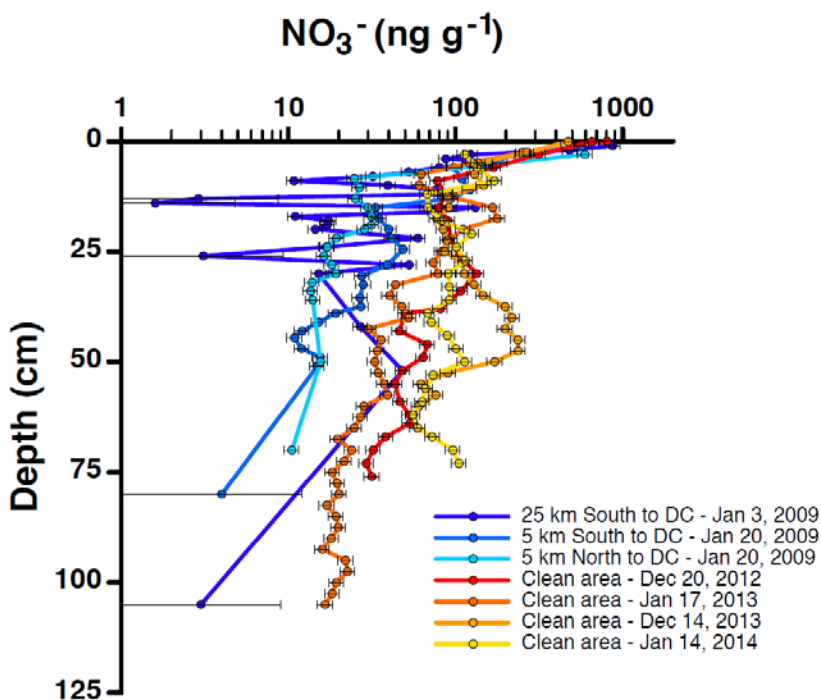
Figure 9. Nitrate concentration in snow pits in proximity (≈ 20 m) to the snow towers at the border of the clean air sector (warm colors), and sampling locations up and downwind of Concordia (cold colors). Sampling dates are indicated in the figure legend. Horizontal error bars depict the estimated uncertainty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

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261 however, there appears to be a tendency that the four snow pits within the camp have somewhat higher,
262 as well as more variable snow NO_3^-. Deeper into the snowpack the difference between the two groups of
263 data becomes stronger. At 1 m depth, the snow age is approximately ten years, and therefore
264 approximately corresponds to the start of permanent and year-round activities in 2005 (note that summer
265 activities at Concordia Station were established in 1996). Similar vertical NO_3^- concentration profiles in
266 the Antarctic snowpack have previously been documented [*France et al.*, 2011]. Further, relatively higher
267 NO_3^- concentrations (approximately 5 times) are observed in the upper layers of the snowpack during the
268 Antarctic summer (Supplement Figure S-2) than during the winter. This NO_3^- enhancement in surface
269 snow and the seasonal cycle have been linked to the production of HNO_3 in the photoactive summer
270 months from reaction of OH with NO_2, with the NO_3^- enhancement being the result of HNO_3 deposition to
271 the snow surface [*Erbland et al.*, 2013]. Elevated NO_3^- concentrations observed at the surface of the
272 snowpack are a common feature at low accumulation regions, with the concentration values depending
273 strongly on the strategy for collection of the first few cm of the snowpack [*Erbland et al.*, 2013; *Shi et al.*,
274 2018]. With the sensitivity of surface snow NO_3^- to the seasonal cycle and, the high variability of NO_3^-
275 observed in surface snow and vertical profiles, the currently available data do not allow a conclusive
276 quantitative assessment of the degree to which the snowpack at Concordia is chemically impaired by
277 ventilation of the snowpack with pollution-NO_x enriched air. Contamination of the snowpack around
278 Concordia station has been noted in previous investigations. *Warren et al.* [2006] reported an > 3-fold
279 increase in snowpack black carbon concentration after the station was established in 2003, with black
280 carbon levels in pre-2003 snow (from deeper depths) also being in closer agreement with snow collected
281 from further distance to the station. Black carbon is one of the contributing factors for a decrease in light
282 penetration into the snowpack [*Warren et al.*, 2006; *France et al.*, 2011; *Libois et al.*, 2013]. Consequently,
283 the increased presence of black carbon causes a shallower e-folding depth compared to pristine,
284 uncontaminated snow. In addition to the experiments described above, during the 2014 campaign a
285 number of dynamic flow-through snow chamber photochemistry experiments were conducted to
286 investigate if there were differences in the reactive chemistry in the snow from near the snow tower site
287 compared to snow sampled 25 km away from camp. These measurements showed on the order of 10-
288 20% higher NO_x and less ozone in the outflow of chambers filled with the snow from further away from
289 the camp. We did not conduct a high enough number of repeats for evaluating the repeatability and
290 statistical significance of these results to gauge if and how much of this signal was due to the experimental
291 setup or due to differences in the snowpack chemical composition. Nonetheless, these preliminary
292 findings point towards possible differences in the chemical behavior that potentially are linked to
293 differences in the snow sampling locations and contaminant levels resulting from camp influences that
294 warrant further investigation.
295

296 **Summary and Conclusions**
297 With our snowpack sampling manifold we were able to sample snowpack air to a maximum depth of 70
298 cm below the surface. Up to ≈2 ppb enhancements in NO_x were observed at that depth from exhaust
299 infiltration. While our experiment was not able to access air deeper (than 70 cm), the observed
300 concentration gradients imply that this transport and contamination extends well beyond the depth that
301 was probed in these measurements.

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

306 Several other previous studies have noted challenges in sampling clean air at polar research sites that
307 stem from pollution caused by camp exhaust. For atmospheric sampling, this interference can be
308 mitigated by careful postprocessing/filtering of the monitoring data, or by interrupting the sampling
309 during unfavorable wind conditions, which is particularly critical for integrated aerosol collection [*Wolff*
310 *and Cachier*, 1998; *Wolff et al.*, 1998]. Our experiments from Concordia Station emphasize the
311 pronounced and longer-lasting influence that station exhaust can have on NO_x levels inside the snowpack
312 air (compared to ambient air). A tendency of potentially enhanced snowpack NO_3^- levels in two snow pits
313 collected at the camp, compared to data from three sites at further distance, supports the suspicion that
314 the snowpack chemical oxidized nitrogen composition at the station may be compromised (i.e.
315 contaminated) from the re-occurring ventilation of the snowpack with polluted air. A similar conclusion
316 was derived from $d^{15}N$ nitrate analyses of snow at Summit: Samples collected in the predominant
317 downwind direction of the station generator showed an isotopic signature that had a stronger association
318 with engine exhaust than samples collected at further distance [*Fibiger et al.*, 2016]. Even in the Summit
319 clean air sector elemental carbon in snow was 1.8 – 2.4 times higher than in snow collected at 10-20 km
320 distance from the camp [*Hagler et al.*, 2008]. The associations shown in our study argue for further
321 investigation, for instance by a high resolution spatial survey of surface snow composition within and
322 beyond camp boundaries. Given the strong seasonality of NO_3^-, this survey should be done with as close
323 as possible concurrently conducted snow sampling at selected locations to minimize the influence of
324 temporal changes on the NO_3^- signature.

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

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Author contribution:

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

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

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

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

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