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Responses of surface ozone to future agricultural ammonia emissions and subsequent nitrogen deposition through terrestrial ecosystem feedbacks

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S1 Implementation of soil NO_x and NH_3 emission in CLM4.5-BGC

S1.1 Soil NO_x

We incorporate new equations to calculate NO_x released as by-products of nitrification and denitrification. Default CLM estimates the amount of N_2O leakage during nitrification by applying a constant scale factor to the nitrification rate (Li et al., 2000) while that from denitrification is variable and evaluated using the Century approach (Del Grosso et al., 2000). Building on the work of previous studies (Parton et al., 2001, 2004; Zhao et al., 2017), we compute a ratio of NO_x to N_2O to account for the leaking of the former during nitrification and denitrification using the following equations:

$$\mathrm{NO}_x\!:\mathrm{N_2O} = 15.2 + \frac{35.5\tan^{-1}[0.68\pi(10D_\mathrm{r} - 1.86)]}{\pi} \qquad \text{Eq. 1}$$

where D_r is the relative gas diffusivity of soil vs. air and is calculated as a function of air-filled pore space (AFPS) of soil (Davidson and Trumbore, 1995):

$$D_\mathrm{r} = 0.209\mathrm{AFPS}^{\frac{4}{3}} \qquad \text{Eq. 2}$$

$$\mathrm{AFPS} = 1 - \frac{\theta_\mathrm{V}}{\theta_\mathrm{V,sat}} \qquad \text{Eq. 3}$$

where θ_V and $\theta_\mathrm{V,sat}$ are instantaneous and saturated volumetric soil water content (in $m^3\ m^{-3}$), respectively.

In addition, we also rectify a coding mistake in CLM by restoring a missing 20% of microbial mineralized nitrogen for nitrification to correct the rapid denitrification in previous versions (Parton et al., 2001), and applied a temperature factor to correct the overestimation at high latitudes as suggested in some previous studies (Xu and Prentice, 2008; Zhao et al., 2017):

$$f_T = \min\left(1, e^{308.56\left(\frac{1}{68.02} - \frac{1}{T_\mathrm{soil}+46.02}\right)}\right) \qquad \text{Eq. 4}$$

where T_soil is soil temperature in Kelvin (K).

S1.2 Soil NH_3

We add into this model a new NH_3 emission scheme consistent with another standalone biogeochemical model, DNDC version 9.5 (Li et al., 2012), which has been used for studying agricultural NH_3 emission (Balasubramanian et al., 2015, 2017; Zhang and Niu, 2016).

For each model soil layer, NH_3 volatilization is considered as a multistage process, which is formulated as:

$$\frac{\mathrm{d}\left[\mathrm{NH_{3\,(g)}}\right]}{\mathrm{d}t}_\mathrm{soil} = \left[\mathrm{NH_{4\,(soil)}^{+}}\right](1 - f_\mathrm{ads})f_\mathrm{dis}f_\mathrm{vol}(\frac{1}{\Delta t}) \qquad \text{Eq. 5}$$

where $[\mathrm{NH_4^+}_{\text{(soil)}}]$ (in g-N m^{-2}) is the amount of soil $\mathrm{NH_4^+}$; Δt is model time step size in CLM (default = 30 min or 1800 s).

Due to electrostatic attraction, a portion of soil $\mathrm{NH_4^+}$ adsorbs on the naturally negatively charged surface of soil particles. Our scheme estimates the fraction of $\mathrm{NH_4^+}$ adsorbed, f_{ads}, as:

$$f_{\mathrm{ads}} = 0.99(7.2733 f_{\mathrm{clay}}^3 - 11.22 f_{\mathrm{clay}}^2 + 5.7198 f_{\mathrm{clay}} + 0.0263) \qquad \text{Eq. 6}$$

where f_{clay} is soil clay fraction as prescribed by the CLM surface data (Bonan et al., 2002).

The non-adsorbed $\mathrm{NH_4^+}$ dissociates reversibly into aqueous $\mathrm{NH_3}$ and hydrogen ion ($\mathrm{NH_4^+}_{\text{(aq)}} \rightleftharpoons \mathrm{NH_3}_{\text{(aq)}} + \mathrm{H^+}$). The fraction of such $\mathrm{NH_4^+}$ dissociated into aqueous $\mathrm{NH_3}$, f_{dis}, is determined by the following equations (Li et al., 2012):

$$f_{\mathrm{dis}} = \frac{K_{\mathrm{w}}}{K_{\mathrm{a}}[\mathrm{H^+}]} \qquad \text{Eq. 7}$$

$$K_{\mathrm{w}} = 10^{0.08946 + 0.03605 T_{\mathrm{soil}}} \times 10^{-15} \qquad \text{Eq. 8}$$

$$K_{\mathrm{a}} = (1.416 + 0.01357 T_{\mathrm{soil}}) \times 10^{-5} \qquad \text{Eq. 9}$$

$$[\mathrm{H^+}] = 10^{-\mathrm{pH}} \qquad \text{Eq. 10}$$

where K_{a} (in mol L^{-1}) and K_{w} (in mol L^{-2}) are dissociation constants for $\mathrm{NH_4^+/NH_3}$ and hydrogen-/hydroxide-ion equilibria, respectively; T_{soil} (in ºC) is soil temperature; $[\mathrm{H^+}]$ (in mol) is the concentration of aqueous hydrogen ion in the soil calculated from soil pH. The model has yet to be capable of calculating soil pH implicitly, and $\mathrm{NH_3}$ volatilization is sensitive to soil pH, so we perform our simulations using a constant pH of 6.8, as is adopted by DNDC, for a more concise analysis.

Lastly, we use this equation to calculate the fraction of aqueous $\mathrm{NH_3}$ volatilized as gaseous $\mathrm{NH_3}$, f_{vol}:

$$f_{\mathrm{vol}} = \left(\frac{1.5s}{1+s}\right)\left(\frac{T_{\mathrm{soil}}}{50 + T_{\mathrm{soil}}}\right)\left(\frac{l_{\mathrm{max}} - l}{l_{\mathrm{max}}}\right) \qquad \text{Eq. 11}$$

where s (in m s^{-1}) is surface wind speed; T_{soil} (in ºC) is soil temperature; l and l_{max} (both in m) are the depth of each particular soil layer and the maximum depth of a soil column, respectively.

S2 Supplementary figures

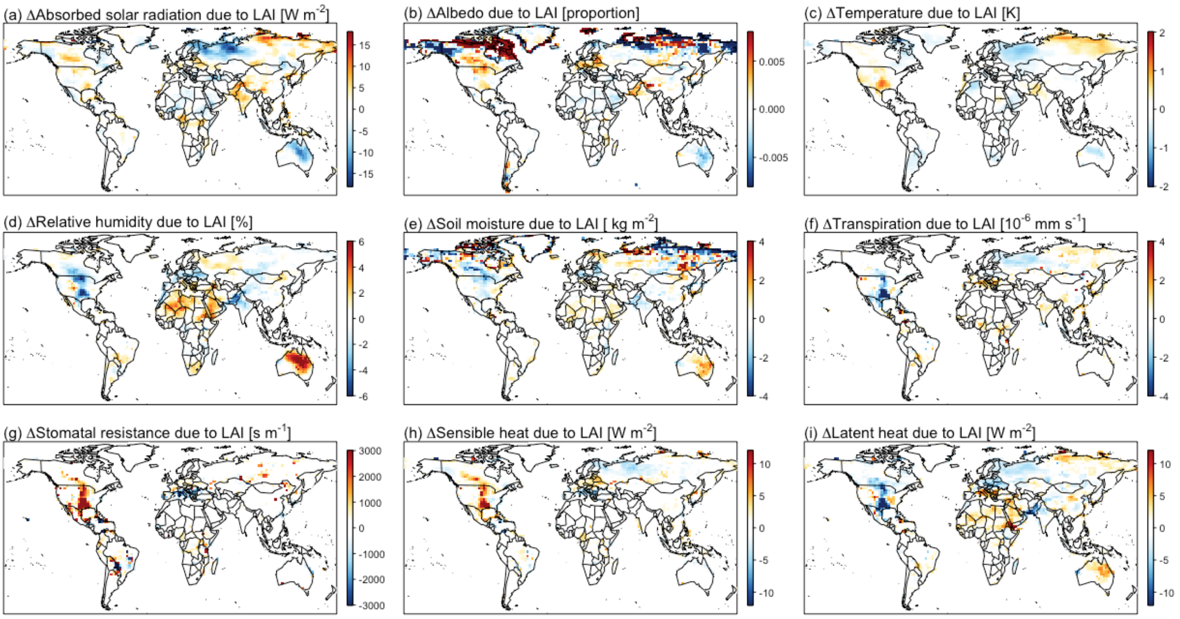

Figure S1. Summertime changes in **(a)** absorbed solar radiation, **(b)** albedo, **(c)** 2-meter surface temperature, **(d)** 2-meter relative humidity, **(e)** soil moisture, **(f)** vegetation transpiration, **(g)** stomatal resistance, **(h)** sensible heat flux, and **(i)** latent heat flux driven by LAI increase under dynamic meteorology.

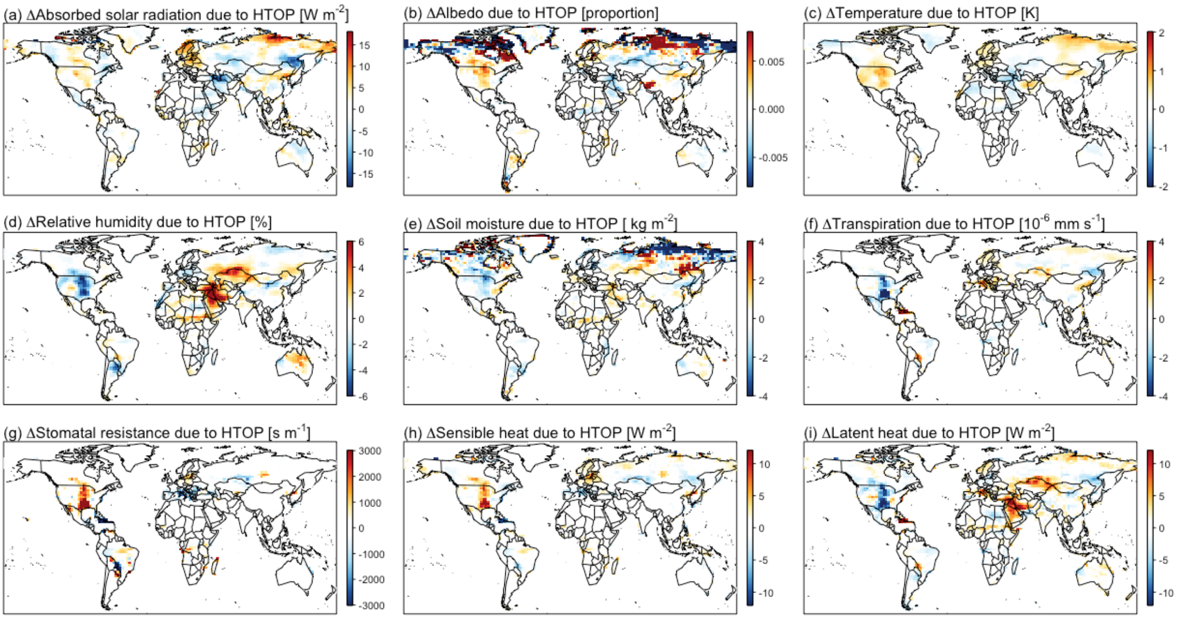

Figure S2. Same as Fig.S1 but driven by canopy height increase.

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