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Atmospheric
Chemistry
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Discussions

Interactive comment on "Application of thermal dissociation-laser induced fluorescence (TD-LIF) to measurement of HNO_3, Σalkylnitrates, Σperoxy nitrates, and NO_2 fluxes using eddy covariance" *by* D. K. Farmer et al.

D. K. Farmer et al.

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We thank the referee for the interesting and detailed response. We agree with the referee that the observed patterns are interesting and surprising. It is the counter-intuitive nature of the observations that encouraged us to investigate the validity and potential errors of our measurement technique in such detail. The result of these investigations is this paper, which has the sole intention of providing a detailed description of the TD-LIF - eddy covariance measurement technique. As the referee realizes, a full explanation of the chemical mechanisms behind our observations is beyond the scope of this paper, which is focussed on the technique, with several examples of observations

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to demonstrate the potential of this system to provide interesting and useful data. A more detailed manuscript including a quantitative discussion of the observations and timescales involved in upward HNO_3 and ΣPN fluxes has been submitted for review, and we will be excited to receive further commentary from the referee and the rest of the community when this paper is published. A more detailed discussion was not possible within the context of this paper.

With regards to the major scientific comments:

The referee points out that the proposed technique cannot distinguish between gas and aerosol phase HNO_3. While we agree this must be taken into consideration in interpreting the data, and have added several sentences to this effect in the discussion of patterns in fluxes, the NH_3 - and thus NH_4NO_3 - mixing ratios are expected to be very small at Blodgett Forest. There are no local sources in the area, and the emissions from agricultural sources in the Central Valley will likely have deposited by the time the air mass reaches Blodgett Forest (7 hours). The presence of any NH_3, though, would likely produce NH_4NO_3, having an effect on both mixing ratios and fluxes. However, as particles tend to deposit, albeit with a significantly smaller deposition velocity (V_{dep}) than their gaseous counterparts, the result would likely be to diminish the observed deposition flux, and not to cause an upward observed HNO_3 flux. We agree with the referee that in other environments, the effect of NH_4NO_3 be significant, and should be considered in the interpretation of observations.

We agree with the referee that in order to achieve the observed HNO_3 fluxes, significant within-canopy chemistry is required within the canopy residence time (10 minutes). An alternative explanation of the upward HNO_3 flux might be more palatable to the community. However, we have not found any other more rational explanations for the observations, and have submitted a separate manuscript (Farmer and Cohen, 2006) to address the possible mechanisms behind these observations. As the referee agrees, the gas-particle partitioning typically invoked to explain the fluxes cannot be used to explain the TD-LIF observations. Further, we thank the referee for drawing our attention to the intriguing paper regarding the presence of organic nitrates in biogenic aerosols. We do not believe that the presence of particulate organic nitrates could explain the observed upward HNO_3 fluxes. However, such particles may be measured in the Σ ANs channel, likely resulting in a slow deposition component to that flux.

Minor Comments.

The referee made some very useful suggestions for the paper. We have corrected all typographic errors, SI unit inconsistencies, and mistaken figure references, and added several references as per the referee's suggestion. We have also clarified several points regarding our methodology, which we expect to answer most of the referee's minor scientific comments. With regards to specific minor scientific comments, and in answer to the referee's specific questions:

1. Comments on observations/fluxes. The referee raises the question of whether a physiological compensation point can be observed for NO_2. While there is no obvious correlation between atmospheric mixing ratio and NO_2 flux, there are several complicating factors (namely separating NO_2 flux resulting from $NO+O_3$ reactions from flux resulting from direct emission) that must be considered in searching for an ecosystem-scale compensation point. This is an interesting question, but is beyond the scope of this paper, in which we merely hoped to point out that this technique could be used, and provides interesting data. However, we intend to address this point in future manuscripts.

With regards to the referee's suggestion that we describe the concentration statistics in more detail, the revised manuscript will specify that the concentration ranges given are typical. We will also add a reference to Murphy et al.'s ACPD paper [2006], which describes the concentration statistics in detail.

With regards to the referee's comment that NO fluxes are biologically controlled, we understand that NO fluxes are controlled by soil microbes, with some contribution from plant emissions, which likely has different implications on the nighttime u_* correlations from fluxes solely controlled by plant gas exchange. However, we have clarified our wording to focus on our point that the extent of biological control of NO_2, ΣANs, ΣPNs, and HNO_3 is unknown.

The referee suggests using μmol m^{-2} s^{-1}, rather than ppb m s^{-1}, as the units of flux. However, we find that the ppb m s^{-1} units provide an easier link to the observed mixing ratios; further, these units are more common in consideration of fluxes of reactive trace gases which may be affected by tropospheric chemistry, which we believe to be important to these species. However, we will provide the conversion factors in a footnote at the first use of flux units in the revised manuscript.

As stated in the paper, the average diurnal fluxes for the season were integrated (by calculating the area under the average daily time series of total $\Sigma NO_{y,i}$ flux, to provide a net average daily deposition), and then multiplied by the number of days in the given season to attain a total, net seasonal deposition. We do this rather than calculating the product of the average flux by the time period in order to account for the diurnal changes in the flux. Thus we feel that the term ‘integrated’ is appropriate.

Unfortunately we know of no measurements of soil NO emissions for the pine plantation at Blodgett Forest, and agree with the referee that this would be an interesting number for comparison to our observed fluxes.

The referee provided an excellent suggestion of putting our error terms in the perspective of other measurements. We will do so in a revised version of this paper.

2. Methods/Instrument comments. The referee suggests that the inlet temperature would volatilize ammonium nitrate aerosol. This is extremely unlikely, as the residence time (milliseconds) in the inlet is very short. Even if some NH_4NO_3 were volatilized, the HNO_3 would not dissociate to NO_2 in any oven other than the hot (550°C) channel, and thus would not be measured in any channel other than the HNO_3 channel.

We have clarified our wording regarding lagtime calculations in a revised manuscript, as the referee's suggestion describes our method. For a given pump/tubing configuration, we used lagged covariance plots to determine a typical lagtime for each of the four channels, and applied this lagtime to all the data for a given configuration. The pump and tubing configurations changed several times throughout the multi-year campaign when pumps failed and parts were cleaned or exchanged.

3. Spectral Analysis comments. The referee suggests that as the measurements are made in the surface roughness layer, they may deviate from the -5/3 / -4/3 slopes. Our understanding is that this is still in the 'constant flux layer', and that one can still make reasonable eddy flux measurements in the roughness sublayer with the Komolgorov slopes for power- and cospectra. However, the referee may be correct in thinking that this may have contributed to our slopes deviating slightly from the expected.

We evaluated the underestimation due to sensor separation by comparing observed cospectra that had been corrected by the transfer function to uncorrected, observed cospectra; we will specify the use of observed cospectra in the revised paper.

The referee points out that the flux loss due to the half-power dampening frequency of the sampling tube is large (2-7$\%$) compared to the flux loss from instrument response time (3.6$\%$). The instrument response time loss was theoretically calculated as per Horst (1997), and is independent of observations. The flux loss due to sampling tube damping was calculated by applying a transfer function to observed cospectra. As we point out in the paper, under most operating circumstances, the flux loss due to sampling tube dampening is <2$\%$, and thus likely smaller than the loss due to instrument response time. As we highlight elsewhere in the paper, different ways of calculating error, either experimental or theoretical, seem to provide quite different estimates. We provide all these numbers so that the reader can make their own assessment of the error and validity of the TD-LIF eddy covariance technique. As the referees observed, these errors are relatively small, and will not affect the sign of the flux.

While the referee suggests that flow distortion may be more important than removal of sticky compounds as an effect of the tower during nighttime, downslope flow, both ideas are at this point speculative, and in the absence of further evidence, we will continue to include both as potential sources of error in the fluxes.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 2923, 2006.

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