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ACPD

8, S8876–S8878, 2008

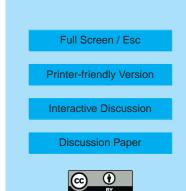
Interactive Comment

Interactive comment on "Eddy covariance fluxes of acyl peroxy nitrates (PAN, PPN, and MPAN) above a Ponderosa pine forest" *by* G. M. Wolfe et al.

Anonymous Referee #2

Received and published: 6 November 2008

The paper presents an evaluation of measurements of acyl peroxy nitrates (APN) fluxes and gradients above and within a pine forest canopy focussing on the role of surface deposition and chemical conversions inside the canopy. The paper addresses the quantification of the contribution of the APN fluxes to NOy deposition to ecosystems and understanding the role of chemical production, thermal decomposition versus surface deposition, including stomatal and non-stomatal uptake. The presented work also complements other recent studies on atmosphere-biosphere exchanges, e.g., Karl et al., 2004 (VOCs) and Ganzeveld et al., 2006 (peroxides) indicating that the removal of reactive compounds seems to quite different from that estimated based on approaches (Wesely, 1989) commonly applied in large-scale (air quality, chemistry and transport



models). It stresses the point that such approaches need to revised not only modifying the resistance approach but the explicit consideration of canopy interactions between emission, deposition, chemistry and turbulent exchanges. The paper is well written, describing very interesting measurements and an extensive evaluation to nail down the controlling processes including biological, chemical and physical components. As such the paper is well suited for publication in ACP and I have only some minor comments to be addressed by the authors.

The method section is very informative and essential to give the details on these challenging measurements but think it is distracting from the main point to be made in this paper on the APN fluxes and role of controlling processes. Consequently, I would suggest to consider to move most of the details of the methodology section to a supplement section (if possible) and only describe in section 2 some of the key features.

At page 17514 there is a discussion about how to appreciate the observed deposition rates of > 0.5 cm s-1 compared to upward exchange rates of 0.7 cm s-1 by Farmer and Cohen at the same site. It is discussed that these differences might be due to different meteorological conditions and also having a more mature canopy structure resulting in a more efficient deposition and suppressed turbulent transport for the here presented data compared to those by Farmer and Cohen. It is difficult to conceive that these differences can have such a pronounced impact resulting in the canopy being an effective source turning into an effective sink. It appears that this could only be studied using explicit canopy exchanges models that include the processes as described in this paper. Reading the last sentence of the conclusions, this is indeed what the authors will further pursue and it would be useful to explicitly mention this already here.

At page 17520 there is a discussion about the role of thermal decomposition in the fluxes mentioning that part of the downward flux of PAN could reflect the more efficient thermal decomposition (TD) at the surface compared to the air aloft. Calculation of the significance of the TD in explaining the fluxes compared to the role of surface deposition (stomatal uptake) raises the very interesting point about establishing the

ACPD

8, S8876–S8878, 2008

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relative importance of chemistry versus turbulent transport. Turnispeed et al. (2006) did not consider the role of TD in effecting the PAN fluxes based on the fact that, using the commonly applied approach of comparing the turbulent and chemical timescale, the TD timescale is much slower than that of turbulence. Wolfe et al. state such as assessment should not use the average loss rate but vertical gradient in the loss rate, which for the presented measurements actually indicates an important role of TD in explaining the observed gradients (and fluxes). This discussion raises the issue about a chemical flux divergence versus chemistry explaining part of the flux. Reading over carefully the text it becomes clear that the authors (and Turnispeed et al.) do not aim at assessing the importance of a flux divergence (so a deviation from the log profile) but really focus on how much the chemistry explains the surface removal. This could be stressed more specifically in the text.

Karl, T., Potosnak, M, Guenther, A, et al., Exchange processes of volatile organic compounds above a tropical rain forest: Implications for modeling tropospheric chemistry above dense vegetation, J. Geophys. Res., 109, D18306, doi:10.1029/2004JD004738, 2004.

Ganzeveld, L., Valverde-Canossa, J., Moortgat, G., Steinbrecher, R., Evaluation of Peroxide Exchanges over a Coniferous Forest in a Single-Column Chemistry-Climate Model, Atmos. Environ., 40, S68-S80, 2006.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17495, 2008.

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