soil systems

Article

Supplementary Information for

Summertime Soil–Atmosphere Ammonia Exchange in the Colorado Rocky Mountain Front Range Pine Forest

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S1. Additional measurements made by ambient ion monitoring system coupled with ion chromatographs (AIM-IC).

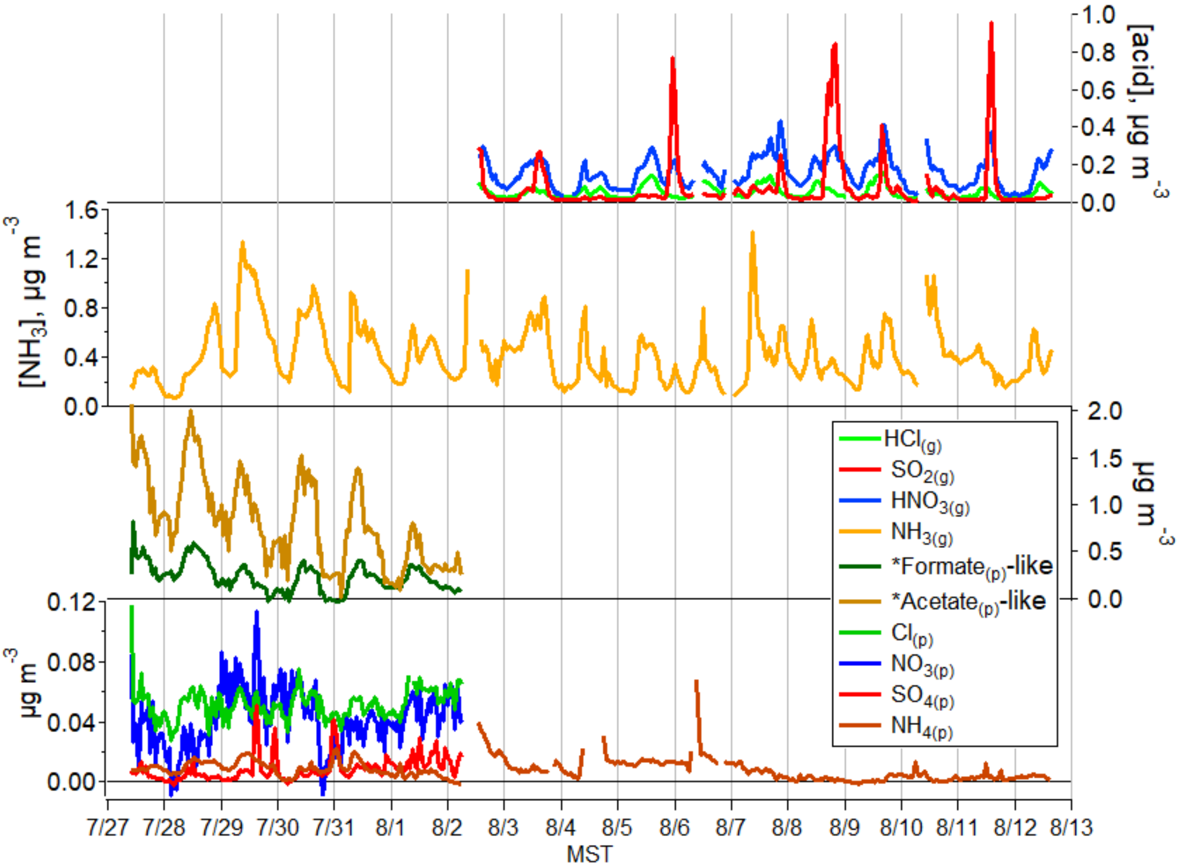

Figure S1. Ambient concentrations of trace gases (HCl, SO_2, HNO_3, and NH_3) and average $PM_{2.5}$ composition (pCl, pNO_3, pSO_4, pNH_4, and *organics) observed in MEFO by the AIM-IC from 27 July to 13 August 2015.

S2. Flux calculation based on compensation point resistance model

S2.1. Soil fluxes and in-canopy transfer velocity

The variable χ represents the air concentration, either as an equilibrium point in the context of a compensation point or as a measured ambient concentration, such as a mixing ratio measured by the AIM-IC. The transport velocity represents the transport of air masses through the canopy and is composed of the in-canopy aerodynamic resistance (R_{ac}) and the quasi-laminar boundary layer resistance at the forest ground surface (R_{bg}):

$$v_{tr} = R_{ac} + R_{bg}. \tag{S1}$$

Following the approach by Shuttleworth and Wallace (1985), R_{ac} was calculated as

$$R_{ac} = \frac{h_c \cdot \left(e^n - e^{n \cdot \left(1 - \frac{d + z_0}{h_c}\right)}\right)}{\kappa \cdot u_* \cdot n \cdot (h_c - d)}, \tag{S2}$$

where u_* is the friction velocity measured above the forest canopy and κ is the von Kármán constant (=0.41) [2]. The parameter n is a function of the leaf area index and described further in Massad et al. (2010).

The quasi-laminar boundary layer resistance at forest ground is given by Schuepp et al. (1977) as

$$R_{bg} = \frac{Sc - ln\left(\frac{\delta_0}{z_l}\right)}{\kappa \cdot u_{*g}}, \tag{S3}$$

where δ_0 is the distance above ground where the molecular diffusivity of NH_3 (D_{NH3}) [4] equals the eddy diffusivity and is thereby defined as $\delta_0 = D_{NH3}/\kappa \cdot u_{*g}$. The upper height of the logarithmic wind profile above the ground surface (z_l) was estimated as ~7 m from the in-canopy wind profile measurements. Sc is the Schmidt number, a strong function of the molecular diffusivity of the trace gas, and ~0.66 for NH_3. Assuming a logarithmic wind velocity profile, the friction velocity above the forest ground (u_{*g}) was determined as

$$u_{*g} = \frac{u_{2m} \cdot \kappa}{\ln\left(2 - z_{0g}\right)} \tag{S4}$$

by using the lowest wind speed measurement available at ~2 m a.g.l. and a roughness length at the ground surface (z_{0g}) of 0.01 m.

S2.1. Stomatal and cuticular fluxes

The stomatal resistance (R_s) was derived after Weseley et al. (1989) as

$$R_s = \frac{400 \cdot R_{s\_min} \cdot \left(\frac{200}{0.1 + G}\right)^2 \cdot \frac{D_{H2O}}{D_{NH3}}}{T_c \cdot (40 - T_c)}, \tag{S5}$$

where G is the global radiation measured above the forest canopy and D_{H2O} and D_{NH3} are the molecular diffusivities of water and NH_3 in air, respectively [4]. The canopy temperature (T_c) was estimated by the average of ambient air temperatures measured at 1.8 m, 7.0 m, and 14.1 m a.g.l.. The minimal stomatal conductance (R_{s_min}) was set to 130 s m^{-1}, which is suggested by Weseley et al. (1989) for a coniferous forest in midsummer .

The deposition of NH_3 to the pine needles' cuticles (F_{cut}) was determined by the ratio of χ_c and the cuticular resistance R_{cut}:

$$F_{cut} = -\frac{\chi_c}{R_{cut}}. \tag{S6}$$

According to Massad et al. (2010), R_{cut} can be described as a function of the relative humidity and the ratio of acids and bases in ambient air:

$$R_{cut} = \frac{31.5 \cdot e^{a \cdot (100 - rH_c)}}{AR}. \tag{S7}$$

The acid ratio (AR) was calculated as

$$AR = \frac{2 \cdot \chi_{SO2} + \chi_{HNO3} + \chi_{HCL}}{\chi_{NH3}}, \tag{S8}$$

using the mixing ratios measured by the AIM-IC within the forest canopy. In Equation (S7), the in-canopy relative humidity (rH_c) was determined by the average of the relative humidity measured at 1.8 m, 7.0 m, and 14.1 m a.g.l.. The parameter a is given as 0.0318 for forests [2] .

The canopy compensation point (χ_c) is needed in both Equation (6) in the main text and Equation (S6) for the determination of the stomatal and cuticular canopy fluxes, respectively. It represents the NH_3 mixing ratio at the pine needle surface, which governs the uptake or release of NH_3 by the stomata and the deposition of NH_3 to the cuticle. Following the compensation point approach described by Nemitz et al. (2001), we reformulated the equation for χ_c to be independent from NH_3 measured above the canopy and the above canopy aerodynamic resistance as

$$\chi_c = \frac{\chi_{zo+d} + \chi_s \cdot \frac{R_b}{R_s}}{1 + \frac{R_b}{R_s} + \frac{R_b}{R_{cut}}}. \tag{S9}$$

We assumed that the mixing ratio at the canopy top due (χ_{z0+d}) was similar to the NH_3 mixing ratio measured by the AIM-IC due to the relatively open forest canopy structure. While all other terms in Eq. (S9) are described above, the quasi-laminar boundary layer resistance (R_b) which limits the exchange at the pine needle surface was determined as

$$R_b = \frac{2 \cdot \left(\frac{Sc}{Pr}\right)^{\frac{2}{3}}}{\kappa \cdot u_*}, \tag{S10}$$

where Pr is the Prandtl number, defined as the ratio between momentum and thermal diffusivities (for air ≈0.72).

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