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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The Morning NO_x maximum in the forest atmosphere boundary layer" *by* M. Alaghmand et al.

Anonymous Referee #3

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Review of "The morning NOx maximum in the forest atmosphere boundary layer," by Alaghmand et al.

Summary Comments:

The paper considers several potential explanations for a morning maximum in NOx commonly observed at a remote site in the northern lower peninsula of Michigan. The authors come down on the side of the importance of distributed surface emissions into a stable nocturnal boundary layer that accumulate in the few hours before sunrise, giving rise to a peak that starts to rise prior to sunrise, and which decays with the onset of the morning breakup of the stable layer. The paper merits publication but could

be improved by a more critical assessment of this favored explanation, especially with regard to the timing of the initial NOx increase and how this relates to what is known about the formation, and its timing, of the stable NBL.

Two of the alternative explanations may be non-starters (more details below): (1) Why consider HONO (section 3.1) to be a source of NOx if 2 NOx are required to from 1 NOx? There may be a way to address this by the timing of the NOx consumption, but the authors do not consider this. On its face, this is a sink and not a source. (2) How can transport from Detroit and Chicago (section 3.4) give rise to a peak that occurs at a certain time of day? This requires quite a meteorological coincidence.

Main Comments:

[A] The paper could benefit from a more critical assessment of the preferred explanation for the morning maximum, that being that it is due to surface emissions accumulating in the stable nocturnal boundary layer over some hours prior to NBL breakup at sunrise. It is critical to ask what determines the start time of the rise to the peak. It seems that NOx should start to increase as soon as the boundary layer becomes stable. What time is this typically? What is the dynamical meteorology? Is it consistent with the observed onset of the NOx increase? This can be address in general terms, with regards to what it typical. In addition, it could be addressed on a per-night basis. Fig. 4 indicates that there is relevant data. Is there a correlation between NBL stability and the NOx increase, both with regard to onset time, as well as to magnitudes? For example, if the NBL becomes stable at 10 PM, then would expect NOx to start to increase then, but this is not generally seen in the plots. The increase is generally much later. There is some evidence related to this point plotted in Figure 4, but this is just for one day. Is this typical? The authors do not focus on the timing of stability onset. This seems a critical point not brought out in the argument. If the onset of the NOx increase coincides with the onset on NBL stability, this strengthens the authors' case. To be specific, here are questions that Fig.2 raises: Why is there no increase in NOx from, say, 4 AM to 5 AM. Is there not a stable NBL at this time? If there is, then

why no evidence of accumulation of soil emissions into the NBL. Why even a decrease from 3 AM to 4 AM? Is not the NBL stable during this time? Does this argue against the authors' case? What is known, both in general terms and from contemporaneous tower temperature data, about boundary layer stability as a function of time? This points to further work that could readily be done to quantitatively assess the preferred explanation, and potentially strengthen (or weaken) the authors' argument.

[B] There are many allusions sprinkled throughout the paper about the potential significance of anthropogenic emissions, but there is little, if any, correlation of NOx with CO. My general feeling is that anthropogenic sources are given greater likelihood than is warranted by the lack of a correlation with CO. Why give this so much credence if there is no CO peak at sunrise? This was a recurring notion as I read through the paper.

Detailed Comments:

p.29253, lines 21-24: Incompatibility: "continental boundary layers have 1-3 ppbv" vs. "remote locations have 4-50 pptv." Only true if all remote locations are non-continental, but can't a continental location be remote? Are the subject measurements from a remote site? Are there remote sites on the Antarctic continent? Could improve clarity of phrasing.

p. 29254, lines 3-5: The way this is written, it is suggest that the presence of BVOCs is required for NOx chemistry to generate HNO3. Could improve clarity of phrasing.

p. 29255, line 25-end: Why is this called an artifact test? Sounds like what some would call a zero.

p. 29256, line 11: detection limit is given here, but some lines later (21-22), a definition of detection limit is given. Better to give the definition at first use.

p. 29256, lines 25-26: tube diameters are given. Are these ODs or IDs? They look like ODs, but IDs are more relevant to what matters (indeed what is given elsewhere), such as residence time in the tubing.

p. 29258, line1: The increase in NO is discussed as if it has nothing to do with the increase in NOx. For a reader not too familiar with the subject, the question arises as to how much the NOx increase contributes to the NO increase. Please say something explicit about this. (Is it negligible? Is it a 10% effect?)

p.29258, bottom: How can HONO be considered a NOx source? R4 and R5 show that two NOx molecules are required to produce one NOx molecules. Looks more like a sink than a source, just looking at these reactions. If, however, the NO2 consumption occurs over a long time scale prior to HONO photolysis, then it can be a source on a short time scale. The authors should be more thorough here. The burden is on them to spell this out a bit more since on its face this is a sink.

p.29262, start of section 3.4: I don't see how transport of polluted air from Detroit or Chicago can be responsible for a morning peak at the site unless the transport patterns are locked into a daily cycle. Again, I'll focus on timing of the peak. The timing of a NOx peak from Detroit or Chicago depends entirely on back trajectories, and what the wind speed is, and when it changes directions. It would be a phenomenal coincidence (though interesting) if the routinely observed morning peak at the site were routinely due to the onset of the arrival at the site of air from those cities. Offhand I would expect transport from these cities to give a rise in NOx that could occur at random times of the day. Why consider this as a credible, likely source of a peak that occurs at a fixed time of day?

p.29263, first line of conclusions: Again seems odd that NO peak is address with no connection whatsoever to NOx peak. Same point as above.

Fig. 4: Are these times on a 24-hr clock? Or AM/PM? Esp. is this 12 noon or midnight?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 29251, 2011.