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Eddy covariance fluxes of acyl peroxy nitrates (PAN, PPN and MPAN) above a Ponderosa pine forest

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Abstract. During the Biosphere Effects on AeRosols and Photochemistry EXperiment 2007 (BEARPEX-2007), we observed eddy covariance (EC) fluxes of speciated acyl peroxy nitrates (APNs), including peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and peroxymethacryloyl nitrate (MPAN), above a Ponderosa pine forest in the western Sierra Nevada. All APN fluxes are net downward during the day, with a median midday PAN exchange velocity of −0.3 cm s^{-1}; nighttime storage-corrected APN EC fluxes are smaller than daytime fluxes but still downward. Analysis with a standard resistance model shows that loss of PAN to the canopy is not controlled by turbulent or molecular diffusion. Stomatal uptake can account for 25 to 50% of the observed downward PAN flux. Vertical gradients in the PAN thermal decomposition (TD) rate explain a similar fraction of the flux, suggesting that a significant portion of the PAN flux into the forest results from chemical processes in the canopy. The remaining "unidentified" portion of the net PAN flux (~15%) is ascribed to deposition or reactive uptake on non-stomatal surfaces (e.g. leaf cuticles or soil). Shifts in temperature, moisture and ecosystem activity during the summer – fall transition alter the relative contribution of stomatal uptake, non-stomatal uptake and thermochemical gradients to the net PAN flux. Daytime PAN and MPAN exchange velocities are a factor of 3 smaller than those of PPN during the first two weeks of the measurement period, consistent with strong intra-canopy chemical production of PAN and MPAN during this period. Depositional loss of APNs can be 3–21% of the gross gas-phase TD loss depending on temperature. As a source of nitrogen to the biosphere, PAN deposition represents approximately 4–19% of that due to dry deposition of nitric acid at this site.

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