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Observations of HNO_3, ΣAN, ΣPN and NO_2 fluxes: evidence for rapid HO_x chemistry within a pine forest canopy

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Abstract. Measurements of exchange of reactive nitrogen oxides between the atmosphere and a ponderosa pine forest in the Sierra Nevada Mountains are reported. During winter, we observe upward fluxes of NO_2, and downward fluxes of total peroxy and peroxy acyl nitrates (ΣPNs), total gas and particle phase alkyl and multifunctional alkyl nitrates ($\Sigma ANs_{(g+p)}$), and the sum of gaseous HNO_3 and semi-volatile NO_3^- particles ($HNO_{3(g+p)}$). We use calculations of the vertical profile and flux of NO, partially constrained by observations, to show that net midday ΣNO_{yi} fluxes in winter are –4.9 ppt m s^{-1}. The signs and magnitudes of these wintertime individual and ΣNO_{yi} fluxes are in the range of prior measurements. In contrast, during summer, we observe downward fluxes only of $\Sigma ANs_{(g+p)}$, and upward fluxes of $HNO_{3(g+p)}$, ΣPNs and NO_2 with signs and magnitudes that are unlike most, if not all, previous observations and analyses of fluxes of individual nitrogen oxides. The results imply that the mechanisms contributing to NO_y fluxes, at least at this site, are much more complex than previously recognized. We show that the observations of upward fluxes of $HNO_{3(g+p)}$ and σPNs during summer are consistent with oxidation of NO_2 and acetaldehyde by an OH x residence time of 1.1×10^{10} molec OH cm^{-3} s, corresponding to 3 to 16×10^7 molecules cm^{-3} OH within the forest canopy for a 420 to 70 s canopy residence time. We show that $\Sigma AN_{(g+p)}$ fluxes are consistent with this range in OH if the reaction of OH with ΣANs produces either HNO_3 or NO_2 with a 6–30% yield. Calculations of NO fluxes constrained by the NO_2 observations and the inferred OH indicate that NO_x fluxes are downward into the canopy because of the substantial conversion of NO_x to HNO_3 and σPNs in the canopy. Even so, we derive that NO_x emission fluxes of ~15 ng(N) m^{-2} s^{-1} at midday during summer are required to balance the NO_x and NO_y flux budgets. These fluxes are partly explained by estimates of soil emissions (estimated to be between 3 and 6 ng(N) m^{-2} s^{-1}). One possibility for the remainder of the NO_x source is large HONO emissions. Alternatively, the 15 ng(N) m^{-2} s^{-1} emission estimate may be too large, and the budget balanced if the deposition of HNO_3 and σPNs is slower than we estimate, if there are large errors in either our understanding of peroxy radical chemistry, or our assumptions that the budget is required to balance because the fluxes do not obey similarity theory.

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