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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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General comments

We appreciate Referee #1's constructive feedback. 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** font.

We like to point out that the data presented in this manuscript are one of the most extensive and highly resolved seasonal measurements of ozone and nitrogen oxides at this site. We believe that the presentation of these observations is the core of this manuscript and of high value by itself and warrants publication. Additionally, we included a modeling component to expand the discussion of our data and previous measurements done by others at this site (e.g., studies from the PROPHET campaign as referenced in Carroll et al. 2001; some of the studies listed as part of the ACP/ACPD special issue of the CABINEX campaign).

Specific comments

32519 L.25 While it is true that NOx is a large fraction of NOy in urban areas, this sampling site is far from urban. How can the authors justify using the catalytic channel of the TEI instrument as a measure of NOx? Wouldn't it be some fraction of total NOy?

> The Model 42C-TL instrument used in this study uses a heated molybdenum oxide (MoO) catalyst to produce NO from oxidized nitrogen gases. This reviewer is correct in that the NO_x values reported by this instrument are actually a fraction of total NO_y due to the limited selectivity of the MoO converter. Winter et al. (1974) reported that aside from NO_2, other reactive nitrogen species are converted to NO by the MoO catalyst and then reported as NO_2. A recent intercomparison of different NO_x measurement techniques within the ACTRIS project (Gilge et al. 2013) showed that instruments using a catalyst (e.g., MoO) differed from other measurement techniques (e.g., photolytical converter) by — on average — 2% for ambient NO and 3% for ambient NO_2 measurements. This intercomparison by Gilge et al. (2013) was done at the Hohenpeissenberg Meteorological Observatory, which is a semi-rural site for monitoring background level air, quite comparable to UMBS. The results from Gilge et al. (2013) give additional confidence that the NO and NO_2 values reported by the Model 42C-TL are usable for our study. We do not disregard the probability that in a complex mixture of oxidized nitrogen gases, the NO_2 values reported by the Model 42C-TL may be more realistically a fraction of NO_y. In the revised manuscript, we added discussion of the intercomparison study by

Gilge et al. (2013) to provide further explanation of our measurements; we also changed the nomenclature for NO_2 to $NO_{2,MO}$ and for NO_x to $NO_{x,MO}$ to clearly indicate that the NO_2 and NO_x results in our study are those measured with a MoO-type converter instrument.

We also like to re-emphasize that the primary findings presented in this study build around the timing and relative changes of the morning NO_x peak, and not on absolute concentrations and relative ratios and distribution of NO/NO_y.

Modified text P.32520 L.1: **A recent intercomparison of NOx measurement techniques showed that instruments using the molybdenum converter yielded NO and NO2 values that differed from instruments using other techniques (e.g., photolytical converter) by 2% and 3% respectively, for ambient air measurements at a semi-rural site in Germany (Gilge et al. 2013).**

32520 L.8 It would be clearer if the 5% accuracy error is specified as analytical accuracy and not overall measurement uncertainty. Does this value hold for both NO and "NOx"?

This error value holds for NO. The Model 42C-TL has only one detector that detects NO. The accuracy error of the instrument for standard measurements was determined to be approximately 5%. The NO_x conversion efficiency was determined to be 99.9% (P.32520 L.2-3) for NO_2. Consequently, the $NO_{2,MO}$ uncertainty is very similar to that of NO. However, as stated above, there is a potential for other oxidized nitrogen gases to be converted and reported as NO_2 by the instrument. Since this portion of the signal cannot be determined directly, the quantification of NO_2 and NO_x is associated with an overall higher uncertainty.

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Interactive Discussion

Discussion Paper

Modifed text P.32520 L.6-8: **After propagating the uncertainties of the mass flow controllers and the NO gas standard, we estimate the uncertainty in the NO determination to be ∼5%.**

32521 Bias in sampling line: how important was NOx photochemistry inside of the PFA tubing? The lower inlets that were coiled inside the building experienced less sunlight. How does this bias correction factor into overall uncertainty of the measurement?

Unfortunately we do not have experimental observations that will allow us to quantitatively assess this potential error. We believe this effect to be minor, if at all noticeable. The Teflon sampling lines used had 1/16 inch wall thickness and most of the sampling lines were below canopy, with the excess tubing coiled near the forest floor. There is a significant attenuation of light in this forest and available radiation below the canopy is a small fraction of the above-canopy irradiance.

32522 L.22 The dynamical behavior of gases through the canopy are going to be influenced by in-canopy turbulence and air movement. How do the authors justify using above-canopy processes such as boundary layer dynamics and cloud formation to simulate in-canopy behavior, i.e. assuming that canopy acts as a uniform source of soil or foliar emissions. Can the importance of canopy-scale movement be addressed?

Our model system is described in great detail by Ganzeveld et al. (2002, 2006, 2008); this includes the description of in-canopy transport. In the manuscript, we describe that our model simulates various in-canopy processes, i.e., chemistry, turbulence, dynamics, etc. (please see P.32522 L.5-27). The canopy is not considered a uniform source of soil or foliar emissions in our model, but instead sources change with time and height inside the canopy.

Corrected text, P.32523 L.27: **Note that the canopy does not act as a uniform source of soil or foliar emissions in our model and source (and sink) strengths change with time and height inside the canopy.**

32523 L.20 The Zhou et al. reference is different from the one listed in Table 1.

Yes, the references are different. The one listed in Table 1 is the one from which we obtained the value used in our model; the one listed on P.32523 L.20 describes the motivation for us to consider the photolysis of nitrate on leaf surfaces in our model.

Corrected text, P.32523 L.20: **The model also considers the potentially relevant contribution to canopy NO$_x$ by photolysis of nitrate that has accumulated on leaf surfaces (e.g., Zhou et al., 2003; Zhou et al., 2011).**

32526 L.22 Is the buildup of BVOC inside the canopy an observation or an inference? It is discussed here as though it is commonly seen in this forest.

The accumulation of biogenically emitted trace gases inside the canopy is inferred based on the temperature lapse rate and the previously reported BVOC emissions (e.g., Ortega et al., 2007; Pressley et al., 2003).

Corrected text, P.32526 L.20-22: **The divergence in the lapse rates also indicates that the layers appear to be decoupled. These conditions suppress vertical mixing, and cause accumulation of biogenically produced trace gases inside the canopy.**

32526 L.26 Is there evidence of a canopy layer in this forest even in the winter?

The purpose of using the term “canopy layer” even for the November month is for us to use a consistent term to describe this height interval of the forest for both summer and winter seasons. We provide our definition of the “canopy layer” on P.32519 L.1âĂŤ2 (and see Fig. 1).

32528 L.25 Does the “spatial and temporal evolution” refer to vertical motion or also some measure of horizontal composition?

It means vertical motion. Our measurement was a vertical profile at a fixed point (or Eularian measurement); we did not have a horizontal component in our measurement. The model is a 1-D system that assumes horizontal homogeneity.

32528 L.27 typo “suggests”

P.32528 L.27 corrected to: **This behaviour suggests that the ozone loss and NO enrichment are controlled**. . .

32528 L.28 It appears the authors are inferring process from correlation. I think they might want to be a bit more circumspect.

P.32528 L.25-P.32529 L.2 changed to: **It is notable that the temporal evolution of the night-time O_3 loss near the ground coincided with the night-time accumulation of $NO_{x,MO}$. The main connecting processes here are limited turbulent transport and soil NO emissions explaining the accumulation of NO_x near the soil surface. It also partly explains the decrease in O_3 due to a reduced resupply of O_3 from higher up in the canopy and surface layer. The resupply of O_3 is insufficient to**

compensate for surface deposition and chemical destruction from reaction with soil-emitted NO. The NO mixing ratios are so small that the titration of O_3 would only be a minor term in O_3 destruction. Similar to the $NO_{x,MO}$ diurnal cycle, the daily amplitude in the O_3 mixing ratio was smaller in November than in August.

32530 L.16 I'm not sure I follow the logic that the lack of large-scale sources of NOx in the region, the morning peak cannot be local. This is an important assertion but it's not clear that it follows from the data.

We will include our definitions of local and non-local sources in the text. Our definition of local sources is "sources from soil, foliar, and downward transport from aloft air mass (boundary layer evolution)." The time scale of local sources is the duration of turbulent mixing and in-situ photochemical production/destruction (< 1 hr). Non-local sources are defined as advected air mass or long-range transport. The time scale for those processes is on the order of 15 hrs to days.

The peaks of NO and $NO_{x,MO}$ are exclusive of each other. The $NO_{x,MO}$ peak is associated with non-local sources while the NO peak is associated with local sources. To address the reviewer's comment, here (P.32530 L.16+), we are making the point that winds coming from the north-westerly direction are associated with low levels of $NO_{x,MO}$. In contrast, we saw high levels of $NO_{x,MO}$ with winds from the southerly direction. Our results corroborate findings and analyses done by Cooper et al. (2001), Thornberry et al. (2001), and Alaghmand et al. (2011). Alaghmand et al. (2011)'s back-trajectory analyses showed that air masses from the south had passed through major urban areas. High $NO_{x,MO}$ concentrations were more frequent during southerly winds (Supplemental Fig. A1). Therefore, we concluded that the $NO_{x,MO}$ source cannot be local but appears to be dominated by non-local contributions.

32530 L.25 I wonder if the treatment of timing for the NOx peak is oversimplified. Figure 4 shows that the NOx begins to increase before sunrise on most days. Is this so?

Around 03:00 hrs local time, $NO_{x,MO}$ increases can be noted; the $NO_{x,MO}$ maximum itself occurred around 08:00 hrs. But $NO_{x,MO}$ in general was elevated during night-time, i.e., 20:00 to ∼04:00 hrs relative to the afternoon (12:00 to 19:00). This is shown in Fig. 4. Conditions in November were less consistent; there are multiple peaks, one at 03:00 and later at ∼08:00 and ∼10:00.

32533 L.0 Is the disagreement of model and observations related to the fact that the authors are not measuring NOx per se, but a fraction of NOy?

As we have addressed in the first question, the results from the intercomparison study by Gilge et al. (2013) give us confidence that the Model 42C-TL $NO_{x,MO}$ measurements are sufficiently accurate for the purpose of our study and model runs.

32534 L.27 While it appears that soil NOx emissions have little influence in the model, it's not clear how to understand the spatial variation in this value given that Nave et al. reports a value 10x lower than the one used by Alaghmand et al.

The difference between the Nave et al. (2011) and Alaghmand et al. (2011) reported NO emission fluxes express the large (temporal and spatial) variability in soil NO emission fluxes. Alaghmand et al. (2012) used unpublished data by Carleton et al. (2003). Initially, we also used this unpublished dataset for our model runs. However, we adjusted the Carleton et al.

(2003) data by excluding the rain events in the data set. Coincidently, this adjustment that we made with the Carleton et al. (2003) data resulted in agreement with the soil NO emission data that Nave et al. (2011) reported for the summer of 2008, which is the same period when we conducted our measurements (P.32534 L.18-19).

Our model did not yield agreement with observed $NO_{x,MO}$ in the canopy even using a substantially larger soil NO emission flux comparable to that reported by Alaghmand et al. (2011). This demonstrates that soil NO flux is no a major driver of NO_x in the canopy.

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