

Referee #1

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Reidmiller, D. R., D. A. Jaffe, E. V. Fischer and B. Finley: Nitrogen oxides in the boundary layer and free troposphere at the Mt. Bachelor Observatory, Atmos. Chem. Phys. Discuss., 10, 5751-5801.

General Comments

(1) REVIEWER

This paper presents a thorough overview of NO_x measurements from a mountaintop observatory in the northwestern US for 5 seasonal intensives. The measurements appear to be of high quality and are carefully segregated, using time of day, into those representative of the free troposphere (FT) vs. those with a boundary layer influence. Novel meteorological profile measurements are used to justify this segregation. Use of the FT data allows a characterization of the background NO_x mixing ratios for this region as well as an assessment of Asian influences, including a meteorological analysis, in an averaged sense, of dynamical conditions which favor Asian Long-Range Transport. Additionally the top 20 high-NO_x events are examined to determine likely source regions. The treatments of the measurements and data are thorough. The analysis of the observed variations in mean and median NO_x levels, while adequate for a "data paper" such as this, tends to be somewhat qualitative (see items 7, 11, 12 below), and therefore not entirely convincing. To put this on firmer ground would require a modeling effort that I acknowledge is beyond the scope of the present effort. Overall this is a high quality piece of work, clearly written, and should be published more or less as is, subject to only minor changes.

(1) RESPONSE

We agree with and appreciate this reviewer's assessment of our study.

Specific Comments

(a) REVIEWER

p. 5753, deep convection and lightning NO_x occur not only in tropics

(a) RESPONSE

We have removed the text in parentheses that states: "(i.e., the tropics)"

(b) REVIEWER

p. 5754, line 16: 15% of emitted NO_x gets to FT, presumably as NO_x (not yet PAN). Does a significant portion get converted to PAN in the BL, then to be transported to FT? BL too warm? Depend on season?

(b) RESPONSE

A review of Koike et al. (2003) and references therein did not discuss NO_x-to-PAN conversion in the BL. However, Koike et al. (2003) explicitly state that, "...15% of NO_x emitted over the northeastern part of China remained as NO_y at 2–7 km (free troposphere)". So, implicit in this statement is BL conversion of NO_x to PAN. We have clarified the text in our paper to now read, "only a small percentage (15%) of NO_x emitted in the Asian BL is exported to the FT as NO_y."

(c) REVIEWER

p. 5759: UV Pen-ary lamp? Is mentioned out of the blue. How used? Context?

(c) RESPONSE

We have added text to clarify the use of the UV Pen-ray lamp: “This UV lamp produces O₃ from hydrocarbon-free air for the gas phase titration of NO to NO₂. This allows for an instrument calibration of NO₂.”

(d) REVIEWER

p. 5759, line 26: minimum recorded when under repair. Not clear. Might think that "under repair" means not in use, but must be being used while in compromised condition.

(d) RESPONSE

The system has two O₃ generators. When maximum O₃ is produced the sensitivity of the system is maximized. When one of these generators is down for repair, O₃ is still being provided to the system, but in about half the concentration as when the system is operating normally. As a result, the sensitivity is at a minimum when less O₃ is made available for the chemiluminescent reaction necessary for detection of [NO]. We have added text to clarify this statement.

(e) REVIEWER

p. 5760: How is detection limit defined?

(e) RESPONSE

Following the work of previous group members [e.g., Honrath 1991; Beine 1996], we define the detection limit of an analytical method as 3x the standard deviation of a blank measurement [e.g., Winefordener and Long, 1983; Keith 1991]. For our purposes, the “blank measurement” can be described by the expression:

$$\frac{1}{Sensitivity} * \sqrt{\frac{2 * Zero_counts}{N}}$$

where N is the averaging time (in seconds) of the counts during the zero mode. Rather than describing this in detail in the text, we have added a reference to Reidmiller, 2010 which is the corresponding author’s PhD dissertation and describes the instrumentation, data reduction and calibration statistic derivations in complete detail.

Honrath, R. E.: Nitrogen Oxides in the Arctic Troposphere, PhD dissertation, University of Alaska, Fairbanks, AK, USA, Sept 1991.

Beine, H. J.: NO_x Photochemistry in High Northern Latitudes during Spring, PhD dissertation, University of Alaska, Fairbanks, AK, USA, Aug 1996.

Winefordener, J. D. and G. L. Long: Limit of detection, *Anal. Chem.*, 55, 712, 1983.

Keith, L. H.: Report results right!, *Chemtech*, 486-489, 1991.

(f) REVIEWER

Overall the authors present a very thorough description of data reduction procedures and error analysis.

(f) RESPONSE

We appreciate the reviewer’s positive assessment of our presentation.

(g) REVIEWER

p. 5765, lines 12-25: Plausibility arguments are given for why the NO/NO₂ ratio varies as it does, but without any quantitative analysis, the reasons are not very convincing.

E.g., what is quantitative effect of snow on J?, what is quantitative effect of being closer to solstice?, etc.

(g) RESPONSE

We have added the following text to this section: “As Brasseur et al. (1999) show, J_{NO2} at the altitude of MBO can increase by 25-50% as the solar zenith angle changes from 70° to 0°... Honrath et al. (2000) found that irradiated snowpack can enhance NO₂ concentrations by up to 300 pptv and Mt. Bachelor is snow-covered during spring, but bare during autumn.”

Brasseur, G. P., J. J. Orlando and G. S. Tyndall: *Atmospheric Chemistry and Global Change*, Oxford University Press, New York, 654pp, 1999.

Honrath, R. E., M. C. Peterson, M. P. Dziobak, J. E. Dibb, M. A. Arsenault and S. A. Green: Release of NO_x from sunlight-irradiated midlatitude snow, *Geophys. Res. Lett.*, 27(15), 2237-2240, 2000.

(h) REVIEWER

p. 5766: I have trouble understanding/appreciating the message in Fig. 5. Possible to offer more explanation?

(h) RESPONSE

We have added the following text: “It follows, then, that a change in airmass type (i.e., a BL-influence) could be detected by a change in the slope of q vs. θ as it approaches zero.”

(i) REVIEWER

p. 5770: An INTEX-B flyby is noted but the region for INTEX-B in Fig. 6 does not overlap with MBO location.

(i) RESPONSE

The NW-to-SE and SW-to-NE purple boxes labelled “D” (the INTEX-B campaign domain in Fig. 6) do indeed cover MBO, but it is masked by the overlapping of regions “E” (PHOBEA campaign) and “F” (ITCT-2k2 campaign).

(j) REVIEWER

p. 5770: Is a stretch to compare NO₂ from 2007-2008 to NO₂ for same month in 2006, but I guess that is best that can be done. Ranges are comparable but really not a valid (ie, direct) comparison.

(j) RESPONSE

The authors agree, which is why we have explicitly stated that “... as opposed to direct NO₂ comparisons...” However, we have added the following text to the end of this section: “We recognize, as Chameides et al. (1990) stated, that large, random variations are associated with NO_x measurements in the remote FT, making comparisons of NO₂/NO from individual time intervals statistically meaningless. However, this is the best we can do with the available data.”

Chameides, W. L., D. D. Davis, J. Bradshaw, S. Sandholm, M. Rodgers, B. Baum, B. Ridley, S. Madronich, M. A. Carroll, G. Gregory, H. I. Schiff, D. R. Hastie, A.

Torres and E. Condon: Observed and model-calculated NO₂/NO ratios in tropospheric air sampled during the NASA GTE/CITE-2 field study, J. Geophys. Res., 95(D7), 10,235-10,247, 1990.

(k) REVIEWER

p. 5771: Is plausible that warmer Ts had an effect via shorter PAN lifetime, but, again, not quantitative. How much warmer? Is this enough to actually make a difference?

(k) RESPONSE

We have further cited Fischer et al. (2010) as they quantify PAN-to-NO_x decomposition in this region during this time and included text to read: “The anomaly of +4°C corresponds to a change in mean temperature in this region at this altitude of -12°C to -8°C, which corresponds to a decrease in PAN lifetime from ~680 sunlit hours to ~200 sunlit hours. As Fischer et al. (2010) show, this change could result in a substantial re-partitioning of NO_y from PAN to NO_x in the NE Pacific during spring.”

(l) REVIEWER

And same applies to wind speed argument. Probably acts in the right direction, but enough to be significant quantitatively?

(l) RESPONSE

This is difficult to quantify because it would determine on a number of factors. However, the paragraph following the one in question (and Table 4) describes the use of the LRT3 index, which is a quantitative measure of the intensity of Asian long-range transport based on sea-level pressure anomalies. This evidence supports the wind speed argument and corroborates the finding that a significant quantitative difference in inter-annual differences in the trans-Pacific transport of Asian pollution. As a result, we have made no changes to the text.

(m) REVIEWER

p. 5777, line 8: 5 found to have a NA influence. Or is 5+2 = 7? Since the 2 had mixed sources.

(m) RESPONSE

We elected not to include the 2 “mixed” sources into either “Imported” or “North American” because the patterns they displayed were not as evident as the 10 Imported or 5 North American events. Therefore, we have not changed the text in regard to this comment.

Technical Comments

(1) REVIEWER

p. 5759: Buhr describes

(1) We have changed the text accordingly.

(2) REVIEWER

p. 5767, line 12: 5,h

(2) We have changed the text accordingly.