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Interactive comment on “Diode laser-based cavity ring-down instrument for NO₃, N₂O₅, NO, NO₂ and O₃ from aircraft” by N. L. Wagner et al.

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We thank the reviewers for their constructive and useful comments. In particular the referees identified three areas which needed improvement and rewriting. First, we have rewritten the description of the inlet transmission measurement and emphasized when and where NO additions are made and when the heaters and scrubbers are needed. Second, we have added a paragraph which uses in flight data to determine detection limits for each of the five measurements. These in-flight detection limits can be compared with laboratory detection limits and previous instruments. Third, we have added a paragraph discussing the accuracy of each of the measurements. Below are the referee comments in blue and our responses in black.

Anonymous Referee 1 Received and published: 27 March 2011

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General Comments: The article “Diode laser-based cavity ring-down instrument for NO₃, N₂O₅, NO, NO₂ and O₃ from aircraft” by Wagner, et al. describes an impressive new tandem instrument that combines several types of chemical and thermal modulation with two robust optical measurements (of nitrate radical and nitrogen dioxide) to produce determinations of five key atmospheric species suitable for airborne sampling.

This impressive achievement is described reasonably well (except for a few problem sections that I identify below) with a careful description of most of the conceivable problems and limitations. What is missing is an overall assessment of the measurement capabilities (limit of detection, measurement precision and accuracy) of the instrument as deployed in the CalNex field measurements. I understand that capabilities have a tendency to improve with time, but there appears to be enough data from the flights and preflight experiments to provide a detailed characterization of the instrument as it was in June 2010. Specifically, I’ll highlight the statement in the Abstract “The measurement precision for both NO₃ and N₂O₅ is below 1 pptv (2σ , 1s) and for NO, NO₂ and O₃ is 170, 46, and 56 pptv (2σ , 1s) respectively.” since these specifications are (or seem to be in the case of the latter three measurements) detection limits based on optical-only deviations in the zero baseline, which is only minimally related to the overall uncertainty of the instrument (at least for NO₃ and N₂O₅). My comment is based on an assertion (using quoted effects within the paper) that the uncertainty associated with the actual measurement of optical loss within any of the measurement cells is one of the smallest contributors to the overall uncertainty of the measurement. I’ll note some specific areas of concern in the next section, but I wish to close with the statement that this is a good paper and that the uncertainty issue can easily be addressed in an edit and that I recognize that the reported instrument appears to be working quite well in the challenging airborne measurement situation.

We thank the reviewer for these constructive comments. We have added paragraphs in which detection limits are determined from in-flight data and the overall accuracy of each measurement is stated and discussed.

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Rewritten discussion of detection limits and accuracy:

“Figure 6 shows a representative measurement of the NO_3 and N_2O_5 instrument baseline precision in our laboratory while sampling zero air. The Allan variance plot gives a detection limit under 1 pptv (2σ) in 1 s for both species. For NO_3 , this sensitivity is comparable to, but slightly worse than that reported by Dubé et al. (2006) (e.g., 0.5 pptv, 1 s, 2σ) using the Nd:YAG/dye laser instrument. For N_2O_5 , the sensitivity is slightly improved over the pulsed laser version (e.g., 2 pptv, 1s, 2σ), although the improvement derives more from reduction in the optical noise associated with the fast flow in the heated channel than with any change in the optical system itself. Due to environmental effects (e.g. vibrations on the aircraft) and variations in the ambient air (e.g. temperature gradients), the precession of the instrument is reduced while sampling ambient air in flight. The in-flight detection limits are determined from daytime measurements during CalNex, when the ambient mixing ratios of both NO_3 and N_2O_5 were below the laboratory detection limits and were 3 pptv (2σ) in 1 s for both NO_3 and N_2O_5 . The laboratory detection limits for the NO_2 and O_3 measurements have been reported in a separate publications (Washenfelder et al., 2011) and are 46 pptv and 56 pptv (1s, 2σ) respectively. Our previously reported, ground based NO_x instrument (Fuchs et al., 2009) exhibits a better precision of 22 pptv (2σ , 1s). In-flight baseline precision can be determined during zero measurements, which are 10-15 s in duration. For NO , NO_2 , and O_3 the in-flight detection limits were 140 pptv, 90 pptv, and 120 pptv, respectively. These detection limits are the average precision of 140 zero measurements from an 8 hour flight on June 3rd, 2010. The aircraft measurements of NO , NO_2 and O_3 also suffer from an optical instability in flight that leads to drifts on the order of 0.1 – 0.3 ppbv in flight. We anticipate improvements, primarily in the data acquisition software, to improve the precision of the NO_x and O_3 channels on the aircraft instrument. The longer-term baseline instability is most likely related to the mechanical stability of the optical cavity alignments on these channels. Investigation into the source of this instability and potential solutions is ongoing, although it could be addressed by simply increasing the frequency of zero measurements from the current 5 minute interval. The

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inaccuracy of the NO_3 and N_2O_5 measurements were described in detail by Fuchs, et al. (Fuchs et al., 2008), are unchanged by modifications described here. The N_2O_5 inaccuracy ranges from -8% to +11% (1σ). The major uncertainties contributing to the inaccuracy are uncertainty in the cross-section, R_i , inlet loss and filter aging. Because the filter aging can only decrease the measured mixing ratios, it only contributes to the upper limit of the inaccuracy. The same factors contribute to the inaccuracy of the NO_3 measurement (-9%, +12%, 1σ). However, the inlet loss of NO_3 is more uncertain leading to an increased inaccuracy compared with N_2O_5 . For measurements of NO , NO_2 and O_3 , the inaccuracy is dominated by the measurement of the effective cross-section which is directly related to the $\pm 2\%$ accuracy of the UV ozone monitor used to measure the cross-section as describe in section 3.1. There is additional uncertainty ($\pm 1\%$) in the dilution associated with the NO addition required to convert the O_3 to NO_2 . The total inaccuracy for all three measurements is $\pm 3\%$ (1σ)."

Specific Comments: An interesting question (in my opinion) is whether the incorporation of the relatively broad-band diode laser sources into the CRD measurement really resulted in an improvement of the instrument. Note that this issue can be considered in isolation from the other revisions to the instrument that allowed for the three NO_2 -related determinations. Clearly, in the case of the shift from 532 nm to 405 nm, a significant improvement in the nitrogen dioxide measurement was realized based on the increase in the effective absorption cross section and avoidance of ozone interference (and probably the breadth of the spectral features/spectral filling under the diode laser bandwidth). It is interesting that there is an unexpectedly (?) strong dependence on pressure observed in the NO_2 channels and some suggestion of the origin of this effect would be useful. With the proviso that the pressure dependence is properly represented and is relatively constant, the move to a diode laser appears to have improved these measurements.

We agree. Using a 405 nm diode laser has improved the NO_2 measurement and allowed for additional measurements of O_3 and NO .

The pressure dependence of the effective NO_2 cross-section is surprising to us as well. Our calibration scheme determines the effective cross-section, which is the integrated cross-section weighted by the laser spectrum and divided by R_l . R_l is the ratio of the cavity length to the length over which the absorber is present. It is possible that the pressure dependence is in R_l rather than cross-section. We have revised both the manuscript and figure 3 to allow for this possibility. Regardless of the source of the pressure dependence, the effective cross-section is still valid for the NO_2 measurements.

On the other hand, the move from a narrow-band dye laser source to the diode laser appears to have significantly degraded the NO_3 measurements. One aspect is that the effective absorption cross section is smaller, due to the incorporation of less strongly absorbed wavelengths into the ring-down signal. More problematic (in principle) is the suggestion that non-exponential ring-down decays are observed. This is attributed to the presence of underlying water absorptions, but in fact, the variation of absorption cross section within the bandwidth of the diode laser can result in multi-exponential decay signatures (the decay rate of some photons is larger than others). This could also be a problem in the NO_2 measurements, but is apparently not observed? Even more problematic is that possibility that the active mode structure produced by the diode lasers might change with time. Note that these effects would probably not be observed in an empty cavity unless there were large enough differences in the losses of the different cavity modes excited, so the Allan analysis might not have been useful in characterizing the problem.

We agree that the current implementation of the instrument has reduced sensitivity (precision) for NO_3 and N_2O_5 compared with previous instruments based on pulsed lasers. However, it is not clear to us that the reductions are due to the implementation of diode lasers alone, so we have refrained from an explicit comparison. For example, several components of the current instrument, including the composite optical bench and the ring-down mirrors, experienced reduced performance during the CalNex in-

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tensive. Until we are able to resolve these issues, a comprehensive assessment of the precision difference due to the diode lasers alone is not likely feasible. We have added the following sentence to the manuscript: “The reduction in precision compared to the previously reported, pulsed laser instrument is due to a combination of factors, including reduced performance from the composite optical bench and cavity ring-down mirrors experience during the CalNex field intensive, and is not due solely to the introduction of diode lasers.”

On the second point regarding multi-exponential decays, the manuscript does address these concerns. We carried out a theoretical analysis of the accuracy degradation associated with the presence of water vapor in the backgrounds and found it to be negligible (section 3.2). We have further shown that the calibrations are quantitative and linear, especially for NO_2 , indicating no degradation in analytical performance associated with potentially variable absorption cross section underneath the laser bandwidth. Additionally, absolute fit errors show no variation with NO_2 and NO_3 concentrations. The use of an effective cross section thus appears to be sufficient to characterize any effects associated with the use of a relatively broad diode laser. We have added two sentences to this effect to the manuscript as well.

I'm not sure how important the discussion in the second paragraph (line 4) on page 1568 is, since the reactions that drive NO and ozone into NO_2 are probably quantitative, but that paragraph is very difficult to understand. I read it carefully several times and I still am not sure that I understand the argument. Please rewrite this to make it clearer.

We have rewritten this paragraph to clarify it. The paragraph is copied below. Maintaining a constant number density is important because, while the conversion is quantitative, the excess reagent (NO or O_3) introduces a dilution of the ambient air. By carefully considering the effect of variation of pressure, we can simultaneously insure that the conversion is quantitative and minimize the dilution.

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“Maintaining a constant conversion efficiency of O_3 and NO to NO_2 is a potential challenge for sampling from an aircraft platform since the ambient pressure (and hence the reactant concentration and reactor residence time) is variable with aircraft altitude. Flows on all three 405 nm channels are controlled at constant volumetric rates, rather than constant mass flow rates, to maintain constant residence time and reactant number density in each reactor. Addition of a constant, mass flow of the excess reactant with a well-defined mixing ratio to the variable, volumetric flow produces a constant number density in each reactor as the aircraft ascends and descends. For example, the number density of NO in the O_x sample cell is the product of mixing ratio of the NO standard cylinder (MR), the total number density in the sample cell (Nd) and the ratio of the volumetric flows (F_{NO}^{vol} and F_{cell}^{vol}) as shown in eq. 2. Here, P is the pressure in the sample cell, P_0 is the standard pressure, k is Boltzmann’s constant, T is the sample cell temperature, and F_{NO}^{vol} is the volumetric flow of the reactant at standard pressure and temperature which is directly proportional to the mass flow and independent of pressure. Because the flow through the sample cell is maintained at a constant volumetric rate, the only pressure dependences in eq. (2) are the number density and the reactant volumetric flow, and they cancel each other. The result is a reactant number density that is independent of pressure. Thus, the conversion efficiencies outlined above do not vary with aircraft altitude.”

$$[NO_2] = MR \times Nd \times \frac{F_{NO}^{vol}}{F_{cell}^{vol}} = MR \times \frac{P}{kT} \times \frac{F_{NO}^{std} P_0}{F_{cell}^{vol}}$$

The discussion that spans pages 1575 and 1576 appears contradictory, hearkening back to the comment above about global uncertainty. The pptv levels quoted in the Abstract for NO , NO_2 and O_3 are cited as detection limits but then 100 to 300 pptv drifts are cited as a problem. If the drift has been characterized and is linear (or at least deterministic) I could see how it could be included in the background subtraction procedure and would thus be a minor contributor to the uncertainty. Is this the case?

There is always some drift of the background with cavity ring-down instruments. These

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background drifts are due to temperature changes, small changes in the optical alignment, etc. These drifts are accounted for by frequent zero measurements. Such drifts can be accounted for by increasing the frequency of the zero measurements. Additionally, these baseline drifts were more pronounced at specific times during the CalNex field study, while at other times they were less important.

There are number of contributions to the uncertainty of each of the measurements that should be considered in quoting the accuracy and precision of the instrument: for example, the conversion of N_2O_5 to NO_3 , the transmission (and the variation of the transmission during use on short and longer time-scales) of NO_3 to and through the measurement cell, and the uncertainty of the absorption cross section at elevated temperature all contribute to possible inaccuracy (and in some cases imprecision) of the dinitrogen pentoxide concentrations determined. A similar analysis should be conducted for each of the analytes. I believe that Dube and Brown have worked through these analyses to produce valid figures of merit for the older instrument, so it should be possible to follow their template. Since the Abstract represents a synthesis of the results of the paper, it would be more appropriate to quote the better, more global characteristics there.

We have added a paragraph discussing the accuracy of each measurement and the factors contributing to the uncertainty. See response to the comments above.

Technical Corrections: In both of the corrections (for water and pressure) second order polynomials are used, not third, as is stated in the text and figure captions.

We were in error and have replaced '3rd order' polynomials with '2nd order' in the text and captions.

An inset to Fig.1 showing the zero air / inlet combination would be helpful in visualizing it.

Please see the response to the comment below.

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Likewise, the discussion on line 12, page 1573 would be clearer if Fig. 1 showed the heater and NO inlet and the text said that the heater was followed by the NO addition (before the nylon NO₃ scrubbing). I assume that is what is going on: 1) add NO to turn ambient NO₃ into NO₂ or 2) heat and then add NO to turn NO₃ from ambient+N₂O₅ into NO₂. If the conversion of NO₃ by NO is quantitative, why is the scrubber even needed? (If it isn't quantitative, isn't there a larger problem?)

The measurement of the inlet transmission is not a simple procedure and requires a careful explanation. We have rewritten the section describing the transmission efficiency measurement to clarify the steps in the measurement, the additions and their locations. With the improved description in the text, no modifications to Fig. 1 were made. The rewritten section is below:

“Each measurement of NO₃ transmission efficiency has five steps shown in Fig. 5. First, the zero of the instrument is measured as discussed above. Second, the NO₃ source is added to the tip of the NO₃/N₂O₅ inlet and the mixing ratio NO₃ is measured in 662 nm channels. The amount of NO₂ coming from the source directly is measured in the NO₂ channel. As described above, for ambient sampling, the inlet for the NO₂, NO_x and O_x channels is separate from the NO₃ and N₂O₅ inlet; however, during the transmission measurements the NO₂ channel must be connected to the NO₃/N₂O₅ inlet. This connection is made via the three-way valve shown in Fig. 1, which switches the instrument between sampling and calibration mode. Unlike the previously described pulsed laser instrument, in which the NO₃ and NO₂ measurements were in series, they are in parallel in this instrument, such that measurements of NO₃ or N₂O₅ occur simultaneously with that of NO₂. The third step of the transmission efficiency measurement is to add NO₃ and NO simultaneously to the NO₃/N₂O₅ inlet. The reaction of NO₃ and NO quantitatively converts NO₃ into NO₂ producing two molecules of NO₂ for each molecule of NO₃ added to the inlet. During this step the NO₂ channel measures NO₂ from three sources: NO₂ coming directly from the N₂O₅ calibration source, NO₂ produced by the reaction of NO₃ and NO, and the NO₂ impurity present in the NO addition.

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The fourth step is to shut off the $\text{NO}_3/\text{N}_2\text{O}_5$ addition from the calibration source, but leave the NO flow present to measure the NO_2 impurity present in this NO. The fourth step accounts for this contamination. The fifth step is a second zero measurement, with no addition of either NO or $\text{NO}_3/\text{N}_2\text{O}_5$. The N_2O_5 transmission efficiency can be measured by a similar five step procedure with the addition of N_2O_5 to the inlet instead of NO_3 ; however, during the third step a heater is used to convert the N_2O_5 into NO_3 which is then converted to NO_2 by reaction with NO. This heater is along the connection between the $\text{NO}_3/\text{N}_2\text{O}_5$ inlet and the NO_2 sample cell and is followed by a short section of nylon tubing which acts as an NO_3 scrubber, as described in Fuchs et al. (2008). In this configuration, the scrubber serves to remove NO_3 from the flow produced by thermal decomposition of N_2O_5 when the NO addition is off during step 2, so that the NO_2 channel measures only the NO_2 arising from thermal dissociation of N_2O_5 and not any optical extinction from NO_3 . It also prevents recombination of NO_3 with NO_2 in the NO_2 sample cell. (Both the heater and scrubber are necessary for the NO_3 transmission measurement as well, because our source can not produce pure NO_3 . It is unavoidably contaminated with N_2O_5 .) During addition of NO, all NO_3 produced in the heater between the inlet and the NO_2 sample cell is converted to 2 NO_2 , which is not affected by the scrubber.”

I assume that all tubing in the system is Teflon? It would be prudent to say this from the outset, since materials (and the word tubing) are otherwise omitted in many places.

All of the tubing in the system is Teflon. We have inserted “the inlet is constructed from Teflon tubing and fittings.” to clarify the tubing material used. We have also inserted the word ‘tubing’ where it was omitted.

Line 5 on page 1571 isn't very clear. There are stated uncertainties of 1.5, 4, and 6% for what appears to be the same thing. Also, when heated, the absorption cross section for NO_3 changes – presumably the uncertainty also increases?

We have rewritten this section to clarify the meaning of these uncertainties. The cross-

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sections measured by Yokelson and Osthoff are accurate to $\pm 4\%$. The variability of the diode laser line shape leads to an additional uncertainty of $\pm 1.5\%$. When these uncertainties are added in quadrature the total accuracy of the effective cross-section is $\pm 6\%$.

The temperature dependence of the cross-section has been measured by Osthoff and does not lead to decreased accuracy.

The caption for Fig. 8 is wrong as regards the colors.

We have changed the caption to reflect the layout and colors of the figure.

The suggestion that elimination of methanol-based dye solutions was a major increase in safety for an instrument that generates ozone and carries high pressure zero air and NO (and solid N₂O₅?) is a bit dubious.

The dye laser solution, consisting of a flammable liquid and a carcinogenic dye, has been an important issue in certifying this instrument for flight safety. Its elimination is a significant improvement. The other hazardous materials, including the ozone generation, pressurized gas cylinders, and N₂O₅ calibration source are independent of this improvement and cannot be considered in terms of a tradeoff against the methanol / dye solution. This aspect of the diode vs. dye laser optical sources has represented a “major” improvement in safety, at least from point of view of those who certify this instrument for aircraft use.

Anonymous Referee 2 Received and published: 18 April 2011

The authors present a new, two-colour, laser-diode-powered multi-channel CRD set up for airborne measurement of NO_x, NO₃ / N₂O₅ and O₃. The device combines features of previously described 400 nm laser-diode instruments for NO_x and O₃ and also presents for the first time use of 662 nm laser-diodes for the NO₃ and N₂O₅ channels. The detection limits and precision are more than adequate for most environments and the use of a single instrument (with a single calibration standard) for airborne investi-

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gation of nighttime chemistry is an important development.

The operational features of the new device are described clearly and in sufficient detail and are backed up with data from an airborne campaign. The authors should consider following comments and minor corrections.

P157 L4 delete “NO₃ then“

We have removed this unnecessary wording.

P1557 L8 very modest ? Be more quantitative

We have added “(less than 1 pptv)”.

P1558 L17 please include the weight, footprint and power consumption of the pulsed laser system for comparison

We have added “(30 kg and 0.5 kW)” for the weight and power consumption of the pulsed laser system.

The footprint of the Nd:YAG plus dye laser system used 600 cm² of space on the optical bench. The pulsed laser system also required a power supply and cooler which consumed 3U of the 19” rack to a depth of 20”.

P1559 L20 As the authors are fully aware, NO is rarely the most important reactive partner for NO₃ in remote or rural locations. NO is also not a DIRECT sink for N₂O₅. Please elucidate.

We have replaced “Measurement of NO characterizes one of the most important nighttime sinks for NO₃ and N₂O₅.” with “Measurement of NO characterizes the most important nighttime sink for NO₃ in near source regions (e.g., low altitude over urban areas).”

P1560 L1 “quickly turned off” Please be more quantitative (even if hard numbers appear later).

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We have replaced “the laser is quickly turned off” with “the laser is turned off quickly compared with the decay of optical intensity in the cavity”.

[P1560 L7 “centre wavelength”](#) Not sure what this means in the context of a multi-mode laser.

We have replaced “Here, σ is the absorption cross-section corresponding to the absorber, the center wavelength and the spectrum of the laser,” with “Here, σ is the absorption cross-section corresponding to the absorber, averaged under the spectrum of the laser,”

[P1560 L14 “centered at”](#)

We have replace “diode laser centered at 662 nm” with “662 nm diode laser”

[P1561 L21 Does the laser mode structure vary with modulation frequency \(as described on page 1562 L19\)?](#)

Yes, the modulation frequency does affect the mode structure. The laser was modulated at the same frequency throughout the course of the field experiment. If a different frequency were used, new temperature setpoints for the tuning of the laser would need to be determined and the cross-sections would need to be recalibrated.

[P1565 L1 The O₃ cross section is 10000 times smaller than that of NO₂. However, 30ppb O₃ is 3000 times the mixing ratio of 10 ppt NO. How does this influence the LOD for NO ?](#)

At 405 nm, the cross-section for NO₂ is $6.2 \cdot 10^{-19} \text{ cm}^2$ (this work). The cross-section for O₃ is $1.49 \cdot 10^{-23} \text{ cm}^2$ (Fuchs, EST, vol. 43, pg. 7831, 2009). Based on these cross-sections 30 ppb of O₃ would appear as a 0.72 pptv of NO₂, much smaller than even the better detection limits reported in the Fuchs paper. However, if future improvements lower the detection limit, then it will be necessary to correct for the extinction of O₃.

[P1567 L2 0.3 % is better than 3 ppthv ?](#)

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We have changed “3 ppthv ozone” to “0.3 % ozone”.

P1568 The measurements rely on zero air for ring down times in the absence of NO₂. How do you know that the “zero air” has zero NO₂. 50 ppt of NO₂ is not untypical in zero air. This implies an underestimation of NO₂ by the amount in the “zero air” bottle, which is an important source of potential error at low NO₂ mixing ratios.

The reviewer raises an important point. Contamination of the zero air is a source of potential error in the current zero scheme for this instrument. It is difficult to quantify this error using the instrument described here. Separate, chemiluminescence based measurements of the NO₂ contamination of the Scott-Marin, grade ultrazero air have shown it to be < 10 ppt (Eric Williams, personal communication).

Currently, this instrument is configured to measure polluted urban air masses and an offset of 10 ppt would not be significant. Optimization of the instrument for a cleaner or more remote environment would require a more active scrubbing scheme for NO_x.

We have added “The potential for an NO₂ impurity in the zero air limits the applicability of this zero scheme for sampling in remote environments, where ambient NO_x may be comparable NO_x impurity in commercial zero air. Chemiluminescence measurements at our laboratory have found the zero air (Scott-Marin ultrazero) to have less than 10 pptv of NO_x. “ to acknowledge this source of potential error.

P1575 calibration The inlet transmission (calibration) for NO₃ is performed using several ppbv of NO₃. NO₃ at these high levels could have a passivating effect on the walls (e.g. oxidation of organics) and thus result in lower loss rates than would be determined at an atmospheric mixing ratio of e.g. 20 ppt. How can you be sure that this loss rate is transferable. I guess that simultaneous measurements of N₂O₅ and equilibrium calculations could help here. Might be worthwhile mentioning this aspect.

We have added the following sentence to the manuscript: “In field calibrations during CalNex showed no dependence of NO₃ transmission efficiency on NO₃ mixing ratio

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over the range 0.3 – 4.3 ppbv, although calibrations on any given day were normally performed at a single concentration.”

Fig 5 caption. “The N₂O₅ calibration is 99 %“ (transmission is 99 %)

We have replaced “The N₂O₅ calibration is 99%“ with “the N₂O₅ transmission is 99%”.

Fig 6. The upper and lower captions appear to have got muddled (integration time on log scale ?)

We modified the figure so that the labels from the upper panel and the lower panel are both visible.

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 1555, 2011.

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