Atmos. Chem. Phys. Discuss., 12, C13865–C13874, 2013
www.atmos-chem-phys-discuss.net/12/C13865/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Dynamics of nitrogen oxides and ozone above and within a mixed hardwood forest in Northern Michigan" *by* B. Seok et al.

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Received and published: 22 April 2013

General comments

The suggestions from Referee #2 were considered as detailed below, and are appreciated for improving the quality of our manuscript. The referee's comments are printed in *italics* followed by our response indented in regular font. Text changes made to the manuscript are in **bold** fonts.

Specific comments

The authors use profile measurements and a single-column model to simulate the

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Interactive Discussion

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diurnal behavior of the vertical distribution (over a 40 m height) of NOx and O3 at a forest site in northern Michigan. The months of August and November are simulated and contrasted, as the biology and weather differ significantly between these 2 months. An interesting feature in the observations is a morning peak in NO and also a morning peak in NOx. It is concluded that the morning peak in NO is due to the photolysis of NO2 advected to the site from urban areas to the south. However, the results are very unclear as to what causes the peak in NOx

In my view, the paper comes up very short on this important objective.

In the introduction, the objectives of our study are stated (P.32517, L.27 to P.32518 L.5) as (1) to investigate the cause for the observed morning peak mixing ratios of NO_x and (2) to assess the sensitivity of in-canopy NO_x (and O_3) to potentially relevant in-canopy sources and sinks under atmospheric conditions encountered at UMBS. However, it appears from the referee's comments that the steps we have made to present these objectives are not all that clear. To address these comments we propose to introduce in the revised the following changes:

(1) to investigate the cause for the observed morning peak mixing ratios of NO_x differentiating between the role of local- versus distant sources of NO_x and (2) to assess the sensitivity of in-canopy NO_x (and O_3) to potentially relevant in-canopy sources and sinks under atmospheric conditions encountered at UMBS.

Additionally, we have altered our conclusions section. P.32542 L.4+:

The dynamical behavior in $NO_{x,MO}$ and O_3 at a deciduous forest site at UMBS was investigated. We combined concentration gradient and micrometeorological measurements with a canopy-boundary layer exchange model for a detailed analysis of the role of local sources and sinks (biogenic emissions, dry deposition, chemistry) and turbulent

ACPD
12, C13865–C13874, 2013

Interactive Comment

transport, versus the role of advection in the observed NO_x and O_3 mixing ratio changes.

Our data analyses show that the morning NO maximum at UMBS is associated with the increase in solar radiation after sunrise, and most likely due to photolysis of $NO_{2,MO}$. The model simulations indicate that soil NO emissions are not sufficient to explain the morning $NO_{x,MO}$ peak concentrations. Also, sensitivity analyses with the SCM showed that foliage NO_x emissions via nitrate photolysis do not appear to explain the observed morning NO_x (and NO) maxima above the canopy as these processes yielded a misrepresentation of the observed diurnal variability in NO_x. Instead, the SCM analyses suggests that a leaf-level NO_2 compensation point seems to play a role in the observed NO and $NO_{x,MO}$ dynamics.

Observed and simulated $NO_{x,MO}$ data indicate that the morning $NO_{x,MO}$ maximum is associated with local and non-local transport events such as entrainment from aloft air masses and advection of polluted air. The sensitivity analysis of the SCM and the analysis of air mass advection suggest that despite UMBS being located in a relatively remote area far from major urban sites, most of the $NO_{x,MO}$ seen at UMBS is of anthropogenic origin and that its impact is significant on the chemistry observed at the site.

To understand the dynamics of $NO_{x,MO}$ at UMBS, not only should we consider large scale advection, boundary layer dynamics, and entrainment, we should also consider leaf-scale processes as biologically mitigated processes seem to contribute to the observed $NO_{x,MO}$ dynamics at UMBS. Therefore, more studies on leaf-scale processes and their effect on the biosphere-atmosphere exchange are needed for further evaluation of this question.

ACPD
12, C13865–C13874, 2013

Indeed when the authors address the cause of the NOx peak toward the end of the paper, this is the claim: "the observed morning NOx maximum appears to be caused by (1) the photolysis of NO2 . . ., or (2) . . ." I may be missing something, but I think the authors may not mean this. Photolysis of NO2 to NO does not cause any change in NOx. Is this a mis-statement or what the authors really intend?

If it is intended, it merits further explanation, as many will interpret as I have done. I find it frustrating to have a lack of clarity on what is such a fundamental point of the paper.

Yes, there indeed was an error in the text at this point. There are two peaks and each peak is driven by different process. The peak in NO is due to the photolysis of NO_2. The $NO_{x,MO}$ peak appears to be due to transport/entrainment and a foliar source most likely due to the existence of an NO_2 compensation point.

Also, the authors fail to address, head on, the fact that the high levels of NOx, which they attribute to advection from urban areas to the south, have a diurnal peak that consistently falls shortly after sunrise. This is bewildering. It seems that back trajectories are called for, along with a determination of transit times from the urban areas.

Cooper et al (2001), Thronberry et al (2001), and Alaghmand et al. (2011) provided evidence in their analyses (and back trajectory analyses (Alaghmand et al. (2011)) for the determining transport from the south. Therefore, we applied simple wind and pollution rose diagrams for supporting our argument that a significant fraction of $NO_{x,MO}$ is transported to the site long distance.

I find it very puzzling, indeed interesting, that there is such a tight correlation of the

ACPD

12, C13865–C13874, 2013

Interactive Comment

timing of the NOx peak and sunrise. Why is it not much more variable? On some days, does the peak occur at a different that can be explained by differences in transport?

Our supplemental Fig. A2 shows that the $NO_{x,MO}$ maxima occur very close to sunrise. Also, Fig. A1 shows that it is during the sunrise period when there are winds from the south, which we assume carry polluted air (based on analyses by Cooper et al. (2001), Thornberry et al. (2001), and Alaghmand et al. (2011)). The spread in the $NO_{x,MO}$ (unlike for the NO) (Fig. A2) implies that the occurrence of the $NO_{x,MO}$ peak is not exclusively associated with a source process that depends on solar irradiance but that there is a combination of sources that supply $NO_{x,MO}$ over a prolonged period.

Have the authors considered boundary layer development/growth (hence dilution)?

Yes, we have considered the role of boundary layer development in our analysis. We had to rely heavily on the model analysis due to fact that we did not have direct observations higher up in the residual layer or growing mixed layer to assess the role of entrainment versus advection.

In summary, I find the paper lacking in two important respects, important since they relate to a fundamental objective of the paper, and that is to explain the diurnal pattern in NOx,

The two issues: (1) a claim that the NOx peak is due to photolysis of NO2 (2) if the NOx has an urban source, then why is its peak so tightly correlated with sunrise? (any relation to boundary-layer evolution?)

As mentioned previously, this will be corrected. The NO peak is due to NO_2 photolysis. Our analyses further show that the $NO_{x,MO}$ peak appears

ACPD

12, C13865–C13874, 2013

to be due to transport/entrainment and a foliar source that most likely is associated with the existence of a foliar NO_2 compensation point. This latter finding also relies on the model simulations that incorporate the role of transport and local-sources but that can unfortunately not be thoroughly evaluated due to missing observations on the chemical composition higher up in residual layer.

p 32516, line 18: "on" –> "to"

Corrected.

p 32517, line 2: Soil emissions are not too significant, so why list that one first?

We were simply listing the main sources of NO_x in no particular order. We reordered the list so that its significance goes from most to least.

Updated text (P.32517 L.2): **Nitrogen oxides (NO_x = NO + NO_2), which originate from combustion, lightning, and soil emissions, play a critical role in regulating the photochemical production of ozone (O_3) in the troposphere...**

p 32519, line 20: "including" –> "and" (since NO2 does not include the other species)

Corrected.

p 32519, line 28, and following: This depends on age. It is a reasonable estimate at young age, but is not reasonable, even for anthropogenic source, at old age (since NOx has been converted to other species).

ACPD
12, C13865–C13874, 2013

The interpretations in the manuscript primarily build around the timing and relative changes of the morning $NO_{x,MO}$ peak, and not that much on absolute concentrations and NO_x/NO_y relative ratios and distribution. Therefore, the deficiency in using the Model 42C-TL instrument in measuring NO_x should not deter from the main conclusion that we draw.

Moreover, a recent intercomparison study of various NO_x instruments by Gilge et al. (2013) showed that Model 42C-TL data deviated by 2∼3

p 32520, line 9: How is detection limit defined?

(P.32520 L.9) The following sentence defining the term "detection limit" was added: **The detection limit was determined by taking three times the standard deviation of the blank (the ultra-zero air).**

p 32554, fig 3 caption: "dotted" –> "dashed"

Corrected.

p 32528, line 12: It is said that understory NO [at <=20 m?] is larger than above canopy NO. I do not see this in fig. 4.

The colors of the contour plot will be reworked so that the levels are more distinct. (We have added contour lines that are in 0.02 ppbv increments in the updated figure.) Closer inspection of this graph indicates lighter shades of blue [∼0.1 ppbv NO] below canopy (< 21m) than above the canopy (> 21 m, 32 m - 40 m) [darker shades of blue, ∼0.05 ppbv NO] (slightly better visible between hrs 18 and 24).

Please find the updated Fig.4 included in this reply.

ACPD

12, C13865–C13874, 2013

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Interactive Discussion

Discussion Paper

p 32532, line 10: What is the "stability effect"?

We have reworded this to "atmospheric stability."

section 4.3: I can see why there is a tendency for the NO peak to be tied to sunrise, but why the NOx peak? If the NOx peak is due to transport from polluted regions, is this just a coincidence then? And related to the transit time from the urban areas. I would not expect such close correlation with sunrise. This is puzzling.

The correlation between the timing of the NO_x peak and change in wind direction may be a coincidence, but our data suggest that the $NO_{x,MO}$ peak is due to transport by entrainment and a NO_2 compensation point in foliar emissions.

p 32536, line 9: add 's' to 'mean'

Corrected.

p 32541, last 3 lines: "the observed morning NOx maximum appears to be caused by (1) the photolysis of NO2 : : :" This must not be what the authors really mean. Photolysis of NO2 does not alter NOx. It converts one form of NOx to another form of NOx.

This is an error as stated in the replies to previous comments. P.32541 L.27 to P.32542 L.1 will be changed to: **In summary, the observed morning NO maximum appears to be caused by the photolysis of NO_2. NO_2 arises primarily from anthropogenic sources, and is transported into the UMBS canopy by advection and entrainment.**

ACPD
12, C13865–C13874, 2013

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Interactive Discussion

Discussion Paper

ACPD
12, C13865–C13874, 2013

Interactive Comment

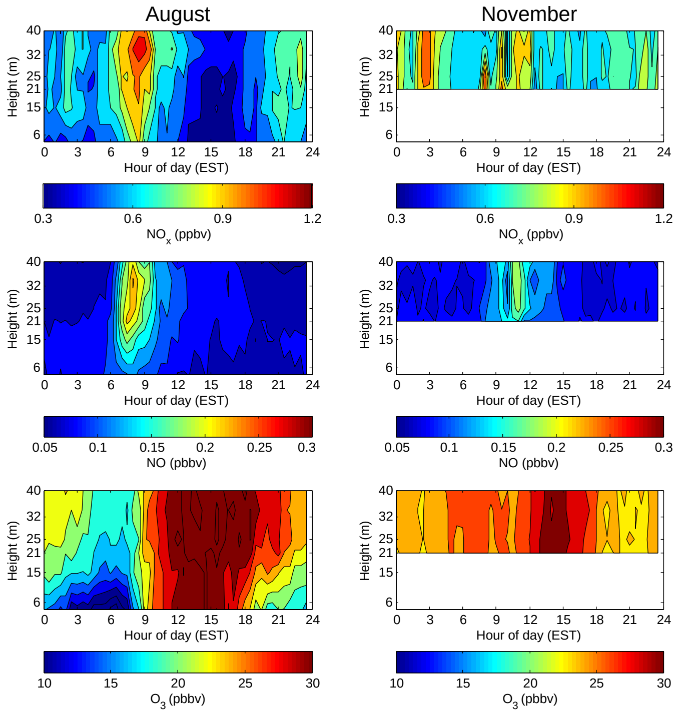

Fig. 1. Fig.4 updated to show contour lines.

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Interactive Discussion
Discussion Paper