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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Aerosol flux measurements above a mixed forest at Borden, Ontario” *by* M. Gordon et al.

Anonymous Referee #2

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The manuscript by Gordon et al. presents size-segregated aerosol flux measurements above a Canadian mixed forest, made with a relatively new fast (1 Hz) particle spectrometer (FMPS). It also contains some of the first chemically resolved aerosol flux measurements by eddy-covariance, using an Aerosol Mass Spectrometer (AMS). The current understanding of the dry deposition process of particles remains incomplete with large differences between models and measurements and unexplained variability between sites and studies. As such the measurements make a useful contribution to the literature, especially because the study attempts to link size-segregated observations with chemically speciated observations, albeit from measurements conducted during different summers. The data analysis is mainly sound and the English is clear. However, there are a number of major scientific concerns that need to be addressed before the paper can be considered for publication in ACP.

Major Comments:

(1) In my opinion the authors miss the most likely explanation for upward fluxes. Nemitz and Sutton (2004) refer to several studies that have observed simultaneous apparent (measured at the reference height) emission of small particles, while larger particles showed deposition. They continue to show that this behaviour is consistent with the effect of ammonium nitrate (AN) evaporation during the deposition process, if fluxes are measured with an instrument with fixed bin sizes. Because particles undergo shrinkage during the deposition process, fluxes are derived according to a parameter (i.e. diameter) that is no longer conserved with height. This is the same effect as caused by water loss due to RH gradients discussed by the authors. The earlier AMS flux measurements at this site appear to confirm that deposition velocities were much larger for nitrate than for sulphate, a fact that suggests that AN evaporation was affecting chemical bulk fluxes. Thus it is also highly likely that this process was also affecting particle number fluxes. As such the information on the sulphate / nitrate exchange is in my opinion central to understanding the particle number fluxes, and rather than omitting Sections 5.6 and 5.7 as suggested by Reviewer 1, I suggest to fully integrate the AMS measurements into the paper, with more information on the methodology given in the methods section. I believe that after these earlier studies have been considered, the conclusions of the paper will change significantly.

(2) Overall, the structure of the paper is unusual in that the Discussions Section accounts for 9 Figures out of a total of 15. As a result a lot of experimental detail is introduced only very briefly where measurements are referred to or it is missing altogether. All experimental details should be moved into the Method section, not only on the AMS flux approach, but also on the SMPS, the leaf wetness measurements (what kind of sensor was used?), the NH3 and SO2 measurements etc. The basic flux, AMS and SMPS measurements (Figs. 11, 13 & 15) should be shown in the Results section and only figures that refer to the interpretation of the results (e.g. Fig 14) should remain in the Discussion Section.

(3) The authors present fluxes for individual particle sizes throughout the manuscript, which is not meaningful. For example, C62nm and F62nm are probably zero as there are no particles with a diameter of exactly 62 nm. Instead, the measured fluxes actually represent the flux within a size-range as given by the size bins of the FMPS. Therefore, throughout the paper, any quantification of a flux needs to be accompanied by the width (or better range) of the size bin to which it refers, or it needs to be normalised by the bin width, i.e. presented as dC/dlogDp or dF/dlogDp (cf Fig. 4c; Ahlm et al., 2010). For the same reason, Fig. 2 should be presented as dC/dlogDp in order to make it more generic and independent of the bin width of this particular instrument, and Fig 4a should be represented as dF/dlogDp. This is not applicable to exchange velocities where the width of the bin cancels out when dividing the flux by the concentration.

(4) It remains unclear, what corrections were applied to the data for which part of the analysis and what the rationale was. For example, were the data corrected for the effect of RH fluxes? Were fluxes corrected for storage error (Section 4.3) prior to further analysis (e.g. for Table 1)? The authors should more stringently distinguish between (i) fluxes as measured at the measurement height, (ii) best-estimate fluxes at the measurement height, corrected for hygroscopicity (if required, depending on whether the FMPS measures dry or wet size, see below) and the effect of NH4NO3 volatilisation on size (see above) and (iii) the best estimate of the actual surface / atmosphere exchange (corrected for chemistry and storage between vegetation and measurement height). Although the authors may not be able to quantify all these effects explicitly, these issues should nevertheless be discussed with these differences in mind. The authors should make it more explicit where they are talking about the (uncorrected) fluxes measured at the measurement height. For example, the upward fluxes are only ‘apparent’ upward fluxes, they are unlikely to be emissions of particles from the vegetation surface. It is also not completely clear for which analyses the data were filtered, e.g. for low u* and for which they were not. This has implications for the interpretation of the results (see below).

(5) I find the discussion of the effect of particle growth on fluxes (Sections 5.1, 5.7 and Conclusions) confusing as it appears to combine horizontal and vertical transport phenomena. The particle growth detected by the SMPS is a regional scale phenomenon that presumably occurs over large areas. Thus, changes at the measurement height are more likely to reflect processes that occur along horizontal gradients rather than provide information on in-canopy processes below the measurement height. The main effect of the horizontal changes on fluxes would be through the storage error which the authors quantify separately.

This has important implications; for example, the decrease in nitrate (p22488, l4) is likely to have been due to an increase in temperature overall, shifting the equilibrium from the aerosol towards the gas phase. Rather than being driven by vertical gradients this is again a regional phenomenon. In addition, temperature is only one factor affecting the nitrate partitioning and its change with height, the others being gradients in RH and, importantly, the removal of NH3 and HNO3 by the canopy, which results in very small gas-phase concentrations near and within the canopy. Without simultaneous flux measurements of NH3 and HNO3, the effect cannot fully be quantified. Further, the vapour pressures of NH3 and HNO3 also respond to other aerosol components such as sulphate.

(6) Linked to this, the discussion of the effect of NH4NO3 evaporation and the attempt to quantify the effect is incomplete. The authors imply that the additional flux induced by the evaporation is constrained by the increased in NH3 storage within the canopy. This argument misses two facts: firstly, as the authors concede later in the text, other factors are much more likely to dominate the variability in the NH3 concentration, such as the gas/aerosol partitioning at the regional scale, changes in the competing HNO3 concentration (not measured), changes in boundary layer height and, most basically, changes in air masses that are advected to the measurement site. Secondly, and more importantly, the argument ignores that an increase in the deposition rate also increases the NH3 deposition flux and thus NH4NO3 volatilisation can increase the effective (or

apparent) NO3 deposition rate without increasing the NH3 concentration. For example, van Oss et al. (1998) modelled the effect of NH4NO3 volatilisation on bulk chemical fluxes, based on the data of Wyers and Duyzer (1997).

(7) In the present analysis there is disagreement between the total mass fluxes derived from the FMPS fluxes and those derived from the AMS. The possibility of some organic fluxes not having been resolved by the AMS provides a convenient explanation. However, in my mind it is much more likely that if the FMPS fluxes were properly corrected for the effects of storage (it is unclear whether this correction was applied, see above) and changes in size due to NH4NO3 volatilisation, these difference may be resolved.

Minor Scientific Comments:

Abstract. The abstract talks about a “net production rate” of 75 nm particles. At no point does the manuscript claim that 75 nm particles are produced (indeed, there is unlikely to be a mechanism for this). In addition, it does not make sense to quantify the flux of a size for the reasons stated above. Thus, the sentence should use wording such as “the size-distribution of the net apparent upward flux at the measurement height peaked at a particle size of 75 nm”.

P22471, l1. This sentence is somewhat imprecise. SO4= cannot lead to eutrophication only to acidficiation, but NH4+ can also contribute to eutrophication.

P22472, l15. The historical summary of aerosol flux measurements is incomplete. There are other eddy-covariance datasets of size-segregated particle number fluxes, many of which are summarised in the review of Pryor et al. (2008b). Key datasets include those of Gallagher et al. (1997) and Ahlm et al. (2010). Overall, the application of optical particle counters to the measurement of size-segregated particle number fluxes predates the application of CPCs to the measurement of total number fluxes, e.g. Sievering (1987), although some of the earliest measurements were not made over forest.

P22473, l14. Although the FMPS reports data at 1 Hz, was this the actual response time of the system (inlet + analyser)? Has this been validated by inducing step changes in concentration and looking at the response?

P22473, l19. What was the flow rate of the FMPS through the 1/4” inlet? What was the Reynolds number?

P22474, l5. If for the larger sizes, concentrations from several bins were bulked together, it may be possible to derive fluxes for larger sizes. This may show the bi-directional flux behaviour with simultaneous apparent emission of the smaller sizes at times when the larger particles show emission, as would be expected for NH4NO3 evaporation.

P22477, l1. To what extent are particles dried during sampling by the FMPS? Was dry sheath air used? The answer to this question determines whether the hygroscopicity correction is applicable or not. Related to this, Khlystov et al. (1996, 1997) noted that NH4NO3 evaporation may occur in DMPS/SMPS systems. Are FMPS systems likely to be affected also? What would be the effect on the measurement?

P22477, l21. How can the size range around 62 nm (again this should refer to the bin, rather than a single size) be a good representation for the total size range if it reflects the peak (and thus an extreme) in the size distribution? Why not calculate the total flux over the range and use this for most of the analysis?

Section 5. The authors may want to consider relating their work to the observations of Whitehead et al. (2010) over South-East Asian tropical rainforest who present a similar time-scale analysis of decoupling.

Section 5.3, Fig. 10 & Eq. 11. What is the effect of filtering for low turbulence on Eq. 11? Presumably FStg is not equally distributed over day and nighttime conditions, and thus periods of high and low turbulence.

P22486, l22. In the expanded method section (see above), the authors need to clarify that the AMS flux mode is distinct from the standard AMS JMS mode in that it keeps the beam open for 28 minutes.

P22486, l27 & Fig. 15. Presumably m/z 43 was not the only organic fragment monitored by the AMS? Were the fluxes of the other fragments consistent with the behaviour of m/z 43? Could they be integrated into the analysis to derive more robust total organic fluxes?

Technical Comments

P22470, l20: "... range from a few nm to tens of"

P22475, l18: " ... used to rotate the anemometer measurements ..."

P22475, l25: "... of the signal carried by frequencies > 1 Hz due to ..."

P22476, l12: "Swietlicki"

P22478, l10: "Rannik et al. (2009) demonstrated that ..."

Further literature.

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Khlystov, A., Ten Brink, H.M., Toivonen, A.: Evaporation of ammonium nitrate aerosol in DMPS/SMPS. J. Aerosol Sci. 27 (Supp. 1), S75-S76, 1996.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 22469, 2010.