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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of reactive nitrogen oxide fluxes by eddy covariance above two mid-latitude North American mixed hardwood forests" *by* J. A. Geddes and J. G. Murphy

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We thank the reviewer for their careful consideration of our manuscript. Our responses to their comments are below (original comment in small indented text).

Comments:

> 1) The authors state, that one focus of the paper is "on reporting the instrumental methods" (p895, line 9). While the molybdenum converter (MoC) is a crucial method in the present study, it is not adequately introduced, described and dis-

cussed:

a) Section 1 or Section 2.2: The general ability of molybdenum to convert NOy should be introduced in more detail, including literature references if possible.

b) Section 2.2: For eddy covariance NOy measurements, it is crucial to make sure that the MoC system not only has a high conversion efficiency, but also a fast response even for problematic compounds like HNO3. Problems with fast response sampling of HNO3 have been reported e.g. by Horii et al. (2006). Therefore it is important to accurately describe the design of the sample air inlet and the MoC (geometry, wall materials, heating, ...) used in this study.

c) Section 4: Since this is (to my knowledge) the first study using a MoC for EC measurements of NOy, the usefulness of this converter type should be discussed (e.g. in comparison to the gold converter).

The reviewer brings up several good points. We agree that a longer introduction about the molybdenum converter and its use is warranted, and have added the following material to the introduction:

"This converter is identical to that described in the Environmental Science and Engineering (ESE) instrument reported by Williams et al. (1998). An alternative method for the conversion of NOy is the gold tube converter (among other metal and alloy converter tubes that have been tested, such as platinum, nickel, and stainless steel (Fahey et al., 1985; Kliner et al., 1997)), usually heated in the presence of a reducing gas such as CO or H2. Comparisons of NOy conversion by Mo or Au converters have been discussed in the literature (e.g. Williams et al. (1998)), in addition to studies comparing multiple Mo converters with themselves (e.g. Fitz et al. (2003); Xue, et al. (2011)). Differences in NOy conversion between the conventional techniques have been reported to be within 5%, and with an adequate quality control program should not result in significant differences. Critically, there is consensus that non-NOy interferences (e.g. NH3) and ideal operating temperatures must be assessed for each instrument individually under the relevant conditions. In the present work, the MoC was operated at a set

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temperature of 300 C. The conversion efficiency for our system was tested for NO2, HNO3, and NH3 before and after the campaigns. Conversion of NO2 and HNO3 was found to be within 10% of unity, while the NH3 interferences were minimized to less than 30% and less than 10% at HFWR and PROPHET respectively.

"Time response through the inlet system of problematic compounds such as HNO3 must be considered. The converters are located in a detachable inlet component in order to minimize sampling losses, and components of the inlet made of steel are silco-coated in order to improve transmission. Lab tests were performed to determine the instrument time response. By alternating ambient sampling with zero air overflow at the inlet, the decrease in signal was well represented by exponential decay with a 1 second time constant. However, in experiments where the instrument was exposed to prolonged (hours) high HNO3 concentrations from an HNO3 permeation device, the decrease in signal was well represented by a bi-exponential decay, with a fast time constant governed by the overall time response (1 s), and slower time constant around 1-2 minutes. In our HNO3 experiments, the amplitude of the fast decay was more significant than the amplitude of the slow decay. These results are broadly similar to the experiments reported for NOy flux measurements by gold catalyst converter (Munger et al. 1996). Problematic fast sampling of HNO3 has also been reported elsewhere (e.g. Horii et al. (2006)), so that HNO3 fluxes in eddy covariance observations of NOy may be under-represented. Based on our experiments, and the cospectra presented in Section 2.3.3 that suggest most of the flux at each site was dominated by eddies of frequencies less than 0.1 Hz, we expect that there may be some underestimate of the HNO3 fluxes at each site."

> 2) p901, line 11.: The WPL correction is not overestimated if it is applied after the high frequency correction of the NOy flux, and if a similar damping of H2O and NO in the sampling tube is assumed (which would be a very reasonable assumption).

We understand the reviewer's point. In our case, since the high frequency corrections

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as we discuss in Section 2.2.3 are on the order of 10% or less, we expect a similarly low effect on the dampening of the H2O flux for calculating the WPL correction. Therefore, we have added this wording in our discussion of this issue.

> 3) p905, line 23: Obviously, in Fig. 5 average cospectra were calculated over different wind speed and stability conditions!? This is very problematic and may result in erroneous interpretations of the spectral slopes. Averaging of cospectra should only be performed within certain stability classes (at least separately for stable and unstable cases) and, also important, the individual cospectra should be described as a function of the normalized frequency f*z/u (instead of just using the frequency f).

The reviewer has identified an important issue with our interpretation of the cospectra. To address this, we have performed a systematic re-analysis of the cospectra. The new results are show in our updated Figure 5 of the manuscript (also shown here, see Figure 1 below; note the caption in the updated manuscript includes more detail). The manuscript now reads:

"For an ideal cospectrum, we use the w'Ts' cospectrum, where Ts is the temperature measured by the sonic anemometer. If modeled correctly, the attenuated cospectrum should agree with the observed w'NOy' cospectral shape. To investigate this, Fig. 5 shows average normalized cospectra of w'NOy' from 31 July to 6 August for HFWR, and from 27 July to 2 August for PROPHET. These cospectra were calculated separately for stable conditions (z/L > 0.05) and unstable conditions (z/L < 0.05), and only for similar mean wind conditions (1–3 m/s), plotted based on the normalized frequency (n = fz/u). The HFWR plots are based on N=92 and N=50 half-hour periods for the stable and unstable conditions, while the PROPHET plots are based on N=84 and N=34 half-hour periods for stable and unstable conditions respectively. Displayed on the top right panel is the dampening coefficient we expect in the w'NOy' cospectrum based on the transfer function calculated by Equation 3 (and is generally consistent with our understanding of instrument time response).

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"In all cases, the slopes of the cospectra of w'NOy' from the peak maximum to a normalized frequency of approximately 4 compare well with the slopes of the w'Ts' ("ideal") cospectra. In the case of HFWR, the unstable conditions show a pronounced increase in cospectral power beyond this frequency, when we expected a dampening according to tube attenuation, followed by a sharp decrease. For stable conditions, an increase is also observed at higher frequencies although it is not as dramatic. This behaviour could be expected in instruments with a large amount of noise in the high frequency. If noise is truly random, there should not be significant covariance with fluctuations in vertical wind, however this has been observed in other situations (e.g. methane fluxes reported in Querino et al., 2011; Smeets et al., 2009). In the case of PROPHET, we see a less marked increase in cospectral power at the high frequencies, indicating that perhaps noise was less of an issue during this campaign. However, we still note the absence of the expected decrease in cospectral power that would result from the signal dampening (and given our understanding of instrumental time response) compared to the "ideal" cospectrum. In all four panels, we plot a straight dashed line at the normalized frequency of 4.5. Given the mean wind conditions for the half-hour periods that were averaged to make these plots (2 ± 0.5 m/s), this corresponds to a natural frequency of 0.3 Hz.

"Given the evidence in Fig. 5 that the spectral shapes close to the maximum cospectral power are similar for w'NOy' and w'Ts', and that it appears the tube-attenuation transfer function will not correctly account for cospectral issues at the higher frequencies, we apply a correction based on cospectral similarity instead of using the tube attenuation transfer function. This correction is applied by comparing the integrated area under the non-normalized cospectra of w'NOy' up to 0.3 Hz with the ratio of the total covariance of w'Ts' to the integrated area under the non-normalized cospectra of w'Ts' up to 0.3 Hz ... "

4) p909, line 20/21: I doubt if this interpretation is correct. Considering the very steep increase and decrease in the NOy concentrations (at midday of 7 Oct., I

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estimate a decrease of about 12'000 ppt within 2 hours), the storage change below the flux measurement height can play an important role. The mentioned decrease results in a pure storage change related flux of about 45 ppt*m/s during 2 hours! This should be taken into account here.

The reviewer makes an excellent point. We have added the following to the manuscript:

"During this period, very steep changes in the atmospheric concentrations are observed. Under such conditions. it is unlikely that the storage term can be ignored in calculating the flux, making the eddy covariance observations alone unrepresentative of true flux. In the absence of vertical profile observations, the storage term can be estimated to a first order by the equation:

$$F_S = \frac{dC}{dt} h \tag{1}$$

where Fs is the storage term, dC/dt is the change in mixing ratio over time dt, and h is the measurement height. For example, the decrease in NOy concentrations from 0730 to 1100 on the morning of October 7 leads to an average storage flux term of around -30 ppt m/s. This term is roughly equal to the positive eddy covariance flux measured. The interpretation of the flux measurements during this time is therefore problematic without measurements of NOy at multiple heights to accurately determine the storage term. For this reason, we exclude observations during this time from the discussion of the rest of the campaign."

5) Section 4.1: It would make more sense to discuss the influence of wind direction (advection source areas) not only in terms of fluxes but also to include the respective concentrations and deposition velocities.

The reviewer makes a fair suggestion, and we have investigated the influence of wind direction on concentrations and deposition velocities. As a result of this investigation,

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we also found a minor error in the analysis; where we intended to use results from the campaign excluding the flux observations during the high pollution event (where storage cannot be ignored), the data shown in the original Figure 11 included these observations. After correcting for this error (see Figure 2 below), the general conclusions from HFWR regarding wind direction were not altered, but mean values shifted.

We have now included a new Table (Table 2 in the updated manuscript, see Figure 3 below) to accompany Figure 11, where median mixing ratios, fluxes, and deposition velocities are summarized for each direction at PROPHET and HFWR.

We have elaborated on the influence of transport, and the data summarized in the new table, as follows:

"At PROPHET, flow from the southwest (from the direction of the Milwaukee and Chicago areas across Lake Michigan) is associated with the highest despotion. Observations from this direction were also associated with the highest NOy mixing ratios, and the highest vdep. Deposition is also enhanced when flow from the southeast (from the direction of Detroit, Cleveland, and populated regions in south-western Ontario) is observed, but the calculated vdep was not as high. This may be a result of the higher NOx/NOy ratios that were observed coming from this direction. Observations from the north are still of deposition on average, although with less skew towards high values. NOx and NOy mixing ratios were lowest coming from this direction. Despite a similar NOx/NOy mixing ratio as that coming from the southwest, the vdep is much lower (in fact, the lowest). Investigation of this data showed that flow from the north was associated with the most (and highest) observations of NOy emission, which will counteract deposition and complicate the interpretation of vdep.

"At HFWR, deposition looks approximately normally distributed around zero when flow is coming from the north, whereas deposition is enhanced when wind comes from the south (from the direction of of the greater Toronto area in southern Ontario) and skewed towards high values. Observations from the southwest and southeast have

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similarly high NOx and NOy mixing ratios, and comparable vdep. When air is coming from the north, deposition velocities were found to be near zero. Like at PROPHET, these data were associated with more observations of emission. However, in this case it was also found that afternoon observations from this direction occurred rarely, so that this deposition velocity reflects night-time conditions more heavily (such an issue was not observed for PROPHET). This selection bias does not seem to be a result of a diurnal pattern in wind direction, but rather is likely a result of spike removal due to observed generator effects.

"The differences in vdep at HFWR and PROPHET, when comparing observations with similar NOx/NOy mixing ratios (e.g. .5-0.6 in Table 2), could be explained by several mechanisms: differences in canopy and understory structure; differences in NOz (=NOy-NOx) composition; differences in NOy emission strengths; and differences in turbulence or mixing mechanisms."

6) Table 1: Add average concentrations if available.

We agree that average concentrations would be useful in this table, unfortunately these are not easily found (especially values that could be properly compared). However we did note that the order of magnitude in average daily flux does seem to roughly correspond to the order of lowest to highest NOy mixing ratios (i.e. the Harvard and Duke studies were subject to generally higher NOy, while Schefferville was clearly subject to the lowest concentrations). This qualitative detail has been added to the text.

7) Fig. 5: Indicate at least the (different) data sources of (a) and (b) in the figure caption. Referring to the main text should only be used for extensive details/explanations.

We have added the appropriate details to the figure caption (note Figure 5 is now different given our updated analysis of cospectra).

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Technical and language comments

p895, line 5/6: This sentence appears somewhat inconsistent. NO and NO2 are also "individual NOy species".

p897, line 7: I guess that 'Pneucleus' is the name of a company? Please specify more clearly.

p900, line 19/24: better write "water vapor" instead of just "water"

p900, Eq. 2: This equation is not very clear: what is the difference between lowercase "c" and uppercase "C" here?

p909, line 18: replace "or" by "are"

p915, line 16: correct to "interferences"

We have addressed all of these technical comments in the updated manuscript accordingly.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 27891, 2013.

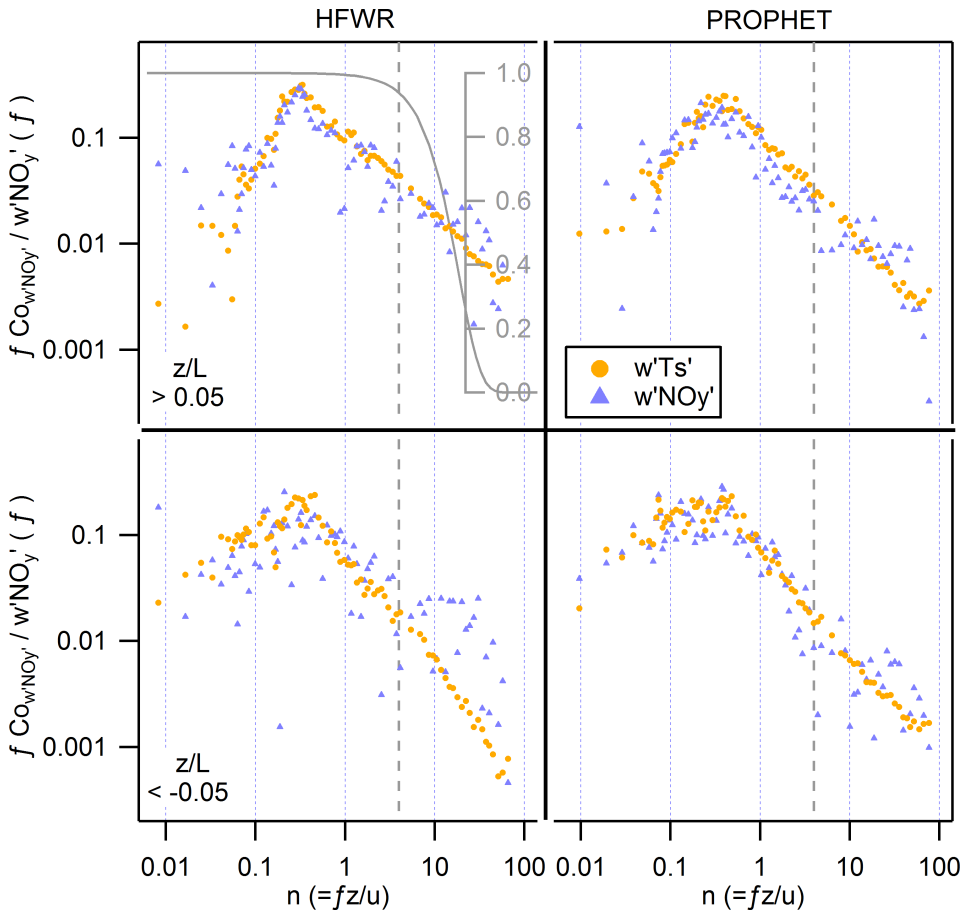

Fig. 1. Normalized cospectra for HFWR and PROPHET (left and right panels respectively) separated into stable and unstable conditions (top and bottom panels respectively).

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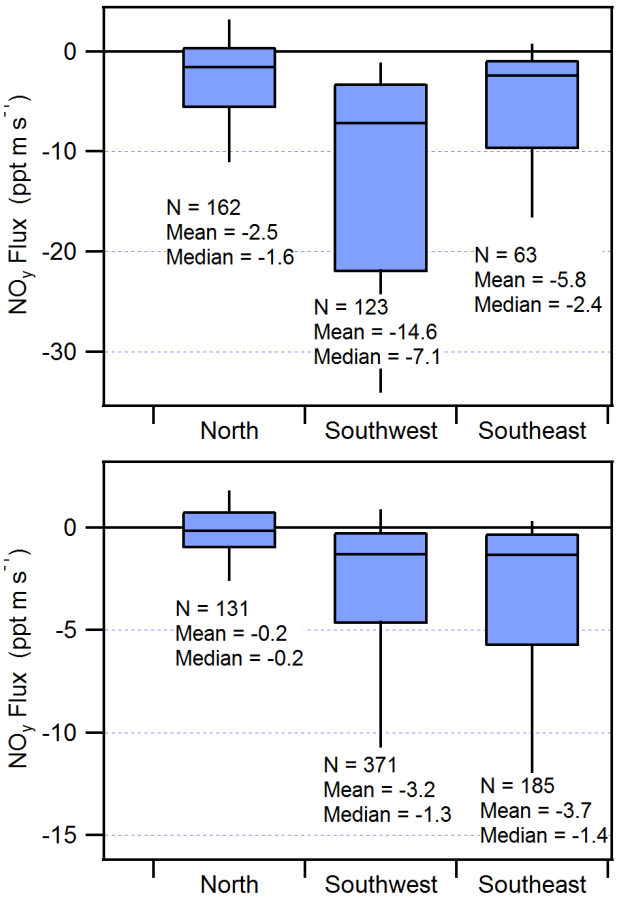

Fig. 2. Updated Figure 11

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Table 2. Median observed quantities as a function of wind direction. NO_x and NO_y mixing ratios in ppt, fluxes in ppt $m s^{-1}$, and v_{dep} in $cm s^{-1}$.

		NO_x	NO_y	NO_x/NO_y	NO_y Flux	v_{dep}
PROPHET	N	420	815	0.51	-1.6	-0.17
	SW	1058	2440	0.52	-7.1	-0.42
	SE	890	1271	0.73	-2.4	-0.19
HFWR	N	377	769	0.57	-0.2	-0.02
	SW	633	1099	0.61	-1.3	-0.14
	SE	554	939	0.56	-1.4	-0.14

Fig. 3. Added Table to Manuscript describing observations as a function of wind direction

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