

Author's responses to reviewer's comments and relevant author's changes in the manuscript are provided here. A marked-up manuscript, detailing all the changes made to the main text in the manuscript is provided at the end of the document.

### ***Responses to reviewer 1***

This manuscript reports on the first year-round measurements of NO<sub>x</sub>, PAN and NO<sub>y</sub> made on the Greenland ice sheet, plus select NMHC measurements made with an automated GC system, and combines them with ongoing measurements of ozone provided by NOAA. The nitrogen oxide data are very interesting by virtue of being unique. Data interpretation focuses on the seasonality of the different N oxides, the speciation of NO<sub>y</sub>, and the sources of short-lived plumes that are superimposed on the relatively smooth seasonal variations. Source attribution relies heavily on FLEXPART "retroplume" analysis to identify enhancements in the N-oxides and some NMHC that can be linked to anthropogenic emissions and/or biomass burning in north America versus Europe versus Asia. All of the N oxides show broad peaks from late winter into spring and then decrease through summer into fall, with NO<sub>x</sub> staying elevated later into summer than PAN and NO<sub>y</sub>. PAN is the dominant fraction of NO<sub>y</sub> throughout the year, with the PAN/NO<sub>y</sub> ratio peaking near 0.8 in April and remaining ~ 0.5 even at its minimum in July. These findings are qualitatively similar with previous results from long-term stations in the Arctic basin, so probably were broadly expected (certainly not surprising to me), but confirmation is still valuable. Authors note that NO<sub>x</sub>/NO<sub>y</sub> increases from ~ 0.04 in winter to a little over 0.1 in summer, with the summer time increase tentatively ascribed to release of NO<sub>x</sub> from sunlit snow. They also point out that the sum of NO<sub>x</sub> plus PAN never accounts for all of measured NO<sub>y</sub>, with unmeasured species contributing 20-38% of NO<sub>y</sub> throughout the year. This shortfall is termed "odd NO<sub>y</sub>" and amounts to nearly 50 ppt in summer and nearly 100 ppt in winter (for monthly averages). Authors suggest that odd NO<sub>y</sub> probably represents alkyl nitrates, nitric, pernitric, and nitrous acids; with the first 3 potentially transported to Summit from remote sources at lower latitudes, while snowpack emissions may account for some fraction of the 3 acids during summer. One previous study found that the sum of C1 to C4 alkyl nitrates reaching Summit increased from ~ 10 ppt in July/Aug to a max < 35 ppt in Feb. This would imply that the sum of nitric, pernitric and nitrous acids ranges from 65 ppt in winter down to 30-40 ppt in summer. There are no wintertime measurements, but several campaigns have measured all three acids at Summit during summer and 30 ppt for monthly averaged sum would be quite a bit higher than reported values (Grannas et al., 2007 summarize most of these studies and provide references to original studies). Perhaps the calculated odd NO<sub>y</sub> is not inconsistent with these results if the uncertainties are considered, or perhaps 2008-2010 captured different conditions than these other studies. Authors suggest that it would be worthwhile to measure all of the candidate N oxides simultaneously to clarify the NO<sub>y</sub> budget, but should acknowledge that this was the objective of the 1998 and 1999 campaigns when the MTU group first went to Summit (there were no measurements of pernitric acid in that study, but the sum of alkyl nitrates plus nitric and nitrous acids was in the 15-20 ppt range and it is not likely that average pernitric exceeded 10 ppt). The NMHC observations are very consistent with previous results based on canister samples reported in Swanson et al. (2003). This is encouraging, but it appears that these results have been highlighted in 2 papers from the Helmig group already, so I am not sure they need to be included in this manuscript as well. To me, they add very little to the present story and none of the main points of this paper would be impacted if the NMHC were removed. The source attribution effort for plumes reaching Summit relies heavily on FLEXPART, which is an appropriate and well validated tool. However, I find that this section of the manuscript (3.2) is not very well presented, verging on confusing in places. Specific examples will be pointed out below, but at a high level I find it disturbing that several times the authors seem to suggest that errors in FLEXPART transport can be so large that they mistrust it (in general) juxtaposed to a paragraph where they are interpreting changes from one time step to the next as valid. Following is a commingled list of specific and technical

comments, keyed to the page and line numbers in the “printer friendly” version downloaded from the ACPD site.

The authors would like to thank the anonymous reviewer for the helpful comments and providing detailed suggestions. The manuscript has been revised based on the suggestions given and we feel that this has significantly improved the analysis and results presented in the manuscript. Responses to each comment are given below, with details on revisions to the manuscript. Page and line numbers stated here are based on the revised manuscript.

13819/12 as noted above, 40 ppt for the sum of N acids plus alkyl nitrates seems high for summer at Summit. Consider confidence level of these calculated differences, and perhaps whether they should be highlighted in the abstract.

Uncertainty estimates for odd  $\text{NO}_y$  were calculated from the propagation of uncertainties in the  $\text{NO}_y$ ,  $\text{NO}_x$  and PAN data. Figure 2, in the manuscript has been changed to a bar plot to show the monthly mean  $\text{NO}_y$  and  $\text{PAN}+\text{NO}_x$  (with measurement uncertainties) and Figure 3 now shows the monthly mean odd  $\text{NO}_y$  and uncertainty levels.

The odd  $\text{NO}_y$  levels are no longer highlighted in the abstract and the text in the abstract has been updated. Page 1, Lines 9-11 now read:

*...we find that odd  $\text{NO}_y$  species (odd  $\text{NO}_y = \text{NO}_y - \text{PAN} - \text{NO}_x$ ) contribute a large amount to the total  $\text{NO}_y$  speciation.*

The text on page 15 has also been re-written to discuss the odd  $\text{NO}_y$  levels at Summit. Page 15, Lines 8-18 now read:

*Fig. 2 shows the monthly averaged mole fractions of  $\text{NO}_y$  and  $\text{PAN}+\text{NO}_x$  during the measurement period. The results show that the sum of PAN and  $\text{NO}_x$  cannot always account for the monthly averaged  $\text{NO}_y$  within the measurement uncertainty range, suggesting a significant source of odd  $\text{NO}_y$  at Summit. When considering the 30 minute averages, ~66% of the data show significant odd  $\text{NO}_y$  levels (i.e. cannot be accounted for by total measurement uncertainty alone). What is particularly striking about the  $\text{NO}_y$  speciation is that odd  $\text{NO}_y$  levels can be very large over winter (Fig. 3). From December 2009–April 2010, the monthly mean odd  $\text{NO}_y$  was always above  $70 \text{ pmol mol}^{-1}$ , reaching a maximum of  $93 \pm 31 \text{ pmol mol}^{-1}$  (mean  $\pm$  uncertainty) in February 2010. Odd  $\text{NO}_y$  decreased to  $\sim 30\text{-}56 \text{ pmol mol}^{-1}$  in the summer months; however, this still accounts for up to  $\sim 40\%$  of the total  $\text{NO}_y$  during this period.*

13821/7-8 quite a few additional TOPSE and POLARCAT references also make the point regarding different source regions near surface versus mid/upper trop, and could be added.

The authors thank the reviewer for pointing out the missing references. The following relevant references have been added to the manuscript on Page 5, lines 1-3.

Atlas et al., 2003; Lamarque and Hess, 2003; Fisher et al., 2010; Singh et al., 2010; Bian et al., 2013.

13821/11-12 is North Asia a recognized region? Do you mean Siberia? That seems more common usage

The reviewer is correct. Siberia is the region we are discussing. This has been changed on page 4, line 6, in the manuscript

13821/18 emissions from the → emissions in the

This sentence has been updated as suggested on page 4, line 12

13822/5 should “high altitude Arctic” be “high latitude”? It is true that high altitude Arctic is not impacted strongly by local sources, but also true for high altitudes pretty much everywhere.

This is a good point. Please see the response to the comment below regarding the change of high altitude to high latitude.

13822/19 and 20 here it seems authors did mean altitude above, but one could debate whether 3 km elevation of Summit is really “high altitude”, and both of these sentences would also make sense if latitude replaced altitude.

The authors agree that the use of high latitude would make more sense and altitude has been changed to latitude on Page 5, lines 10 and 12.

13823/15 Pretty sure the instrument that went to PICO was built for studies at Summit in 1998 to 2001, so it seems odd not to mention it. Mike Dziobak would know for sure.

The reviewer is correct. An earlier version of the instrument was used during the campaigns at Summit. The PICO instrument was highlighted as it demonstrated the use of the instrument for long-term measurements. However, it is important to mention the instrument at Summit. The text on page 6 lines 6-10 now reads:

*The instrument was developed at Michigan Technological University and is based on the same design that was used in Newfoundland in 1996 (Peterson and Honrath, 1999), subsequently installed at Summit during campaigns in 1998, 1999 and 2000 (Honrath et al., 1999, 2002, Dibb 2002), and at the Pico Mountain Site from 2002 to 2010 (Val Martín et al., 2006).*

13824/3-16 This paragraph briefly outlining the calibration of the NO<sub>x,y</sub> instrument is misleading. Details in the supplement clear things up, but need to also be accurate here. Specifically, you cannot assess the LED NO<sub>2</sub> convertor efficiency just by challenging it with NO, and you should mention that you challenged the Au convertor with NO<sub>2</sub> twice a day, and with HNO<sub>3</sub> and NPN every 3 days.

This paragraph has been re-written to clarify the details regarding the NO<sub>x,y</sub> instrument. The text on page 6 line 27 - page 7, line 10, has been updated to state:

*Calibrations were performed every 12 hours to determine the sensitivity of the instrument to NO via standard addition (10 cm<sup>3</sup> min<sup>-1</sup>) of ~1 mmol mol<sup>-1</sup> of NO in nitrogen (N<sub>2</sub>) (Scott Marrin,*

*Scott Specialty Gases) to the sample flow (650 cm<sup>3</sup> min<sup>-1</sup>) at the inlet on the tower. A known amount of NO<sub>2</sub>, generated via gas phase tritration of NO with O<sub>3</sub>, was also added to the to the sample flow during the calibration cycle, to determine the conversion efficiencies of the NO<sub>2</sub> and NO<sub>y</sub> converters. In addition to the standard calibrations, every three days the conversion efficiency of the NO<sub>y</sub> converter to HNO<sub>3</sub> and n-propyl nitrate (NPN) were determined and artifacts for NO<sub>y</sub>, NO and NO<sub>2</sub> were measured via sampling NO<sub>x</sub> free air (Breathing air grade, Airgas, Radnor, PA, USA). The final datasets were corrected for this artifact.*

13824/24-25 The second “additional filter” is confusing. Seems it is based on subjective or arbitrary assessment of too much variability, but not enough to be caught by the objective Poisson filter. Please explain this better.

The second additional filter was utilized to remove potentially polluted measurements or those with unrealistic high values or high variability that was not removed in the first filter. It was noted that enhancements in the NO<sub>x,y</sub> were occasionally observed during periods coinciding with the logged start and end times of skiway grooming. To be conservative the filter removed all measurements during skiway grooming times. However, on closer inspection of the skiway periods (since the manuscript was submitted), it was observed that some of the data did not show large deviations when compared to neighboring measurements (most likely as a result of the wind direction), therefore ~ 1% of the data that were originally filtered may not necessarily be impacted by skiway grooming. In the updated data analysis and final manuscript only those measurements made during logged skiway grooming times, with obvious enhancements relative to neighboring data points, have been included in the skiway filter. Changing this filter has a very low impact on the final results, with the campaign mean levels changing by only 1 pmol mol<sup>-1</sup> for NO<sub>x</sub> and NO<sub>y</sub>.

A second additional filter was also used to remove outliers that were not filtered with the Poisson filter, or no instrument malfunction was logged. These outliers were determined via threshold values for NO, NO<sub>2</sub>, NO<sub>x</sub> and NO<sub>y</sub> based on very high values or large standard deviations. The filtered points were double checked as outliers by comparing to adjacent observations.

We thank the reviewer for noting that the filter techniques were not clear. We also noted that there was an error in the original manuscript regarding the total number of measurements, which was stated to be 90–91% but is actually 87–88 %. The manuscript has been revised and the text on page 7, line 12–21 now reads:

*Approximately 8% of the final dataset was removed due to known instrument issues. Additional filtering procedures were applied to remove points potentially contaminated by local camp pollution. Variability in the 20 and 30 s averaged data was compared to the expected value from photon counting statistics which are treated as a Poisson distribution. Measurements with variability greater than 3 times the Poisson value were then removed from the final dataset (~ 4 %). Evaluation of these periods show that they typically occur when the wind direction was from the main camp, confirming that local pollution was the main source of the variability. Erroneous data points as a result of unknown instrument issues, or periods when the skiway was groomed, were also removed. Less than 0.2% of the total data were classified as erroneous and each point was manually checked by comparing to adjacent observations. Finally, large negative mole fractions, as a result of large variability between modes during the measurement cycle, were removed (≤ 1 %).*

13826/24-25 Seems likely that the % uncertainty for PAN measurements varied somewhat

depending on the ambient mixing ratio (most likely higher as detection limits approached). To be consistent with 2.2.1 (and to be more useful to reader), should state the ppt levels where the 16 and 22% estimates are valid.

The reviewer is correct. At low PAN ambient mixing ratios measurement precision is an important factor when considering the total uncertainty. At higher mixing ratios errors associated with accuracy of the calibrations and flows are greater. To clarify these points, page 9, lines 10-22, of the manuscript has been re-written with the following text:

*Similarly to the NO<sub>x</sub> and NO<sub>y</sub> data, the PAN measurements were averaged over 30 min. The total uncertainty for the 30 min averaged PAN mole fractions was determined from the root sum of the squares of the precision of the instrument (estimated as  $2\sigma N^{0.5}$ , where N is the number of points averaged in 30 min (N = 3)) and the uncertainty in the calibration standard. The precision is < 57 pmol mol<sup>-1</sup> with a mean (median) value of 6.7 pmol mol<sup>-1</sup> (5.6 pmol mol<sup>-1</sup>). Uncertainty in the PAN calibration standard is associated with uncertainties in (a) the calculation of the NO addition, (b) the conversion of NO to PAN from the calibration unit, and (c) variability in the PAN sensitivity between calibrations. The uncertainty in the calibration standard is 15% during normal operation. This value increased to 21% during the period in spring 2009 when there were no calibrations. Using the mean precision, the total uncertainty in the PAN measurements at 150 pmol mol<sup>-1</sup> is estimated to be approximately 16% during normal operation and 22%, during spring 2009.*

13827/8-27 As noted above, consider removing the NMHC from this paper. If that recommendation is not taken, this section needs to describe the duty cycle and time resolution of these measurements. Simple math (6000 measurements over 25 months) suggests nearly 8 data points per day, so maybe 3 hour resolution but how long is sample actually concentrated? Did it work all the time for 25 months? How often calibrated (if 1000 blanks/standards = 500 each, that works out to less than 1/day)? Perhaps most critical, how were the 30 minute N oxide measurements merged with the NMHC measurements that clearly do not have 48 observations/day?

As the reviewer stated, the NMHC method and data have been presented in Helmig et al., 2014. However, the Helmig et al. 2014 publication primarily focused on processes within snowpack measurements of NMHC, with little discussion and interpretation of the ambient air behavior of NMHC. We feel that the NMHC data are a critical part of this study as the NMHC ambient air relative ratios provide important information on the rate of photochemical processing. This analysis yields confirmation of fast transport to the measurement site during periods when low ozone levels were observed in the winter. Additionally, the NMHC provide information on the interannual variability of O<sub>3</sub> precursors at the site, which is less clear in the other data due to a gap in the NO<sub>x,y</sub> measurements and high PAN uncertainties over winter 2008/2009. A direct comparison was not performed between individual NMHC and N oxide measurements. However, when calculating enhancements due to fire or anthropogenic pollution, both the NMHC and N oxide data (when available) were averaged over the same time period of the event.

The reviewer is correct with the calculations. The NMHC system provide approximately 8 measurements a day, with each measurement representing a collection/sample integration time during the sample pre-focusing step of ~ 45 min. In addition, one blank sample was analyzed ~daily, and a standard every ~ 2 days.

The text on Page 10, lines 8-11, has been revised to read:

*The NMHC system provided ~8 ambient measurements of C<sub>2</sub>–C<sub>6</sub> hydrocarbons each day, with each measurement representing a collection/sample integration time during the sample pre-*

*focusing step of ~45 min. In addition, one blank sample was analyzed ~daily, and a standard every ~2 days.*

13829/1 Not clear how the simple treatment of BC scavenging would cause “under-estimation” of the BC tracer reaching Summit. Not including aging effects making BC more hydrophilic would seem to decrease scavenging by any precipitation along the transport path, which ought to lead to overestimates of the concentration still in the air mass(es) reaching Summit.

We thank the reviewer for pointing out how this sentence may be misleading. The underestimation in the BC tracer at Summit is a result of the use of wet scavenging coefficients in the model which are more representative of a hydrophilic aerosol. Close to the source region, the BC would be more hydrophobic, therefore the wet scavenging would be greater than expected. As the BC ages the scattering coefficients are more realistic. However, the overall result is an underestimation. The text has been updated and pg 12, lines 1-5 read as:

*The wet scavenging coefficient used in the model is more representative of a hydrophilic aerosol, however, there is no conversion from hydrophobic to hydrophilic properties with aging BC in the model, therefore greater scavenging may occur closer to the source region, resulting in an underestimation of the BC tracer at Summit (Stohl et al., 2013).*

13829/8 Why choose to create monthly averages of ozone for 3 full years, rather than just the 2 years (or 25 months) with overlapping NO<sub>x</sub> and PAN data?

As a full 3 year data set was available for ozone we included all measurements in the seasonal cycle in Figure 1. However, Figure 1 has now been revised and the 25 months of overlapping data are presented separately for NO<sub>x</sub>, NO<sub>y</sub>, PAN and O<sub>3</sub>.

13829/18-22 As written, this sentence seems to imply that Liang et al. (2011) claim that STE is a source of PAN in the Arctic upper troposphere (implying enhanced PAN in the lower stratosphere). What they actually believe they observed was production of PAN in stratospherically influenced air masses in the troposphere above 5 km that had high NO<sub>x</sub> and HNO<sub>3</sub> transferred from the stratosphere. Suggest redrafting this sentence to clarify this point.

We thank the reviewer for capturing this error. This sentence has been revised in the manuscript. The text on page 13, lines 4-8 has been changed to:

*Observations from the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) mission in 2008, show that mixed stratospheric-tropospheric air masses, above 5 km, have elevated levels of O<sub>3</sub> precursor, such as NO<sub>x</sub> and HNO<sub>3</sub>, which can subsequently be converted to PAN (Liang et al., 2011).*

13831/5 detection—→ detection

This typographical error has been corrected on page 4, line 22.

13831-13833 (end of section 3.1.1) The 2.5 paragraphs discussing the “odd NO<sub>y</sub>” strike me as more speculative than they need to be. Granted, no one has yet measured nitric, pernitric, and nitrous acids through the winter but they have been measured during campaigns in summers of 2003, 2007, 2008, 2010, and 2011 and during a spring campaign in 2004. (Earlier campaigns in 1998-2002 did not include pernitric acid, but did include canister sampling for NMHC and usually quantified the C<sub>1</sub>-C<sub>4</sub> alkyl nitrates.)

The 2008 GSHOX campaign ended ~9 July so may not overlap the observations discussed herein, but the 2010 campaign lead by M. Hastings extended from mid May till late June. I suspect that the PIs who made measurements of snow sourced NO<sub>y</sub> compounds during these experiments would be pleased to provide statistical summaries (perhaps even complete data files) that would allow quantitative comparison to your calculated odd NO<sub>y</sub> in summer 2010 and semi quantitative assessment for the summer and spring seasons more generally.

We are very grateful to the reviewer for providing the information regarding the snow sourced NO<sub>y</sub> compounds at Summit. The authors have contacted the PIs of the 2010 and 2011 campaigns at Summit and data has been provided for a comparison to the odd NO<sub>y</sub> from this study. The measurements were performed in the clean air sector at Summit with the inlet set at approximately 1.5 m above the snow surface (J.E. Dibb and M.G. Hastings, personal communication. Data from 2010 is only available during the months of May and June and although some overlaps with our NO<sub>x</sub> and NO<sub>y</sub> data in 2010, PAN data was not available after April, so a direct comparison with odd NO<sub>y</sub> is not possible. However, the data provides an estimate of the HNO<sub>3</sub> and HONO levels during late spring/summer.

The median HNO<sub>3</sub> and HONO values were calculated for the campaign period during May-June 2010 and compared with the odd NO<sub>y</sub> at Summit. Additionally, a statement was added discussing the HONO and HNO<sub>3</sub> levels during previous measurement campaigns. The following text has now been added to the revised manuscript on page 16, line 24 – pg 17, line 18.

*Ambient HNO<sub>3</sub> and HONO have been measured at Summit during a number of spring and summer campaigns. Levels of HNO<sub>3</sub> are typically on the order of a few tens pmol mol<sup>-1</sup>, and HONO levels are lower with mole fractions of ~10 pmol mol<sup>-1</sup> or less (Dibb et al., 1994, 1998; Honrath et al., 1999; Dibb et al., 2002; Ford et al., 2002; Yang et al., 2002; Dibb et al., 2007; Chen et al., 2007; Liao et al., 2011). Median mixing ratios of HNO<sub>3</sub> and HONO, measured during May and June, 2010, with a mist chamber/ion chromatography (MC/IC) system (~1.5 m above the snowpack), were 7 pmol mol<sup>-1</sup> and 13 pmol mol<sup>-1</sup>, respectively (J.E. Dibb and M.G. Hastings, personal communication). Note that HONO measurements by MC/IC in polar regions should be viewed as an upper limit to the true value, due to potential interferences from other species (Chen et al., 2004; Liao et al., 2006). A direct comparison of HNO<sub>3</sub> and HONO with calculated odd NO<sub>y</sub> levels is not possible for 2010 because PAN measurements were unavailable after April. Monthly mean odd NO<sub>y</sub> levels calculated for May and June in 2009 were 50 and 36 pmol mol<sup>-1</sup>, respectively. Summer levels of alkyl nitrates are expected to be low at Summit with Swanson et al. (2003) measuring monthly mean levels (total C<sub>1</sub>-C<sub>4</sub>) of ~10–20 pmol mol<sup>-1</sup> between May and August. Assuming alkyl nitrate levels of ~15 pmol mol<sup>-1</sup> during May/June, the sum of HNO<sub>3</sub>+HONO+alkyl nitrates are comparable to the odd NO<sub>y</sub> levels measured at Summit (when considering measurement uncertainties). Particulate nitrate may also contribute a small*

amount to the total  $\text{NO}_y$ , however, this contribution is expected to be small as ambient  $\text{p-NO}_3^-$  levels are typically lower than  $\text{HNO}_3$  at Summit (Dibb et al., 1994). A recent study in Antarctica, during polar winter, has shown that absorbed  $\text{HO}_2\text{NO}_2$  can be emitted into the atmosphere above the snowpack when temperatures increase (Jones et al., 2014). Therefore,  $\text{HO}_2\text{NO}_2$  may also contribute to the odd  $\text{NO}_y$  measured at Summit, during winter and summer.

A section of text has also been added to the revised manuscript to support the statement regarding the photochemical source of  $\text{NO}_x$ . On page 15 line 1-7, the updated text reads:

*This conclusion is supported by results from an investigation focusing on  $\text{NO}_x$  and  $\text{O}_3$  levels in the snowpack at Summit. Measurements of  $\text{NO}_x$  were performed at various levels within and above the snowpack, during the same period as this study. The data, supported by model results from a newly developed 1-D process scale model, show that  $\text{NO}_x$  levels, in the upper regions (0-30 cm) of the snowpack, peak around solar noon as a result of  $\text{NO}_3^-$  photolysis (Van Dam et al., 2014; Murray et al., 2014).*

13833/1-3 Can the larger uncertainty in PAN due to instrument degradation after spring 2009 not be propagated into the uncertainty of calculated odd  $\text{NO}_y$ ? This would be particularly important if you are able to compare the sum of measured  $\text{NO}_x$ , PAN,  $\text{HNO}_3$ ,  $\text{HO}_2\text{NO}_2$ , HONO and assumed sum of  $\text{RONO}_2$  (~10 ppt) to measured  $\text{NO}_y$  during summer 2010 as suggested immediately above.

The authors agree with the reviewer and have calculated measurement uncertainties for odd  $\text{NO}_y$  as discussed in the responses above.

13833-13834 (section 3.1.2) as noted earlier, I do not feel the NMHC add much to this paper, especially if they “have previously been presented in detail (Helmig et al., 2014a,b” (lines 18-19 on 13833)

As mentioned in response to an earlier comment, we feel that the NMHC data are an important part of the study. This statement in the manuscript, however, may be misleading, as the publication by Helmig et al. 2014 focused primarily on processes within the snowpack. This statement will be re-phrased in the revised manuscript on page 17, lines 21-22, to read:

*Measurements of primarily firn air conducted with this system were presented by Helmig et al. 2014.*

Additionally, Figure 5 now shows the two years of NMHC data separately as a box-and-whisker plot as suggested by reviewer 2.

13834/13-23 Strongly suspect that Figure 4 would show quite similar features if  $\text{NO}_x$  and  $\text{NO}_y$  replaced the NMHC.

The reviewer is correct and similar variability is observed in the  $\text{NO}_x$  and  $\text{NO}_y$  measurements as a result of polluted air masses sampled at the site. In this section we focused on NMHC as a comparison could be made between the two winters. This was not possible for  $\text{NO}_x$  and  $\text{NO}_y$  as a result of the gap in measurements from November 2008 through February 2009. The text on the variability in the NMHC levels, has been moved to section 3.1.2 on page 18,



lines 5-12. The text has also been updated to read:

*A comparison between the two winters shows monthly mean NMHC levels were consistently higher from November–March 2008/2009 when compared to 2009/2010. However, the standard deviation values during the second winter are typically higher, suggesting greater variability in the NMHC levels in 2009/2010. The non-averaged NMHC data (Figure S5, supplementary material), show there is considerable short term variability in the NMHC mole fractions superimposed on the seasonal cycle, in particular during the winter months. Short term elevated NMHC levels were observed during both winters and indicate fast transport of polluted air masses to the site.*

13835/17 to the total,—→ of the total,

The text has been updated as suggested on pg 19, line 16.

13833-13838 section 3.2.1 This section intends to focus on winter/early spring (DJFM), which may be fine, but as it unfolds the authors do not stick to their own script and it gets a little confusing at times. Perhaps there should be more material in section 3.2 sort of setting the context and summarizing what FLEXPART thinks about seasonal patterns of transport from different source regions/types, plus any marked differences between the 2 years. Once it is established that urban/industrial plumes dominate DJFM and that 10/13 apparent BB smoke plumes reached Summit in the summer, drilling down into the 2 different seasons could follow.

As suggested by reviewers 1 and 2, section 3.2 has been substantially re-written to improve the manuscript. The first part of section 3.2 now provides an introduction to the source contribution from FLEXPART and discusses the seasonal patterns in the transport and sources. Figure 6 now shows a barplot of the relative contributions to the BC anthropogenic and fire tracer levels at Summit from North America, Europe and Asia. We feel that this introduction will help clarify the focus on individual seasons in the subsections that follow. As a result of the discussion on the seasonality of anthropogenic tracers, the analyses in section 3.2.1 now includes events in November, 2008 and 2009, as the BC<sub>anthro</sub> tracer was found to be high during these months.

The only full paragraph on page 13835 focuses exclusively on FLEXPART analyses in the DJFM season, and specifically on where this model thinks its BC<sub>anthro</sub> tracer originated in plumes it advects to Summit. This is fine, but it would be useful to compare the FLEXPART source attribution to similar analyses done with a range of different modeling tools as part of the POLARCAT project (especially considering that Stohl was co-leader of POLARCAT and Burkhardt provided FLEXPART forecasts to several of the aircraft campaigns that were mounted under the POLARCAT banner). Do the results reported here apply only to Summit/central Greenland, especially the very low impact from Asian sources? Law et al. (in press, and available on-line) provides a nice summary that would facilitate putting Summit into the context of the wider Arctic, probably needing just an additional sentence or two.

The author's agree with the reviewer's comments. Section 3.2 now contains a discussion on the transport to Summit during this study and how it relates to previous studies. We have

also added a discussion based on MODIS fire observations, to help clarify the variability observed in the FLEXPART  $BC_{fire}$  tracer simulations at Summit.

The text on page 19, line 20 to page 20, line 21 now reads:

*Fig. 6 shows that the contribution to the total  $BC_{anthro}$  from Asia is low year-round. Hirdman et al. (2010) investigated the contribution of pollutants from different sources to various Arctic surface sites from 2002-2007. The authors show that Summit is less sensitive to emissions from the surface in the Arctic region, than low elevation surface stations, and air masses transported to Summit from outside of Greenland are likely to originate from Europe and North America.*

*In contrast to the anthropogenic tracer, North American emissions dominate the total  $BC_{fire}$  tracer with 69% of the total  $BC_{fire}$  tracer originating from this region from July 2008-July 2010. This result is expected as air masses arriving at Summit typically originate from North America during the summer months (Kahl et al., 1997). Previous studies have also shown that North America is a major source of biomass burning emissions transported to Summit (e.g., Whitlow et al., 1994; Legrand and de Angelis, 1996; Fuhrer and Legrand, 1997; Alexander et al., 2004; Stohl et al., 2006). The high Asian contribution to the total  $BC_{fire}$  tracer in spring 2008 is in agreement with observations during the POLARCAT campaigns in 2008, when a number of biomass burning plumes were observed from Siberia (Law et al., 2014, and references therein). During the measurement period, however, the contribution from Asian biomass burning emissions at Summit was low, compared to North America. European biomass burning emissions were also low, except during a period in March, when European fires dominated the total  $BC_{fire}$  tracer. In 2008 and 2010 the contribution from total biomass burning emissions peaked in August. In 2009, however, there was no significant peak in biomass burning emissions at Summit, and  $BC_{fire}$  tracer levels during the summer were much lower overall.*

*Variability in  $BC_{fire}$  tracer can be a result of a change in emissions or transport pathways. Overpass and cloud-corrected MODIS Terra (MOD14CMH) and Aqua (MYD14CMH) fire pixel counts from the Climate Modeling Grid (CMG) product were downloaded from the University of Maryland ftp server (<ftp://fuoco.geog.umd.edu>) to investigate the variability in fire emissions. The monthly total fire pixel count and total Fire Radiative Power (FRP), over the zonal region 40-75 N, were determined from March to September for 2008, 2009, and 2010 separately. The results (Figures S6a-d, supplementary material) show that there was a reduction in total fire counts and FRP in summer 2009, when compared to 2008 and 2010.*

The next paragraph extends onto the next page, and presents enhancements of  $NO_x$ , PAN,  $NO_y$ , ozone and ethane measured at Summit during the pollution episodes identified by FLEXPART. Each of the tracers actually decreases 20-26% of the time that FLEXPART thinks pollution reached Summit, a result which “may be associated with erroneous transport by FLEXPART”. Authors need to expand a little on this, else they risk convincing the reader that much of this entire section of the manuscript should be discounted. Did all or most of the tracers decrease in the same episodes? With tracers each showing the “wrong” response 20% of the time it is possible (but not likely) that transport was erroneous nearly all of the time. Could some of the FLEXPART “misses” be “hits” if the time window was expanded a little bit (+/- 3, 6, or 9 hours)? Even a 12 hour offset could be explained if the mean wind speed (in the met fields driving FLEXPART) during 11 days of transport was off by just 4%.

We found that many of the negative enhancements were the result of using background values for the gas species based on monthly statistics from the 2 years of data combined. Background levels were not the same each year, so the data was re-analyzed using a background value from each month and year, separately, for each gas. The text was updated on page 21, line 19 to page 22, line 2, to reflect these changes.

*During each event, the mean PAN, NO<sub>y</sub>, NO<sub>x</sub>, O<sub>3</sub>, and C<sub>2</sub>H<sub>6</sub> were calculated, where is the enhancement above background levels (determined as the 20<sup>th</sup> percentile for each species, for each month and year). Care must be taken when defining a background level as the enhancement ratios are strongly dependent on this value. Initial analyses used a single background value for each month, determined from the 20th percentile of data from all years, however, this resulted in many negative or low enhancement ratios which were not consistent with the observations. A background value for each individual month and year was found to be more appropriate, as these levels change slightly from year to year. For the 52 anthropogenic events identified during winter, the median (and range) value of the enhancements were 24 (-22 to 312) pmol mol<sup>-1</sup> for PAN, 7.0 (~0 to 54) pmol mol<sup>-1</sup> for NO<sub>x</sub>, 67 (-17 to 273) pmol mol<sup>-1</sup> for NO<sub>y</sub>, 1.1 (-6.7 to 7.6) nmol mol<sup>-1</sup> for O<sub>3</sub>, and 148 (-244 to 1120) pmol mol<sup>-1</sup> for C<sub>2</sub>H<sub>6</sub>.*

Enhancement in the ozone precursors that were still negative after applying the new background are discussed in the revised manuscript on page 22, lines 14-20.

*Over the two winters, negative mean ΔNO<sub>y</sub> values were observed during 3 events (event 72, 78, and 79), negative ΔPAN during 5 events (18, 65, 69, 72, and 78) and negative ΔC<sub>2</sub>H<sub>6</sub> during 4 events (64, 72, 73 and 79). Negative Δ values were associated with, 1) events when the peak BC<sub>anthro</sub> level was low (relative to BC<sub>anthro</sub> peak levels during all events), indicating a small impact from anthropogenic pollution, 2) missing data points during the event, or 3) events when small enhancements in PAN and NO<sub>y</sub> occurred, however, low mole fractions were also observed during the same event period.*

The reviewer has made an important point regarding the time window and errors in FLEXPART. The data has been re-analyzed to compare enhancement levels in ozone precursors using a ± 3, 6, 9 and 12 hour offset in the time window. The analysis showed that increasing the offset only has a small impact on the enhancement levels, when they were initially low, but at higher levels, the increase in the offset resulted in lower enhancements, due to “dampening” the impact of the event through the inclusion of background levels. Page 22, lines 3-13, discuss the effect of including an offset in the time window.

*Tests were performed to determine whether temporal mismatches occurred between the simulated plume arrivals and peaks in the measured species as a result of errors in the wind fields used in FLEXPART. Each event identified above was extended in time by 3, 6, 9, and 12 hours prior to and after the event, and new Δ values for the O<sub>3</sub> precursors were calculated. The analyses showed that extending the event window did not have a large impact on the mean values when mole fractions were low, i.e. levels were typically near the background already and extending the event time did not result in additional plumes being captured. During those events with large peaks in O<sub>3</sub> and precursors, Δ values decreased, with increasing window lengths as a result of capturing lower background levels. Thus, the event times calculated using the original threshold appear to be in agreement with the pollution plume arrival times.*

The next paragraph (all on 13836) is quite confusing. First 2 sentences start by focusing on detailed time series for the DJFM period in the 2 years, but then analysis of the full 2 year record is interjected, followed by a summary of low ozone events in April-Sept. (Recall that section 3.2.1 is supposed to be focused on winter/spring.) The following paragraph (extending onto 13837) also starts by considering the full record, but then comes back to winter/spring, except that it expands winter to include Oct and Nov along with DJFM (the months that motivated the investigation of anthropogenic plumes). More confusing than jumping back and forth between intervals or seasons of interest are some of the numbers in these two paragraphs. First we are told that 45 low ozone events were identified in summer months (Apr-Sept), of these 10 lined up with FLEXPART pollution plumes (some anthro, some BB, not specified how many of each). Then it is stated that over the full observation period there were 28 events where ozone decreased when the FLEXPART BCanthro tracer increased, with 21 of these in the expanded Oct-Mar winter. This would seem to imply that the other 7 cases had to occur during Apr-Sept, further implying that 3 of the 10 summer time events had to be linked to BB plumes. However, Table 3 lists all of the BB events and only 2 show ozone decreases > 2 ppb. There is a 3rd BB event with ozone decrease (too small), but that occurs during March, and would also qualify as an anthro plume. Note that it is not easy to try to follow the links between these different numbers, making it that much more disappointing that the simple math does not work out.

The reason for the differences in the statistics is due to the way the analyses is performed when identifying low ozone periods. When focusing only on low ozone events, periods were selected based on when the O<sub>3</sub> measurements < 2ppb for at least 12 hours. The event was classified as “polluted” if the mean BC<sub>anthro</sub> level during the event period was above the 75<sup>th</sup> percentile. However, the BC<sub>anthro</sub> may not have been enhanced for at least 12 hours (which is the classification used when identifying anthropogenic pollution events) so may result in different events. As this section was not clear, we decided to address the issue of the low ozone events in a different way and only focus on specific low ozone events during the winter period. The text has been revised and the number of low ozone events is discussed on page 22, lines 21-24, which reads:

*Analyses of  $\Delta O_3$  and FLEXPART BC tracer masses show decreases in O<sub>3</sub> ( $\Delta O_3 < 0 \text{ nmol mol}^{-1}$ ), coinciding with anthropogenic pollution events, were observed during 20 periods in total from July 2008 to July 2010, with 16 of these events occurring between November and March, when sunlight is at a minimum.*

Additionally, tables for all anthropogenic events (including event time, event length and trace gas measurement statistics) have now been included in the revised supplementary material.

Coming back to the paragraph bridging pp 13836-13837, the final 4 sentences zoom in on just 8 days in Jan 2010 and focus closely on 23 Jan. Here it is argued that FLEXPART really nails the transport and suggest that decrease in ozone in an anthro plume advected quickly from Europe probably reflects titration by NO close to the source. Could be, but why do you (why should I) believe FLEXPART here but not so much on the top of page 13836 (see earlier

comment)?

The next paragraph (ends on page13838) continues to basically accept FLEXPART as truth, and starts by presenting evidence (enhanced  $\ln(\text{propane/ethane})$  ratio) that would be consistent with rapid transport from source region to Summit on both 23 and 31 Jan 2010. However, the authors go on to say that we probably should not be real confident that the propane/ethane ratio is truly reflecting age since emission (13837/14-16). Yet, the remainder of the paragraph implicitly assumes that the retroplume analysis can be accepted and interpreted nearly on a time step by time step basis. However, the final paragraph of section 3.2.1 points out that there were intervals when the tracer measurements at Summit jumped up as if they were impacted by a pollution or BB plume while neither of the FLEXPART BC tracers showed any increase, and again suggest that the FLEXPART transport may be significantly in error.

Clearly, FLEXPART is not perfect, but it is also clear that it is useful. To me, it kind of feels like different people wrote different paragraphs in this section, with some biased to take the model results as gospel and others biased strongly against the model. I think it would help the presentation if an objective assessment of FLEXPART skill capturing plume transport to Summit was included in the expanded section 3.2 suggested above, and if a single author carefully edited section 3.2.1 to have all the paragraphs show appropriate appreciation of both the strengths and limitations of FLEXPART (or any other model).

With any transport model, there will be uncertainties in the transport, as a result of errors in the wind fields and missing/errors in source emissions. As suggested by the reviewer, the revised manuscript now includes a more detailed discussion of FLEXPART transport and plume analyses at the start of section 3.2, as discussed in the responses above. The text at the beginning of section 3.2.1 (originally on pg 13839, lines 14-20) has been revised, to clarify some of these points. The text on page 26, lines 19-25 now reads:

*The  $BC_{\text{fire}}$  tracer from FLEXPART was used to identify periods at Summit that were potentially impacted by BB emissions. Potential inaccuracies with the FLEXPART simulation of transport pathways, fire identification, and tracer emission uncertainties may result in BB events being under or overestimated, however, FLEXPART has been successfully used to identify long range transport of biomass burning emissions in many studies (e.g. Brioude et al., 2007; Stohl et al., 2007; Lapina et al., 2008; Quennehen et al., 2011, 2012; Schmale et al., 2011; Cristofanelli et al., 2013).*

13840/line 3 and line 21. First one states that the combination of BC<sub>fire</sub> and BC<sub>anthro</sub> tracers identifies 6 smoke plumes with small anthro signature, but second one says there were only 5 “nearly pure” smoke plumes. Note that Table 3 suggests that 2 smoke plumes had high anthro contribution, 6 had medium influence and 5 had low. Seems that line 3 is wrong, and also line 1 that claims 5 medium events (should be 6).

We thank the reviewer for noticing the error here. As shown in table 3, there are 5 plumes with low anthropogenic impacts, 6 plumes with medium anthropogenic impacts and 2 with high anthropogenic contributions. The statements in line 3 and line 21 are wrong in the text and these numbers have now been corrected on page 27, lines 3-8 in the revised manuscript.

13840/4-12 This paragraph makes a nice, and convincing, case that most of the BB plumes reaching Summit come from North America. This is consistent with a pretty long list of previous studies based on Greenland firn/ice cores but none of these are mentioned. It also seems that Stohl and Burkhart have earlier paper that reaches similar conclusion. Would be good to add some of these citations to this paragraph.

We thank the reviewer for pointing out that some references are missing. This paragraph has been updated and moved to the section 3.2 on page 20, lines 1-4 and reads:

*Previous studies have also shown that North America is a major source of biomass burning emissions transported to Summit (e.g., Whitlow et al., 1994; Legrand and de Angelis, 1996; Fuhrer and Legrand, 1997; Alexander et al., 2004; Stohl et al., 2006).*

13842/4 anlyses-->analyses

This typographical error has been corrected on page 29, line 17.

13842/14-23 Are these really conclusions from this paper? Do they not just confirm Swanson et al. (2003) and repeat findings in Helmig et al. (2014a,b)?

As suggested, these sections of text have been removed from this section.

13843/2-4 and 18-21 These 4 sentences seem to say the same thing. Probably better to kill the first 2 and keep the BB stuff in just one paragraph.

We agree with the reviewer's suggestion. These sentences have been removed and the summary has been revised, as a result of changes in the main body of the manuscript.

13844/10-11 HNO<sub>3</sub> determine--->HNO<sub>3</sub> to determine would probably want to add RONO<sub>2</sub> to this list, and possibly HO<sub>2</sub>NO<sub>2</sub> (comparable to HNO<sub>3</sub> in summer)

This section has been rewritten, to clarify the need for future measurements to assess pollution impacts at Summit. This section on, page 31, lines 2-4, reads:

*Future studies, with coincident CO, O<sub>3</sub>, and O<sub>3</sub> precursor measurements at Summit, would be valuable to determine enhancement ratios with respect to CO and evaluate the potential for ozone production in the region.*

## **Responses to reviewer 2**

The paper presents two years of NO<sub>x</sub>, NO<sub>y</sub>, and PAN data taken at Summit, Greenland along with showing ozone and hydrocarbon data over the same period. This is combined with FLEXPART analysis to understand the influence of anthropogenic and biomass burning (BB) sources. The paper contains very interesting data that should be published, however there are some problems with the manuscript in its current form. The first reviewer has done a very good job pointing out both scientific and technical issues with the manuscript. Therefore, those comments will not be repeated here. Unlike the first reviewer, I find it may be worth to include the NMHC measurements in the paper. This is specifically addressed below (comment 3).

We would like to thank reviewer 2 for the valuable comments. Each comment has been addressed and a discussion given on the revisions made.

1. The paper begins by showing two years of data as monthly averages (months 1-12) for NO<sub>x</sub>, NO<sub>y</sub>, PAN, and ozone. However, later the entire NMHC record is shown for the same

time period later. The authors should decide if they want to focus on averaging together these two years of data as representative of the seasonal cycle (as is done in Figure 1 and 2) or if they want to show the actual time series as the basis for the analysis (Figure 4). In my opinion averaging the two years removes some of the valuable information in this dataset. Why not show NO<sub>x</sub>, NO<sub>y</sub>, PAN, and ozone as monthly averages separately for each year in Figures 1 and 2. The same applies to Tables 1 and 2; are the values different for the two years of data, or is the average representative of both years?

The reviewer has made an excellent suggestion. Figure 1 has now been revised to show the data as monthly averages over each year separately. Tables 1 and 2 have also been updated to include the statistics for each year as separate columns. We feel that the updated plots and tables will provide more information on the differences between the two winters which is particularly important for the discussion in section 3.2.1. Monthly statistics for O<sub>3</sub> and precursors, which were stated in the main text and the abstract, have been updated appropriately, due to the updated analyses.

2. Figure 3 is not very useful as it is presented. If the authors want to show some information about the diurnal cycles of NO<sub>x</sub>, NO<sub>y</sub>, and PAN they should show data for each month (not a three month average). The amount of sunlight at Summit changes radically between April and June. Given the influence of snow on NO<sub>x</sub> levels it's not fair to average all of this data together to give one diurnal profile.

We agree with the reviewer and have separated the diurnal plots in Figure 4 to show data for April and May and June, separately. We have also included the diurnal cycle for March to cover the early spring period. The text in the manuscript has been revised on page 16, lines 4-23 to read:

*Results from this study show, despite the odd NO<sub>y</sub> levels decreasing from late spring to summer, odd NO<sub>y</sub> species can contribute over twice as much as NO<sub>x</sub> to the total NO<sub>y</sub>. To investigate the source of the odd NO<sub>y</sub> species and the possible impact from snowpack photochemistry we analyzed the diurnal variability of NO<sub>x</sub>, NO<sub>y</sub>, and odd NO<sub>y</sub> at Summit separately for March, April, May, and June, 2008–2010, at a height of ~7.5m (Fig. 4). The amplitude of the diurnal cycles for NO<sub>x</sub>, NO<sub>y</sub>, and odd NO<sub>y</sub> (determined as the difference between the minimum and maximum 2 h median values), peaked in April/May. For all 4 months, the amplitude of the NO<sub>y</sub> diurnal cycle is greater than that of NO<sub>x</sub>. Diurnal amplitudes, in April, were 36 pmol mol<sup>-1</sup> and 16 pmol mol<sup>-1</sup> for NO<sub>y</sub> and NO<sub>x</sub> respectively. Odd NO<sub>y</sub> is shown to peak just after solar noon (Fig. 4i, j, k, l) suggesting a photochemically produced odd NO<sub>y</sub> species may be present. It has been hypothesized that HNO<sub>3</sub> and HONO, may account for some of the NO<sub>y</sub> diurnal variability at Summit (Ford et al., 2002). The diurnal variability of ambient NO<sub>y</sub> species above the snowpack, however, is further complicated by vertical mixing and boundary layer dynamics, which may vary with season. For example, the downward transportation of pollution from aloft due to a growing boundary layer may result in a daytime maxima in NO<sub>x</sub> and NO<sub>y</sub>, which then decreases at night due to surface uptake. There is also a possible contribution to odd NO<sub>y</sub> in the summer from long range transport of reactive nitrogen species such as HNO<sub>3</sub> and alkyl nitrates as these species have previously been observed in anthropogenic and biomass burning plumes in the Arctic (Liang et al., 2011; Wespes et al., 2012).*

3. I do find it appropriate to have some information about NMHCs directly in the paper (even if it's already been published elsewhere). However, the authors should use the same box/whisker plot analysis for Figure 4 as in Figure 1 (two years of monthly average data, with the two years of data presented separately). Otherwise, the plot is almost the same as already presented in Helmig et al., 2014a and provides nothing in addition to what has already been published.

The authors agree with the reviewer and now show the six NMHC as box-and-whisker plots

separated for the 2 years of measurements (Figure 5), to be consistent with Figure 1 and the updated tables. A plot of the non-averaged NMHC is now provided in the supplementary material (Figure S5).

The text in section 3.1.2 has been updated to discuss the new plot. Page 17 line 20 – page 18, line 4, reads:

*Figure 5 shows the results for the C<sub>2</sub>–C<sub>5</sub> alkane NMHC measured during 2008–2010 at Summit in ambient air. Measurements of primarily firn air conducted with this system were presented by Helmig et al. (2014). NMHC show a strong seasonal cycle with maximum mole fractions during the winter and early spring period and a rapid decline towards the summer, due to an increase in photochemical processing. The monthly averages for the C<sub>2</sub>–C<sub>5</sub> NMHC are given in Table 2. During the summer period, measured mole fractions of the heavier NMHC were below or close to the detection limit. As expected, the phase of each NMHC is shifted due to the rate of reaction with OH. The lightest of the NMHC shown in Fig. 5a, ethane (C<sub>2</sub>H<sub>6</sub>), peaks in March with a monthly mean of  $2100 \pm 151 \text{ pmol mol}^{-1}$  (mean  $\pm 1\sigma$ ) in 2009, and  $1835 \pm 174 \text{ pmol mol}^{-1}$  in 2010, and declines to a minimum of  $\sim 600 \text{ pmol mol}^{-1}$  in July/August. Heavier NMHC have lower mole fractions, peak earlier in the year, and reach a minimum earlier in summer due to their faster rate of reaction with OH.*

4. The FLEXPART analysis given in Figures 5 and 6 is questionable given that the paper does not focus on black carbon or aerosols. CO source contributions are a more appropriate choice because they do not suffer from the same wet removal issues.

The BC tracer was used here for the retroplume analysis as simulations are available for both the anthropogenic and fire tracers as part of the POLARCAT campaign. Simulations using CO were only performed for the anthropogenic tracer. Using the BC tracer allowed for consistency between biomass burning and anthropogenic investigations. A comparison was made between the CO and BC anthropogenic tracers to determine whether pollution events were missed. A time series and correlation plots for the two tracers from summer 2008 to 2010 are now provided in the supplementary material (Figures S1 and S2).

The result suggests that although there may be some differences in the magnitude of the FLEXPART tracers, the transport simulated with the BC tracer is very similar to the CO tracer.

Text has been added to the revised manuscript to include a discussion on the CO and BC tracers. Page 12, lines 7-18, reads:

*Carbon monoxide can also be used as a tracer for pollution transport. Simulations using CO were performed for the anthropogenic tracer, however, the BC tracer was used in this study as simulations were available for both anthropogenic and fire tracers as part of the POLARCAT campaign, and thus allowed for consistency between the biomass burning and anthropogenic analysis. A comparison was made between the CO and BC anthropogenic tracers to determine whether pollution events were missed when using the BC tracer, as a result of deposition. A time series and correlation plot for the two tracers from summer 2008 to 2010 are shown in Figures S1 and S2 in the supplementary material. The result suggests that although there may be some differences in the magnitude of the FLEXPART tracers, the transport simulated with the BC tracer correlates well with the CO tracer (Pearson's correlation coefficient,  $R=0.97$ ), therefore, significant pollution events were unlikely to be missed.*

5. Figures 4 and 5 also show that anthro and BB sources contribute different amounts during the different years studied. This is further motivation to present the data from each year separately in Figures 1 and 2 (discussed in comment 1). Why are source contributions only shown for December through March? It would be useful to also show a period in summer for



the BB tracer contribution.

This is a very good point. Figure 6 in the revised manuscript now includes the monthly source contributions from FLEXPART for each month separately, from 2008-2010, for both anthropogenic and fire sources. Additionally, section 3.2 has been re-written to include a detailed discussion on the contributions to the  $BC_{\text{anthro}}$  and  $BC_{\text{fire}}$  tracer from different source regions during different times of the year. Further details are given in the responses to reviewer 1.

6. The paper should specify what version of FLEXPART and what emissions are used for the anthro and BB sources.

We thank the reviewer for noting the missing information regarding the FLEXPART model and have added this information to the revised manuscript

On page 11, line 11, the sentence now reads:

*The Lagrangian particle dispersion model FLEXPART (version 8.2) was utilized....*

On page 11, lines 21-26, the following text has been added:

*For the BC anthropogenic tracer the Emissions Database for Global Atmospheric Research (EDGAR) UNEP BC report 2005 data (UNEP, 2011; Shindell et al., 2012) was used. To estimate the BC fire emissions, MODIS hot spot data (Justice et al., 2002; Giglio et al., 2003) was used to estimate the area burned (180 hPa per MODIS hot spot) and combined with a combustion efficiency, emission factor, and fuel load, which were all based on land use type*

7. Figures 7 and 8 are interesting because they contain a portion of the measured time series, so pollution events can be seen in the data. The authors should include a full time series in the electronic supplement and only show the portion of the time series discussed in detail in the main portion of the paper.

We agree with the reviewer and the full time series of the measurement species have been included in the supplementary material (Figures S4 and S5). Table 3, containing information on the BB events, remains in the main manuscript. A table with details on each of the anthropogenic pollution events has been provided in the electronic supplement (Table S1). Time series of individual events are still included (Figures 7, 9, 10 and 11) in the main text.

8. Figures 9, 10, and 11 use column integrated FLEXPART retroplume analysis to study air mass origin. This is a good approach to understand features that originate from long-range transport in the  $NO_x$ ,  $NO_y$ , and PAN data. However, the figures as presented are confusing. What information does the altitude of the plume provide (given that the gray points are hardly visible on the plots)? Is the gray the altitude 10 days prior to release, or the altitude where the particles reside for more than ten days? This portion of the paper is very confusing.

The figures of the FLEXPART retroplume include 10-day particle centroid locations. Only the locations from 1-10 days upwind are shown on the plot for simplification, however, retroplumes include simulations 20 days prior to arriving at Summit. FLEXPART is not a back-trajectory model, but rather a Lagrangian Particle Dispersion Model. As such, at any point in time there are thousands (in this case 10s of thousands) of particles in the model domain.

In the manuscript the FLEXPART simulated total column sensitivity plots in Figures 8-11 have

been re-plotted to show the altitude of the plume and trajectory location every 3 hours, up to 10 days prior to arriving at Summit. FLEXPART figures in the supplementary material use the original plotting method. However, the captions have been revised to clarify the data presented in the figures.

9. Figures 10 and 11 study specific events, however the portion corresponding to the particle release is not indicated on the measurement plots. I found myself trying to shade in the periods from 7/26/2008-7/27/2008 and 8/4/2008-8/5/2008 on Figures 10 and 11 the correspond to the FLEXPART release times. The authors should put the effort into making these plots understandable for the reader.

We thank the reviewer for noting this issue. Figures 9, 10 and 11 now include vertical bars, to identify the release time for the FLEXPART retroplume.

10. Page 13838 - Lines 20 to end of page: The case of the FLEXPART BC not coinciding with enhanced PAN, NO<sub>y</sub>, and ethane is a bit of a mystery. This will be less confusing if the authors change to using CO source contributions, since BC is subject to wet removal. CO is a more straightforward to compare with PAN and ethane since they experience more similar atmospheric processing. If the disagreement still persists after looking into CO by source, then the authors should look into differences in plume altitude compared with other similar plumes. Are there emissions missing that can explain this? Is there a difference in transport pathways (e.g. residence time in the boundary layer or upper troposphere/lower stratosphere) that can explain this?

As discussed in the response to comment 4 above, the simulations do not appear to be missing any events when using the BC tracer instead of the CO tracer. It is possible that FLEXPART is missing some sources, or, as mentioned in the manuscript, the pollution originated prior to the 20 day simulation. The retroplumes for some of these periods have been investigated, and discussed in the manuscript. This section of text has been revised on page 25, lines 3-26, and reads:

*In this study, the impact from anthropogenic emissions, as identified through FLEXPART retroplume analyses, were the primary focus. However, enhancements in the measured species were also observed during periods which are not correlated with pollution events simulated by FLEXPART. For example, on 15 February and 24-28 February 2010, (Fig. 7), enhancements in PAN, NO<sub>y</sub>, and ethane are observed that do not coincide with high FLEXPART BC<sub>anthro</sub> tracer levels. The BC<sub>fire</sub> tracer from FLEXPART during this period is low, suggesting that the event was not the result of biomass burning emissions. The retroplume shows the air masses from these two events were transported over north Canada and remained in the Arctic for many days before arriving at Summit (not shown here). It is unlikely that the air sampled was from stratospheric origin, as ethane levels were high and ozone decreased during these events. It is possible that there may be missing sources in FLEXPART, or that the pollution originated prior to the 20 day simulation.*

*Enhancements in O<sub>3</sub> precursors that do not coincide with high FLEXPART tracer simulations were also observed during the spring months, however, O<sub>3</sub> was typically enhanced during these events, suggesting a different source than those in February 2010. FLEXPART analyses indicate the air masses were well aged, therefore, mixing with air masses originating from the upper troposphere/stratosphere is possible. For example, the highest PAN and NO<sub>y</sub> levels during spring 2010 were observed between 22-24 April, when FLEXPART retroplumes show that the air masses were transported between 3300 and 4300 m.a.s.l (Fig. 9). During this same period, ethane and O<sub>3</sub> were also high. This event may be an example of tropospheric air, with high levels of NMHC, mixing with stratospheric air rich in O<sub>3</sub> and NO<sub>y</sub>, resulting in PAN formation*

*(Liang et al., 2011). The determination of the sources that result in enhancements in O<sub>3</sub> and its precursors, that cannot be attributed to pollution transport, requires further investigation.*

11. The retroplume altitudes as a function of plume age should be included in Figures 9, 10, and 11. Can the authors comment on the amount of NO<sub>x</sub> observed during spring and summer for observations that were likely influenced by interactions with snow (i.e. retroplumes that stay in the boundary layer for some time)?

The revised manuscript now includes clearer plots and descriptions of retroplume altitudes, as discussed in the response to point 8 above.

The suggestion by the reviewer, regarding the NO<sub>x</sub> levels, is an excellent one. Retroplumes that spend a greater time at low altitudes over the Greenland ice sheet may be influenced by interactions with snowpack. However, further research beyond the scope of this study is required, in order to accurately determine the residence time over the Greenland ice sheet and perform a detailed analysis.

12. The text describes some information, which is not adequately presented in the figures. For example, P13835 states that 42 events were identified as influenced by anthropogenic pollution using the FLEXPART BC<sub>anthro</sub>. These events should be indicated on the times series of measurements (NO<sub>x</sub>, PAN, NO<sub>y</sub>, ozone) and also in Figures 5 and 6 or the time periods should be listed in the electronic supplement. Similarly, the source contribution/sensitivity to fire emissions should be shown somewhere in a figure or in the electronic supplement (similar to Figures 5 and 6, but for fires).

As discussed in the responses to points 5, and 11 above, information on the events observed, including, start time, event length and peak BC<sub>anthro</sub> tracer level, have been included in a table in the electronic supplement and a plot of the FLEXPART fire tracer contributions, during the measurement period, is given in Figure 6.

13. For the cases studied in spring and summer – how does the lifetime of PAN compare for thermal decomposition vs. photolysis (at the relevant temperatures/SZA along the trajectories)?

The primary loss process for PAN is the result of thermal decomposition. At Summit, thermal decomposition is expected to be very low as a result of the low temperatures (<0°C) throughout the year. PAN decomposition is possible during transport from lower latitudes and is expected to be the primary loss mechanism for PAN during transport to Summit. Talukdar *et al.*, 1995 showed that thermal decomposition dominates over photolysis in the low- to mid-troposphere. The retroplumes analyzed in this study indicate that pollution plumes arriving at Summit are typically transported below 6-7km and loss from photolysis is unlikely, however, it is possible that some plumes may be transported at higher altitudes before descending to Summit. The chemical transformation of the measured species during transport to and from Summit is the focus of a future study; therefore we do not feel it would be necessary to include the analyses here.

During the BB event in August 2008, the PAN levels did vary when the air mass moved to lower altitudes and may be the result of thermal decomposition during transport. The following text discussing this event has been added on page 29, lines 4-10:

*During the main peak of this event (~August 4–7) a decrease in PAN mole fractions was*

observed even though the  $BC_{fire}$  tracer remained elevated. The FLEXPART trajectories indicate that the decrease in PAN coincided with a decrease in the altitude of the pollution plume over the Greenland ice sheet. It is possible, at these lower altitudes, thermal decomposition of PAN occurred, resulting in the formation of  $NO_2$  and possible photochemical production of  $O_3$  near to Summit. However, this cannot be concluded from the available measurements.

14. Is there any indication how much particulate nitrate may be contributing to  $NO_y$ ?

The  $NO_y$  system used at Summit is based on the same instrument design deployed at Pico from 2004-2010. Val Martin *et al.*, 2008 discussed the contribution of particulate matter to the total  $NO_y$  measured by the instrument at Pico. The authors stated that the instrument does not allow sampling of aerosols  $> 10 \mu m$ . These details have been added to section 1 in the supplementary document.

Fine particulate may still be sampled, but previous studies have shown that ambient  $p\text{-NO}_3^-$  levels at Summit are typically low. The following text has been added to the manuscript, to clarify this point. Text on page 17, lines 12-14, now reads:

*Particulate nitrate may also contribute a small amount to the total  $NO_y$ , however, this contribution is expected to be small as ambient  $p\text{-NO}_3^-$  levels are typically lower than  $HNO_3$  at Summit (Dibb *et al.*, 1994).*

15. The increase in the uncertainty of the PAN measurements in spring 2009 provides even further motivation to look at the years separately. Do the increased uncertainties in 2009 impact what we can learn from the seasonal data before/after this date?

Monthly averages with measurement uncertainties were plotted for PAN and provided in the supplementary material (Figure S3). The data shows that the differences in the monthly mean value during the spring time peaks (i.e. in April) are within the uncertainty levels. However, the individual PAN measurements indicate very high levels in April 2010. The manuscript has been updated to include a discussion on the seasonality of PAN and measurement uncertainties. The text on page 13 lines 11-17 reads:

*Table 1 gives a statistical summary for the monthly averages of PAN,  $NO_y$ ,  $NO_x$ , and  $O_3$  during 2008–2010. Maxima in monthly mean mole fractions of PAN occur in April with mean levels of  $233 \pm 68 (1\sigma) \text{ pmol mol}^{-1}$  and  $280 \pm 102 \text{ pmol mol}^{-1}$ , for 2009 and 2010, respectively. The difference between monthly mean PAN levels observed in April 2010 and April 2009 are within the measurement uncertainties (as shown in Figure S3, supplementary material), however, the 30 minute averages (shown in Figure S4) indicate high levels of PAN,  $NO_y$ , and  $NO_x$  in April 2010. These high levels are explored further in Sect. 3.2.1.*

16. A more detailed discussion of relevant POLARCAT papers is needed. Key examples include: Roiger *et al.*, 2011 and Alvarado *et al.*, 2010.

The section which previously included references to Roiger *et al.*, 2011 and Alvarado *et al.*, 2010 has been re-written, as the revised manuscript now includes a discussion on a plume transported across the North Pole. This event is comparable to one discussed in Roiger *et al.* and the revised manuscript includes this information on page 28, line 23 – page 29, line 2. The revised text reads:

*For example, during event 7, FLEXPART indicates that an aged plume (mean age ~16 days) originating from Asia, was transported over the North Pole between ~3000- 4200 m.a.s.l. A similar transport pattern was observed during the POLARCAT campaign, during which a plume, originating from Asia, was lifted within a warm conveyor belt over the North Pole towards Greenland (Roiger et al., 2011). The plume was then transported into the lower stratosphere, resulting in a well mixed tropospheric-stratospheric air mass with high O<sub>3</sub> levels. The plume during event 7 was transported at lower altitudes, however mixing with air from stratospheric origin is not impossible and may be the cause of the O<sub>3</sub> ( $\Delta O_3=10.7 \text{ nmol mol}^{-1}$ ) and PAN ( $\Delta \text{PAN}=68.5 \text{ pmol mol}^{-1}$ ) levels observed.*

17. Section 3.2 should be significantly rewritten/reworked. Motivation for why the seasons and events were chosen should be clearly presented at the beginning of Section 3.2. For example, the Paragraph started on line 24 Page 13834 should be presented earlier, so it's clear why the anthropogenic emissions are the focus in winter. The specific cases that are the focus of this section should be explained more clearly and the authors should endeavor to answer the question: What did we learn about anthro and BB events and their influence on NO<sub>x</sub>, PAN, and NO<sub>y</sub> at Summit by doing these measurements?

The authors agree with reviewers 1 and 2 regarding section 3.2. As discussed in the responses to reviewer 1, a more detailed discussion on the FLEXPART source contributions and variability between the two winters has provided at the start of section 3.2. Sub-sections 3.2.1 and 3.2.2 have been substantially re-written and additional analyses performed on individual events. We feel that the new analyses and revised manuscript provides an improved discussion on the impact of polluted plumes on ozone and ozone precursors at Summit.

Technical corrections:

- Arctic should be capitalized

Corrected

- Space missing between the delta NO<sub>x</sub> and Delta ozone on page 13835 (line 24).

Corrected

- The paper should be reviewed for other typos and readability.

The revised paper has been reviewed prior to submission.

### **Responses to reviewer 3**

The data set presented here is unique and valuable and should be published. It will be particularly useful if the NO<sub>x</sub>, NO<sub>y</sub>, O<sub>3</sub> data (Fig.1) is shown consistently with the NMHC data (Fig. 4), in particular if the full time series is shown, not averaged over the 2 years (as is currently in Fig. 1). If the authors address the other reviewers comments I expect the paper will be acceptable for publication.

We thank reviewer 3 for the comments regarding the manuscript. As suggested, the revised

manuscript now includes monthly averaged NMHC, NO<sub>x,y</sub>, PAN and O<sub>3</sub> separated for the two years in the main manuscript. A full time series of each species is also provided in the supplementary material. Further details on changes that were made are provided in the responses to reviewers 1 and 2 above.

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# Seasonal variability of atmospheric nitrogen oxides and non-methane hydrocarbons at the GEOSummit station, Greenland

**L. J. Kramer<sup>1</sup>, D. Helmig<sup>2</sup>, J. F. Burkhardt<sup>3,4</sup>, A. Stohl<sup>5</sup>, S. Oltmans<sup>6,7</sup>, and R. E. Honrath<sup>1,†</sup>**

<sup>1</sup>Atmospheric Sciences Program/Dept. of Geological and Mining Engineering and Sciences, Michigan Technological University, Houghton, Michigan, USA

<sup>2</sup>Institute of Arctic and Alpine Research, University of Colorado, Boulder, CO, USA

<sup>3</sup>Department of Geosciences, University of Oslo, Norway

<sup>4</sup>Sierra Nevada Research Institute, University of California, Merced, USA

<sup>5</sup>Norwegian Institute for Air Research (NILU), Kjeller, Norway

<sup>6</sup>NOAA Earth System Research Laboratory, Boulder, CO, USA

<sup>7</sup>CIRES, University of Colorado, Boulder, Colorado, USA

<sup>†</sup>deceased

Correspondence to: L. J. Kramer (lkramer@mtu.edu)

## Abstract

Measurements of atmospheric [nitrogen oxides](#)  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), peroxyacetyl nitrate (PAN),  $\text{NO}_y$ , and non-methane hydrocarbons (NMHC) were taken at the GEOSummit Station, Greenland (72.34° N, 38.29° W, 3212 m.a.s.l.), from July 2008 to July 2010. The data set represents the first year-round concurrent record of these compounds sampled at a high latitude Arctic site [in the free troposphere](#). Here, the study focused on the seasonal variability of these important ozone ( $\text{O}_3$ ) precursors in the Arctic [free-troposphere](#) and the impact from transported anthropogenic and biomass burning emissions. Our analysis shows that PAN is the dominant  $\text{NO}_y$  species in all seasons at Summit, varying from [4945 %](#) to [7881 %](#), however, we find that odd  $\text{NO}_y$  species (odd  $\text{NO}_y = \text{NO}_y - \text{PAN} - \text{NO}_x$ ) contribute a large amount to the total  $\text{NO}_y$  speciation [with monthly means of up to 95 in the winter and ~40 in the summer, and that the level of odd species at Summit during summer is greater than that of](#). We hypothesize that the source of this odd  $\text{NO}_y$  is most likely alkyl nitrates [and nitric acid](#) ( $\text{HNO}_3$ ) from transported pollution, and photochemically produced species such as [and](#) nitrous acid (HONO).

FLEXPART retroplume [analysis and analyses and black carbon \(BC\)](#) tracers for anthropogenic and biomass burning [emissions, \(BB\) emissions](#) were used to identify periods when the site was impacted by polluted air masses. Europe contributed the largest source of anthropogenic emissions during the winter [and spring months, with up to 82 months \(November–March\) with 56 %](#) of the [simulated anthropogenic black carbon originating from this region between December total anthropogenic BC tracer originating from Europe in 2008/2009 and March 2010, whereas, 69 % in 2009/2010](#). The polluted plumes resulted in [mean enhancements above background levels up to 273 pmol mol<sup>-1</sup>, 312 pmol mol<sup>-1</sup>, 54 pmol mol<sup>-1</sup>, and 1120 pmol mol<sup>-1</sup> for  \$\text{NO}\_y\$ , PAN,  \$\text{NO}\_x\$ , and ethane, respectively, over the two winters. Enhancements in  \$\text{O}\_3\$  precursors during the second winter were typically higher, which may be attributed to the increase in European polluted air masses transported to Summit in 2009/2010 compared to 2008/2009.  \$\text{O}\_3\$  levels were highly variable within the](#)

sampled anthropogenic plumes with mean  $\Delta\text{O}_3$  levels ranging from  $-6.7$  to  $7.6$  nmol mol $^{-1}$  during the winter periods.

North America was the primary source of biomass burning emissions. ~~Polluted air masses were typically during the summer, however, only 13 BB events were observed as the number of air masses transported to Summit, with significant BB emissions, was low in general during the measurement period. The BB plumes were typically very aged, with median transport times to the site from the source region of 11 days for anthropogenic events in winter, and 14 days for BB plumes. Overall we find that the transport of polluted air masses to the high-altitude Arctic typically resulted in high variability in levels of  $\text{O}_3$  and precursors. During winter, plumes originating from mid-latitude regions and transported in the lower troposphere to Summit often result in lower mole fractions than background levels. However, plumes transported at higher altitudes can result in positive enhancements in levels. It is therefore likely that the air masses transported in the mid-troposphere were mixed with air from stratospheric origin. Similar enhancements in  $\text{O}_3$  and its precursors were also observed during periods when FLEXPART indicated that biomass burning emissions impacted Summit. The analysis of anthropogenic events over summer show that emissions of anthropogenic origin have a greater impact on  $\text{O}_3$  and precursor levels at Summit than biomass burning sources during the measurement period.~~ precursor levels during the BB events indicate that some of the plumes sampled impacted the atmospheric chemistry at Summit, with enhancements above background levels of up to 16 for and 237 and 205, 28 and 1.0 for, PAN, and ethane, respectively. observed in all measured species.

## 1 Introduction

The seasonality of ozone ( $\text{O}_3$ ) and its precursors for photochemical production, such as nitrogen oxides, i.e.  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), peroxyacetyl nitrate (PAN), and non-methane hydrocarbons (NMHC), in the remote Arctic troposphere is governed by a combination of transport pathways, photochemistry, and stratospheric influx (Klonecki et al., 2003; Stohl et al., 2006; Law and Stohl, 2007; Liang et al., 2011). Improving our knowledge on the

seasonality of O<sub>3</sub> and its precursors and the relative importance of source regions and transport variability is essential as recent studies have suggested that tropospheric O<sub>3</sub> may have a large impact on radiative forcing and climate feedbacks in the Arctic region (Shindell et al., 2006; Shindell, 2007; Quinn et al., 2008).

Polluted air masses originating from anthropogenic and biomass burning sources in the mid-latitude regions can transport long-lived reservoir species of NO<sub>x</sub>, such as PAN, and nitric acid (HNO<sub>3</sub>) ~~to the arctic~~, to the Arctic region (Wofsy et al., 1992; Wespes et al., 2012), which may reform NO<sub>x</sub> and result in enhanced levels far downwind from the emission sources (Beine et al., 1997; Walker et al., 2010). NMHC may also be transported in air masses from anthropogenic and biomass burning sources. The mole fractions of NMHC in the Arctic atmosphere can vary greatly during the year due to seasonal variability in emissions, transport pathway variability and the reaction with OH radicals (Jobson et al., 1994; Blake et al., 2003; Swanson et al., 2003).

Studies of pollution plumes with airborne, satellite- and ground-based observations, and model simulations show that long-range transport from Europe and North America to the lower Arctic troposphere may constitute a large source of tropospheric O<sub>3</sub> and O<sub>3</sub> precursors, whereas at higher ~~altitudes~~altitude, pollution plumes transported from Asia ~~become important~~ are an important source (e.g. Atlas et al., 2003; Klonecki et al., 2003; Lamarque and Hess, 2003; Law and Stohl, 2007; Shindell et al., 2008; Fisher et al., 2010; Singh et al., 2010; Walker et al., 2012; Wespes et al., 2012; Bian et al., 2013). A large contribution to the seasonality of O<sub>3</sub> and O<sub>3</sub> precursors in the Arctic troposphere is due to variability in the location of the Arctic polar front (Klonecki et al., 2003; Stohl, 2006). During winter in the Northern Hemisphere, the polar front expands southward over North America, Europe and ~~North Asia~~ Siberia allowing direct transport of polluted air masses from sources within these latitudes to the Arctic. The Arctic polar front recedes in summer, reducing the impact of these pollution sources on the Arctic lower troposphere. However, it has been shown that the transport of emissions from biomass burning regions to the Arctic is possible during summer (Stohl, 2006) and that they can strongly impact the atmosphere above Summit Station in Greenland (Stohl et al., 2006). Results from a modeling study by Walker et al.

(2012) using tagged emissions ~~from in~~ the global chemical transport model GEOS-Chem show that during summer the primary emissions that impact the production of O<sub>3</sub> in the Arctic region were from high latitude regions, whereas, during the fall and winter periods, transport of emissions from mid-latitude regions in North America and Europe is possible.

A number of studies have discussed the seasonality of surface O<sub>3</sub> (Bottenheim et al., 1994; Beine et al., 1997; Monks, 2000; Browell et al., 2003; Helmig et al., 2007b; Walker et al., 2012), nitrogen oxides (Barrie and Bottenheim, 1991; Honrath and Jaffe, 1992; Bottenheim et al., 1994; Muthuramu et al., 1994; Beine et al., 1997; Solberg et al., 1997; Dibb et al., 1998; Munger et al., 1999; Beine and Krognes, 2000; Stroud et al., 2003; Thomas et al., 2011) ~~and NMHC~~ (Jobson et al., 1994; Blake et al., 2003; Klonecki et al., 2003; Swanson et al., 2003; ?), ~~and NMHC~~ (Jobson et al., 1994; Blake et al., 2003; Klonecki et al., 2003; Swanson et al., 2003) ~~+~~ the Arctic ~~region~~. However, due to the logistical difficulties in measuring at remote Arctic locations, the majority of seasonal studies have taken place at coastal sites in Northern Europe, Canada, and Alaska, or focused on the late spring/summer periods. Seasonal and interannual studies of nitrogen oxides in the remote Arctic ~~free~~ troposphere are largely missing. The high ~~altitude~~ ~~latitude~~ Arctic has negligible impact from local pollution sources, and local production of NO<sub>x</sub> from PAN decomposition is expected to be small in this cold region. Therefore, enhanced mole fractions of nitrogen oxides are primarily a result of long-range transported pollution from anthropogenic or biomass burning sources in Europe, North America, and Asia, or of downward transport from the stratosphere (e.g. Liang et al., 2011). A build-up of O<sub>3</sub> precursors during winter in the Arctic free troposphere may have important implications for the tropospheric O<sub>3</sub> budget in the mid-latitudes during late spring and early summer (Gilman et al., 2010). ~~Modelling~~ ~~Modeling~~ studies have postulated that air masses originating from the Arctic region can result in the transport of NO<sub>y</sub> and NMHC to the North Atlantic and enhance tropospheric O<sub>3</sub> in this region due to the thermal decomposition of PAN (Honrath et al., 1996; Hamlin and Honrath, 2002).

This study utilizes 2 ~~years~~ of continuous measurements and model results to characterize the seasonally varying magnitude of O<sub>3</sub> and its precursors in the re-

mote high ~~altitude~~-~~latitude~~ Arctic and the potential impact from transported pollution. Year-round measurements of  $\text{NO}_x$ ,  $\text{NO}_y$ , PAN,  $\text{O}_3$  and NMHC from the high ~~altitude~~-~~latitude~~ Greenland Environmental Observatory at Summit (GEOSummit) station in Greenland are presented. The paper is structured as follows: in Sect. 2, the techniques to measure  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_y$  (total reactive nitrogen oxides  $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{PAN} + \text{HNO}_3 + \text{HONO} + \text{others}$ )  $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{PAN} + \text{HNO}_3 + \text{HONO} + \text{others}$ ) PAN, and NMHC are presented and the FLEXPART Lagrangian particle dispersion model utilized in this study is discussed. ~~Section 3.1 discusses~~ Sect. 3.1 presents the seasonal cycles of  $\text{O}_3$  precursors at the measurements site and the  $\text{NO}_y$  speciation is investigated. In Sect. 3.2, the ~~interannual variability and~~ source contributions to enhanced  $\text{O}_3$  precursors from anthropogenic emissions and biomass burning are discussed. Finally, a summary of the main findings is given in Sect. 4.

## 2 Experimental methods

### 2.1 GEOSummit Station

Measurements of  $\text{NO}_x$ ,  $\text{NO}_y$ , ~~PAN~~- PAN, and NMHC were performed at the GEOSummit Station (hereafter called Summit), Greenland (72.34° N, 38.29° W, 3212 m.a.s.l.), from July 2008 to July 2010. Inlets for the instruments were installed ~ 7.5 m above the snowpack on a meteorological tower located approximately 660 m south-west of the main camp within the “clean air” sector. Tubing and cables were routed through a heated pipe to a buried laboratory facility.

### 2.2 Measurements

#### 2.2.1 Nitrogen oxides

##### ~~Measurement~~

Measurements of NO, NO<sub>2</sub>, and NO<sub>y</sub> were performed with an automated O<sub>3</sub> chemiluminescence detection system (Ridley and Grahek, 1990). The ~~system-instrument~~ was developed at Michigan Technological University and is based on the same design that was used in Newfoundland in 1996 (Peterson and Honrath, 1999) and subsequently installed at Summit during campaigns in 1998, 1999 and 2000 (Honrath et al., 1999, 2002; Dibb et al., 2002), and at the Pico Mountain ~~Site-Observatory~~ from 2002 to 2010 (Val Martín et al., 2006). NO<sub>2</sub> and NO<sub>y</sub> were detected by chemiluminescence after reduction to NO using a photolytic NO<sub>2</sub> converter (Kley and McFarland, 1980) and a gold-catalyzed NO<sub>y</sub> converter in the presence of CO, ~~respectively (Bollinger et al., 1983; Fahey et al., 1985)~~ (Bollinger et al., 1983; Fahey et al., 1985), respectively. NO<sub>y</sub> is given as the sum of reactive nitrogen oxides. In the Arctic, NO<sub>y</sub> is primarily comprised of NO, NO<sub>2</sub>, PAN, HNO<sub>3</sub>, HONO and particulate nitrate (p-NO<sub>3</sub><sup>-</sup>). For the instrument used in this study, a photolytic blue LED NO<sub>2</sub> converter (Air-Quality Design Inc., Colorado) was installed. Photolytic converters have lower conversion efficiencies than molybdenum converters, however, interferences from other species photolyzing to NO, such as HONO and PAN, are reduced (Pollack et al., 2011; Villena et al., 2012). The sample mass flow controllers (MFC) and the NO<sub>2</sub> and NO<sub>y</sub> converters were housed inside the inlet box on the tower to minimize the residence time of NO<sub>y</sub> species inside the PFA tubing.

During each measurement cycle of 10 min, the NO and NO<sub>2</sub> signals were recorded as 30 s averages and NO<sub>y</sub> signals as 20 s averages, after a period of equilibration in each mode. Zero measurements of NO were performed at the start and end of each measurement cycle by mixing O<sub>3</sub> with the sample upstream of the reaction chamber. The zero signals were measured to determine the interference signal in the reaction chamber, which was then subtracted from the measured signals. ~~Calibration cycles, Calibrations were performed every 12 hours~~ to determine the sensitivity of the instrument to NO ~~and converter efficiency, were performed every 12 through the~~ via standard addition (10 cm<sup>3</sup> min<sup>-1</sup>) of ~ 1 mmol mol<sup>-1</sup> of NO in nitrogen (N<sub>2</sub>) (Scott Marrin, Scott Specialty Gases) to the sample flow of 650 cm<sup>3</sup> min<sup>-1</sup> at the inlet on the tower. A known amount of NO<sub>2</sub>, generated via



gas phase titration of NO with O<sub>3</sub>, was also added to the sample flow during the calibration cycle, to determine the conversion efficiencies of the NO<sub>2</sub> and NO<sub>y</sub> converters. In addition to the standard calibrations, a calibration was performed every 3 days to determine every three days the conversion efficiency of the NO<sub>y</sub> converter and to HNO<sub>3</sub> and n-propyl nitrate (NPN) were determined and artifacts for NO<sub>y</sub>, NO<sub>x</sub> and NO<sub>2</sub> were measured via sampling NO<sub>x</sub> free air (Breathing air grade, Airgas, Radnor, PA, USA). The final datasets were corrected for this artifact.

~~The variability~~ Approximately 8% of the final dataset was removed due to known instrument issues. Additional filtering procedures were applied to remove points potentially contaminated by local camp pollution. Variability in the 20 and 30 s averaged data was compared to the expected value from photon counting statistics which are treated as a Poisson distribution. Measurements with variability greater than 3 times the Poisson value were then removed from the final dataset (~~~4~4% were removed with this filter~~). Evaluation of these periods ~~shows show~~ that they typically occur when the wind direction was from the main camp, confirming that local pollution ~~is was~~ the main source of the variability. ~~Additional filtering processes were implemented to remove bad data caused by (1) spikes from electronic noise or intermittent instrument malfunctions; (2) high variability due to~~ Erroneous data points as a result of unknown instrument issues, or periods when the skiway was groomed ~~or periods not captured in the Poisson statistics filter and (3), were also removed. Less than 0.2% of the total data were classified as erroneous and each point was manually checked by comparing to adjacent observations. Finally,~~ large negative mole fractions, ~~due to short term fluctuations as a result of large variability between modes during the measurement cycle. After the application of all the filtering procedures described above, 90–91, were removed (<1% of the NO<sub>x</sub> and measurements were included in the final dataset).~~

The final NO, NO<sub>2</sub>, NO<sub>x</sub>, and NO<sub>y</sub> data used in this work were further averaged over a 30 min period. NO<sub>x</sub> was determined as the sum of the NO and NO<sub>2</sub> measurements during each 10 min cycle. The overall uncertainty for the 30 min data is calculated from the root sum of the squares of the measurement accuracy, artifact uncertainty, and precision.

Maximum uncertainties for NO, NO<sub>2</sub>, and NO<sub>x</sub> at 50 pmol mol<sup>-1</sup> are 10%, 17%, and 19%. For NO<sub>y</sub>, the ~~uncertainty~~ total uncertainty is also dependent on the conversion efficiencies of the NO<sub>y</sub> species, which is estimated to be ~ 6% based on the NO<sub>y</sub> levels expected at Summit. The total uncertainty in NO<sub>y</sub> is estimated to be ~ 9% at 200 pmol mol<sup>-1</sup>. ~~is < 20 and typically 9.~~

Detection limits for the 30 min averages were determined from the 2σ precision of the instrument and error in the artifact. Detection limits for NO, NO<sub>2</sub>, NO<sub>x</sub>, and NO<sub>y</sub> ~~are were~~ 4 pmol mol<sup>-1</sup>, 8 pmol mol<sup>-1</sup>, 9 pmol mol<sup>-1</sup>, and 7 pmol mol<sup>-1</sup>, respectively. ~~Measurements~~ Mole fractions below the detection limit, including small negative mole fractions (as a result of uncertainties in the zero measurement and artifact corrections) were included in all averaging calculations to ensure the final values were not biased. Further details on the calibrations performed and the precision and accuracy of the measurements are ~~given in the Supplement~~ provided in the supplement.

## 2.2.2 Peroxy-acetyl nitrate

A commercial PAN gas chromatography analyzer (PAN-GC, Metcon, Inc., Boulder, CO) was installed alongside the NO<sub>xy</sub> instrument to determine atmospheric PAN mole fractions. The PAN instrument is based on gas chromatography with electron capture detection (GC-ECD). The instrument was equipped with a preconcentration unit to improve the detection limit whilst allowing for PAN sampling every 10 min. The preconcentration unit traps PAN and carbon tetrachloride (CCl<sub>4</sub>) on a ~~peltier-cooled~~ Peltier-cooled (5 °C) capillary column prior to injection onto the main GC column, which was set to a ~~temperature~~ temperature of 13 °C to reduce the thermal decomposition of PAN. Ultra-pure nitrogen gas (99.9999% purity) was used as the carrier gas for the PAN-GC.

The instrument was calibrated approximately every week using a known amount of PAN, which was photochemically produced from the same NO-calibration gas used for the NO<sub>xy</sub> instrument described in Sect. 2.2.1. The NO gas was delivered to a reaction cell inside the PAN calibration unit which contained a UV mercury lamp to photolyze an excess of acetone (in zero air) ~~which-that~~ reacts with the NO gas to form PAN. The PAN calibration

gas was sent to the inlet on the tower and then sampled by the GC-ECD. The conversion efficiency of NO to PAN was determined at the beginning and end of the measurement period through the standard addition of NO/NO<sub>2</sub> to the NO<sub>xy</sub> instrument. The conversion efficiency remained relatively constant throughout the measurement period at  $96 \pm 1\%$ .

The sensitivities determined from the weekly PAN calibrations were interpolated to the measurements to take into account any drifting. CCl<sub>4</sub> was also used as an internal reference during periods when calibrations were not taken (Karbiwnyk et al., 2003). The atmospheric concentration of CCl<sub>4</sub> should be relatively constant; therefore any changes in the CCl<sub>4</sub> peak area would be caused by changes in the instrument sensitivity. During a period between 28 February 2009 and 17 May 2009 there was a gap in the calibrations caused by a blockage in the tubing that delivered the PAN calibration gas to the inlet. During this period the relationship between the CCl<sub>4</sub> peak area and PAN sensitivity from the previous calibrations was used to obtain the PAN sensitivity. Over the duration of the measurement period the detector became dirty resulting in drifting and a noisy baseline. Due to this issue no data after 28 April 2010 were included in the analyses here.

Similarly to the NO<sub>x</sub> and NO<sub>y</sub> data, the PAN measurements were averaged over 30 min. The total uncertainty for the 30 min averaged PAN mole fractions was determined from the root sum of the squares of the precision of the instrument (estimated as  $2\sigma N^{0.5}$ , where  $N$  is the number of points averaged in 30 min ( $N = 3$ )) and from the uncertainty in the calibration standard. The precision was < 57 pmol mol<sup>-1</sup> with a mean (median) value of 6.7 pmol mol<sup>-1</sup> (5.6 pmol mol<sup>-1</sup>). Uncertainty in the PAN calibration standard is associated with uncertainties in (a) the calculation of the NO addition, (b) the conversion of NO to PAN from the calibration unit and, (c) variability in the PAN sensitivity between calibrations. The total uncertainty was estimated to be 16% uncertainty in this calibration standard was calculated to be 15 % during normal operation. This value increased to 221 % during the period in spring 2009 when there were no calibrations. Using the mean precision, the total uncertainty in the PAN measurements at 150 pmol mol<sup>-1</sup> was estimated to be approximately 16 % during normal operation, and 22 % during spring 2009.

The limit of detection (LOD) of the instrument was estimated from the peak to baseline noise ratio. The LOD is defined as the mole fraction giving a signal to noise ( $S/N$ ) ratio of 3. The baseline noise was determined from a region just after the PAN peak for each chromatogram. The limit of detection was highest during the first few months of operation up to November 2008 with a median value of 41 pmol mol<sup>-1</sup>. Despite the high LOD, 88 % of chromatograms were above the LOD during 2008. The LOD improved after this period with a median value of 15 pmol mol<sup>-1</sup>. The final PAN data set was not filtered for wind direction as analyses showed that there was no obvious influence from camp pollution on the PAN measurements.

### 2.2.3 Non-methane hydrocarbons

NMHC were continuously sampled from June 2008 to July 2010 using a fully automated and remotely controlled GC system that was specifically designed for this study. Details of the setup at Summit are given in [Helmig et al. \(2014\)](#). The GC is a further development of the instrument operated at the Pico Mountain Observatory and described in detail by (Tanner et al., 2006). The ~~instrument provided ~ 6000~~ NMHC system provided ~ 8 ambient measurements of C<sub>2</sub>–C<sub>6</sub> hydrocarbons ~~; in addition to ~ 1000 blank and standard runs from June 2008 to July 2010. each day, with each measurement representing a collection/sample integration time during the sample pre-focusing step of ~ 45 min. In addition, one blank sample was analyzed ~ daily, and a standard every ~ 2 days.~~

The inlet for the GC instrument was installed on the same tower as the PAN, NO<sub>y</sub>, and NO<sub>x</sub> inlets. The instrument ~~relies~~ relied on a cryogen-free sample enrichment and injection system. All consumable gases were prepared at the site with a hydrogen generator, compressor, and air purification system. Aliquots of the sample stream were first passed through a ~~water~~ Peltier-cooled trap to dry the air to a dew point of -30 °C, then through an ozone scrubber, and NMHC were then concentrated on a Peltier-cooled (-25 °C) multi-stage adsorbent trap. Analysis was accomplished by thermal desorption and injection onto an aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) porous layer open tubular (PLOT) column for cryogen-free separation on a SRI Model 8610 GC with flame ionization detection (FID). Blanks and stan-

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standard samples were injected regularly from the manifold. The gravimetric and whole air standards that were used were cross-referenced against our laboratory scale for volatile organic compounds, which has been cross-referenced against national and international scales, including through two previous audits by the World Calibration Centre for VOC ~~(http://http://imk-ifu.fzk.de/wcc-voc/)~~. At 100 pptv mole fraction, analytical accuracy and precision ~~are~~ were typically better than 3–5%, yielding a combined uncertainty estimate of ~ 5%. The instrument ~~achieves~~ achieved low single digit pmol mol<sup>-1</sup> detection limits. During summer, when NMHC levels for C<sub>4</sub>–C<sub>5</sub> NMHC at times dropped below the detection limits, for the statistical and whisker plot calculations those data were treated as 1/2 of the detection limit.

#### 2.2.4 Ozone

Surface O<sub>3</sub> was measured by an O<sub>3</sub> analyzer located in the Temporary Atmospheric Weather Observatory (TAWO) building a few hundred meters from camp by the National Oceanic and Atmospheric Administration (NOAA) as part of the core atmospheric measurements that began in 2000 (Petropavlovskikh and Oltmans, 2012). Hourly averaged data for 2008, 2009, and 2010 were downloaded from the Earth System Research Laboratory Global Monitoring Division (ESRL-GMD) website (<http://www.esrl.noaa.gov/gmd/dv/data/>).

#### 2.2.5 FLEXPART

The Lagrangian particle dispersion model FLEXPART (version 8.2) was utilized to identify potential periods when polluted air masses impacted the measurement site. FLEXPART simulates atmospheric transport using wind fields from global forecast models to determine source to receptor pathways of air masses (Stohl et al., 2005). The model was driven with meteorological analysis data from the European Centre for Medium Range Weather Forecasts (ECMWF) and ~~run~~ ran backward in time in so-called “retroplume” mode (Stohl et al., 2003). Every 3 h, 40 000 particles were released from the measurement site location and followed backwards in time for 20 days. Sensitivities to anthropogenic and fire emissions

were determined during the backwards simulations and are proportional to the particle residence time over the source areas. In this work, a black carbon tracer was used to simulate both anthropogenic ( $BC_{\text{anthro}}$ ) and biomass burning emissions ( $BC_{\text{fire}}$ ). For the BC anthropogenic tracer the Emissions Database for Global Atmospheric Research (EDGAR) UNEP BC report 2005 data (UNEP, 2011; Shindell et al., 2012) was used. To estimate the BC fire emissions, MODIS hot spot data (Justice et al., 2002; Giglio et al., 2003) was used to estimate the area burned (180 hPa per MODIS hot spot) and combined with a combustion efficiency, emission factor, and fuel load, which were all based on land use type. The BC tracer was susceptible to both wet and dry deposition during transport. The wet ~~deposition process is simplified in the simulations (no ageing of BC with scavenging coefficient used in the model is more representative of a hydrophilic aerosol, however, there is no conversion from hydrophobic to hydrophilic properties ) and may result with aging BC in the model, therefore, greater scavenging may occur closer to the source region, resulting~~ in an underestimation of the BC tracer at Summit (Stohl et al., 2013). However, for this study the tracer was only used to identify events; therefore, absolute BC values were not required. Carbon monoxide can also be used as a tracer for pollution transport. Simulations using CO were performed for the anthropogenic tracer, however, the BC tracer was used in this study as simulations were available for both anthropogenic and fire tracers as part of the POLARCAT campaign, and thus allowed for consistency between the biomass burning and anthropogenic analysis. A comparison was made between the CO and BC anthropogenic tracers to determine whether pollution events were missed when using the BC tracer, as a result of deposition. A time series and correlation plot for the two tracers from summer 2008 to 2010 are shown in Figures S1 and S2 in the supplementary material. The result suggests that although there may be some differences in the magnitude of the FLEXPART tracers, the transport simulated with the BC tracer correlates well with the CO tracer (Pearson's correlation coefficient,  $R=0.97$ ), therefore, significant pollution events were unlikely to be missed.

## 3 Results and discussion

### 3.1 Seasonal cycles

#### 3.1.1 Reactive nitrogen oxides

Figure 1a–d shows the statistical analyses of the monthly averaged  $\text{NO}_y$ ,  $\text{NO}_x$ , and PAN,  $\text{PAN}$ , and  $\text{O}_3$  ambient mole fractions, respectively, during the measurement period from July 2008 to July 2010, and results for from January 2008 to December 2010. A malfunction with the  $\text{NO}_{xy}$  instrument resulted in missing  $\text{NO}_x$  and  $\text{NO}_y$  data from 24 November 2008 to 30 March 2009, hence the number of 30min averages included in the monthly distribution is much lower for December to March than for other months as indicated by the values at the top of each plot. 2009. Seasonal cycles are observed in measured ambient mole fractions of  $\text{NO}_x$ ,  $\text{NO}_y$ , and PAN, for all measured species, with higher levels for all species during the late winter/early spring period and lower mole fractions from summer to fall. The positively skewed whiskers indicate that air masses with elevated levels of the measured species were sampled year-round.  $\text{NO}_x$ ,  $\text{NO}_y$ , and PAN were sampled year-round. Anthropogenic and biomass burning emissions transported to the site from North America and Europe are a major source of these enhancements in  $\text{NO}_x$ ,  $\text{NO}_y$ , and PAN (see Sect. 3.2). Observations from the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) mission in 2008 show that the transport of air from the Arctic stratosphere to the upper troposphere may also result in mixed stratospheric-tropospheric air masses, above 5 km, have elevated levels of  $\text{O}_3$  precursors such as  $\text{NO}_x$ ,  $\text{NO}_y$ , and  $\text{HNO}_3$  and PAN above 5, which can subsequently be converted to PAN (Liang et al., 2011). Therefore, high mole fractions observed in PAN,  $\text{NO}_y$ , and  $\text{NO}_x$ , may also be the result of sampling air masses mixed with those originating from the stratosphere and upper troposphere.

Table 1 gives a statistical summary for the monthly averages of PAN,  $\text{NO}_y$ ,  $\text{NO}_x$ , and  $\text{O}_3$  during 2008–2010. Maxima in monthly mean mole fractions of PAN and were observed occur in April with mean levels of  $241 \pm 77$ – $233 \pm 68$  ( $1\sigma$ )  $\text{pmol mol}^{-1}$  and  $321 \pm 98$ – $280 \pm 102$   $\text{pmol mol}^{-1}$  respectively. PAN mole fractions at, for 2009 and 2010,

respectively. The difference between monthly mean PAN levels observed in April 2010 and April 2009 are within the measurement uncertainties (as shown in Figure S3, supplementary material), however, the 30 minute averages (shown in Figure S4) indicate high levels of PAN,  $\text{NO}_y$ , and  $\text{NO}_x$  in April 2010. These high levels are explored further in Sect. 3.2.1. Monthly mean  $\text{NO}_y$  mole fractions also peaked during April 2010 at  $356 \pm 103$  pmol mol<sup>-1</sup>. PAN mole fractions at Summit and the magnitude of the PAN spring-time peak are consistent with observations at other high latitude sites such as Zeppelin Mountain, Svalbard (Beine et al., 1997; Solberg et al., 1997; Beine and Krognes, 2000), and Alert, Northwest Territories, Canada (Worthy et al., 1994; Dassau et al., 2004). There is a rapid transition towards lower levels of PAN in the summer, with a The minimum mean monthly average of  $66 \pm 29$  in July occurred in July with PAN levels of 64 pmol mol<sup>-1</sup> and 68 pmol mol<sup>-1</sup> for 2008 and 2009, respectively.  $\text{NO}_y$  mole fractions do not decrease as quickly as PAN from spring to summer as PAN and reach a minimum monthly average of 400 in during September. We find that the PAN and  $\text{NO}_y$  summer mole fractions observed here are comparable to previous measurements performed at the same site in 1998 and 1999, when observed PAN levels were typically 20–150 pmol mol<sup>-1</sup>, and  $\text{NO}_y$  levels ranged between 100–300 pmol mol<sup>-1</sup> (Honrath et al., 1999; Ford et al., 2002). The slower decrease in  $\text{NO}_y$  from spring to summer, compared to PAN, is a result of the presence of  $\text{NO}_x$  and odd  $\text{NO}_y$  (odd  $\text{NO}_y = \text{NO}_y - \text{PAN} - \text{NO}_x$ ) over the summer months and is discussed further below.

The seasonal cycle of PAN is governed by the rate of thermal decomposition and transport patterns. The warmer summer temperatures result in the decomposition of PAN during long range transport; additionally, during the summer months the polar front recedes north, thus reducing the potential for anthropogenic emissions to reach the measurement site (Beine and Krognes, 2000; Stohl, 2006). Measurements have shown that PAN is typically the largest contributor to  $\text{NO}_y$  in the Arctic, due to the rapid formation of PAN near the source region and a long lifetime in the free troposphere (Solberg et al., 1997; Munger et al., 1999; Ford et al., 2002; Alvarado et al., 2010; Singh et al., 2010; Liang et al., 2011).



However, there have been very few studies on the seasonal variability of the  $\text{NO}_y$  speciation in the Arctic due to limited measurements over winter months.

The full annual cycle of  $\text{NO}_y$  contributions from PAN and  $\text{NO}_x$  during this study provides some information on the  $\text{NO}_y$  speciation, year-round-year-round, at Summit. The results plotted in Fig. 2 show Table 1 shows that PAN is the dominant form of  $\text{NO}_y$  all year-round, with monthly average-mean  $[\text{PAN}]/[\text{NO}_y]$  ratios above 60% in spring and fall, reaching a maximum of 78.81% in April and 2010. The lowest  $[\text{PAN}]/[\text{NO}_y]$  ratios occurred during the summer, with a minimum of 49% monthly mean of 45% in July .Over the summer, 2008. The seasonal cycle for  $\text{NO}_x$  contributes approximately 10–13% to the total does not follow PAN and  $\text{NO}_y$ . In winter this decreases at Summit. As shown in Table 1, monthly mean  $\text{NO}_x$  levels peak one month later than  $\text{NO}_y$  and PAN, coinciding with an increase in solar radiation. Thus, the contribution of  $\text{NO}_x$  to  $\text{NO}_y$  maximizes over the summer (9–14%). The  $\text{NO}_x$  contribution decreased to  $\lesssim 4\%$  over winter and often  $\text{NO}_x$  levels were below the detection detection limit of the instrument. The thermal decomposition of PAN is a possible local source of ambient  $\text{NO}_x$  during spring and summer months (Beine et al., 1997), however, the contribution is expected to be very low at Summit as ambient temperatures during the measurement period were always below  $0^\circ\text{C}$ .

Studies have hypothesized that photochemical reactions within the snowpack result in the release of  $\text{NO}_x$  and also HONO to the overlying atmosphere (e.g., Honrath et al., 1999, 2000a, b, 2002; Munger et al., 1999; Beine et al., 2002; Dibb et al., 2002). Thus, the increase of  $\text{NO}_x$  with radiation in spring suggests a possible photochemical source. This conclusion is supported by results from an investigation focusing on  $\text{NO}_x$  and  $\text{O}_3$  levels in the snowpack at Summit. Measurements of  $\text{NO}_x$  were performed at various levels within and above the snowpack, during the same period as this study. The data, supported by model results from a newly developed 1-D process scale model, show that  $\text{NO}_x$  levels, in the upper regions (0–30 cm) of the snowpack, peak around solar noon as a result of  $\text{NO}_3^-$  photolysis (Van Dam et al., 2014; Murray et al., 2014).

Fig. 2 shows the monthly averaged mole fractions of  $\text{NO}_y$  and PAN+ $\text{NO}_x$  during the measurement period. The results show that the sum of PAN and  $\text{NO}_x$  cannot

always account for the monthly averaged  $\text{NO}_y$  within the measurement uncertainty range, suggesting a significant source of odd  $\text{NO}_y$  at Summit. When considering the 30 minute averages,  $\sim 66\%$  of the data show significant odd  $\text{NO}_y$  levels (i.e. cannot be accounted for by total measurement uncertainty alone). What is particularly striking about the  $\text{NO}_y$  speciation ~~shown in Fig. 2~~ is that odd  $\text{NO}_y$  levels can be ~~significant, particularly over winter, when they reach a maximum monthly mean of  $95 \pm 36$~~  very large over winter (Fig. 3). From December 2009–April 2010, the monthly mean odd  $\text{NO}_y$  was always above  $70 \text{ pmol mol}^{-1}$ , reaching a maximum of  $93 \pm 31 \text{ pmol mol}^{-1}$  (mean  $\pm$  SD uncertainty) in February 2010. Odd  $\text{NO}_y$  ~~decreases to approximately 30–50~~ decreased to  $\sim 30 - 56 \text{ pmol mol}^{-1}$  in the summer months; however, this still accounts for  $\sim 20-38$  up to  $\sim 40\%$  of the total  $\text{NO}_y$  during this period.

Snowfall rates increase during the summer months ~~over—Summit (Dibb and Fehsenfeld, 2004) therefore at Summit (Dibb and Fehsenfeld, 2004)~~ therefore, an increase in deposition of water-soluble species such as  $\text{HNO}_3$  to the snowpack may result in the depletion of ambient odd  $\text{NO}_y$  in the summer. The increase in solar radiation may also play an important role in the reduction of odd  $\text{NO}_y$  species in the summer. Solberg et al. (1997) observed a decrease in odd  $\text{NO}_y$  with increasing solar UV radiation in Spitsbergen, Norway. The authors suggested that species such as  $\text{HONO}$ ,  $\text{HNO}_3$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HO}_2\text{NO}_2$ , and alkyl nitrates may contribute to  $\text{NO}_y$  over the winter with the impact reducing in spring due to an increase in photolysis. A study on the seasonal variability of alkyl nitrates at Summit in 1998–1999 found that the light  $\text{C}_1\text{--C}_4$  alkyl nitrates ~~peak through late winter until April with total mole fractions between 30 and 42~~ peaked over winter (Swanson et al., 2003). The monthly mean total  $\text{C}_1\text{--C}_4$  mole fraction during February 1999 was  $33 \text{ pmol mol}^{-1}$  (Swanson et al., 2003). Therefore, Assuming a similar level during February 2010, alkyl nitrates ~~could account for a large portion~~ would account for  $\sim 1/3$  of the odd  $\text{NO}_y$  observed during the winter months at Summit. However, there still remains this month. Taking into account measurement uncertainties, there remains, therefore, a large fraction of  $\text{NO}_y$  unaccounted for over winter, and further measurements are required during this period to determine both the species and sources of this odd  $\text{NO}_y$ .

~~The seasonal cycle for does not follow PAN and~~ Results from this study show, despite the odd  $\text{NO}_y$  at Summit. As shown in Table 1, monthly mean levels peak one month later than and PAN, increasing from  $6 \pm 11$  in February to  $29 \pm 24$  in May, coinciding with an increase in solar radiation. Thus, the relative contribution of to maximizes over the summer when is still high but PAN levels decrease. The thermal decomposition of PAN is a possible source of during spring and summer months; however, the contribution is expected to be very small in this high latitude region as temperatures during the measurement period were always below 0C (Beine et al., 1997). Thus, the increase of with radiation in spring suggests a possible photochemical source. The role of snowpack emissions on species within the arctic boundary layer is still uncertain, however, studies have suggested that photochemical reactions within the snowpack may result in the release of and HONO to the overlying atmosphere (e.g., Honrath et al., 1999, 2000a, b, 2002; Munger et al., 1999; Beine et al., 2002; Dibb et al., 2002).

During levels decreasing from late spring to summer, odd  $\text{NO}_y$  species can contribute over twice as much as  $\text{NO}_x$  to the total  $\text{NO}_y$ . To investigate the source of ~~these the odd~~  $\text{NO}_y$  species and the possible impact from snowpack photochemistry we ~~have~~ analyzed the diurnal variability of  $\text{NO}_x$ ,  $\text{NO}_y$ , and odd  $\text{NO}_y$  at Summit. ~~Our measurements of and mole fractions separately for March, April, May, and June, 2008–2010,~~ at a height of  $\sim 7.5$  m above the snowpack display clear diurnal cycles from April–June (Fig. 3a, b). ~~It is observed that~~ 4). The amplitude of the diurnal cycles for  $\text{NO}_x$ ,  $\text{NO}_y$ , and odd  $\text{NO}_y$  (determined as the difference between the minimum and maximum 2 h median values), peaked in April/May. For all 4 months, the amplitude of the  $\text{NO}_y$  diurnal cycle is greater than ~~for that of~~  $\text{NO}_x$ , with average diurnal amplitudes of 33. Diurnal amplitudes, in April, were 36  $\text{pmol mol}^{-1}$  and 1416  $\text{pmol mol}^{-1}$  for  $\text{NO}_y$  and  $\text{NO}_x$  respectively. ~~It has been hypothesized that~~ Odd  $\text{NO}_y$  is shown to peak just after solar noon (Fig. 4i, j, k, l) suggesting a photochemically produced odd  $\text{NO}_y$  species ~~such as~~ may be present. ~~It has been hypothesized that~~  $\text{HNO}_3$  and HONO, may account for some of the  $\text{NO}_y$  diurnal variability at Summit (Ford et al., 2002). ~~An analysis of the diurnal cycle for odd (Fig. 3c) averaged over April–June from~~

2008–2010 shows that the odd peaks just after solar noon in our measurements, suggesting a photochemically produced odd species may be present. The diurnal variability of ambient  $\text{NO}_y$  species above the snowpack, however, is further complicated by vertical mixing and boundary layer dynamics, which may vary with season. For example, the downward transportation of pollution from aloft due to a growing boundary layer may result in a daytime maximum-maxima in  $\text{NO}_x$  and  $\text{NO}_y$ , which then decreases at night due to surface uptake. There is also a possible contribution to odd  $\text{NO}_y$  in the summer from long range transport of reactive nitrogen species such as  $\text{HNO}_3$  and alkyl nitrates as these species have previously been observed in anthropogenic and biomass burning plumes in the Arctic (Liang et al., 2011; Wespes et al., 2012). It should also be noted that some of the variability in the

Ambient  $\text{HNO}_3$  and HONO have been measured at Summit during a number of spring and summer campaigns. Levels of  $\text{HNO}_3$  are typically on the order of a few tens  $\text{pmol mol}^{-1}$ , and HONO levels are lower with mole fractions of  $\sim 10 \text{ pmol mol}^{-1}$  or less (Dibb et al., 1994, 1998; Honrath et al., 1999; Dibb et al., 2002; Ford et al., 2002; Yang et al., 2000). Median mixing ratios of  $\text{HNO}_3$  and HONO, measured during May and June, 2010, with a mist chamber/ion chromatography (MC/IC) system ( $\sim 1.5 \text{ m}$  above the snowpack), were  $7 \text{ pmol mol}^{-1}$  and  $13 \text{ pmol mol}^{-1}$ , respectively (J.E. Dibb and M.G. Hastings, personal communication). Note that HONO measurements by MC/IC in polar regions should be viewed as an upper limit to the true value, due to potential interferences from other species (Chen et al., 2004; Liao et al., 2006). A direct comparison of  $\text{HNO}_3$  and HONO with calculated odd  $\text{NO}_y$  speciation discussed here may be influenced by uncertainties in the PAN measurements which increased in spring 2009. The year-round measurements obtained from Summit in 2008–2010 provide new insight on the relative role of photochemistry and boundary layer stability on diurnal cycles of nitrogen oxides and is the subject of future investigation. levels is not possible for 2010 because PAN measurements were unavailable after April. Monthly mean odd  $\text{NO}_y$  levels calculated for May and June in 2009 were 50 and 36  $\text{pmol mol}^{-1}$ , respectively. Summer levels of alkyl nitrates are expected to be low at Summit with Swanson et al. (2003) measuring monthly mean levels (total  $\text{C}_1\text{--C}_4$ ) of  $\sim 10\text{--}20 \text{ pmol mol}^{-1}$  between May and August. Assuming

alkyl nitrate levels of  $\sim 15$  pmol mol<sup>-1</sup> during May/June, the sum of HNO<sub>3</sub>+HONO+alkyl nitrates are comparable to the odd NO<sub>y</sub> levels measured at Summit (when considering measurement uncertainties). Particulate nitrate may also contribute a small amount to the total NO<sub>y</sub>, however, this contribution is expected to be small as ambient p-NO<sub>3</sub><sup>-</sup> levels are typically lower than HNO<sub>3</sub> at Summit (Dibb et al., 1994). A recent study in Antarctica, during polar winter, has shown that absorbed HO<sub>2</sub>NO<sub>2</sub> can be emitted into the atmosphere above the snowpack when temperatures increase (Jones et al., 2014). Therefore, HO<sub>2</sub>NO<sub>2</sub>, may also contribute to the odd NO<sub>y</sub> measured at Summit, during winter and summer.

### 3.1.2 Non-methane hydrocarbons

Figure 4-5 shows the results for the C<sub>2</sub>-C<sub>5</sub> alkane NMHC measured during 2008-2010 at Summit. The in ambient air. Measurements of primarily firn air conducted with this system were presented by Helmig et al. (2014). NMHC show a strong seasonal cycle with maximum mole fractions during the winter and early spring period and a rapid decline towards the summer, due to an increase in photochemical processing. The monthly mean averages for the C<sub>2</sub>-C<sub>5</sub> NMHCs are given in Table ??-The 2. During the summer period, measured mole fractions of the heavier NMHC were below or close to the detection limit. As expected, the phase of each NMHC is shifted due to the rate of reaction with OH. The lightest of the NMHC shown in Fig. 4-5a, ethane (C<sub>2</sub>H<sub>6</sub>), which peaks in March with a monthly mean of  $1974 \pm 209$  pmol mol<sup>-1</sup> (mean  $\pm 1\sigma$ ) and reaches a minimum of  $633 \pm 65$  in 2009, and  $1835 \pm 174$  pmol mol<sup>-1</sup> in 2010, and declines to a minimum of  $\sim 600$  pmol mol<sup>-1</sup> in July/August. Heavier NMHC have lower mole fractions and peak earlier in the year, and reach a minimum earlier in summer as their due to their faster rate of reaction with OH is much faster. The seasonal cycle of NMHC at Summit including NMHC firn air measurements from 2008 to 2010 have previously been presented in detail (Swanson et al., 2003; ?; ?).

A comparison between the two winters shows monthly mean NMHC levels were consistently higher from November-March 2008/2009 when compared to 2009/2010.

However, the standard deviation values during the second winter are typically higher, suggesting greater variability in the NMHC levels in 2009/2010. The non-averaged NMHC data (Figure S5, supplementary material), show there is considerable short term variability in the NMHC mole fractions superimposed on the seasonal cycle, in particular during the winter months. Short term elevated NMHC levels were observed during both winters and indicate fast transport of polluted air masses to the site.

The seasonality of NMHC can provide some insight into the potential for the photochemical production of  $O_3$  in the Arctic troposphere. The accumulation of  $O_3$  precursors, such as nitrogen oxides and NMHC over winter has been suggested as a potential in situ source of  $O_3$  that may contribute to the tropospheric  $O_3$  peak observed in spring in the Arctic (e.g., Penkett et al., 1993; Honrath et al., 1996; Monks, 2000; Blake et al., 2003; ?) (e.g., Penkett et al., 2003). Measurements of NMHC and  $O_3$  during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) campaign show that within the mid-troposphere, total NMHC decreased by  $\sim 6.2$  ppbC from February to May, and that  $O_3$  increased by  $\sim 16$  ppbv during the same period (Blake et al., 2003). The data from this study show similar results for NMHC, with the sum of the  $C_2$ – $C_6$  NMHC decreasing by  $\sim 4.4$ – $\sim 4.6$  ppbC from February to May. The magnitude of the  $O_3$  increase, at  $\sim 8$  ppbv, is smaller than observed during TOPSE, however, the photochemical processing of NMHC in spring may contribute to the spring time peak of  $O_3$  over Greenland.

### 3.2 Variability in ozone and its precursors from anthropogenic and biomass burning emissions

In Sect. 3.1, the seasonal cycles for  $O_3$  precursors at Summit were discussed. Short term enhancements in  $O_3$  precursor levels indicated that the site was often impacted by polluted air masses from lower latitudes. In this section the interannual and short term variability in the measured species at Summit, from 2008–2010 due to variability, as a result of changes in transport pathways and the relative source contributions of pollutants from North America, Europe, and Asia are investigated. Anthropogenic and biomass burning emissions are considered separately, over different seasons.

### 3.2.1 Winter/spring anthropogenic impacts

Figure 4 shows that there is considerable variability in the NMHC mole fractions superimposed on the seasonal cycle; in particular during the winter months, suggesting polluted air masses were transported to the measurement site during this period. Mean  $\pm 1\sigma$  mole fractions of ethane were  $1.86 \pm 0.24$  in December Fig. 6 shows the total monthly averaged FLEXPART tracer simulations for  $BC_{anthro}$  and  $BC_{fire}$  tracers for 2008 to March 2009 and  $1.69 \pm 0.31$  for December 2009 to March, 2009, and 2010. The 95th percentile values were the same for the two periods (2.2) suggesting that polluted air masses had a strong impact during both seasons. However, The data show that anthropogenic pollution impacts started to increase in November, peaking over the dark winter period, and then decreased in late spring. The total  $BC_{anthro}$  tracer at Summit is dominated by emissions from North America, Europe, and Asia. Source contributions from each continent can vary month-to-month and year-to-year, however, European emissions were typically the largest contributor to the total monthly  $BC_{anthro}$  during the winter period, when the polar front recedes northwards. During winter (NDJFM) 2008-2009, 56 % of the total  $BC_{anthro}$  originated from Europe, with 32 % from North America and 11 % from Asia. The following winter (NDJFM 2009-2010), European emission were higher at 69 %, with North America and Asia contributing 19 % and 11 %, respectively. A very small contribution ( $\leq 1\%$ ) of the total anthropogenic tracer originated from other continents. Fig. 6 shows that the contribution to the average background level (given by the 20th percentile of the measurements during each period) was lower in 2009/2010 (1.4) than total  $BC_{anthro}$  from Asia is low year-round. Hirdman et al. (2010) investigated the contribution of pollutants from different sources to various Arctic surface sites from 2002-2007. The authors show that Summit is less sensitive to emissions from the surface in the Arctic region, than low elevation surface stations, and air masses transported to Summit from outside of Greenland are likely to originate from Europe and North America.

In contrast to the anthropogenic tracer, North American emissions dominated the total  $BC_{fire}$  tracer, with 69 % of the total  $BC_{fire}$  tracer originating from this

region from July 2008 to July 2010. This result is expected as air masses arriving at Summit typically originate from North America during the summer months (Kahl et al., 1997). Previous studies have also shown that North America is a major source of biomass burning emissions transported to Summit (e.g., Whitlow et al., 1994; Legrand and de Angelis, 1996; Fuhrer and Legrand, 1997; Alexander

The high Asian contribution to the total  $BC_{\text{fire}}$  tracer in spring 2008 is in agreement with observations during the POLARCAT campaigns in 2008, when a number of biomass burning plumes were observed from Siberia (Law et al., 2014, and references therein). During the measurement period, however, the contribution from Asian biomass burning emissions at Summit was low, compared to North America. European biomass burning emissions were also low, except during a period in March, when European fires dominated the total  $BC_{\text{fire}}$  tracer. In 2008 and 2010 the contribution from total biomass burning emissions peaked in August. In 2009 (1.6) suggesting that in 2009/2010 there was a greater number of clean air masses or periods with low emissions impacting the site, however, there was no significant peak in biomass burning emissions at Summit, and  $BC_{\text{fire}}$  tracer levels during the summer were much lower overall.

FLEXPART tracer simulations indicate that during the months December to March, biomass burning events were limited to a ~1 week period in March. Variability in  $BC_{\text{fire}}$  tracer can be a result of a change in emissions or transport pathways. Overpass and cloud-corrected MODIS Terra (MOD14CMH) and Aqua (MYD14CMH) fire pixel counts from the Climate Modeling Grid (CMG) product were downloaded from the University of Maryland ftp server (<ftp://fuoco.geog.umd.edu>) to investigate the variability in fire emissions. The monthly total fire pixel count and total Fire Radiative Power (FRP), over the zonal region 40-75 N, were determined from March to September for 2008, 2009 (see Table 2); therefore, we focus the analysis on anthropogenic emissions between these months, and 2010 separately. The results (Figures S6a-d, supplementary material) show that there was a reduction in total fire counts and FRP in summer 2009, when compared to 2008 and 2010.



In the next two sections, the impact of anthropogenic and biomass burning emissions on  $O_3$  and  $O_3$  precursors are investigated.

### 3.2.1 Anthropogenic impacts

To investigate the source of the observed variability and the impact on ozone precursor levels at Summit, the anthropogenic tracer from FLEXPART retroplume simulations ( $BC_{\text{anthro}}$ ) and NMHC emissions ratios were used to determine changes in the transport pathways and relative source contributions of anthropogenic emissions from different continents.

An event with pollution transport was defined as identified when the  $BC_{\text{anthro}}$  tracer was greater than ~~75th~~ the 75<sup>th</sup> percentile of the total  $BC_{\text{anthro}}$  during the 2 year measurement period (corresponding to  $BC_{\text{anthro}} > 0.0082 \text{ pmol mol}^{-1}$ ) for a minimum of 12 h. The FLEXPART temporal resolution for backward simulations is 3 h, so identifying events when the  $BC_{\text{anthro}}$  was enhanced for at least 12 h ensured that significant polluted air masses impacted the site ~~and also allowed for some temporal mismatches in simulated and observed plume arrivals. Using these thresholds.~~ Using these thresholds, 85 anthropogenic pollution events were observed during the measurement period. Details for each event, including start date, FLEXPART tracer levels, and trace gas enhancements are presented in Table S1 in the supplementary material. The mean weighted age of the plume was also calculated for each FLEXPART retroplume, to determine the typical transport time for the events. As shown in Fig. 6, 42 events were identified in total for the periods December to March anthropogenic impacts are observed year-round, however, during the summer anthropogenic pollution events can be mixed with biomass burning emissions. Therefore, for this study, the focus is on events between November and March when FLEXPART anthropogenic tracer levels peaked and biomass burning emissions were typically low. In total, 52 events were identified during the periods November to March 2008/2009 and December to March 2009/2010 (21 events each season). FLEXPART retroplume analysis also provides information on the source contribution to these events, shown in Figs. 5 and 6. In 2008/2009, the  $BC_{\text{anthro}}$  tracers originating from North America and Europe accounted for 26 and 69, respectively, to the total  $BC_{\text{anthro}}$  tracer mass during the pollution 2009 (events :

In 12-37) and November to March 2009/2010, North American emissions were much lower, contributing only 13 of the total  $BC_{anthro}$  tracer mass, with European emissions dominating with 82. In both years impacts from Asian emissions were low ( $< 6$ ) and negligible from other continents. The mean weighted age of the plume was calculated for each FLEXPART retroplume, to determine the typical transport time for the events. The median time for 2010 (events 55-80). Typical mean transport times for polluted air masses to be transported to the site was approximately 11 in winter were  $\sim 11 - 12$  days.

During each event, the mean  $\Delta PAN$ ,  $\Delta NO_y$ ,  $\Delta NO_x$ ,  $\Delta O_3$ , and  $\Delta C_2H_6$  were determined/calculated, where  $\Delta$  is the enhancement above background levels (determined as the 20<sup>th</sup>-20<sup>th</sup> percentile for each species each month). For the 42, for each month and year. Care must be taken when defining a background level as the enhancement ratios are strongly dependent on this value. Initial analyses used a single background value for each month, determined from the 20<sup>th</sup> percentile of data from all years, however, this resulted in many negative or low enhancement ratios which were not consistent with the observations. A background value for each individual month and year was found to be more appropriate, as these levels change slightly from year to year. For the 52 anthropogenic events identified, the mean enhancements during each event ranged between during winter, the median (and range) value of the enhancements were 24 ( $-35$  and  $+27322$  to  $312$ )  $pmol\ mol^{-1}$  for PAN, 0 to  $+257.0$  ( $\sim 0$  to  $54$ )  $pmol\ mol^{-1}$  for  $NO_x$ , 67 ( $-17$  to  $+336273$ )  $pmol\ mol^{-1}$  for  $NO_y$ , 1.1 ( $-3.9$  to  $7.5$   $6.7$  to  $7.6$ )  $nmol\ mol^{-1}$  for  $O_3$ , and 148 ( $-0.3$  to  $+1.0244$  to  $1120$ )  $pmol\ mol^{-1}$  for  $C_2H_6$ , with negative results representing less than 20 of.

Tests were performed to determine whether temporal mismatches occurred between the simulated plume arrivals and peaks in the measured species as a result of errors in the wind fields used in FLEXPART. Each event identified above was extended in time by 3, 6, 9, and 12 hours prior to and after the event, and new  $\Delta$  values for the events for PAN, ethane, and and 26 for  $O_3$ . Negative enhancement values may be associated with erroneous transport simulated by FLEXPART as the mean enhancement for each species is dependent on the timing and length of the events as determined from FLEXPART. During the winter/spring period, there is a large gradient precursors were calculated. The analyses showed that

extending the event window did not have a large impact on the mean  $\Delta$  values when mole fractions were low, i.e. levels were typically near the background already and extending the event time did not result in additional plumes being captured. During those events with large peaks in  $O_3$  precursors with latitude (e.g. Blake et al., 2003), therefore, the transport of air masses from the south may also result in lower total mole fractions at Summit, despite pollution input from emission sources and precursors,  $\Delta$  values decreased, with increasing window lengths as a result of capturing lower background levels. Thus, the event times calculated using the original threshold appear to be in agreement with the pollution plume arrival times.

Figures 7 and ?? show a time series of the measurements between December and March for 2009/2010. Over the two winters, negative mean  $\Delta NO_y$  values were observed during 3 events (event 72, 78, and 2008/2009, respectively). During these periods, events with elevated ethane, PAN and levels are observed; however, what is particularly interesting is that during some of these events, low mole fractions ( $\Delta < 0$ ) were measured. Analyses of PAN during 5 events (18, 65, 69, 72, and 78) and negative  $\Delta$  and FLEXPART BC tracer masses from July 2008 to July 2010 show that decreases in below the background level (when  $C_2H_6$  during 4 events (64, 72, 73 and 79). Negative  $\Delta$  was negative for at least 12h and reached a minimum  $\Delta$  level below  $-2$ ) were observed throughout the year. During April to September 45 events with low ozone were observed, however, these events were typically associated with low levels of pollution with only 10 out of the 45 events classified as polluted (as indicated by either high FLEXPART values were associated with, 1) events when the peak  $BC_{anthro}$  ( $> 75$ th percentile) or  $BC_{fire}$  ( $> 90$ th percentile) tracers). For the remaining 35 events enhancements in level was low (relative to  $BC_{anthro}$  peak levels during all events), indicating a small impact from anthropogenic pollution, 2) missing data points during the event, or 3) events when small enhancements in PAN and  $NO_y$ , PAN and ethane were either low or negative, suggesting pollution levels were minimal in the sampled air masses occurred, however, low mole fractions were also observed during the same event period.

~~Decreases~~ Analyses of  $\Delta O_3$  and FLEXPART BC tracer masses show decreases in  $O_3$  (where the minimum  $\Delta O_3 < -2 < 0$  nmol mol<sup>-1</sup>) that coincided, coinciding with anthropogenic pollution events, were observed during ~~28 periods~~ 20 periods in total from July 2008 to July 2010, with ~~21~~ 16 of these events occurring between ~~October~~ November and March, when sunlight is at a minimum. Thus, it is possible that the decrease in Negative  $\Delta O_3$  observed during winter/early spring is due to titration of ~~do~~ not always coincide with low  $O_3$  by NO within the sampled air mass soon after emission (Eneroth et al., 2007; Hirdman et al., 2010) precursor levels. For example, from ~~23 to 31~~ January 2010 (indicated by the shaded area in Fig. 7), Figure 7 shows a time series of measurements between January 10 and March 2, 2010. During this period, events with elevated ethane, NO<sub>y</sub>, PAN, and NO<sub>x</sub> levels are clearly correlated with enhancements in the FLEXPART BC tracer, suggesting polluted air masses impacting the site; however, what is particularly striking is that  $O_3$  decreased rapidly during two periods, coinciding with increases in precursors. Using the vertically integrated emission sensitivity (also called the total column sensitivity, measured in nanosecond meters per kg) simulated by FLEXPART, the overall pathways of the air masses during these events can be determined. As shown in Fig. ??a, the air mass on 23 January originated from Northern Europe and was transported to Summit in only a few days. The mean weighted age of the plumes estimated from FLEXPART during this period decreased from ~15 to 8 days (Fig. 7).

mole fractions were low during some events (e.g. events 70, 71 and 74). Studies have shown that NMHC ratios can provide an indication of the photochemical aging of the air mass as the rate of reaction of different NMHC, and hence the ratio, is dependent on the amount of photochemical processing that occurs during transport (Parrish et al., 2004; Helmig et al., 2008; Honrath et al., 2008). High photochemical processing results in a decrease in the ln([propane]/[ethane]) ratio as propane reacts more readily with OH than ethane. The two low ozone events ~~between 23 and 31 January 2010~~ (70 and 71) on ~~22~~ and 29 January, coincided with enhancements in the ln([propane]/[ethane]) ratio, suggesting low photochemical processing, and ~~the impact of~~ fresher air masses, i.e. air that was subjected to more recent pollution before reaching at the site. However, care must be

~~taken when interpreting this result as~~ It is difficult to obtain absolute air mass ages from NMHC ratios, due to dilution of the measured species during transport ~~will also have an impact on the mole fractions measured at the site.~~ PAN and ethane reached peaks of 188, however, the enhancements in the  $\ln([\text{propane}]/[\text{ethane}])$  ratio during the two pollution events coincide with sudden decreases in the mean weighted age of the plumes, estimated from FLEXPART. The vertically integrated emission sensitivity (also called the total column sensitivity, measured in nanosecond meters per kg) simulated by FLEXPART, was used to determine the air mass transport pathway.

Fig. 8a), shows the total column sensitivity from FLEXPART on 23 January (during event 70). The air mass originated from Northern Europe and resided in the lower  $\sim 2$  km during transport, until 1 day upwind when the air mass ascended over the surface of the Greenland ice sheet to the measurement site. Mean  $\Delta$ PAN and  $\Delta$ C<sub>2</sub>H<sub>6</sub> levels during this event were 67.1 pmol mol<sup>-1</sup> and 31037 pmol mol<sup>-1</sup>, respectively, during the event on 23 January, supporting the FLEXPART analyses ~~which indicated a~~ indicating a polluted air mass ~~originating from Europe was sampled at the site was sampled~~ (note there were no NO<sub>y</sub> or NO<sub>x</sub> data available during this period). Ozone, however, decreased ~~by~~, on average, 6.2 nmol mol<sup>-1</sup> below the monthly background level ( $O_{3(\text{bkg})} = 41.6$  ( $O_{3(\text{bkg})} = 45$  nmol mol<sup>-1</sup>) ~~to reach, and reached~~ a minimum level of 35.4 nmol mol<sup>-1</sup>. ~~The FLEXPART retroplume on this day shows that air mass resided in the lower  $\sim 2$  during transport, until 1 day upwind when the air mass ascended over the surface of Greenland to the measurement site (Fig. ??a), thereby reducing the potential to mix with high from stratospheric origin.~~ In contrast, a few hours later the transport patterns quickly changed, and the air masses sampled at Summit originated from high altitudes over North Canada, as shown in Fig. ??8b. As a result, O<sub>3</sub> levels increased and PAN and ethane decreased back toward their background levels ( $\text{PAN}_{(\text{bkg})} = 72_{(\text{bkg})} = 76$  pmol mol<sup>-1</sup>,  $\text{C}_2\text{H}_6_{(\text{bkg})} = 1.55 \text{C}_2\text{H}_6_{(\text{bkg})} = 1442$  pmol mol<sup>-1</sup>). Air originating from the high Arctic region was sampled at the site until 29 January, when the ~~retroplume moved southward~~ air transport moved southward, and air masses residing in the lower troposphere over North America transported polluted air to Summit (Fig. ??8c). From 29–30 January (event 71), ethane, NO<sub>y</sub>, PAN, and NO<sub>x</sub> all increased ~~again by 1.3~~ with mean

enhancements of 1119, 180, 99.0, and 13.8, 267, 146 and 32 pmol mol<sup>-1</sup> respectively, from the calculated monthly background levels, and, respectively. The mean  $\Delta O_3$  decreased by 2 during event 71 was -0.7 nmol mol<sup>-1</sup>, reaching a minimum  $O_3$  level of 39.6 pmol mol<sup>-1</sup>.

~~Analyses of all the pollution events over winter and early spring~~ Background  $O_3$  levels at Summit are typically higher than those observed at lower elevation Arctic sites due to a stronger influence of transport from the stratosphere, a reduction in ozone depletion events from halogens, and low surface deposition rates (Helmig et al., 2007a, b; Hirdman et al., 2010). The decrease in  $O_3$  observed during winter/early spring is likely to be the result of titration of  $O_3$  by NO within the sampled air mass soon after emission (Eneroth et al., 2007; Hirdman et al., 2010) and reduced mixing with the background air. FLEXPART retroplume analyses indicate that low  $O_3$  events ~~from December to March over winter~~ typically coincide when sampling air masses originating from either Europe or North America, which have resided in the lower troposphere ~~until ascending over Greenland and/or are quickly transported over the Greenland ice sheet~~ to the measurement site (examples of FLEXPART retroplumes are shown in Fig. ~~S1a-e in the Supplement~~ S7a-e in the supplement). In contrast, periods ~~identified-identified~~ during winter as pollution events with positive  $O_3$  enhancement values often occurred when the air masses resided in the mid-troposphere during transport to the site (Fig. ~~S2a and b in the Supplement~~ S8a-e), thus allowing for greater mixing with air from high tropospheric or stratospheric origin.

To investigate interannual variability in emissions and their impact on  $O_3$  and  $O_3$  precursors, a comparison of the enhancement values for  $\Delta O_3$ ,  $\Delta PAN$ , and  $\Delta C_2H_6$  was made over the two winters (no comparison was made for  $NO_x$  or  $NO_y$  as measurements were limited during winter 2008/2009). Results show that enhancements in  $O_3$  and  $O_3$  precursors during events were typically higher during the second winter season, with median (mean) values of 12 (37) pmol mol<sup>-1</sup>, 126 (162) pmol mol<sup>-1</sup>, and 1.2 (1.2) nmol mol<sup>-1</sup> in 2008/2009, and 40 (48) pmol mol<sup>-1</sup>, 178 (237) pmol mol<sup>-1</sup>, and 1.5 (1.3) nmol mol<sup>-1</sup> in 2009/2010, for  $\Delta PAN$ ,  $\Delta C_2H_6$ , and  $\Delta O_3$ , respectively. FLEXPART analyses, presented in Sect. 3.2, show that European emissions contributed a greater amount to

the anthropogenic air masses arriving at Summit in winter 2009/2010 compared to the previous year, thus, the higher enhancements are consistent with expectation that European emissions have a larger impact on the Arctic lower atmosphere in winter than North America or Asia.

In this study, the impact from anthropogenic emissions, as identified through FLEXPART retriplume analyses, were the primary focus. However, enhancements in the measured species were also observed during periods which are not correlated with pollution events simulated by FLEXPART. For example, ~~between 12 February and 1 March on 15 February and 24-28 February~~ 2010, (Fig. 7 ~~shows two periods when~~), enhancements in PAN, NO<sub>y</sub>, and ethane are observed that do not coincide with high FLEXPART BC<sub>anthro</sub> tracer ~~are observed. Analysis of the levels. The~~ BC<sub>fire</sub> tracer from FLEXPART ~~also indicated no pollution plume from biomass burning origin during this period is low, suggesting that the event was not the result of biomass burning emissions.~~ The retriplume ~~analysis shows that shows the~~ air masses from these two events were transported over ~~the far north region of north~~ Canada and remained in the ~~arctic Arctic~~ for many days before arriving at Summit (~~not shown here~~). It is unlikely that the air sampled was from a stratospheric origin, as ethane levels were high and ozone decreased during these events. It is possible that there may be ~~an error in the simulated retriplume by FLEXPART missing sources in FLEXPART,~~ or that the pollution originated prior to the 20 day simulation. ~~Further investigations are necessary to determine the cause of these events~~

Enhancements in O<sub>3</sub> precursors that do not coincide with high FLEXPART tracer simulations were also observed during the spring months, however, O<sub>3</sub> was typically enhanced during these events, suggesting a different source than those in February 2010. FLEXPART analyses indicate the air masses were well aged, therefore, mixing with air masses originating from the upper troposphere/stratosphere is possible. For example, the highest PAN and NO<sub>y</sub> levels during spring 2010 were observed between 22-24 April, when FLEXPART retriplumes show that the air masses were transported between 3300 and ~~enhancements in the~~ 4300 m.a.s.l (Fig. 9). During this same period, ethane and O<sub>3</sub> ~~precursors~~ were also high. This event may be an example of tropospheric air, with high

levels of NMHC, mixing with stratospheric air rich in  $O_3$  and  $NO_y$ , resulting in PAN formation (Liang et al., 2011). The determination of the sources that result in enhancements in  $O_3$  and its precursors, that cannot be attributed to pollution transport, requires further investigation.

The study here has focused on anthropogenic impacts during the winter period as this is when FLEXPART anthropogenic tracers peak, however, it should be noted that high  $\Delta O_3$  events occurred in the summer months, in particular between between May and August. Some of the anthropogenic air masses were mixed with BB plumes (as discussed in the next section), however, the largest enhancement in  $O_3$ , during the measurement period ( $\Delta O_3 = 15.0 \text{ nmol mol}^{-1}$ ), occurred from June 4-8 2009, as a result of transport of anthropogenic emissions from Europe to Summit in  $\sim 10$  days.  $O_3$  precursors were also enhanced during this event, indicating that further  $O_3$  production may be possible during subsequent transport.

### 3.2.2 ~~Summer impact from biomass~~ **Biomass burning and anthropogenic events** ~~impacts~~

The extended whiskers shown on the plots in Fig. 1 indicate a large amount of variability in the  $O_3$  precursors during the summer months. Radiation, surface emissions, boundary layer height, and changes in air mass sampling may all contribute to the variability observed; ~~which is typically in the range of hours to days~~. Anthropogenic emission impacts tend to be lower in the summer ~~due to as a result of~~ reduced transport from source regions, ~~however as shown in Fig. 6, however~~, pollution from anthropogenic and, especially, BB emissions can still impact the center of Greenland (Stohl, 2006), resulting in elevated mole fractions for short periods (Stohl et al., 2006). Studies based on aircraft measurements and models during the ARCTAS campaigns in both spring and summer 2008 show that ~~biomass and anthropogenic plumes can result in elevated~~  $NO_x$ ,  $NO_y$ , PAN ~~and hydrocarbons in the Arctic (e.g., Alvarado et al., 2010; Singh et al., 2010; Hornbrook et al., 2011; Liang et al., 2011)~~, and hydrocarbons levels can be elevated in biomass and anthropogenic plumes transported to the Arctic (e.g. Alvarado et al., 2010; Singh et al., 2010; Hornbrook et al., 2011; Liang et al., 2011).



The  $BC_{\text{fire}}$  tracer from FLEXPART was used to identify periods at Summit that were potentially impacted by BB emissions. ~~FLEXPART has been used to identify long range transport of biomass burning emissions in many studies (e.g., Brioude et al., 2007; Stohl et al., 2007; Lapina et al., 2008; Quennehen et al., 2011, 2012).~~ However, due to potential Potential inaccuracies with the FLEXPART simulation of transport pathways, fire identification, and tracer emission uncertainties, ~~BB events identified may be~~ may result in BB events being under or overestimated, however, FLEXPART has been successfully used to identify long range transport of biomass burning emissions in many studies (e.g. Brioude et al., 2007; Stohl et al., 2007; Lapina et al., 2008; Quennehen et al., 2011, 2012). Biomass burning events were characterized as having a FLEXPART  $BC_{\text{fire}}$  tracer  $>90^{\text{th}}$   $> 90^{\text{th}}$  percentile ( $\simeq 7 \text{ pmol mol}^{-1}$ ). In total, 13 events were observed between July 2008 and July 2010 ranging in duration between 12 and 252 h. Details regarding the start date, duration, mean plume age, FLEXPART tracer levels and trace gas levels for each event are shown in Table 23. A more conservative threshold was applied here than for the anthropogenic emissions in Sect. 3.2.1, ~~so~~ consequently, the events identified had significant BB impacts but small anthropogenic signatures. Of these 13 events, 2 were identified as having potentially high anthropogenic signatures ( $BC_{\text{anthro}} > 75^{\text{th}}$ ,  $anthro > 75^{\text{th}}$  percentile) and were most likely plumes of mixed anthropogenic and biomass burning emissions, 5-6 events were identified as having medium anthropogenic signatures ( $75^{\text{th}}$  percentile  $> BC_{\text{anthro}} > 50^{\text{th}}$ ,  $75^{\text{th}}$  percentile  $> BC_{\text{anthro}} > 50^{\text{th}}$  percentile) and the remaining 6-5 events were classified as having low anthropogenic signatures.

~~The analysis of the~~ The source contribution from FLEXPART shows that the majority of the BB events (9 out of 13) originated in North America, with the BB events originating in Europe all occurring in March 2009. ~~To ensure that the results were not biased through only identifying events during the measurement period, a statistical analysis of all the FLEXPART data from 2008, 2009 and 2010 was performed. For these 3,~~ 23 BB events lasting longer than 12h (both with and without anthropogenic mixing) were identified. ~~Of these 23 events;~~

~67 of the  $BC_{fire}$  tracer originated from North America, 15 from Europe and 19 from Asia, confirming that North America is the primary source of BB emissions impacting Summit.

Analyses of  $O_3$  and its precursors at Summit show that the mean enhancements for PAN,  $NO_x$ ,  $NO_{y_2}$  and  $C_2H_6$  during the BB events identified by FLEXPART are highly variable (Table 23). Values ranged between  $-4.4$  and  $12.44$ ,  $6$  and  $13.0$   $nmol\ mol^{-1}$  for  $\Delta O_3$ ,  $-7.9$   $20.6$  to  $90.4$   $pmol\ mol^{-1}$  for  $\Delta PAN$ ,  $0.6$  to  $24.50$ ,  $9$  to  $26.7$   $pmol\ mol^{-1}$  for  $\Delta NO_x$ ,  $-5.6$  to  $141.13$ ,  $4$  to  $153$   $pmol\ mol^{-1}$  for  $\Delta NO_{y_2}$  and  $-22.9$  to  $338.0$ ,  $11.4$  to  $113$   $pmol\ mol^{-1}$  for  $\Delta C_2H_6$ , for the 11 BB events characterized as having low/medium anthropogenic signatures. When considering only those events with low anthropogenic signatures, the results show that air masses sampled with potential BB contributions have Ethane levels were low during the summer in general, and there is a large gradient in NMHC with latitude (Blake et al., 2003), therefore, small or negative  $\Delta$  ranging between  $-4.4$  and  $10.8$ , with positive enhancements during 4 out of 5 events. These enhancements  $C_2H_6$  values are expected at Summit, even with the transport of air masses from the south.

The range of  $O_3$  enhancements observed here are comparable to those by Thomas et al. (2013), who estimated ozone production of up to  $3\ nmol\ mol^{-1}$  in aged BB plumes in the mid to upper-troposphere (peaking at 7 km) over Greenland. Our results suggest that in the lower troposphere the enhancement may even be greater. However, the enhancement values presented here can only be considered as best estimates based on the FLEXPART transport model simulations. Additionally, the long transport times from source region to the measurement site suggest significantly aged BB plumes, with mean weighted plume ages for the events ranging between 9–18 days (median 14 days). These aged plumes will be well mixed with the background air, therefore, separating the pollution impacts from background levels is challenging. For example, in 2008 FLEXPART indicated that a BB event impacted the measurement site from 25–26 July (event 1). The total column sensitivity from the FLEXPART retroplume (see Fig. ??) shows that the air masses arriving at the site during this event in July originated from a region with BB sources over Canada and Alaska and was transported in the lower troposphere over the Arctic Ocean. The air resided over the Arctic Ocean for ~4 days before ascending to Summit; therefore, it is likely that the

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polluted air containing BB emissions mixed with cleaner air from this region. As a result, measurements during this event show small positive enhancements for and, and negative values for  $\Delta$ ,  $\Delta$ PAN and  $\Delta$ .

The largest BB event identified by FLEXPART was observed in August 2008 (event 3), when the  $BC_{\text{fire}}$  tracer indicated BB plumes impacted the site continuously from 3 August to 14 August, peaking at  $\sim 91 \text{ pmol mol}^{-1}$ , as a result of large wildfires in Canada. We find  $O_3$  and its precursors were all positive during this period, with mean enhancements of ~~56.5, 19.4 and 141.1~~ 66.3, 15.0, and 153  $\text{pmol mol}^{-1}$  for  $\Delta$ PAN,  $\Delta$ NO<sub>x</sub> and  $\Delta$ NO<sub>y</sub> respectively, and  $10.5 \text{ nmol mol}^{-1}$  for  $\Delta$ O<sub>3</sub>. A closer analysis of the measurements in Fig. ?? 10 shows that O<sub>3</sub> was consistently high during the event. ~~Analysis of the~~ The FLEXPART total column sensitivity ~~indicates that during this event air masses were often transported at high altitudes in the free troposphere, enhancing the~~ shows that air masses were typically transported between 2500 and 3500 m.a.s.l to Summit. FLEXPART also indicates that anthropogenic pollution was present during this period, therefore, enhancements observed in the gas species may also be the result of anthropogenic pollution.

During the main peak of this event (~ August 4–7) a decrease in PAN mole fractions was observed even though the  $BC_{\text{fire}}$  tracer remained elevated. The FLEXPART trajectories indicate that the decrease in PAN coincided with a decrease in the altitude of the pollution plume over the Greenland ice sheet. It is possible, at these lower altitudes, thermal decomposition of PAN occurred, resulting in the formation of NO<sub>2</sub> and possible photochemical production of O<sub>3</sub> near to Summit. However, this cannot be concluded from the available measurements.

Enhanced PAN, NO<sub>x</sub>, and NO<sub>y</sub> were observed during two BB events on July 17 and 18 July 2009 (event 8 and 9). Plumes during both events were transported at lower altitudes (~1950–2900 m) than the BB plume in August 2008, and had low anthropogenic signatures. Mean  $\Delta$ O<sub>3</sub> levels were 4.6 and 13.0  $\text{nmol mol}^{-1}$  during event numbers 8 and 9, respectively, suggesting the BB emissions resulted in photochemical production of O<sub>3</sub> during transport to the site. Care must be taken when interpreting these results. All the BB plumes sampled during this study have long transport times from source region to

the measurement site, with mean weighted plume ages for the events ranging between 9–18 days (median 14 days). These aged plumes will be well mixed with background air, therefore, separating the pollution impacts from background levels is challenging.

Aged plumes transported at higher altitudes have a higher probability of mixing with high ozone from stratospheric origin, which may contribute to the elevated O<sub>3</sub> levels that were observed (Alvarado et al., 2010; Roiger et al., 2011).

Anthropogenic events during the summer months (April–September) were identified using the same threshold for winter/spring as in Sect. 3.2.1. During the measurement period, 28 events were identified with mean enhancement values up to . For example, during event 7, FLEXPART indicates that an aged plume (mean age ~ 16 days) originating from Asia, was transported over the North Pole between ~3000–4200 m.a.s.l. A similar transport pattern was observed during the POLARCAT campaign, during which a plume, originating from Asia, was lifted within a warm conveyor belt over the North Pole towards Greenland (Roiger et al., 2011). The plume was then transported into the lower stratosphere, resulting in a well mixed tropospheric-stratospheric air mass with high O<sub>3</sub> levels. The plume during event 7 was transported at lower altitudes, however, mixing with air from stratospheric origin is not impossible and may be the cause of the O<sub>3</sub> ( $\Delta O_3 = 10.7, 28 \text{ nmol mol}^{-1}$ ) and PAN ( $\Delta \text{PAN} = 68.5, 237 \text{ pmol mol}^{-1}$ ) levels observed.

BB plumes that are well mixed with background air can result in low precursor levels. In 2008 FLEXPART indicated that a BB event impacted the measurement site from 25–26 July (event 1). The total column sensitivity from the FLEXPART retroplume (see Fig. 11) shows that the air masses arriving at the site during this event originated from a region with BB sources over Canada and Alaska and were transported in the lower troposphere over the Arctic Ocean for ~ 4 days before ascending to Summit. The mean enhancement for O<sub>3</sub> during this event was -4.6, -205, and -1.0 nmol mol<sup>-1</sup> for  $\Delta$  and O<sub>3</sub> precursors have either small or negative enhancements. Similar results were observed in March 2009 (events 4,  $\Delta \text{PAN}$  5, 6), when  $\Delta$  PAN values were all negative and  $\Delta$  and  $\Delta$ , respectively. The air masses of anthropogenic origin primary originated from Europe with a mean plume age ranging between 7 to 15 days O<sub>3</sub> levels were below 4 nmol mol<sup>-1</sup>. During all 3 of these

events, the air masses spent many days in the lower troposphere, over the Arctic ocean and the edge of the Greenland ice sheet, before ascending to Summit in 1–2 days. It is likely, during these events, the aged plumes were well mixed with marine air with low O<sub>3</sub> and precursor mixing ratios. The maximum enhancements during anthropogenic events are much larger than those from the BB events, suggesting that air masses containing anthropogenic emissions may have a larger impact on levels of and precursors at Summit during the summer.

## 4 Summary

These analyses of NO<sub>y</sub>, NO<sub>x</sub>, PAN, NMHC, and O<sub>3</sub> from the high altitude GEO-Summit Station in Greenland show that PAN is the dominant species of NO<sub>y</sub> at the site, year-round, ranging from 49% year-round, with monthly mean contributions ranging from a minimum of 45% in the summer months to 78% in spring. However, the NO<sub>y</sub> seasonal cycle does not follow that of PAN, due to significant contributions from NO<sub>x</sub> in the summer, and odd NO<sub>y</sub> species during both summer and winter. We hypothesize that alkyl nitrates may account for a large portion of the HNO<sub>3</sub>, HONO, and alkyl nitrates are the largest sources of odd NO<sub>y</sub> observed in winter and that photochemically produced species such as HONO within the snowpack may impact the in the summer months. During the winter, mean monthly odd NO<sub>y</sub> budget during summer. However, these hypotheses cannot be confirmed without coincident measurements of individual levels reach 93 pmol mol<sup>-1</sup>. Approximately 1/3 of the odd NO<sub>y</sub> is likely to be alkyl nitrates transported to the site. Previous studies have suggested that HONO, HNO<sub>3</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and HO<sub>2</sub>NO<sub>2</sub> may also contribute to the wintertime NO<sub>y</sub> species and alkyl nitrates above the snowpack levels.

Analyses of the alkane NMHC data show that there is a large build-up of NMHC during the winter period in the atmosphere above Summit which peaks between January and March. The increase in photochemical processing after polar sunrise coincides with a decrease in NMHC levels during subsequent months. Between February and May total NMHC decreased by approximately 4.4 ppbC. The decrease in NMHC may contribute

partly to the spring time peak in observed over the same period. Further analyses using a photochemical model, constrained by the measurements, is needed to evaluate the springtime photochemical production rate at the measurement site and during subsequent transport downwind (Hamlin and Honrath, 2002).

Rapid changes in the origin of sampled air masses, from regions in Europe, North America, and the high latitude Arctic, result in a large variability in the measured species. FLEXPART BC tracers and retroplume simulations show that European sources dominated the anthropogenic emissions impacting the site in December–March contributing to 69 of the anthropogenic BC tracer in 2009 and 82 in 2010. In contrast, North America is the primary source of BB polluted air masses impacting the site in the summer. However BB emissions from Asia and Europe impact the site to a lower degree. Individual pollution events during December–November to March 2008/2009 and 2009/2010 show polluted air masses often result in resulted in elevated ozone precursors above the background level with mean enhancements up to 336273 pmol mol<sup>-1</sup>, 273312 pmol mol<sup>-1</sup>, 2554 pmol mol<sup>-1</sup> and 1.0, and 1120 pmol mol<sup>-1</sup> for NO<sub>y</sub>, PAN, NO<sub>x</sub>, and ethane, respectively. Enhancement values for PAN and ethane during the second winter were higher, possibly as a result of the increase in the contribution of air masses from Europe in 2009–2010 compared to 2008–2009. FLEXPART BC tracers and retroplume simulations indicate that European sources dominated the anthropogenic emissions impacting the site in November–March, contributing up to 56 % of the anthropogenic BC tracer in 2009, and ethane respectively.

69 % in 2010. During the two winter seasons, 16 of the 52 events identified had negative mean ΔO<sub>3</sub> levels at Summit are typically higher than those observed at lower elevation Arctic sites due to a stronger influence of transport from the stratosphere and a reduction in ozone depletion events from halogens (Helmig et al., 2007a, b; Hirdman et al., 2010). Short periods with reduced ozone are observed throughout the year. During the summer months, these low ozone events tend to occur when the sampled air masses contain low levels of pollution. In contrast, during the winter, low ozone levels. These events typically coincided with the occurrence arrival of polluted air masses that have been were transported, possibly quickly to the site, in only a few days, or transported within the lower troposphere.

The reduced O<sub>3</sub> within the plumes was likely due to the occurrence of O<sub>3</sub> titration and reduced mixing with high the higher background O<sub>3</sub> at Summit. Enhanced O<sub>3</sub> levels were also observed during the winter pollution events. These were typically associated with transport up to ~ 3000-4000 m.a.s.l, increasing the probability of mixing with O<sub>3</sub> rich air from stratospheric origin.

FLEXPART tracer simulations indicated that biomass burning emissions transported to Summit during the summer in 2008–2010 primarily originated from North America. ~~Plumes originating from BB events in Biomass burning plumes from~~ Europe were only present during a short period in March 2009. ~~The analyses focused on 11 BB events during the measurement period which did not have large~~ During 2009 measurements were performed over a full summer period, however, BB impacts were low in summer 2009, compared to 2008 and 2010. In total, 13 plumes were identified, and only 5 with low anthropogenic signatures. During ~~these events the events,~~ O<sub>3</sub> and precursor levels were typically enhanced within the BB plumes with ΔO<sub>3</sub> levels up to ~~12.4~~13.0 nmol mol<sup>-1</sup> and ΔPAN, ΔNO<sub>y</sub>, and ΔC<sub>2</sub>H<sub>6</sub> levels enhanced by up to 90.4, ~~141.1~~137 pmol mol<sup>-1</sup> and ~~338~~113 pmol mol<sup>-1</sup>, respectively. ~~However, we cannot say with confidence here whether the enhanced levels observed were directly as a result of biomass burning emissions or whether they occurred as a result of the plumes mixing with background air at high altitudes. In fact, it was found during the summer months that enhancements in all the measured species were greater when sampling air masses from anthropogenic origin rather than BB plumes. High~~ The results presented here show that BB plumes may potentially impact the O<sub>3</sub> at Summit and the Arctic region in general, however, due to the long transport times and limited number of BB air masses transported to Summit during the measurement period, a quantitative analysis of the impact of BB plumes on O<sub>3</sub> and O<sub>3</sub> precursor levels is difficult. Future studies, with coincident CO, O<sub>3</sub>, and O<sub>3</sub> precursor measurements at Summit, would be valuable to determine enhancement ratios with respect to CO and evaluate the potential for ozone production in the region.

Enhanced NO<sub>y</sub> levels observed above the background during the events discussed here may have an important impact on snow photochemistry and the subsequent release of NO<sub>x</sub>,

due to the uptake of NO<sub>y</sub> species ~~such as HN and HONO to the snow pack to the snowpack~~ (Grannas et al., 2007, and references therein). ~~Due~~ Additionally, due to the stability of the Arctic free troposphere, the region is an effective reservoir for O<sub>3</sub> precursors. ~~Therefore, the~~ The high O<sub>3</sub> precursor mole fractions above background levels in ~~the summer spring and summer at Summit~~ may have important implications for NO<sub>x</sub> and O<sub>3</sub> in the mid-latitudes during southerly flow of air masses (Hamlin and Honrath, 2002). ~~However, we find there is a need for future studies to constrain the speciation of above the snowpack, through year-round coincident measurements of, PAN, HONO and determine the sources of odd in the winter and summer.~~

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**Table 1.** Monthly statistics for NO<sub>x</sub>, NO<sub>y</sub>, PAN, O<sub>3</sub> and the NO<sub>y</sub> budget measured at Summit from 2008–2010.

Year	Month	NO <sub>x</sub>	NO <sub>y</sub>	PAN	O <sub>3</sub>	NO <sub>x</sub> /NO <sub>y</sub> <sup>a</sup>	PAN/NO <sub>y</sub> <sup>a</sup>
		(pmol mol <sup>-1</sup> ) Mean ± SD	(pmol mol <sup>-1</sup> ) Mean ± SD	(pmol mol <sup>-1</sup> ) Mean ± SD	(pmol mol <sup>-1</sup> ) Mean ± SD	% Mean ± SD	% Mean ± SD
2008	7	19 ± 12	136 ± 53	64 ± 27	46 ± 5	14 ± 6	45 ± 12
	8	18 ± 9	139 ± 59	93 ± 47	45 ± 7	13 ± 5	55 ± 10
	9	10 ± 6	92 ± 39	60 ± 32	39 ± 5	11 ± 6	60 ± 21
	10	7 ± 12	127 ± 58	88 ± 38	39 ± 4	5 ± 7	66 ± 14
	11	8 ± 15	160 ± 33	103 ± 22	40 ± 4	3 ± 5	59 ± 8
	12	—	—	89 ± 28	40 ± 2	—	—
2009	1	—	—	84 ± 19	44 ± 3	—	—
	2	—	—	119 ± 43	48 ± 4	—	—
	3	12 ± 11	288 ± 36	193 ± 79	49 ± 3	4 ± 4	67 ± 6
	4	17 ± 13	282 ± 74	233 ± 68	55 ± 6	6 ± 5	81 ± 12
	5	24 ± 19	249 ± 65	176 ± 40	56 ± 7	9 ± 6	71 ± 9
	6	20 ± 15	154 ± 51	97 ± 32	49 ± 8	13 ± 8	64 ± 13
	7	16 ± 18	127 ± 56	68 ± 31	43 ± 6	12 ± 12	53 ± 15
	8	13 ± 12	141 ± 41	102 ± 33	42 ± 4	9 ± 7	71 ± 13
	9	7 ± 13	112 ± 46	86 ± 33	40 ± 6	6 ± 8	75 ± 12
	10	5 ± 7	138 ± 43	98 ± 32	40 ± 5	4 ± 7	74 ± 10
	11	2 ± 6	182 ± 40	132 ± 36	42 ± 3	1 ± 3	67 ± 7
	12	5 ± 13	179 ± 52	97 ± 34	45 ± 3	2 ± 5	54 ± 17
2010	1	6 ± 11	181 ± 57	106 ± 35	47 ± 3	2 ± 3	57 ± 10
	2	5 ± 11	242 ± 89	140 ± 78	48 ± 3	2 ± 4	56 ± 14
	3	10 ± 9	245 ± 66	158 ± 77	51 ± 4	4 ± 4	64 ± 18
	4	28 ± 21	356 ± 103	280 ± 102	52 ± 6	8 ± 4	73 ± 11
	5	37 ± 28	275 ± 86	—	52 ± 6	—	—
	6	23 ± 13	190 ± 63	—	47 ± 7	—	—
	7	22 ± 12	241 ± 55	—	50 ± 5	—	—

<sup>a</sup>PAN/NO<sub>y</sub> and NO<sub>x</sub>/NO<sub>y</sub> ratios determined using coincident measurements only.

**Table 2.** Monthly statistics for NMHC measured at Summit from 2008–2010.

Year	Month	Ethane (pmol mol <sup>-1</sup> ) Mean ± SD	Propane (pmol mol <sup>-1</sup> ) Mean ± SD	n-Butane (pmol mol <sup>-1</sup> ) Mean ± SD	i-Butane (pmol mol <sup>-1</sup> ) Mean ± SD	n-Pentane (pmol mol <sup>-1</sup> ) Mean ± SD	i-Pentane (pmol mol <sup>-1</sup> ) Mean ± SD
2008	7	617 ± 37	46 ± 18	7 ± 7	7 ± 7	11 ± 9	22 ± 18
	8	593 ± 0	89 ± 0	10 ± 0	19 ± 0	10 ± 0	44 ± 0
	9	465 ± 113	151 ± 9	37 ± 12	68 ± 21	10 ± 5	7 ± 5
	10	921 ± 264	293 ± 146	47 ± 24	100 ± 49	31 ± 23	22 ± 15
	11	1308 ± 194	502 ± 138	89 ± 35	161 ± 59	51 ± 24	37 ± 18
	12	1574 ± 115	684 ± 85	129 ± 23	230 ± 64	79 ± 21	57 ± 13
2009	1	1884 ± 170	887 ± 118	182 ± 30	335 ± 67	130 ± 27	101 ± 19
	2	1846 ± 147	774 ± 107	139 ± 28	259 ± 51	87 ± 24	68 ± 19
	3	2100 ± 151	822 ± 116	136 ± 29	246 ± 56	75 ± 25	59 ± 18
	4	1779 ± 121	462 ± 91	54 ± 15	90 ± 27	20 ± 8	17 ± 7
	5	1380 ± 187	205 ± 84	17 ± 13	29 ± 19	4 ± 5	4 ± 4
	6	877 ± 98	61 ± 27	3 ± 3	6 ± 5	1 ± 1	1 ± 1
	7	617 ± 47	54 ± 22	5 ± 5	9 ± 7	2 ± 3	2 ± 3
	8	634 ± 65	73 ± 19	5 ± 4	13 ± 7	2 ± 2	2 ± 2
	9	710 ± 44	122 ± 36	15 ± 10	29 ± 18	8 ± 8	8 ± 8
	10	902 ± 113	259 ± 75	43 ± 16	80 ± 31	28 ± 13	24 ± 11
	11	1253 ± 125	482 ± 87	86 ± 20	162 ± 36	62 ± 20	52 ± 17
	12	1459 ± 238	623 ± 182	116 ± 45	220 ± 85	79 ± 35	66 ± 30
2010	1	1707 ± 340	714 ± 208	131 ± 45	245 ± 88	75 ± 33	61 ± 27
	2	1769 ± 324	697 ± 209	128 ± 51	229 ± 93	63 ± 32	53 ± 27
	3	1835 ± 174	619 ± 164	98 ± 43	181 ± 80	42 ± 25	34 ± 21
	4	1785 ± 381	530 ± 276	77 ± 62	138 ± 119	33 ± 34	27 ± 29
	5	1321 ± 113	182 ± 44	14 ± 5	25 ± 9	4 ± 6	3 ± 3
	6	923 ± 98	68 ± 19	3 ± 5	6 ± 4	3 ± 8	3 ± 4
	7	723 ± 36	48 ± 23	3 ± 4	4 ± 4	3 ± 7	3 ± 4

**Table 3.** Biomass burning events and mean enhancements in trace gases measured at Summit.

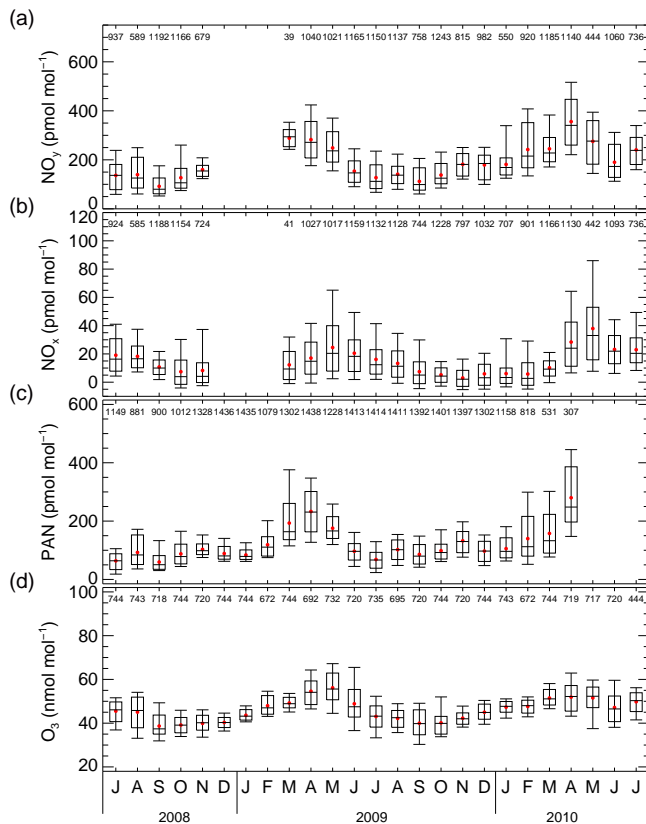
Event	Start Date	Event Length (h)	BC <sub>fire</sub> ( $\mu\text{mol mol}^{-1}$ )	$\Delta\text{O}_3^{\text{a}}$ ( $\text{nmol mol}^{-1}$ )	$\Delta\text{PAN}$ ( $\mu\text{mol mol}^{-1}$ )	$\Delta\text{NO}_x$ ( $\mu\text{mol mol}^{-1}$ )	$\Delta\text{NO}_y$ ( $\mu\text{mol mol}^{-1}$ )	$\Delta\text{C}_2\text{H}_6$ ( $\mu\text{mol mol}^{-1}$ )	Plume age <sup>b</sup> (days)	Source <sup>c</sup>	BC <sub>anthro</sub> <sup>d</sup>
1	25 Jul 2008	33	30.6	-4.6	-4.3	0.9	3.4	48.6	9	NA	med
2	1 Aug 2008	15	25.0	7.0	5.1	1.9	32.8	–	15	NA	low
3	3 Aug 2008	252	90.7	10.5	66.3	15.0	153	–	14	NA	med
4	15 Mar 2009	60	58.6	-0.5	-7.0	–	–	110	12	EU	med
5	18 Mar 2009	33	23.1	3.8	-1.1	–	–	-11.4	15	EU	med
6	21 Mar 2009	21	17.6	3.8	-20.6	–	–	11.3	16	EU	low
7	27 May 2009	30	17.7	10.7	68.5	–	–	–	16	AS	med
8	17 Jul 2009	12	19.9	4.6	90.4	8.8	112	-9.5	13	NA	low
9	18 Jul 2009	15	13.5	13.0	74.3	26.7	137	25.4	14	NA	low
10	16 Aug 2009	18	11.8	-4.1	-1.1	14.8	16.1	–	18	NA	low
11	18 Aug 2009	12	9.5	5.7	71.1	5.2	65.4	113.0	17	NA	med
12	7 Jun 2010	27	11.3	8.9	–	12.2	112	13.9	13	NA	high
13	18 Jul 2010	51	27.4	4.3	–	4.9	97.3	27.8	9	NA	high

<sup>a</sup>  $\Delta$  represents the enhancement over the background level (background = 20th percentile of each species for each month and year).

<sup>b</sup> Mean weighted age from FLEXPART.

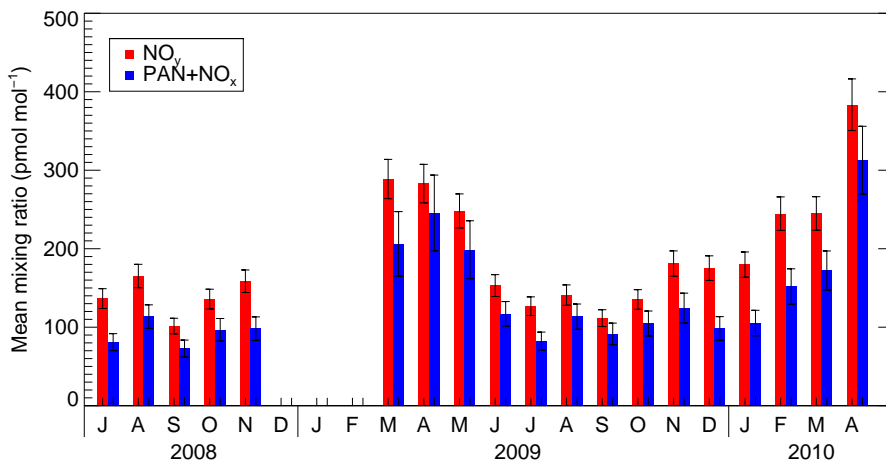
<sup>c</sup> Primary BB source. NA = North America, EU = Europe, AS = Asia.

<sup>d</sup> Indicates potential contribution from anthropogenic pollution. Low: BC<sub>anthro</sub> < 50th percentile, Med: BC<sub>anthro</sub> < 75th percentile, high: BC<sub>anthro</sub> > 75th percentile.

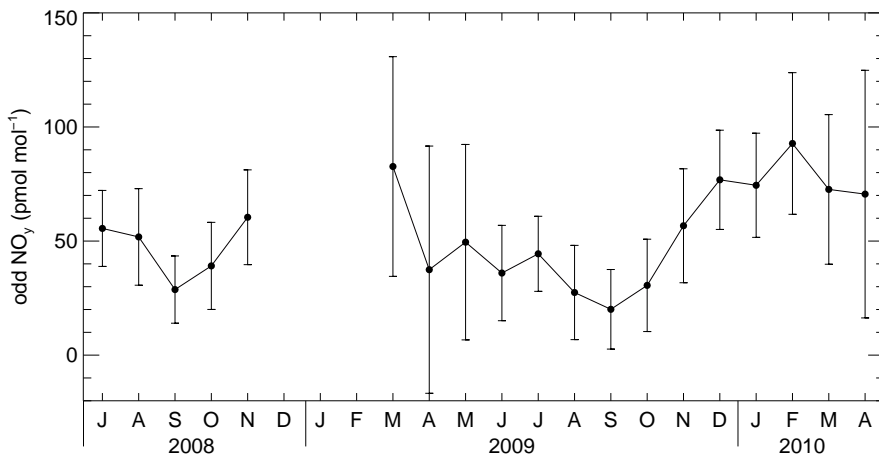


**Figure 1.** Monthly averages of (a)  $\text{NO}_x$ , (b)  $\text{NO}_y$ , (c) PAN, and (d)  $\text{O}_3$  at Summit from July 2008–July 2010. The median and mean of the data are represented by a horizontal line and filled black circle, respectively; the box indicates the middle 67% of the data; and the vertical whiskers indicate the 5<sup>th</sup> and 95<sup>th</sup> percentile of all the data. The numbers at the top of each plot represent the number of 30-min averages included in the distribution.

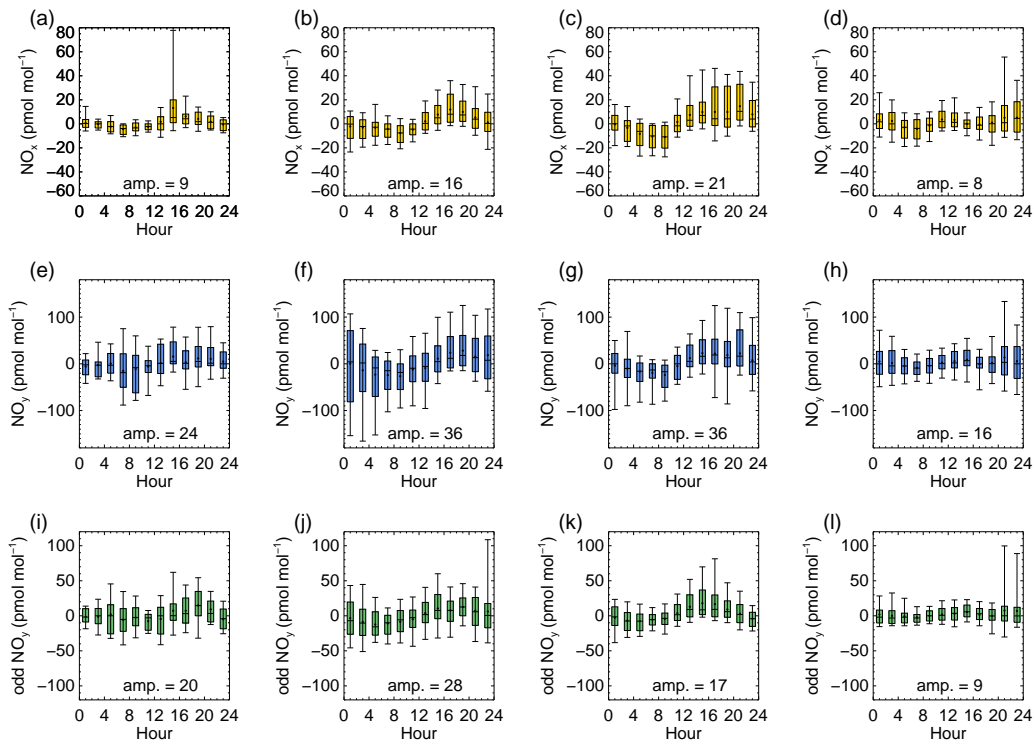




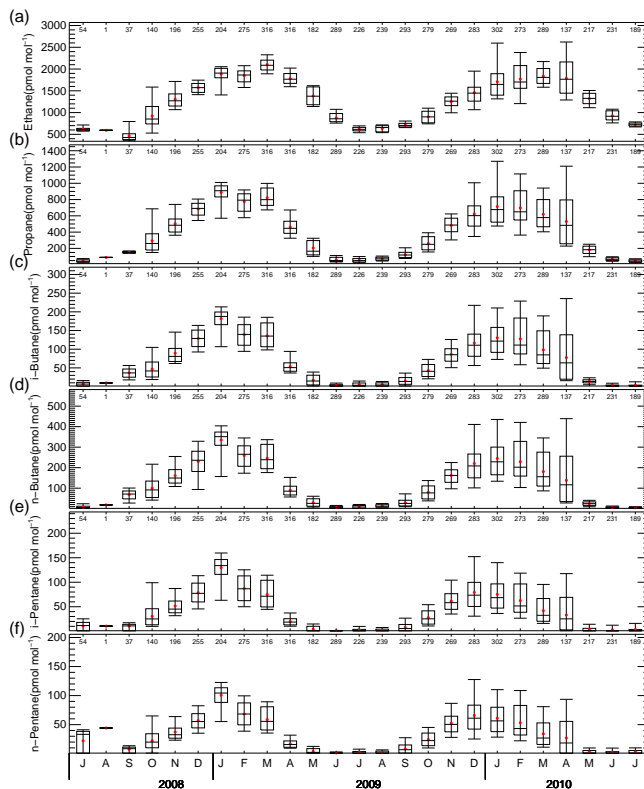
**Figure 2.** Monthly mean levels of  $\text{NO}_y$  and  $\text{PAN}+\text{NO}_x$  at Summit calculated from individual 30 min averages for 2008–2010 at Summit. Error bars represent uncertainty in the measurements resulting from measurement accuracy, calibration uncertainty, and artifact corrections as discussed in sections 2.2.1, 2.2.2, and the supplementary material. Uncertainties in  $\text{PAN}+\text{NO}_x$  were determined from the propagation of errors. Only coincident data are considered in this analysis.



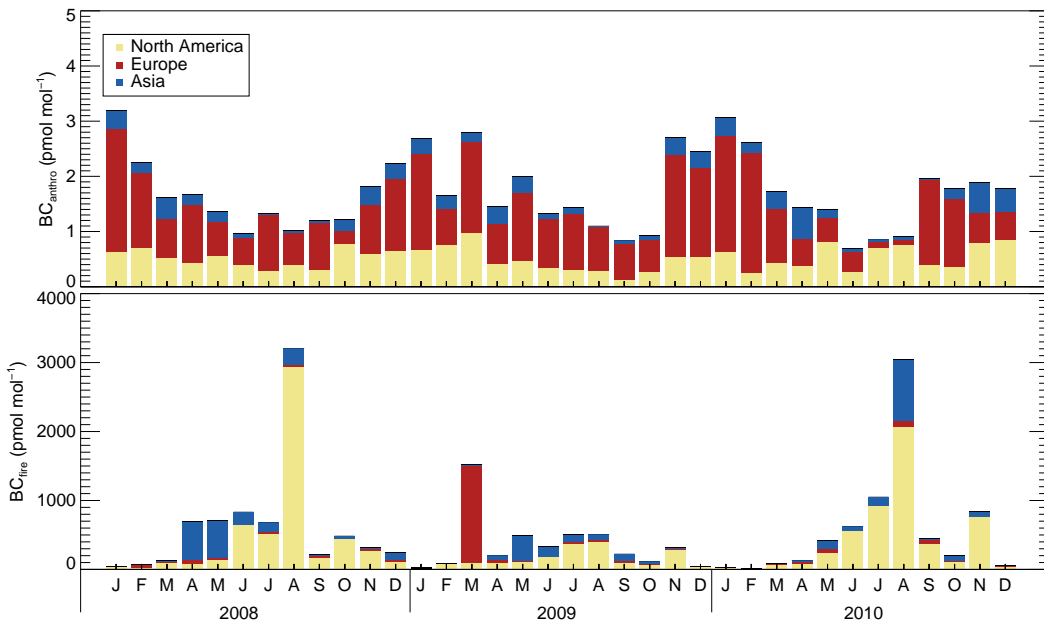
**Figure 3.** Monthly levels of odd NO<sub>y</sub> (calculated from the 30 minute averaged NO<sub>y</sub>, PAN, and NO<sub>x</sub> measurements) at Summit. Error bars represent the uncertainty in odd NO<sub>y</sub> mole fractions, determined from the propagation of errors from PAN, NO<sub>x</sub>, and NO<sub>y</sub>.



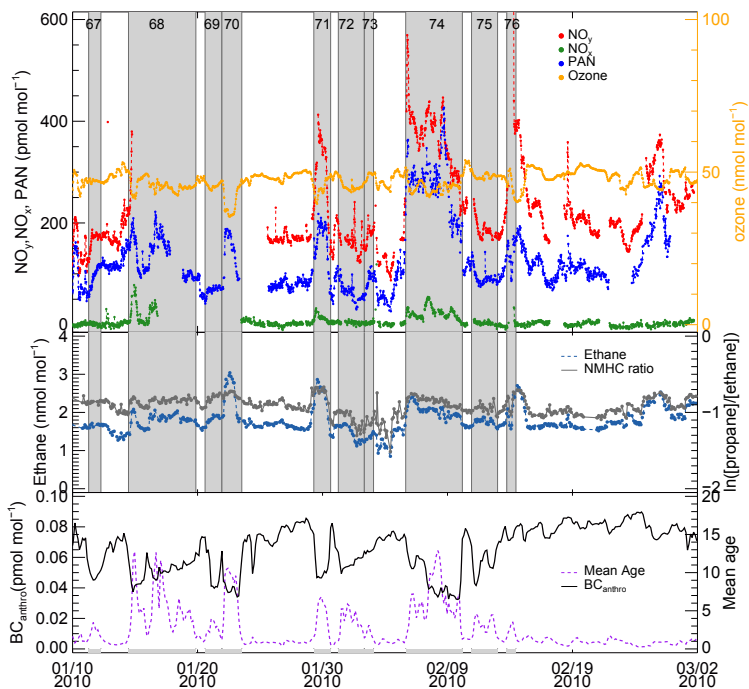
**Figure 4.** Average diurnal cycle of ambient  $\text{NO}_x$  (**a**, **b**, **c**, **d**),  $\text{NO}_y$  (**e**, **f**, **g**, **h**), and odd  $\text{NO}_y$  (**i**, **j**, **k**, **l**) measured at Summit for the months March (1<sup>st</sup> column), April (2<sup>nd</sup> column), May (3<sup>rd</sup> column) and June (4<sup>th</sup> column) 2008–2010. Median ambient levels observed each day were subtracted, to remove any impact from day to day variability. The median and mean of the data are represented by a horizontal line, and filled black circle, respectively; the box indicates the middle 67% of the data; and the vertical whiskers indicate the 5<sup>th</sup> and 95<sup>th</sup> percentile of all the data. Times are shown as local time (UTC). The amplitude of the diurnal cycle (given as the difference between the lowest and highest 2 hour median values, in  $\text{pmol mol}^{-1}$ ) is noted on each subplot.



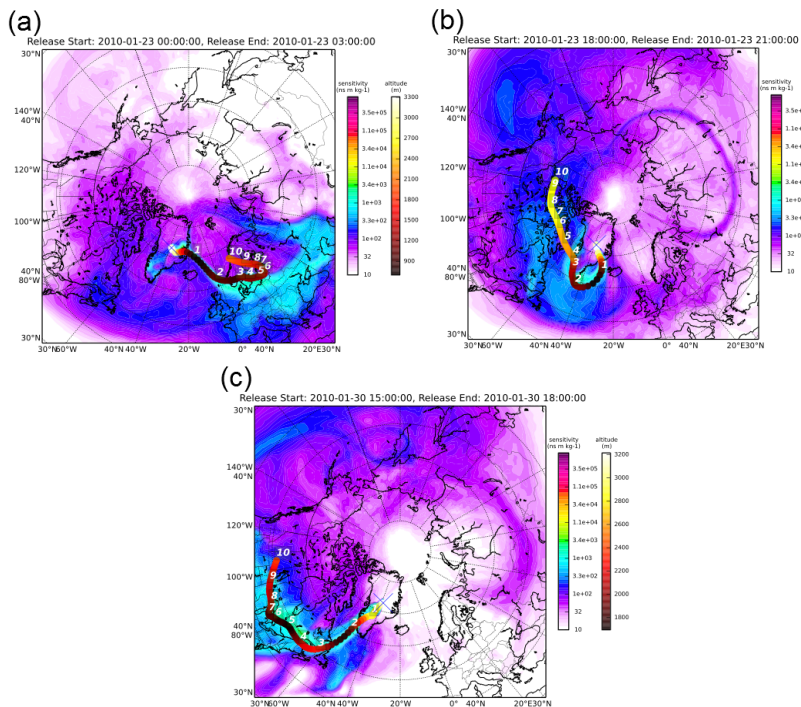
**Figure 5.** Monthly averages of (a) ethane, (b) propane, (c) i-butane, (d) n-butane, (e) i-pentane, and (f) n-pentane, at Summit during from July 2008–July 2010. Median and mean are indicated by a horizontal line and black square, respectively; the box indicates the middle 67 % of the data; and the vertical whiskers indicate the 5<sup>th</sup> and 95<sup>th</sup> percentile of all the data. The numbers at the top of each plot represent the number of measurements included in the distribution.



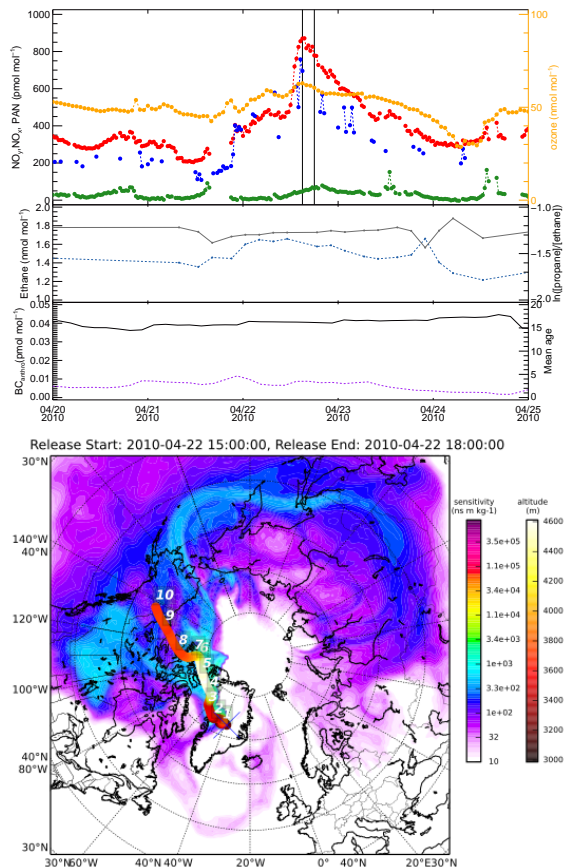
**Figure 6.** Barplot showing the total monthly  $BC_{\text{anthro}}$  (top) and  $BC_{\text{fire}}$  (bottom) tracer from FLEXPART for 2008, 2009, and 2010. The different colors represent the contributions from North America, Europe, and Asia as shown in the legend.



**Figure 7.** The top plot shows 30 min averages of  $\text{NO}_x$ ,  $\text{NO}_y$ , PAN, and 1 h average of  $\text{O}_3$  from Summit between January 10 and March 2, 2010. The middle plot shows ethane mole fraction and  $\ln([\text{propane}]/[\text{ethane}])$ , and the bottom plot shows the FLEXPART  $\text{BC}_{\text{anthro}}$  tracer emissions (from all continents), and mean weighted age, for the same period. The shaded areas indicate the events discussed in detail in the main text and numbers at the top of the plot represent the event number (see supplementary material for details on the events).

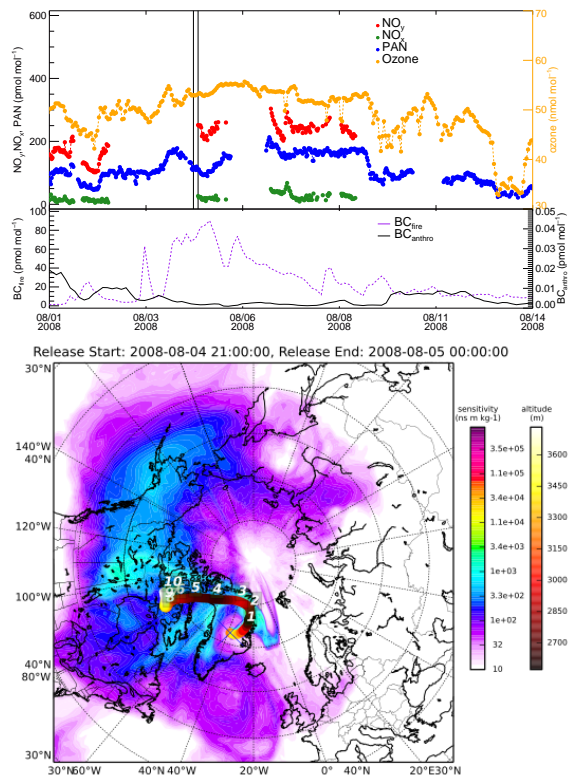


**Figure 8.** Simulated total column sensitivity ( $\text{ns m kg}^{-1}$ ) for retroplumes originating at Summit on (a) 23 January, 2010, at 00:00 UTC, (b) 23 January, 2010, at 18:00 UTC, and (c) 30 January, 2010, at 15:00 UTC. The altitude circles represent the centroid location of the particles in the model domain N days back from the measurement date, where N is the number shown next to the shaded circles (up to 10 days are shown on the plots). The shading represents the altitude at three hourly intervals of the centroid location, given by the heat scale colorbar (note the change in scale for the colorbar).

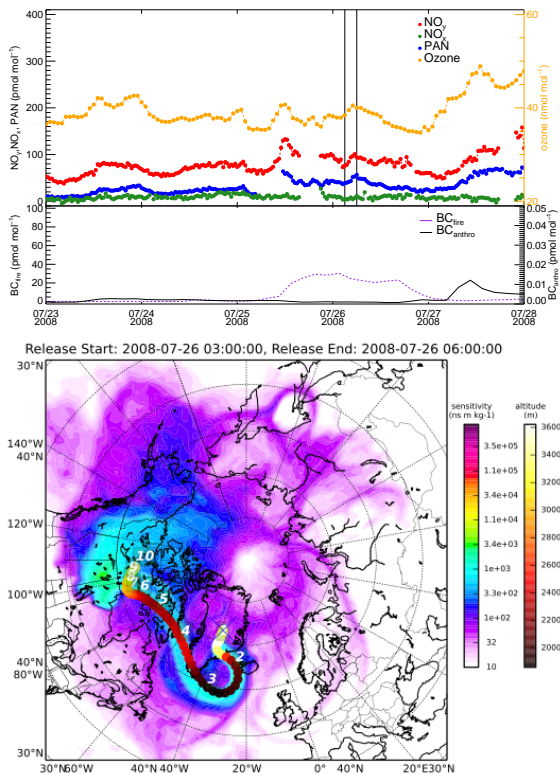


**Figure 9.** 30 min averages of  $\text{NO}_x$ ,  $\text{NO}_y$ , PAN, and 1 h average of  $\text{O}_3$  and FLEXPART  $\text{BC}_{\text{fire}}$  and  $\text{BC}_{\text{anthro}}$  tracer at Summit from 20–25 April, 2010. The vertical lines represent the arrival time of the FLEXPART simulated total column sensitivity at Summit on April 22, 2010, between 15:00–18:00 UTC, as shown in the bottom panel.





**Figure 10.** Top panel: 30 min averages of  $\text{NO}_x$ ,  $\text{NO}_y$ , PAN, and 1 h average of  $\text{O}_3$  and FLEXPART  $\text{BC}_{\text{fire}}$  and  $\text{BC}_{\text{anthro}}$  tracer at Summit from 1–14 August, 2008. The vertical lines represent the arrival time of the FLEXPART simulated total column sensitivity at Summit between 04 August, 2008, 21:00 UTC and 05 August, 2008, 00:00 UTC, as shown in the bottom panel.



**Figure 11.** Top panel: 30 min averages of  $\text{NO}_x$ ,  $\text{NO}_y$ , PAN, and 1 h average of  $\text{O}_3$  and FLEXPART  $\text{BC}_{\text{fire}}$  and  $\text{BC}_{\text{anthro}}$  tracer at Summit from 24–27 July, 2008. The vertical lines represent the arrival time of the FLEXPART simulated total column sensitivity at Summit on 26 July, 2008, between 03:00–06:00 UTC, as shown in the bottom panel