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Atmospheric Chemistry and Physics Discussions

*Supplement of*

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

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## 1 Calibration procedures and uncertainty estimates for the nitrogen oxides instrument

The sensitivity of the instrument to NO was determined via the standard addition of NO, and ranged from 2.3 to 5.9 counts $s^{-1}$ per pmol $mol^{-1}$ (cps $ppt^{-1}$) , with a median value of median 2.7 cps $ppt^{-1}$. To ensure that the instrument operated optimally during periods with limited supervision a number of additional calibrations were performed to determine the zeroing efficiency, the response of the $NO_2$ and $NO_y$ converters and artifact corrections.

The $NO_2$ and $NO_y$ converters were both calibrated for the conversion of $NO_2$ to NO through the standard addition of $NO_2$ at the inlets. $NO_2$ was generated via gas phase titration of the NO standard with $O_3$. The $NO_2$ conversion efficiency remained stable at 52 ± 5 (mean ± 2σ) during the 2 years of measurements. Conversion efficiencies for $NO_2$ in the $NO_y$ converter were > 96% (median 99%). Calibration mole fractions for n-propyl nitrate (NPN, 4.4 to 220 nmol $mol^{-1}$) and nitric acid ($HNO_3$, 1.4 to 9.7 nmol $mol^{-1}$) were determined every 3 days from standard addition of each species with the $NO_y$ converter heated to 300°C (regular operating temperature) and 500°C. At 500°C the conversion efficiency of the $NO_y$ species is expected to be > 95% (Bollinger et al. 1983; Fahey et al. 1985). The conversion efficiencies were calculated to be > 80% (median 95%) for NPN and > 85% (median ~101%) for $HNO_3$. The potential interference due to conversion of non-$NO_y$ species was estimated using the standard addition of acetronitrile ($CH_3CN$), which is typically observed in biomass-burning plumes (de Gouw et al. 2004; Holzinger et al. 2005). Measurements of $CH_3CN$ were obtained twice daily during the regular calibrations and referenced to the calibration standard from two permeation devices used during the measurement period, which were determined using the manufacturer's reported permeation rate (21 and 246 nmol $mol^{-1}$). The $CH_3CN$ conversion was always below 4%, with a median value of 0.9%, confirming that $CH_3CN$ did not significantly contribute to the total $NO_y$ measurements.

The precision of the data is related to the photon-counting noise of the detector. For NO, $NO_2$ and $NO_y$ the precision is estimated as the 2σ standard deviation of the 30 s averages (20 s for $NO_y$) with median values of 4.4 pmol $mol^{-1}$ (NO), 8.2 pmol $mol^{-1}$ ($NO_2$) and 6.2 pmol $mol^{-1}$ ($NO_y$). The data were further averaged to 30 min averages giving a 2σ precision of NO, $NO_2$ and $NO_y$ of less than 3.5 pmol $mol^{-1}$, 6.4 pmol $mol^{-1}$ and 5.2 pmol $mol^{-1}$ respectively.

At low mole fractions uncertainty in the artifact correction is important. The artifact for $NO_y$ was determined once a week, while artifacts for NO and $NO_2$ were performed twice weekly. Artifact values for NO and $NO_y$ were constant during uninterrupted periods of measurements. Small changes in the NO and $NO_y$ artifact occurred after the instrument was switched off for prolonged periods or after instrument maintenance was performed. The artifact corrections applied to the data ranged between -5 to 1.5 pmol $mol^{-1}$ (NO) and 2 to 15 pmol $mol^{-1}$ ($NO_y$). Time-varying artifacts were determined for $NO_2$ as the artifact decreased after time due to a reduction in cell contaminants within the converter. The $NO_2$ artifact applied to the data varied between 14 to 30 pmol $mol^{-1}$ over the two years of measurements. Uncertainty in the artifact corrections are estimated as ± 2 pmol $mol^{-1}$ for NO, ± 5 pmol $mol^{-1}$ for $NO_2$, and ± 5 pmol $mol^{-1}$

for $NO_y$. The uncertainty was larger for NO (±5 pmol $mol^{-1}$) and $NO_2$ (±10 pmol $mol^{-1}$) during the first 6 weeks of measurements while the instrument was stabilizing.

The accuracy in the measurements is also dependent on the uncertainty in the flow rates measured by the sample (1%) and calibration (5%) mass flow controllers (MFCs) and the NO standard calibration gas mole fraction. The NO standards are quoted with an accuracy of 2% traceable to primary standards by the manufacturers. The NO calibration cylinders were also compared to a NIST standard (NIST standard reference 2628a, 10 ppmv) in the field. However, the results from the intercomparisons show a consistent positive bias with mole fractions outside the specified uncertainties. Analysis of the intercomparison tests suggests that the instrument calibration lines did not fully stabilize when switching from the high mole fraction of the NIST standard to the working standard. Therefore, greater confidence is with the manufactures stated mole fractions than those obtained from the intercomparisons with the NIST standard. The total accuracy in the NO and $NO_2$ measurements from the MFCs and calibration standard is estimated to be 6% from error propagation. For $NO_y$, the accuracy also depends on the efficiency of the $NO_y$ converter and biases resulting in the conversion of non-$NO_y$ species, as discussed above. The primary source of error is from the non-conversion of $NO_y$ species to NO. Through the propagation of errors the $NO_y$ accuracy is estimated to be $\leq$ 21% and typically 8%.

## 2. Supplementary Figures

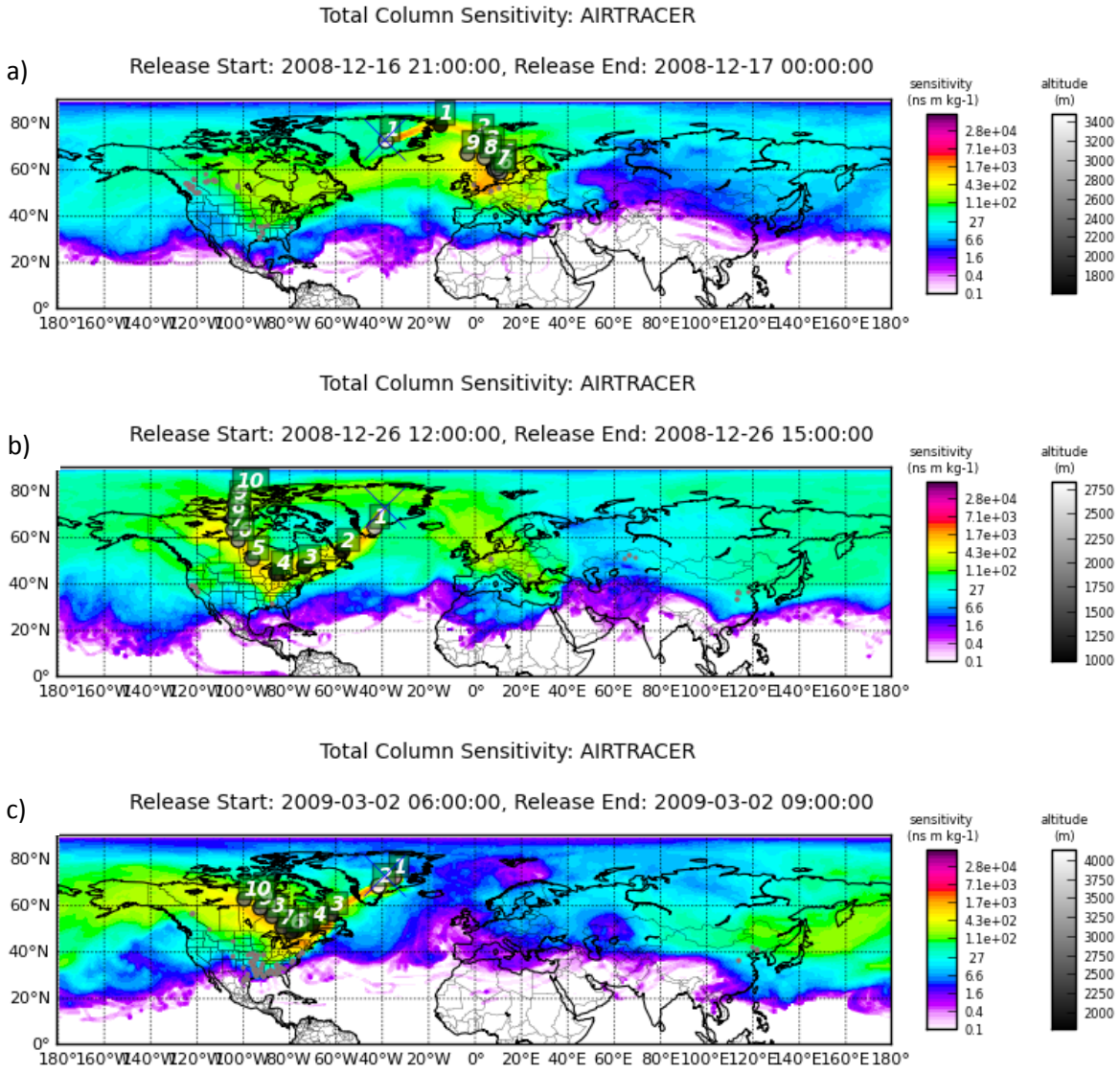


Figure S1: FLEXPART simulated total column sensitivity (ns m $kg^{-1}$) for retroplumes that are representative of the air mass transport during five anthropogenic events with low $O_3$ values (minimum $\Delta O_3$ for these events are all < -2 nmol $mol^{-1}$). Retroplumes originate at Summit on a) 16 December 2008 at 9 pm UTC, b) 26 December 2008 at 12 pm UTC, c) 3 March 2009 at 6 am UTC, d) 15 March 2009 at 9 pm UTC and e) 15 February 2010 at 6 am UTC. The shaded circles are indicative of the approximate position and altitude (grey-shading corresponding to scale) where the air resided up to 10 days (numbered labels) upwind of Summit (further information given in the main text).

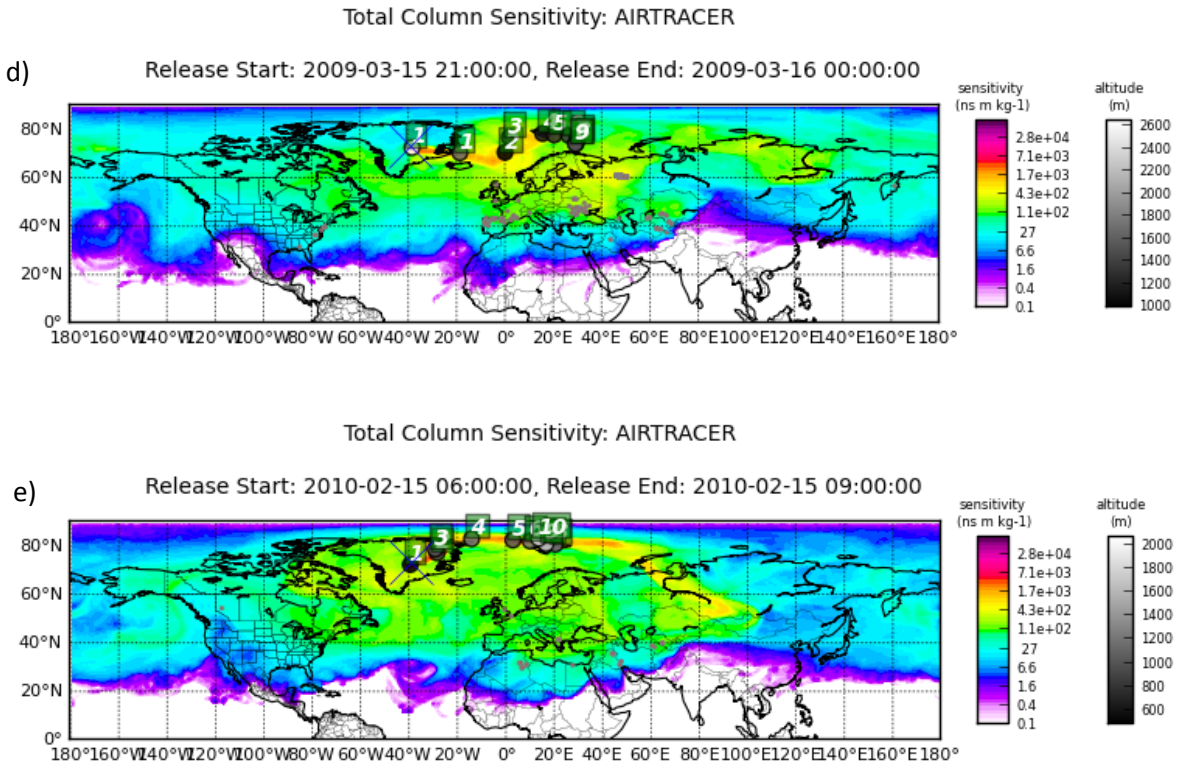


Figure S1: Continued from previous page

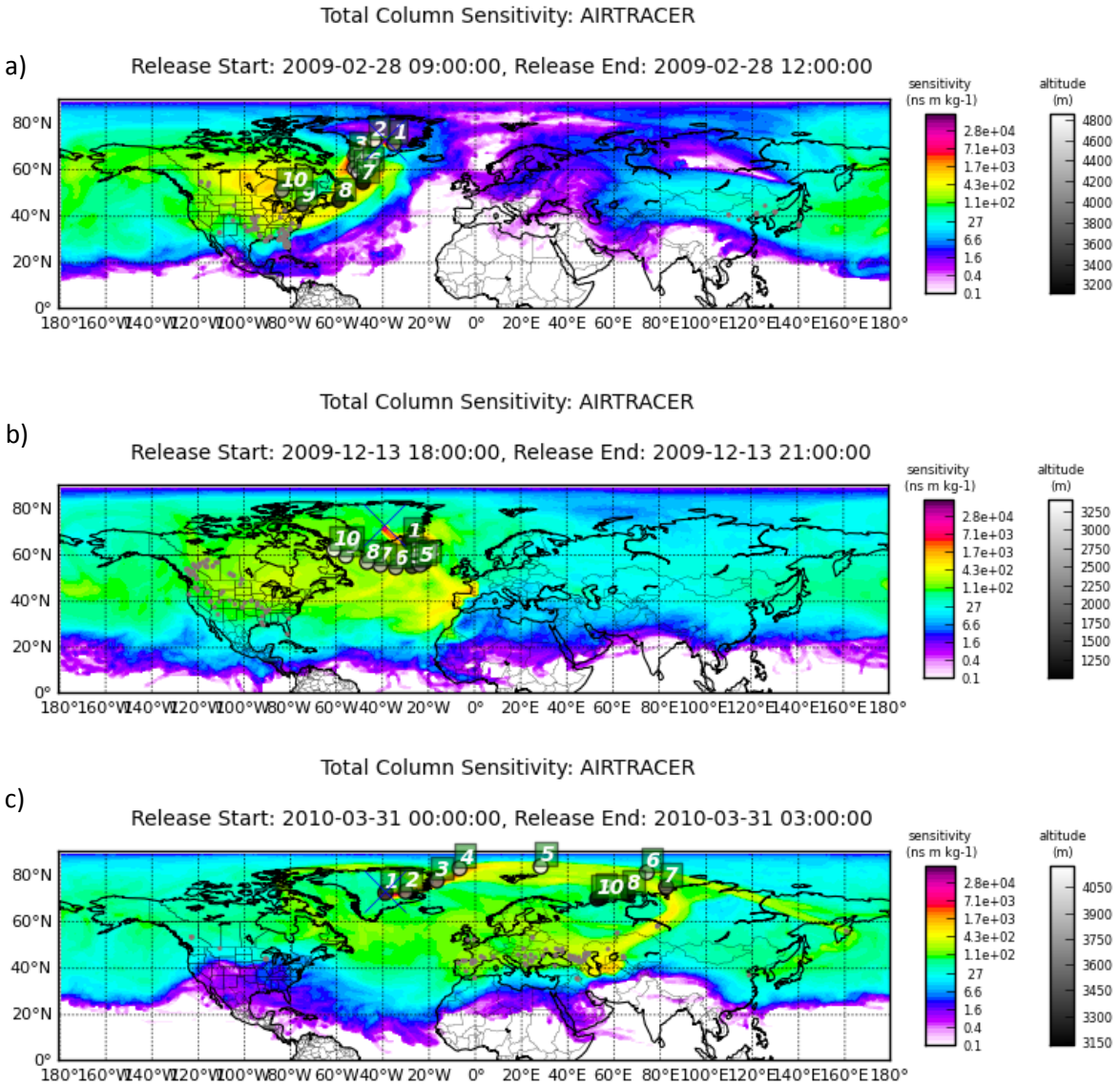


Figure S2: FLEXPART simulated total column sensitivity (ns m $kg^{-1}$) for retroplumes that are representative of the air mass transport during the five anthropogenic events with the largest positive mean $\Delta O_3$ value over winter (ranging from 4.7 to 7.5 nmol $mol^{-1}$). The retroplumes originate at Summit on a) 28 February 2009 at 9am, b) 13 December 2009 at 6 pm, c) 31 March 2010 at 00 UTC, d) 11 January 2010 at 12 UTC and e) 2 February 2010 at 9pm UTC.

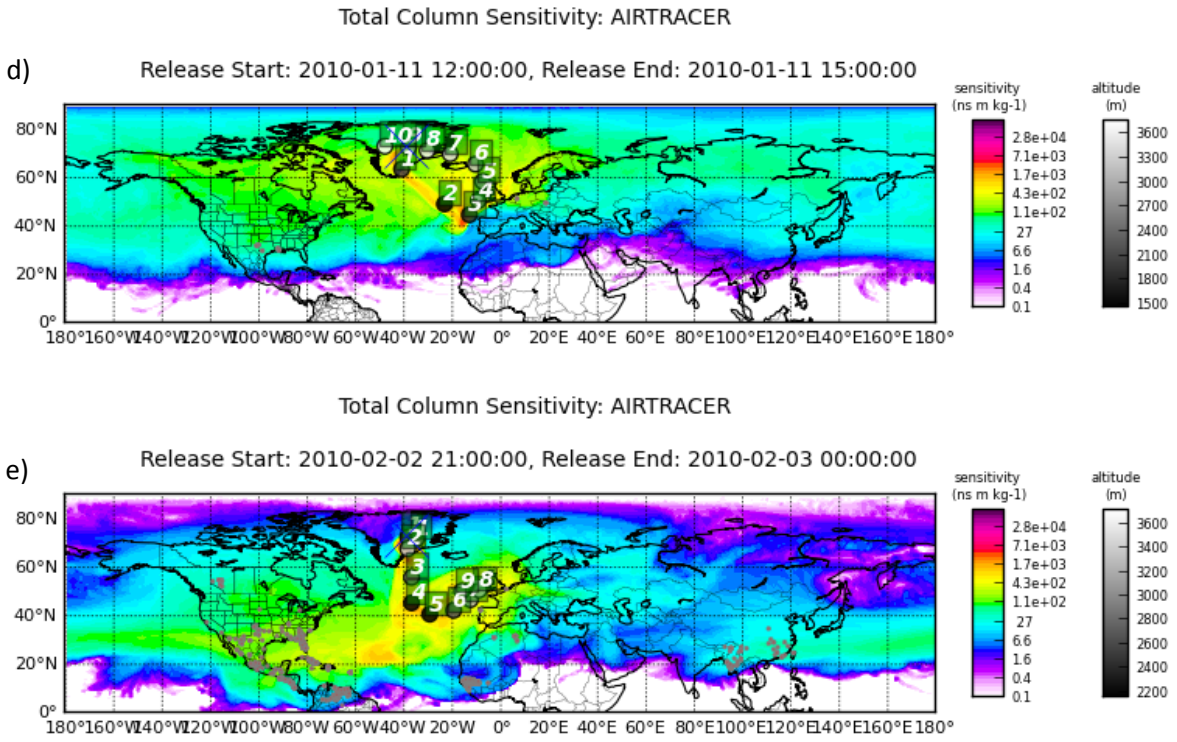


Figure S2: Continued from previous page

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