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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal variability of atmospheric nitrogen oxides and non-methane hydrocarbons at the GEOSummit station, Greenland" *by* L. J. Kramer

Anonymous Referee #1

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Kramer et al., Year-round at Summit

This manuscript reports on the first year-round measurements of NOx, PAN and NOy 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 NOy, and the sources of short-lived plumes that are superimposed on the relatively smooth seasonal variations. Source attribution relies heavily on FLEXPART "retro-plume" 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 NOx staying elevated later into summer than PAN and NOy. PAN is the dominant fraction of NOy throughout the year, with the PAN/NOy ratio peaking near 0.8 in April and remaining $\sim$ 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 NOx/NOy increases from $\sim$0.04 in winter to a little over 0.1 in summer, with the summer time increase tentatively ascribed to release of NOx from sunlit snow. They also point out that the sum of NOx plus PAN never accounts for all of measured NOy, with unmeasured species contributing 20-38% of NOy throughout the year. This shortfall is termed "odd NOy" and amounts to nearly 50 ppt in summer and nearly 100 ppt in winter (for monthly averages). Authors suggest that odd NOy 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 $\sim$ 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 NOy 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

NOy 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.

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.

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.

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

more common usage

13821/18 emissions from the $-\rightarrow$ emissions in the

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.

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.

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.

13824/3-16 This paragraph briefly outlining the calibration of the NOx,y instrument is misleading. Details in the supplement clear things up, but need to also be accurate here. Specifically, you cannot assess the LED NO2 convertor efficiency just by challenging it with NO, and you should mention that you challenged the Au convertor with NO2 twice a day, and with HNO3 and NPN every 3 days.

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.

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.

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 a

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?

13829/1 Not clear how the simple treatment of BC scavenging would cause "underestimation" of the BC tracer reaching Summit. Not including aging effects making BC more hydrophylic would seem to decrease scavenging by any precipitation along the transport path, which ought to lead to overestimates of the concentration still in the airmass(es) reaching Summit.

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 NOx,y and PAN data?

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 NOx and HNO3 transferred from the stratosphere. Suggest redrafting this sentence to clarify this point.

13831/5 dectection—→ detection

13831-13833 (end of section 3.1.1) The 2.5 paragraphs discussing the "odd NOy" 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 C1-C4 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 NOy com-

pounds during these experiments would be pleased to provide statistical summaries (perhaps even complete data files) that would allow quantitative comparison to your calculated odd NOy in summer 2010 and semi quantitative assessment for the summer and spring seasons more generally.

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 NOy? This would be particularly important if you are able to compare the sum of measured NOx, PAN, HNO3, HO2NO2, HONO and assumed sum of RONO2 (∼ 10 ppt) to measured NOy during summer 2010 as suggested immediately 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)

13834/13-23 Strongly suspect that Figure 4 would show quite similar features if NOx and NOy replaced the NMHC.

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

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.

The only full paragraph on page 13835 focuses exclusively on FLEXPART analyses in the DJFM season, and specifically on where this model thinks its BCanthro 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 Burkhart 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 next paragraph extends onto the next page, and presents enhancements of NOx, PAN, NOy, 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 5 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%.

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.

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 page13836 (see earlier comment)?

The next paragraph (ends on page13838) continues to basically accept FLEXPART as truth, and starts by presenting evidence (enhanced ln(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).

13840/line 3 and line 21. First one states that the combination of BCfire and BCanthro 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).

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.

13842/4 anlayses–→analyses

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)?

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.

13844/10-11 HNO3 determine——→HNO3 to determine would probably want to add

RONO2 to this list, and possibly HO2NO2 (comparable to HNO3 in summer)

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 13817, 2014.