

Is the Arctic Surface Layer a Source and Sink of NO_x in Winter/Spring?

B. RIDLEY¹, J. WALEGA¹, D. MONTZKA¹, F. GRAHEK¹, E. ATLAS¹,
F. FLOCKE¹, V. STROUD¹, J. DEARY², A. GALLANT², H. BOUDRIES²,
J. BOTTENHEIM², K. ANLAUF², D. WORTHY², A. L. SUMNER³,
B. SPLAWN³ and P. SHEPSON³

¹*Atmospheric Chemistry Division, National Center for Atmospheric Research, PO Box 3000, Boulder, CO 80307, U.S.A., e-mail: ridley@acd.ucar.edu*

²*Atmospheric Environment Service, 4905 Dufferin St., Downsview, Ontario, Canada, M3H 5T4*

³*Departments of Chemistry and Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907, U.S.A.*

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Abstract. Measurements of NO_x (NO + NO₂) and the sum of reactive nitrogen constituents, NO_y, were made near the surface at Alert (82.5° N), Canada during March and April 1998. In early March when solar insolation was absent or very low, NO_x mixing ratios were frequently near zero. After polar sunrise when the sun was above the horizon for much or all of the day a diurnal variation in NO_x and NO_y was observed with amplitudes as large as 30–40 pptv. The source of active nitrogen is attributed to release from the snow surface by a process that is apparently sensitized by sunlight. If the source from the snowpack is a large scale feature of the Arctic then the diurnal trends also require a competing process for removal to the surface. From the diurnal change in the NO/NO₂ ratio, mid-April mixing ratios for the sum of peroxy and halogen oxide radicals of ≤10 pptv were derived for periods when ozone mixing ratios were in the normal range of 30–50 ppbv. Mid-day ozone production and loss rates with the active nitrogen source were estimated to be ~1–2 ppbv/day and in near balance. NO_y mixing ratios which averaged only 295 ± 66 pptv do not support a large accumulation in the high Arctic surface layer in the winter and spring of 1998. The small abundance of NO_y relative to the elevated mixing ratios of other long-lived anthropogenic constituents requires that reactive nitrogen be removed to the surface during transport to or during residence within the high Arctic.

Key words: active nitrogen, ozone, radicals, snow chemistry, Arctic, surface layer.

1. Introduction

The discovery of depletion or complete removal of surface layer ozone in the Arctic during spring has been one of the more interesting facets of tropospheric chemistry over the past decade (Bottenheim *et al.*, 1986; Barrie *et al.*, 1988; Barrie and Platt, 1997). Investigations made near Alert (82.5° N, 62.3° W), Nunavut, Canada and elsewhere in the Arctic have concluded that catalyzed removal occurs in the stable surface layer over the ocean snow/ice pack when solar insolation becomes

sufficient for activation of reactive halogen constituents. Several mechanisms for halogen activation now favored to originate from sea salt on the ice/snow surface have been suggested (Finlayson-Pitts *et al.*, 1990; McConnell *et al.*, 1992; Fan and Jacob, 1992; Mozurkewich, 1995; Tang and McConnell, 1996; Oum *et al.*, 1998). Chlorine atoms have been shown to have an important effect on the behavior of many alkanes during winter and spring but there is good evidence that active bromine constituents are dominant in ozone removal (Jobson *et al.*, 1994; Muthuramu *et al.*, 1994; Impey *et al.*, 1997, 1999). Indeed, BrO has been measured in the transition stage of ozone depleted air masses (Hausmann and Platt, 1994; Tuckermann *et al.*, 1997; Miller *et al.*, 1997). More recently BrO has been measured in the troposphere at high latitudes over large areas from aircraft (McElroy *et al.*, 1999) and from the European Research Satellite (Richter *et al.*, 1998; Wagner and Platt, 1998).

The efficiency of halogen catalysis is lessened by chain termination reactions of atoms/radicals with hydrocarbons, carbonyls, and NO_x . In previous Polar Sunrise Experiments (PSE) conducted at Alert, instrument uncertainties prevented unequivocal determination of the abundance of NO_x but upper limits of 50–100 pptv were derived in ozone depleted and non-depleted air masses (Bottenheim *et al.*, 1990; Leitch *et al.*, 1994). Measurements of NO_x at Ny-Ålesund, Svalbard (78.9° N, 11.9° E) were reported by Beine *et al.* (1997) in the special issue describing results from the European Arctic Tropospheric Ozone Chemistry (ARCTOC) project (Barrie and Platt, 1997). Median NO_x between 19 Feb.–31 May 1994 was 21.5 pptv and it was reduced to median values of 9–12 pptv in air masses transported to the site in which ozone was partially depleted from about 40 to as low as 4 ppbv. In light of the previous Alert and Ny-Ålesund measurements NO_x has been considered a relatively minor player in Arctic surface layer chemistry. For example, box models having a source of active chlorine and bromine and initialized with as much as 50 pptv of NO_x show removal of NO_x in only a couple of days through transformation to NO_y reservoir constituents. Reservoirs like HNO_3 and BrONO_2 are believed to be rapidly deposited to the snow/ice surface (McConnell *et al.*, 1992; Fan and Jacob, 1992; Sander *et al.*, 1997) while others like PAN are expected to remain in the gas phase (Shepson *et al.*, 1996).

PSE '98 was organized primarily to further investigate carbonyl behavior at Alert (de Serves, 1994; Shepson *et al.*, 1996; Sumner and Shepson, 1999) but it also presented an opportunity for measurements of active nitrogen. Here the behavior of NO_x and NO_y is contrasted between low and higher insolation periods when O_3 mixing ratios were mostly normal (30–50 ppbv). In particular, during the higher insolation of April the behavior of NO_x and NO_y was unusual and one that has not been reported from previous studies at Alert. Results obtained when surface ozone was reduced to zero in an air mass transported to the Alert region will be discussed elsewhere.

2. Measurements

Figure 1 shows the Alert region located on the northern tip of Ellesmere Island. Instrumentation was housed in the Special Studies Trailer (SST) which is located about 5 km southwest of and on a plateau ~190 m higher than Canadian Forces Station (CFS) Alert. CO, PAN, and some meteorological data were acquired at the Atmospheric Environment Service (AES) Baseline Air Pollution Monitoring Network (BAPMoN) station located about 1/2 km to the south of the SST (e.g., Lulis, 1999). An east to west line of four hills with elevations as high as 800 m is located 5–6 km south of the SST and mountains as high as 1500 m are located about 40 km to the west. The land and ocean ice surface are of course snow covered at this time of year but the depth was usually less than 1/2 m except in drifted locations. The snow surface at Alert melts completely during the summer months so the depth during the experiment was the accumulation during the current year. Winds were often light but the prevailing direction was from the southwest sector. Whenever winds were from the north to east sector contamination from the diesel generators or vehicle engines was often observed. ‘High’ NO_x (>50 pptv and as large as 16 ppbv at the SST) could always be attributed to activities at CFS Alert or local vehicle emissions. Both vehicle and CFS Alert contamination are henceforth labeled CFSAC.

NO_{x,y} were measured using a 3-channel chemiluminescence instrument. Each channel had a sensitivity to NO of 8–10 counts s⁻¹ pptv⁻¹ (cps/pptv) and instrument background count rates were near 200 cps after a few days of operation. A Au/CO converter, operated at 300 °C and housed in an insulated container on the edge of the roof of the SST, reduced NO_y to NO. Ambient air entered the converter 1.5 m above the roof through 15 cm of 0.4 cm i.d. teflon tubing which was thermostatted at 50 °C to within a few mm of the tip. Water vapor was added to the flow (resultant of 540 ppmv) a few cm upstream of the converter but periodic tests showed less than 2% difference in the NO_y signal when the water flow was removed. NO_x was sampled from the same height through a teflon filter and similar teflon tubing which was attached to the inside metal skin of the inlet container to keep the temperature near ambient (-15 to -40 °C during the study) to minimize thermal decomposition of possible interferents. Additional tubing (~1.5 m) inside the SST was also insulated to keep the gas flow cool up to where it was split to feed the NO detector and the NO₂ photolytic converter (PC). The PC was modified from that used in our previous studies. The cylindrical pyrex cell of only 62 cm³ volume was immersed in a water bath controlled at 7 °C and illuminated from each end by the beam from two high pressure 300 W xenon lamps having integral parabolic reflectors. The beams passed through dichroic mirrors as usual but were also crudely focused into the PC using 200 and 250 mm focal length lenses. The pressure in the PC was controlled at either 308 or 410 torr to yield a plug flow residence time of 1.5 or 2 sec. Filters that transmitted wavelengths ≥335 nm were used in much of the study but tests showed no difference in the measured mixing



Figure 1. The region around CFS Alert on the northern tip of Ellesmere Island. Instrumentation was housed in the Special Studies Trailer (SST) located inland about 5 km from the main base, about 1/2 km from the Baseline Air Pollution Monitoring Network (BAPMoN) building, and about a 1/2 km from an unused Transmitter Building (TX). The lightly shaded area extending from west to east across the lower third of the figure marks the edge of the 'plateau' between the main base and the measurement sites. Grid lines are at 1 km intervals.

ratio of NO₂ with and without these additional filters. Water vapor was also added to the NO_x inlet tubing (resultant of 240 ppmv) inside the SST most of the time. No difference in the mixing ratio was ascertained with or without the water addition. The channels were calibrated automatically every 8 hours using a small flow of NO directly from a reference cylinder or NO₂ produced by titration of the NO with ozone to 99% completion. The NO_y sensitivity to NO₂ was $\geq 96\%$ of the sensitivity to NO and the data were reduced using the sensitivity to NO₂. The NO₂ channel sensitivity varied with lamp age but was in the range of 50–65% of the NO sensitivity when the 2 sec residence time was employed.

Measurements were made between 4 March and 26 April 1998 (days 63–116). Data were recorded at 5 s intervals but are averaged here to 1 or 5 min. Using the expressions given in Ridley *et al.* (1994), the detection limits for 1 min averages of NO_y, NO, and NO₂ were near 0.5, 0.5 and 1 pptv. The uncertainty of the measurements at mixing ratios approaching the detection limit is dictated by artifacts. These signals were measured every 4 hr by displacing the sample flows with high quality zero air. Artifacts for NO_y, NO, and NO₂ were typically ≤ 5 , ± 1 , and ≤ 2 pptv and were fully subtracted from the raw data using linear interpolation over the 4 hr period. The overall uncertainty of the 1-min averaged data is estimated at: NO_y \pm (3 pptv + 5% of mixing ratio), NO \pm (1 pptv + 7% of mixing ratio), NO₂ \pm (2 pptv + 7% of mixing ratio). It must be emphasized that the measurement of NO₂ by the present technique should be considered an upper limit especially in the cold Arctic environment. For our photolysis lamp and optical configuration we estimate that any ambient NO₃, HONO, or BrONO₂ will be photolyzed with an efficiency relative to NO₂ of 1, 0.3, and ~ 0.11 , respectively. PAN and HNO₃ are not interferences. N₂O₅, HO₂NO₂, and ClONO₂ should not be significant interferences based upon their absorption cross sections and the lamp output spectrum within the PC. For example, at ambient mixing ratios of 50 pptv, none of these constituents should contribute more than 0.2 pptv. Evidence that these possible interferences were negligible at least during some periods of the measurements will be presented in the next section.

3. Low Insolation Period of Early March

Figures 2 and 3 show results for days 64–74 (5–15 March) or prior to spring equinox when solar insolation was absent or very low. Neither irradiance nor actinic flux was measured but possible insolation is shown by the solar zenith angle (SZA) along the top of the figure. The sun was barely above the horizon (or direct sun was blocked by the hills to the south) and only for a few hours each day. During this period O₃ was normal, 30–45 ppbv, and not well correlated with NO_y or other long-lived constituents such as CO. NO_y was near 300 pptv except during days 64–65 when the maximum mixing ratios of ~ 600 pptv for the whole study were measured (excluding CFSAC). This maximum and lesser ones that occurred on days 67–68 (maximum of ~ 400 pptv) and days 82–85 (not shown, maximum of

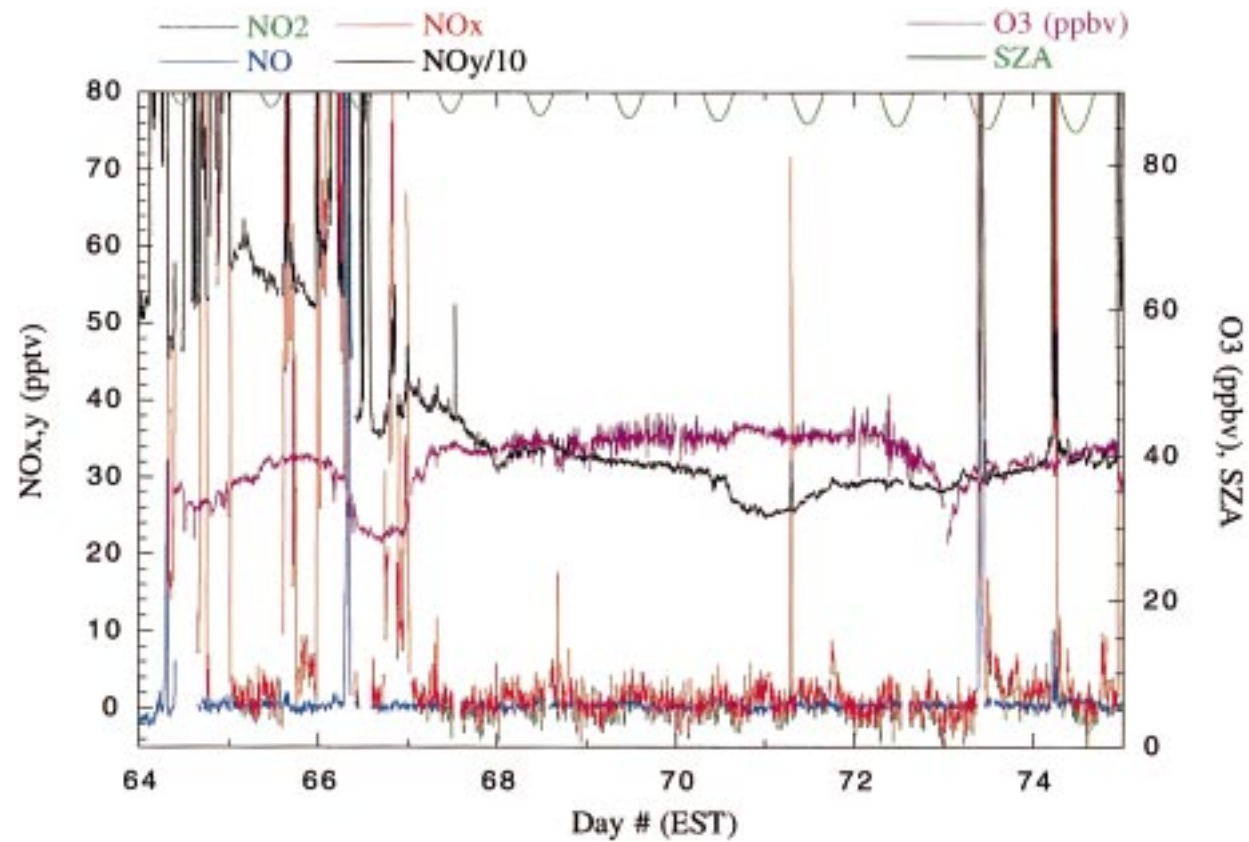


Figure 2. Measurements of NO, NO₂, NO_x, NO_y, and O₃ during the early part of the experiment (5–15 March) when the possible solar insolation was absent or small. The solar zenith angle (SZA) is shown along the top of the figure. On the coarse time scale of the figure contamination from CFS Alert appears as sharp spikes which are sometimes off scale especially on days 64–66. Local time at Alert is Eastern Standard Time (EST) by definition.

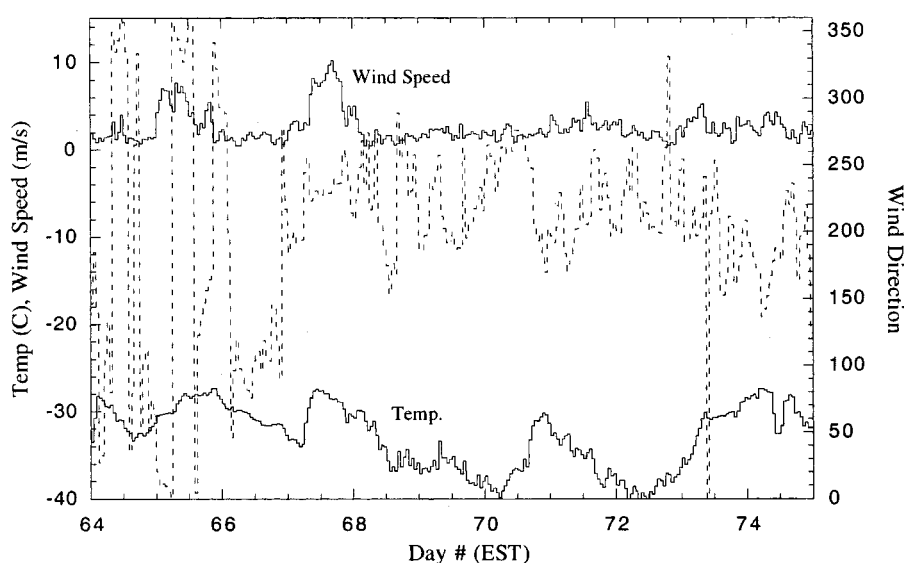


Figure 3. Wind speed, direction and air temperature measured at 10 m elevation at the BAPMoN station corresponding to the days of Figure 2.

~400 pptv) were due to more obvious than normal long-range transport (LRT) events as revealed by an expected good correlation with CO and other long-lived constituents such as CH₄, CO₂, and C₂H₆. NO_y and CO were strongly linearly correlated ($R^2 = 0.9$) for the entire study when CFSAC was filtered from the data. In contrast to the moderate to low mixing ratios of NO_y, NO_x was near zero or near the detection limit of the instrument for much of the period of Figure 2 and notably also during the LRT events. Excluding CFSAC, the average and median values in pptv for the period of Figure 2 were: NO = 0.3 ± 0.7 , median 0.37; NO₂ = 0.7 ± 1.8 , median 0.7, NO_y = 345 ± 38 , median 318; O₃ = 39.4 ± 3.8 ppbv, median 40.3 ppbv. Of course, NO was expected to be near zero when the sun was below the horizon.

Weather conditions during the period of Figure 2 were neither stagnant nor was the snow surface invariant. Wind speed, direction, temperature (Figure 3) and visibility were quite variable although wind direction was mostly from the south to west sector. On day(s) 64 (5 Mar.), 65–67, 71, the afternoon of 72, and 73–75, visibility was low (<1–2 km) due to the presence of ice fog or abundant ice crystals. Blowing, drifting snow occurred on day 67 and light snowfall occurred on day 73 and the afternoon of day 75. In contrast days 68–70, and the morning of day 72 were clear with direct but low insolation. There was no distinct change in the near zero mixing ratios of NO_x between the low visibility and high visibility days although there is a hint of a weak diurnal variation mainly on the high visibility days.

Such low NO_x in the cold Arctic surface layer is not surprising given the near absence of much larger than average NO_y LRT events during PSE '98. The behavior can be easily understood albeit only qualitatively. Based upon preliminary calibration factors for the AES PAN instrument, PAN mixing ratios constituted 83% of NO_y when averaged over the period of Figure 2. This is a larger fraction of NO_y than reported from previous studies made at Alert (Bottenheim *et al.*, 1993). The higher fraction is largely a consequence of observing much smaller mixing ratios of alkyl nitrates in spring 1998. For the 1998 study, the sum of alkyl nitrates constituted only $\leq 6\%$ of NO_y compared to considerably larger fractions of 20–35% measured in earlier studies (Bottenheim *et al.*, 1993; Muthuramu *et al.*, 1994). Thus the median abundance of the sum of other nitrogen constituents such as HNO_3 , HONO , HO_2NO_2 , NO_3 , N_2O_5 , ClONO_2 and BrONO_2 if present was not larger than about 40 pptv. At this mixing ratio, recycling rates to NO_x by photolysis or thermolysis of any of these reservoirs, most of which would be formed primarily at sunlit latitudes prior to transport to the Arctic, are much too slow with the exception of photolysis of BrONO_2 . Even at the maximum temperature of -28°C (range -28 to -40°C) encountered for the period, the rate of PAN decomposition at a mixing ratio as large as 300 pptv would be only ~ 0.7 pptv/day. Furthermore reservoirs like HNO_3 , ClONO_2 and BrONO_2 could be depleted through surface deposition or hydrolysis on ice crystals (Curry and Radke, 1993; Laird and Sommerfeld, 1995; Zondlo *et al.*, 1997; Abbatt, 1997). Assuming that direct surface removal of NO or NO_2 is insignificant, and even without transformation of NO_x to NO_y reservoirs prior to arrival in the Arctic, formation of NO_3 and N_2O_5 and subsequent surface deposition or accommodation of either constituent on the frequently abundant ice crystals must have effectively removed any NO_x initially present in the air masses of the period of Figure 2 (Barrie and Bottenheim, 1991). If the deposition velocity for N_2O_5 is assumed to be similar to that of HNO_3 or $\sim 1\text{--}2\text{ cm s}^{-1}$ (Cadle *et al.*, 1985; Sander *et al.*, 1997) then with a 0.5–1 km deep surface layer the time for removal would be on the order of 1 day. However, formation of N_2O_5 is rate limited (2–3 day time constant) by the reaction of NO_2 with O_3 to produce NO_3 . Previous analyses (Hopper and Hart, 1994; Worthy *et al.*, 1994) have suggested that transit times for LRT from source regions to Alert can be as short as 2–3 days but are more frequently 5 days or longer. Thus, even during relatively direct LRT episodes NO_x could be effectively reduced and with longer residence times in the Arctic during more stagnant meteorological situations the depletion could be complete. The observations demonstrate that the snow surface and perhaps ice crystals can be effective sinks of NO_x from the surface layer when sunlight is low or absent during winter/spring. Unfortunately, the time scale for removal remains poorly defined. The depletion of NO_x in the surface layer as observed during the low insolation period is expected to contrast with the higher altitudes in the troposphere where these effective NO_x removal processes are curtailed. Indeed, evidence for the presence of larger concentrations of NO_x at altitudes above the surface layer will be presented in the next section.

There is further evidence that NO_y constituents are removed from the surface layer. The abundance of other long-lived anthropogenic tracers such as CO and NMHCs was large during the period of Figure 2, indeed over the whole study period, as a result of transport from source regions and the lack of photochemical sinks. Thus, it is very unlikely that the air masses of Figure 2 did not contain significant NO_x initially. Over the whole measurement period of days 63–116, but excluding data obtained during a strong O₃ depletion event of days 107–109, relatively large median values of CO (171 ppbv), acetylene (417 pptv), *n*-butane (133 pptv), ethane (1.96 ppbv) and other constituents were observed. As one example, the median CO/NO_y ratio of 620 (ppbv/ppbv) was considerably larger than has been observed in regions much closer to anthropogenic sources. Liang *et al.* (1998) reported measurements made near Boston for the winter/early spring period (Jan.–April) from which an average CO to average NO_y ratio of only 42 ± 3 can be derived. Their average CO measurements, which ranged from 175–225 ppbv, were not much larger than observed at Alert. The much larger CO/NO_y ratio at Alert is then also consistent with removal of NO_y constituents either during transit to the Arctic or during residence in the Arctic surface layer. Unlike the case for NO_y constituents, CO is removed only through oxidation by free radicals whose concentrations are expected to be very small during darkness. Similar arguments can be made on the basis of the measured hydrocarbon to NO_y ratios.

The low to zero NO_x of Figure 2 has important implications for the measurement technique used here and for the mixing ratios of some other constituents. HO₂NO₂ which would be a stable species in the cold Arctic cannot be a significant measurement interferent if present. Because NO₃ would be photolyzed with nearly the same efficiency, HONO with about 30%, and BrONO₂ with about 11% of the efficiency of NO₂ in our instrument, and using the median NO₂ mixing ratio of ~ 1 pptv for the period of Figure 2, then the mixing ratio of NO₃, HONO, or BrONO₂ would be less than or equal to 1, 3 and 10 pptv, respectively. The result for HONO is different from that of PSE '92 where Li (1994) reported average HONO mixing ratios of 15 pptv (range 0–65 pptv) for mid-Jan. to early March and 5 pptv (range 0–20 pptv) after sunrise in late March to mid-April at Alert. Li suggested that reduction of nitrate in acidic particles was the source of HONO during the dark and sunlit periods. At least during the low insolation period of Figure 2, our measurements are inconsistent with a significant source of HONO from particles or the surface.

4. Higher Insolation Period of April

Figures 4 and 5 present data from days 90–104 (31 Mar.–14 Apr.) when the sun was above the horizon for much or all of a day. Notably, a distinct diurnal variation was observed in NO and NO₂ yielding an amplitude for NO_x of 8–35 pptv depending on the day. The amplitude variation in active nitrogen also closely followed the possible insolation. On the scale of Figure 4, the NO_y mixing ratios appeared more

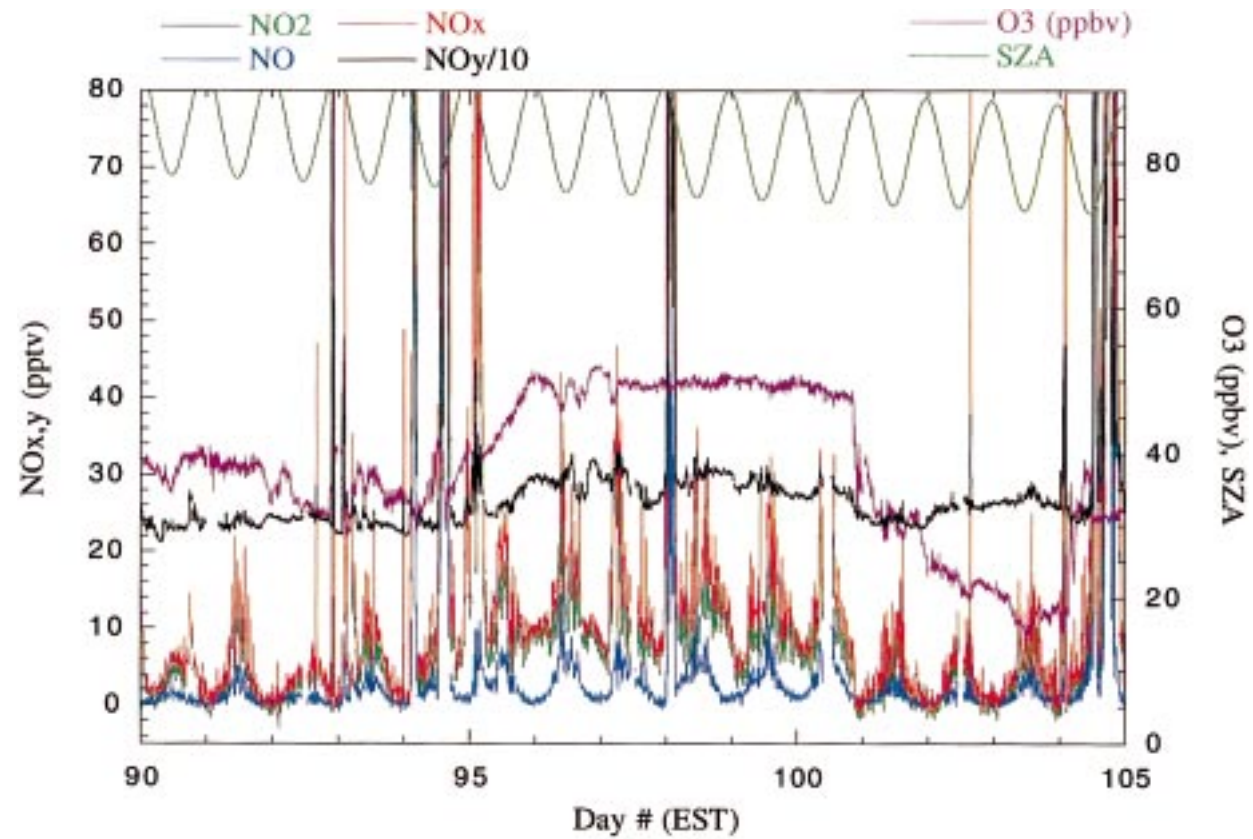


Figure 4. Measurements of NO, NO₂, NO_x, NO_y, and O₃ during 31 March to 15 April (days 90–105) when possible solar insolation was present for all or most of a day. The solar zenith angle (SZA) is shown along the top of the figure. On the coarse time scale of the figure contamination from CFS Alert appears as sharp spikes which are usually off scale.

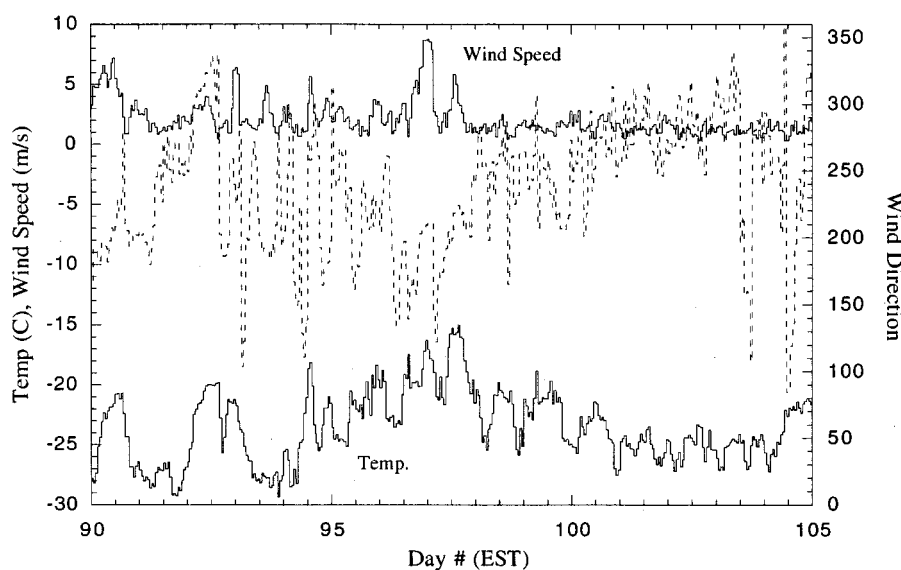


Figure 5. Wind speed, direction and air temperature measured at 10 m elevation at the BAPMoN station corresponding to the days of Figure 4.

uniform and lower than occurred during the low insolation period. Average and median NO_y for the period of Figure 4 were 261 ± 26 and 258 pptv, respectively. Figure 6, however, shows that the diurnal trend in NO_x was followed by one in NO_y.

The diurnal variation in active nitrogen which persisted through to the end of the program remained identifiable under a variety of wind, visibility, and surface conditions although, as shown in Figure 5, wind speeds were frequently lighter and air temperature warmer than occurred during the earlier low insolation period. Some of the meteorological changes are reflected in O₃ where a partially depleted air mass was transported to the SST region on days 101–103 (and 105–106, not shown) and where near maximum O₃ of ~50 ppbv occurred on days 96–100 (6–10 Apr.). Previous analysis (Hopper and Hart, 1994; Hopper *et al.*, 1998) has suggested that these events of larger O₃ are the result of downslope katabatic flow from higher elevations to the west and southwest of Alert which mixes a larger fraction of free tropospheric air into the surface layer. The increase in air temperature supports this argument. The observed increase in O₃ from prior to and during the katabatic flow period implies a substantial gradient of at least 10–15 ppbv across the surface layer/lower free troposphere transition. Commensurate increases in NO_y, the envelope of minimum NO_x, excluding the diurnal amplitude, and PAN and acetylene (not shown in Figure 5) during the katabatic period are also consistent with them having larger mixing ratios above the surface layer. That the period of elevated O₃ was exceptionally bright (direct insolation and high albedo) and clear also supports the katabatic analysis. Days 90 (31 Mar.), 91, 103, the morning of 104, and the

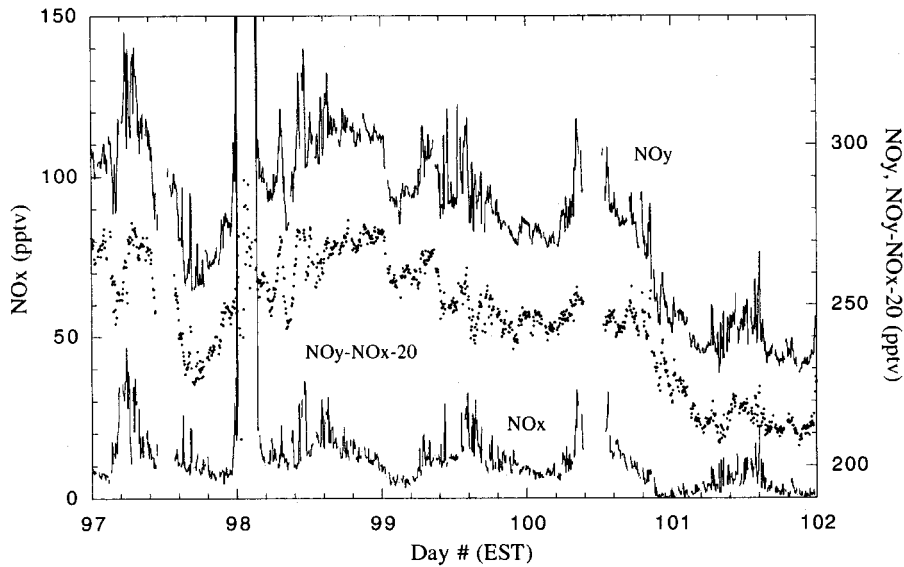


Figure 6. NO_y and $\text{NO}_y - \text{NO}_x$ mixing ratios plotted on an expanded scale to show the diurnal behavior relative to that of NO_x . The $\text{NO}_y - \text{NO}_x$ difference has been offset by -20 pptv for clarity. The large spike in NO_y and NO_x that occurred just after midnight of day 97 is due to emissions from CFS Alert.

afternoon of 105 were also mostly bright and clear. In contrast, low visibility, with overcast sky and light snow occurred on day 92, thick ice fog/fresh snow moved in from the ocean during the late morning and afternoon of day 104, and light snow and lower visibility occurred during the morning of day 105. Although sometimes confounded by CFSAC (when NO_x is off scale in Figure 4), the diurnal change in NO_x persisted during these meteorological and insolation changes. The diurnal change remained with and after a fresh snow surface, a newly drifted snow surface (day 88, not shown) and on days of lower visibility albeit with a range of amplitudes. It also remained when winds occurred from the south to southwest (days 95–97, Figure 5) or from the northwest (days 100–103), directions that would transport air more from the snow covered land surface or from the snow/ice surface over the ocean, respectively.

Several factors could be responsible for the observed diurnal change in NO_x . Mixing ratios of NO_x as large as 16 ppbv were observed at the SST from CFS Alert so that only a very small residual could account for the maximum observed in the diurnal variation. However, it would seem improbable that such regular sampling of highly diluted emissions occurred considering the variety of weather conditions. There was no regular variation in wind speed or direction (Figure 5) or a correspondence between wind direction and SZA. Downward mixing/ventilation from altitudes above the surface layer would be a possible candidate but it is also doubtful that this process occurred on such a regular basis after polar sunrise considering the variety of weather conditions experienced and that the surface layer

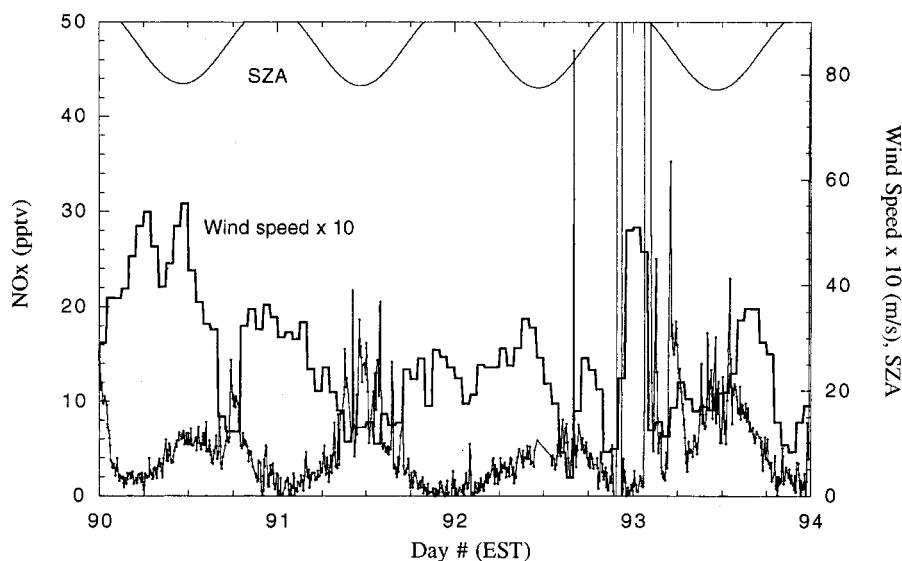


Figure 7. The wind speed, NO_x mixing ratio and solar zenith angle (SZA) for days 90–94. Days 90 and 91 were very bright and clear. Day 93 was marginally less clear due to the presence of some ice crystals. Light snow and lower visibility (2–3 km) occurred until mid-afternoon on day 92. Light ice crystal abundance occurred on day 94.

is usually stable. Furthermore, a diurnal variation corresponding to that of NO_x would be expected for other constituents that were measured with sufficient time resolution and sustained a significant gradient across the top of the surface layer. As discussed previously there was good evidence that O₃, NO_y, PAN, and NO_x all had larger mixing ratios above the surface layer but neither O₃ nor PAN showed a consistent diurnal variation. Indeed, O₃ was remarkably invariant to within a few ppbv at times as shown for days 97–99 in Figure 5. Since from the previous discussion that the gradient in O₃ was at least 10–15 ppbv, and if all of the diurnal amplitude in NO_x was attributed to downward transport, then a diurnal change in O₃ would have been readily measured. A similar argument can be made for PAN. Thus we conclude that vertical ventilation is not responsible for the observed regular diurnal variation in NO_x. There was some correspondence of higher air temperatures with higher NO_x on days 97–100 but not on days 90–96 or 101–105 (Figure 7). Thus it seems unlikely that thermal dissociation of a gaseous constituent was the cause of the diurnal variation in NO_x. Lastly, there were a few days (90, 91, 92) in which small reductions in PAN of 15–20 pptv occurred during the night and early morning but this variation also was not nearly as consistent as the daily diurnal variation in NO_x after equinox. The small changes in PAN were often accompanied by positively correlated changes in CO so that the changes in PAN were most likely due to advective rather than chemical processes. Furthermore, with air temperatures mostly below –20 °C for the days of Figure 4, PAN decomposition

would not contribute more than ~ 1 pptv over the period of the morning increase in NO_x .

Figure 6 also shows that the diurnal variation in NO_x cannot be due to significant recycling from other gaseous reservoirs of NO_y because the variation in NO_y mirrors that of NO_x . Thus, the morning increase has to be due to a new source of reactive nitrogen and one that apparently requires significant insolation, perhaps ultra-violet, since there was no or very little diurnal change during the low insolation period of Figure 2. By default the source is attributed to release from the snow surface with an emission rate sufficient to increase NO_x by 2–8 pptv/hr during morning hours. (The region does have some exposed shale rock mostly on windswept ridges, but its surface area would be very minor compared to that of the snow covered land surface and the snow/ice surface over the ocean to the north.) A source from the snow surface is consistent with the studies of Dibb *et al.* (1998) and Munger *et al.* (1999) where substantial fluxes of unidentified NO_y constituents (other than HNO_3) both into and out of the snow surface were reported from Summit, Greenland. Recently, Honrath *et al.* (1999) have measured fluxes of NO_x from the sunlit snowpack near Summit using an enclosure technique but they did not report whether NO or NO_2 was the dominant constituent within the interstitial air. However, their novel study suggests that the source implied from our measurements is not just an unusual feature of the Alert region. Several studies have shown that the concentration of nitrate is high especially in the upper layers of polar snow (Nefel *et al.*, 1985; Davidson *et al.*, 1989; Dibb *et al.*, 1998). Nitrite concentrations may also be high but measurements have not been reported presumably because it does not survive the usual storage time and procedures used for routine snow analyses. At Alert, for the period of November to May, median concentrations of nitrate in the snowpack are typically 4–6 $\mu\text{equiv./L}$ (Toom-Sauntry and Barrie, 1999). These concentrations would be more than sufficient to account for the observed mixing ratios of gaseous active nitrogen shown in Figure 4 if all of the nitrate was released to the gas phase within a 0.5–1 km stable surface layer (L. Barrie, private communication, 1998). Reduction of nitrate or nitrite to gaseous active nitrogen within the snow is possible by several mechanisms including photolysis: see, for example, Li (1994), Zafiriou *et al.* (1980), Mopper and Zhou (1990), Honrath *et al.* (1999). Presumably the nitrate/nitrite processing occurs in the quazi-liquid water layer on the ice crystals as discussed by Conklin and Bales (1993). Biological activity might also contribute to the release of active nitrogen. Clearly the constituent released from the snowpack has to be either NO or NO_2 directly as measured by Honrath *et al.* (1999), one that is readily photolyzed to NO_x , or some combination thereof. Other primary candidates would be NO_3 , HONO , possibly ClNO/BrNO (Finlayson-Pitts *et al.*, 1990), or BrONO_2 , although the latter would likely suffer hydrolysis within the snow surface. If photolysis of NO_3 or NO_2^- is the source of NO_x , concurrent production of OH radicals in the quazi-liquid layer would make the snowpack potentially very photochemically active (Sumner and Shepson,

1999). Clearly, more detailed study of chemical processes within the snowpack are required.

With a surface source apparently sensitized by sunlight the observed mixing ratio of NO_x will depend on many factors including wind speed, snow temperature and porosity, surface layer stability and depth, and sunlight penetration within the surface. Sufficiently detailed meteorological and snowpack information is lacking for a quantitative examination. However, there are trends in the magnitude of the diurnal behavior that seem to be consistent with a surface source. Overall, wind speeds were sufficiently light to allow observation of the diurnal change and variations in these generally low wind speeds were likely a principal cause of the spikiness in the data. For example, considering Figure 7, days 90, 91, and 93 were bright clear days. With light to calm winds about noon on day 91 peak mixing ratios were 2–3 times larger than occurred near or prior to noon on day 90 when wind speeds were stronger at $\sim 5 \text{ ms}^{-1}$. A significant increase in NO_x was also observed in the late afternoon of day 90 as the wind speed dropped to $\sim 1 \text{ ms}^{-1}$. Similarly, on day 97 of Figure 4, it appears that the change in NO_x did not follow the sun as well as on other days. However, the apparent anomaly is consistent with a change of wind speed that occurred near mid-day. In the morning when NO_x was as large as 35 pptv wind speeds were only 1–1.5 ms^{-1} while starting just before noon the winds increased to over 4 ms^{-1} and NO_x decreased by a factor of 2–3. Figure 7 also qualitatively further demonstrates sensitivity of the NO_x amplitude to sunlight. Light snow/ice fog and low visibility (2–3 km) occurred in the morning to early afternoon of day 92 which was followed by partial clearing in the late afternoon. Although wind speeds were comparable with days 91 and 93, maximum mixing ratios were a factor of 2–3 lower. Since conditions of ice fog and light snow are expected to be accompanied by a reduced surface layer depth, which would tend to increase mixing ratios for the same source strength, the true sensitivity of the emission rate to sunlight could be greater than the factor of 2–3 reduction. However, if a NO_x precursor rather than NO_x itself is released from the surface, then this argument is further complicated by possible removal of the precursor by snow and/or ice crystals and the effect of particles on photolysis rates.

Although there is good evidence that the sunlit snow surface near Alert is a source of active nitrogen, the observed decline of NO_y and NO_x in the late afternoon through ‘nighttime’ period is also interesting. A close examination of Figure 6 reveals that the diurnal amplitude in NO_x is often less than that of NO_y by 5–10 pptv although variations in the minimum or ‘baseline’ of the NO_y observations sometimes mask this small trend. The NO_y–NO_x difference plotted in Figure 6 shows the residual somewhat more clearly. (The difference is offset by 20 pptv in the figure for clarity.) The difference signal is smoother than NO_y indicating that much of the change in NO_y is due to the change in NO_x but that the residual diurnal amplitude of 5–10 pptv is evident especially on days 100–101. Thus, if NO_x is the constituent directly released from the snow surface the residual demonstrates conversion of NO_x to other constituents of which PAN and HNO₃ would be standard

candidates. If NO_x is not the only odd nitrogen species emitted from the snow surface then the difference could also result from incomplete transformation of the emitted precursor to NO_x .

Provided the surface source of NO_x is a large scale feature of the Arctic region, then the decline in NO_x and NO_y later in the day requires that removal processes compete with the surface emissions. The removal process(es) would have to be one(s) that removed NO_x or NO_y from the gas phase, presumably back to the snow surface, with a time constant of the order of a half day. Formation of HNO_3 and subsequent deposition would be a consistent process but the time scale of less than a day would require an OH concentration of the order of 10^6 cm^{-3} . With 24 hr sunlight, removal through $\text{NO}_3/\text{N}_2\text{O}_5$ formation and deposition or particle accommodation would be curtailed because NO_3 would be readily photolyzed. In mid-April the photolysis time constant would be $<20 \text{ s}$ from mid-morning to mid-afternoon. Formation of halogen nitrates and subsequent deposition and hydrolysis at the snow surface could be contributing removal processes. The recent aircraft and satellite analyses mentioned in the introduction reveal that BrO is distributed over very large areas in spring. As well Impey *et al.* (1997, 1999) measured photolyzable bromine (believed to be mostly HOBr and Br_2 but BrONO₂ would be an additional candidate) throughout winter and spring as large as 40 pptv but usually less than 25 pptv. Photolyzable chlorine was as large as 100 pptv but usually less than 15 pptv before polar sunrise and smaller amounts occurred thereafter. Clearly further detailed model studies employing a surface source of NO_x are required to help elucidate the strength of possible removal processes. It is also stressed that if the surface source of NO_x is only a local phenomenon peculiar to the Alert region then ventilation would easily explain the fall-off of NO_x and NO_y later in the day. No unidentified removal process would be required. With the range of meteorological conditions described previously it is, however, unlikely that the consistent decrease in NO_x and NO_y later in the day was always due to ventilation. Whether the source is local or universal obviously requires further study.

5. Implications for Radical Concentration and Ozone Production and Loss

The measurements made during the higher insolation period of Figure 4 can be used to determine limits on some radical concentrations and provide estimates of O_3 production rates when O_3 was near normal springtime levels. Figure 8 shows the diurnal variation of the NO/NO_2 ratio for days 94–100 when the NO and NO_2 signals were large enough to determine a meaningful ratio. On day 101 signals were not much above the detection limit of the instrument and the ratio becomes noisy. At steady state, the expected NO_2/NO ratio is

$$\begin{aligned} \text{NO}_2/\text{NO} = & k_{\text{NO}/\text{O}_3}[\text{O}_3]/J_{\text{NO}_2} + \\ & + (k_{\text{NO}/\text{HO}_2}[\text{HO}_2] + k_{\text{NO}/\text{RO}_2}[\text{RO}_2]) + \\ & + k_{\text{NO}/\text{BrO}}[\text{BrO}] + k_{\text{NO}/\text{ClO}}[\text{ClO}]/J_{\text{NO}_2}, \end{aligned} \quad (1)$$

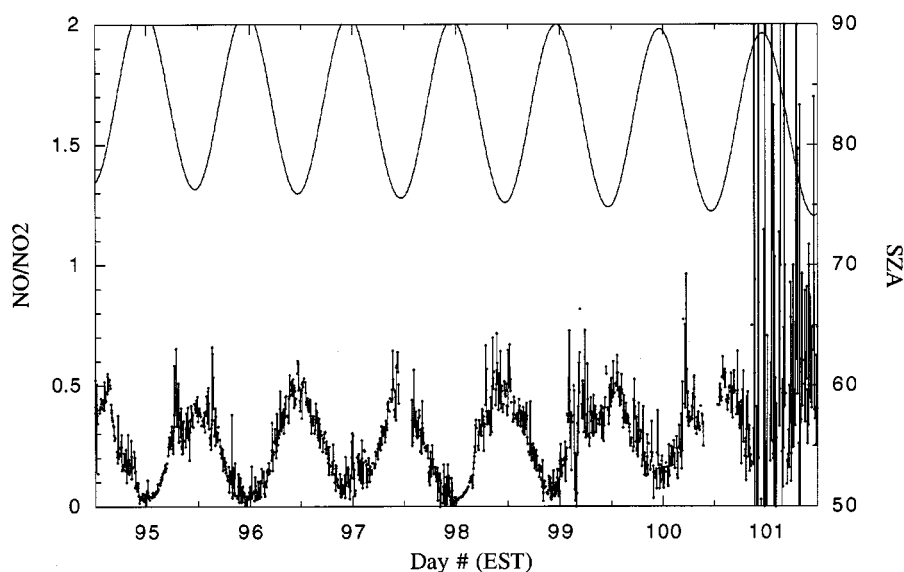


Figure 8. The NO/NO₂ ratio for days 95–101.

where J_{NO_2} is the photolysis frequency of NO₂ and the k 's are the rate coefficients for the subscripted reactants. Allowance has been made for the possibility that halogen radicals are present. At least for small carbon number peroxy radicals (RO₂) $k_{\text{NO}/\text{HO}_2} = k_{\text{NO}/\text{RO}_2}$, $k_{\text{NO}/\text{BrO}} \sim k_{\text{NO}/\text{ClO}}$, and $k_{\text{NO}/\text{BrO}} \sim 2k_{\text{NO}/\text{HO}_2}$ so the ratio can be written as

$$\text{NO}_2/\text{NO} = k_{\text{NO}/\text{O}_3}[\text{O}_3]/J_{\text{NO}_2} + k_{\text{NO}/\text{HO}_2}[\text{RAD}]/J_{\text{NO}_2}, \quad (2)$$

where $[\text{RAD}] \sim [\text{HO}_2] + [\text{RO}_2] + 2[\text{BrO}] + 2[\text{ClO}]$. Using the averages of the noon-time observations of days 98–100, O₃ = 51 ppbv, temperature = –22 °C, NO₂/NO = 2.0, and $J_{\text{NO}_2} = 6.8 \times 10^{-3} \text{ s}^{-1}$ (kindly calculated by S. Madronich using a column ozone of 450 DU and a surface albedo of 90%, private communication, 1998), then RAD = 9.7 pptv. With normal mixing ratios of O₃ present, BrO and ClO are expected to be very small (Hausmann and Platt, 1994; Barrie and Platt, 1997) so RAD is likely best interpreted as the concentration of peroxy radicals HO₂ and RO₂. However, the calculation does provide an upper limit of ≤ 5 pptv for the halogen radical concentration which is consistent with the in situ measurements of BrO of 0–5 pptv during normal ozone periods at Alert in PSE '92 and '97 (Hausmann and Platt, 1994; Impey *et al.*, 1999).

It is also worthwhile examining the local photochemical budget of O₃ during the higher insolation period because the O₃ loss process by photolysis to O(¹D) and reaction with H₂O is expected to be slow compared to more southerly latitudes

due to the relatively low sun angle and the low absolute humidity of the Arctic. The net rate of change of O_3 by photochemical processes can be approximated by

$$\text{Net rate} = k_{\text{NO}/\text{HO}_2}[\text{RAD}][\text{NO}] - (J^* + k_{\text{O}_3/\text{HO}_2}[\text{HO}_2] + k_{\text{O}_3/\text{OH}}[\text{OH}])[\text{O}_3] - 2k_{\text{BrO}/\text{BrO}}[\text{BrO}]^2. \quad (3)$$

The first term on the right hand side of (3) can be identified as the gross production rate $P(O_3)$ and the sum of negative terms as the gross loss rate $L(O_3)$. We have allowed for the possible presence of halogen radicals in the form of BrO. Again considering noon-time averages for days 98–100 where the NO mixing ratio was 6–10 pptv and using the previous estimate for RAD gives $P(O_3) \sim 4\text{--}6 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$. $L(O_3)$ is more difficult to estimate. The second term, $J^*[O_3]$ is the noon-time photolysis coefficient of O_3 to $O(^1D)$ ($J_{O_3} = 8.0 \times 10^{-7} \text{ s}^{-1}$, S. Madronich, private communication, 1998) multiplied by the fraction of the $O(^1D)$ that reacts with water versus being quenched to the ground state (see Ridley *et al.* (1992) for details). A water vapor mixing ratio of 680 ppmv corresponding to a typical saturation of 80% at -22°C was used. $J^*[O_3]$ is then small as expected, $\sim 5.7 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$. An upper limit to the third term of (3) can be determined by assuming that all of RAD is HO_2 . Then $k_{\text{O}_3/\text{HO}_2}[\text{HO}_2][O_3] \sim 6.3 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$. Clearly the third term is sensitive to the actual abundance of RO_2 constituents which unlike HO_2 do not react with O_3 . A factor of two estimate of the fourth term of (3) can be made using model results (Sander *et al.*, 1997) which give an HO_2/OH ratio at high sun of about 400 for the Arctic in mid-April. An upper limit to $k_{\text{O}_3/\text{OH}}[\text{OH}][O_3]$ is then $\sim 0.5 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$. As discussed previously halogen radicals are not expected to be of significant concentration during periods of normal O_3 but at 2 pptv or 5 pptv of BrO the fifth term would be 0.3×10^4 and $1.6 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$, respectively. With BrO less than 5 pptv the third term involving HO_2 dominates $L(O_3)$ and by itself is comparable to $P(O_3)$. The estimates suggest that for air masses at Alert which contain normal mixing ratios of O_3 (30–50 ppbv), both the photochemical production and loss rates of O_3 are equivalent to 1–2 ppbv day^{-1} for the highest sun conditions of mid-April and that the photochemical budget of O_3 in the surface layer is essentially balanced. Without the daytime source of NO_x weak net photochemical destruction of ozone would be anticipated.

6. Summary

In agreement with previous Arctic studies (Worthy *et al.*, 1994; Jobson *et al.*, 1994), the mixing ratios of many long-lived anthropogenic tracers like CO, CO_2 , C_2H_2 , C_2H_6 (and others) during PSE '98 were large due to accumulation from source regions and the lack of photochemical destruction paths during winter. In contrast average NO_y mixing ratios for the whole study were only 295 ± 66 pptv (median 277 pptv, 10500 5-min values). The low abundance relative to other anthropogenic gases at Alert compared to that found in source regions does not support a large accumulation of reactive nitrogen in the surface layer of the high

Arctic in winter, at least during 1998. Instead they imply significant removal of NO_y constituents during transit to the Arctic or within the Arctic. The very small mixing ratios of NO_x observed during early March when solar insolation was absent or small are qualitatively consistent with removal through transformation to NO₃ and N₂O₅ and surface deposition of either constituent or uptake on particles.

Most interesting was the observation of a substantial diurnal variation in NO_x and NO_y when the sun was up for all or most of a 24 hr period. The source was attributed to release of NO_x or constituents that are rapidly transformed to NO_x from the snowpack. It appears that the mechanism for production and emission is sensitized by sunlight but further studies are required to elucidate the processes involved. Considering that the morning to noon increase in NO_x was observed with an aged or fresh snow surface and a newly drifted surface and that emission fluxes of NO_x were recently observed from the snow surface at Summit, Greenland (Honrath *et al.* 1999), there is some evidence that the source is a universal feature of the Arctic in spring. If so, then the observation of the removal of NO_x (and NO_y) in the 'evening to nighttime' period of continuous low elevation sunshine requires loss processes that have not been identified. Understanding whether these processes also occur in winter in addition to NO_x removal through NO₃ and N₂O₅ formation and deposition would help to understand the relatively small mixing ratios of NO_y compared to other long-lived gases. However, we must admit some concern that our observations may not be representative of the pristine Arctic snow surface but rather reflect processes involving contamination accumulated over the winter due to the necessary proximity to emissions from CFS Alert. If so, the unidentified loss process would not be required.

The sum of radical concentrations that can oxidize NO to NO₂ were estimated to be only about 10 pptv during mid-April in air masses in which the O₃ abundance would be considered normal. The small concentrations of peroxy radicals are qualitatively consistent with limited HO_x production through O₃/O(¹D)/H₂O reactions in the dry cold atmosphere where ozone photolysis is also small. Other sources of HO_x from photolysis of formaldehyde, acetaldehyde, peroxides, and perhaps HONO, and halogen atom reactions with hydrocarbons likely play a more important role in HO_x and RO_x production compared to lower latitude atmospheres (Li, 1994; Shepson *et al.*, 1996; de Serves, 1994; Sumner and Shepson, 1999). Although more detailed modeling which contains a diurnal source of NO_x during the 24-hr sunshine of mid-April is required, the rate of photochemical production of O₃ near noon is essentially balanced by the rate of photochemical loss in air masses that contain normal levels of O₃. Without the daytime source of NO_x weak net photochemical destruction of O₃ would be expected.

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