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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nitrogen oxides in the boundary layer and free troposphere at the Mt. Bachelor Observatory" *by* D. R. Reidmiller et al.

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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) REVIWER This paper presents a thorough overview of NOx 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 NOx 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 Trans- port. Additionally the top 20 high-NOx 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 NOx 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 NOx 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 NOx gets to FT, presumably as NOx (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 NOx-to-PAN conversion in the BL. However, Koike et al. (2003) explicitly state that, "...15% of NOx emitted over the northeastern part of China remained as NOy at 2–7 km (free troposphere)". So, implicit in this statement is BL conversion of NOx to PAN. We have clarified the text in our paper to now read, "only a small percentage (15%) of NOx emitted in the Asian BL is exported to the FT as NOy.

(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: (1 / Sensitivity) * [sqrt ((2 * Zero counts)/N)] where N is the averaging time (in seconds) of the counts during the zero mode. Rather than describing this is 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.: NOx 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 fir 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, JNO2 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 NOx 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. ïĄś 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 labeled "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 NOx measurements in the remote FT, making comparisons of NO2/NO from individ-

ual 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 warmers 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-NOx 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 NOy from PAN to NOx 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.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C4183/2010/acpd-10-C4183-2010-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 5751, 2010.