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*Supplement of*

## **A model-based analysis of foliar NO<sub>x</sub> deposition**

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## Supporting information

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**Table S1: Advection concentrations for the UMBS and BEARPEX-2009 scenarios**

Species <sup>a</sup>	UMBS (ppb)	BEARPEX-2009 (ppb)
NO <sub>2</sub>	0.6	0.1-0.35 <sup>b</sup>
O <sub>3</sub>	30	50
CH <sub>2</sub> O	1	1
CH <sub>3</sub> CHO	0.5	0.5

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- a. Species not shown have advection concentrations of zero
- b. For the BEARPEX-2009 case this was the maximum daily advection concentration reached around 17 hrs, based on field observations of higher NO<sub>x</sub> plumes from near-by Sacramento in the afternoon.

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**Table S2: Reactions and rate constants used in the 1D multibox model**

Reaction	Rate constant
$\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$	$3.0 \times 10^{-12} \exp(-1500/T)$
$\text{NO}_2 + h\nu \xrightarrow{\text{O}_2} \text{NO} + \text{O}_3$	See Text
$\text{O}_3 + h\nu \xrightarrow{\text{H}_2\text{O}} \text{O}_2 + 2\text{OH}$	See Text
$\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$	$1.7 \times 10^{-12} \exp(-940/T)$
$\text{HO}_2 + \text{O}_3 \longrightarrow \text{OH} + 2\text{O}_2$	$1.0 \times 10^{-14} \exp(-490/T)$
$\text{OH} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$	$k_0 = 6.9 \times 10^{-31} (T/300)^{-1}$ $k_\infty = 2.6 \times 10^{-11}$
$\text{OH} + \text{HO}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$	$4.8 \times 10^{-11} \exp(250/T)$
$\text{HO}_2 + \text{HO}_2 \xrightarrow{\text{M}} \text{H}_2\text{O}_2 + \text{O}_2$	$3.5 \times 10^{-13} \exp(430/T) + 1.7 \times 10^{33} \times (\text{M} - [\text{H}_2\text{O}]) \times \exp(1000/T) \times (1 + 1.4 \times 10^{-21} \times [\text{H}_2\text{O}] \times \exp(2200/T))$
$\text{H}_2\text{O}_2 + \text{OH} \longrightarrow \text{HO}_2 + \text{H}_2\text{O}$	$1.8 \times 10^{-12}$
$\text{H}_2\text{O}_2 + h\nu \longrightarrow 2\text{OH}$	See Text
$\text{NO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HNO}_3$	$k_0 = 1.49 \times 10^{-30} (T/300)^{-1.8}$ $k_\infty = 2.58 \times 10^{-11}$
$\text{HO}_2 + \text{NO} \longrightarrow \text{OH} + \text{NO}_2$	$3.5 \times 10^{-12} \exp(250/T)$
$\text{NO}_2 + \text{O}_3 \longrightarrow \text{NO}_3 + \text{O}_2$	$1.2 \times 10^{-13} \exp(-2450/T)$
$\text{NO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{N}_2\text{O}_5$	$k_0 = 2.0 \times 10^{-30} (T/300)^{-4.4}$ $k_\infty = 1.4 \times 10^{-12} (T/300)^{-0.7}$
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2\text{HNO}_3$	$2.0 \times 10^{-21}$
$\text{NO} + \text{NO}_3 \longrightarrow 2\text{NO}_2$	$1.5 \times 10^{-11} \exp(170/T)$
$\text{N}_2\text{O}_5 \longrightarrow \text{NO}_2 + \text{NO}_3$	$K_{eq} = 2.7 \times 10^{-27} \exp(1100/T)$
$\text{NO}_3 + h\nu \longrightarrow \text{NO} + \text{O}_2$	See Text
$\text{NO}_3 + h\nu \xrightarrow{2\text{O}_2} \text{NO}_2 + \text{O}_3$	See Text
$\text{CO} + \text{OH} \xrightarrow{\text{M}\text{O}_2} \text{CO}_2 + \text{HO}_2$	$k_0 = 5.9 \times 10^{-33} (T/300)^{-1.4}$ $k_\infty = 1.1 \times 10^{-12} (T/300)^{1.3}$
$\text{CH}_4 + \text{OH} \longrightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	$2.45 \times 10^{-12} \exp(-1775/T)$
$\text{CH}_3\text{O}_2 + \text{HO}_2 \longrightarrow \text{CH}_3\text{OOH} + \text{O}_2$	$4.1 \times 10^{-13} \exp(750/T)$
$\text{CH}_3\text{O}_2 + \text{NO} \xrightarrow{\text{O}_2} \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2$	$2.8 \times 10^{-12} \exp(300/T)$
$\text{CH}_3\text{OOH} + \text{OH} \longrightarrow \text{CH}_2\text{O} + \text{OH} + \text{H}_2\text{O}$	$0.3 \times 3.8 \times 10^{-12} \exp(200/T)$
$\text{CH}_3\text{OOH} + \text{OH} \longrightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	$0.7 \times 3.8 \times 10^{-12} \exp(200/T)$
$\text{CH}_3\text{OOH} + h\nu \xrightarrow{\text{O}_2} \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{OH}$	See Text
$\text{CH}_2\text{O} + \text{OH} \longrightarrow \text{CO} + \text{HO}_2 + \text{H}_2\text{O}$	$5.5 \times 10^{-12} \exp(125/T)$
$\text{CH}_2\text{O} + h\nu \xrightarrow{\text{O}_2} \text{CO} + 2\text{HO}_2$	See Text
$\text{CH}_3\text{CHO} + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{H}_2\text{O}$	$5.4 \times 10^{-12} \exp(135/T)$
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \longrightarrow \text{PAN}$	$k_0 = 9.7 \times 10^{-29} (T/300)^{-5.6}$ $k_\infty = 9.3 \times 10^{-12} (T/300)^{-1.5}$
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO} \xrightarrow{\text{O}_2} \text{NO}_2 + \text{CO}_2 + \text{CH}_3\text{O}_2$	$8.1 \times 10^{-12} \exp(270/T)$
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2 \longrightarrow \text{CH}_2\text{O} + \text{O}_2 + \text{CH}_3\text{OOH}$	$1.3 \times 10^{-12} \exp(640/T)$
$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \longrightarrow \text{O}_3 + \text{CH}_3\text{COOH}$	$4.3 \times 10^{-13} \exp(1040/T)$

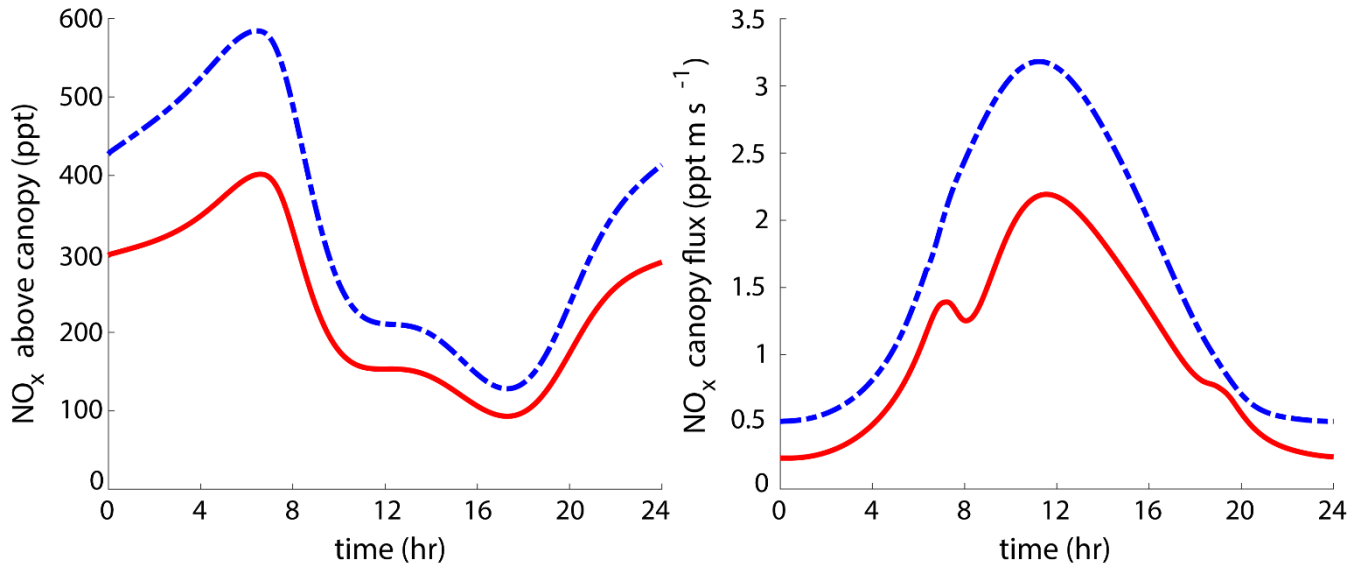
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$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2 \longrightarrow \text{O}_2 + 2\text{CO}_2 + 2\text{CH}_3$	$2.9 \times 10^{-12}\text{exp}(500/\text{T})$
$\text{CH}_3\text{CHO} + \text{NO}_3 \longrightarrow \text{HNO}_3 + \text{CH}_3\text{COO}_2$	$1.4 \times 10^{-12}\text{exp}(-1900/\text{T})$
$\text{PAN} \longrightarrow \text{CH}_3\text{COO}_2 + \text{NO}_2$	$K_{eq}=(9.0 \times 10^{-29}\text{exp}(14000/\text{T}))^{-1}$
$\text{VOC} + \text{OH} \longrightarrow \text{RO}_2$	kOH
$\text{RO}_2 + \text{NO} \longrightarrow (1 - \alpha) \text{HO}_2 + (1 - \alpha) \text{NO}_2 + \alpha \text{RONO}_2$	$2.7 \times 10^{-12}\text{exp}(360/\text{T})$
$\text{RO}_2 + \text{HO}_2 \longrightarrow 0.5 \text{ROOH} + 0.5 \text{O}_2 + 0.5 \text{HO}_2 + 0.5 \text{OH}$	$2.06 \times 10^{-13}\text{exp}(1300/\text{T})$
$\text{RO}_2 + \text{RO}_2 \xrightarrow{\text{O}_2} 1.2 \text{CH}_3\text{O}_2 + \text{products}$	$9 \times 10^{-14}$
$\text{RO}_2 + \text{CH}_3\text{O}_2 \xrightarrow{\text{O}_2} 0.6 \text{CH}_3\text{O}_2 + 0.6 \text{HO}_2 + \text{products}$	$9 \times 10^{-14}$
$\text{VOC} + \text{NO}_3 \longrightarrow \beta \text{RONO}_2 + (1 - \beta) \text{NO}_2 + \text{products}$	kNO <sub>3</sub>

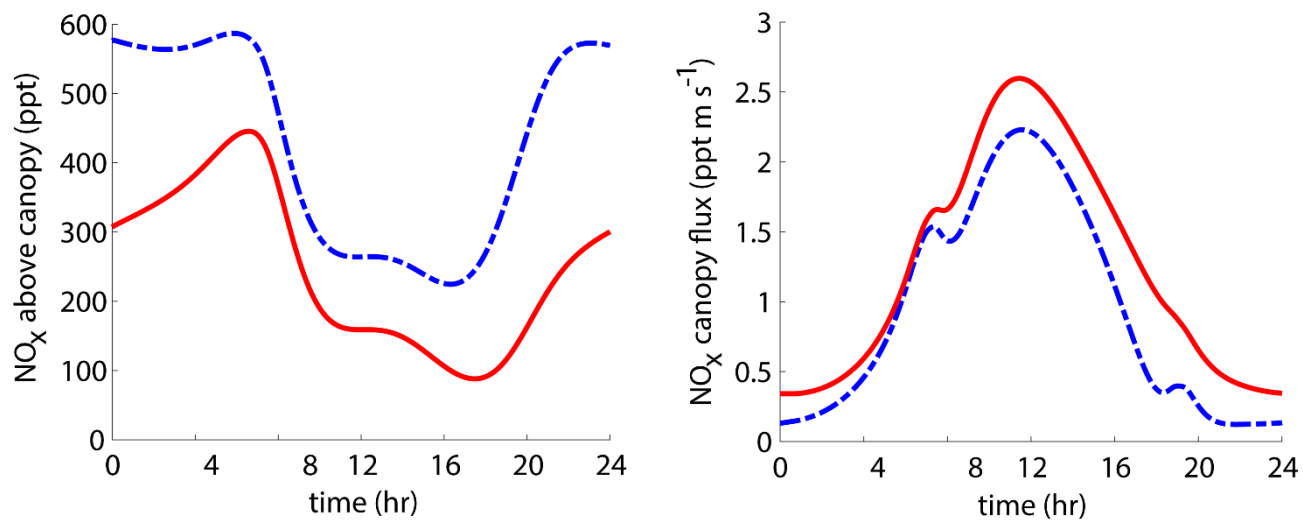
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**Table S3: Reactions and rate constants used in the simplified single box model**

Reaction	Rate constant
$\text{HO}_2 + \text{HO}_2 \xrightarrow{\text{M}} \text{H}_2\text{O}_2 + \text{O}_2$	$2.74 \times 10^{-12}$
$\text{NO}_2 + \text{OH} \xrightarrow{\text{M}} \text{HNO}_3$	$9.2 \times 10^{-12}$
$\text{RO}_2 + \text{NO} \longrightarrow (1 - \alpha) \text{HO}_2 + (1 - \alpha) \text{NO}_2 + \alpha \text{RONO}_2$	$9.0 \times 10^{-12}$
$\text{RO}_2 + \text{HO}_2 \longrightarrow \text{ROOH} + \text{O}_2$	$8.0 \times 10^{-12}$
$\text{RO}_2 + \text{RO}_2 \xrightarrow{\text{O}_2} 1.2 \text{CH}_3\text{O}_2 + \text{products}$	$6.8 \times 10^{-14}$



**Figure S1: Model predictions for the above canopy  $\text{NO}_x$  mixing ratios (a) and fluxes (b) for a LAI scaling factor of 0.25 (blue dash) and 1.5 (red solid).**



**Figure S2: Model predictions for the above canopy NO<sub>x</sub> mixing ratios (a) and fluxes (b) for  $\alpha = 0.01$  (blue dash) and  $\alpha = 0.1$  (red solid).**

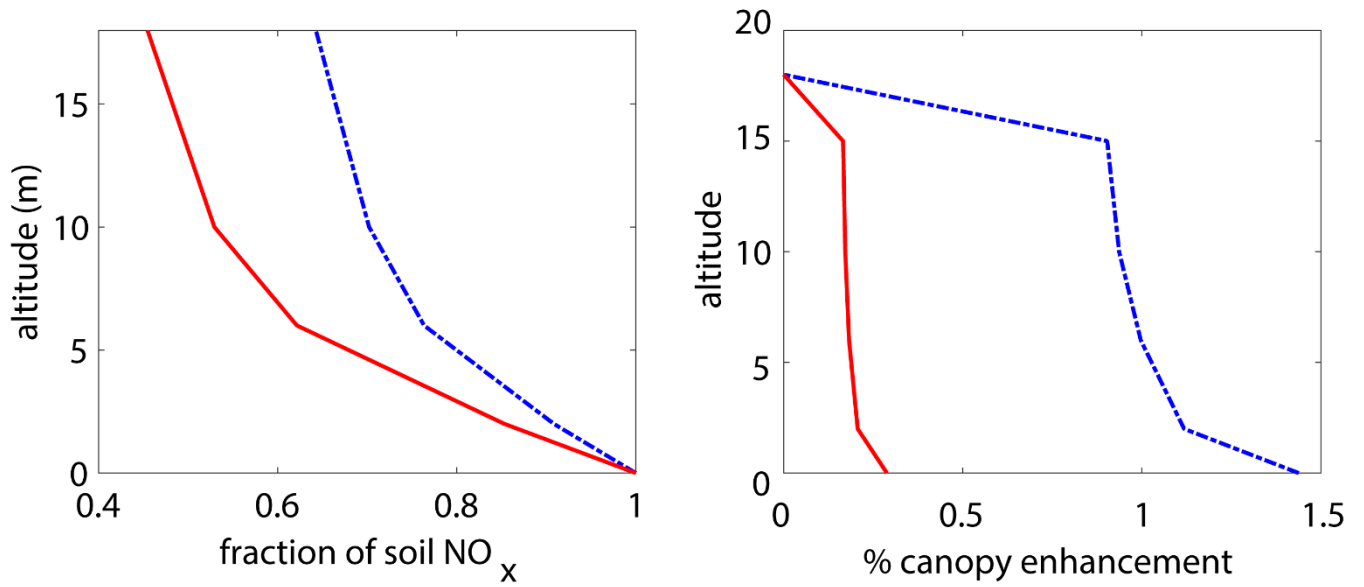


Figure S3: Model predictions for the fraction of soil NO<sub>x</sub> ventilated vertically (a) percent of NO<sub>x</sub> within the canopy relative to above-canopy concentrations (b) for an NO emission rate of 10 ppt m s<sup>-1</sup> (blue dash) and 1 ppt m s<sup>-1</sup> (red solid).



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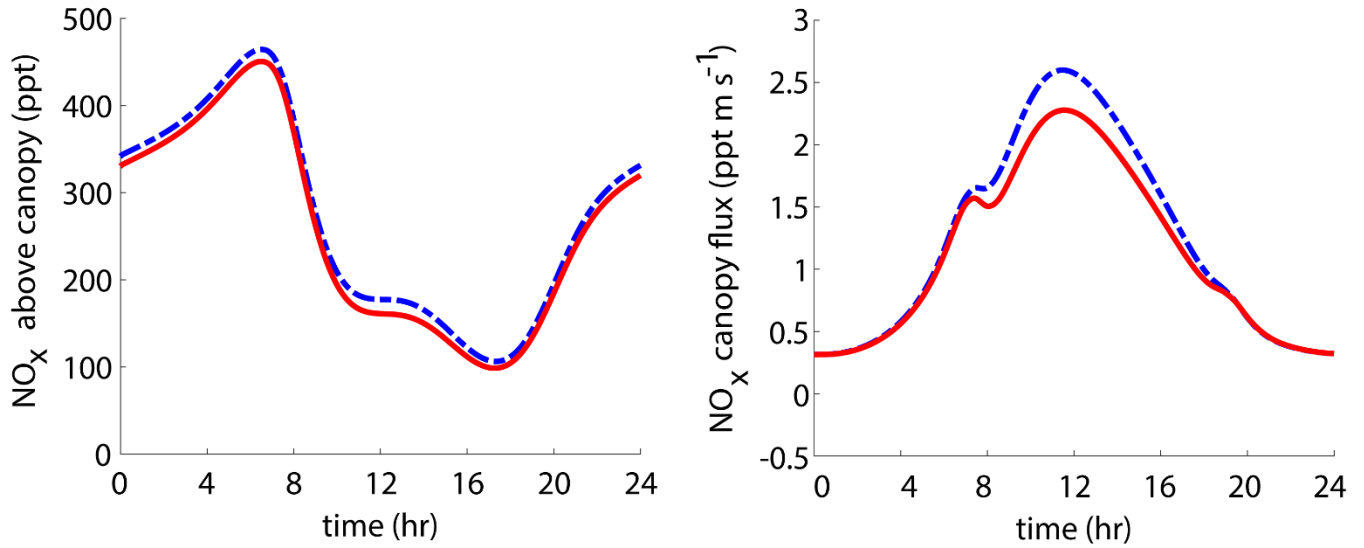
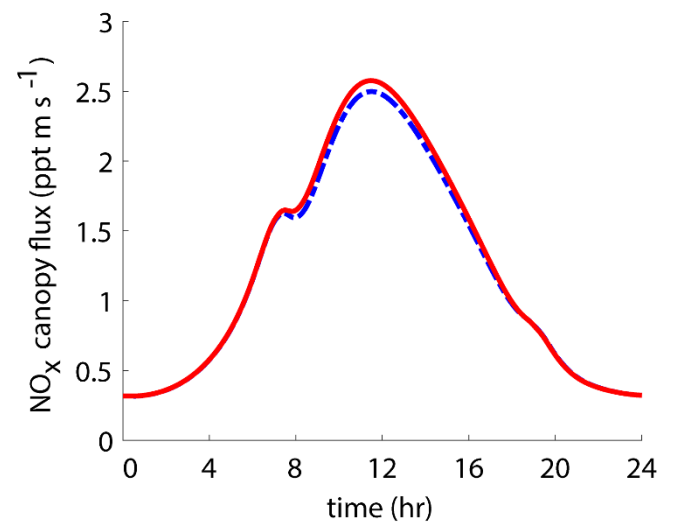
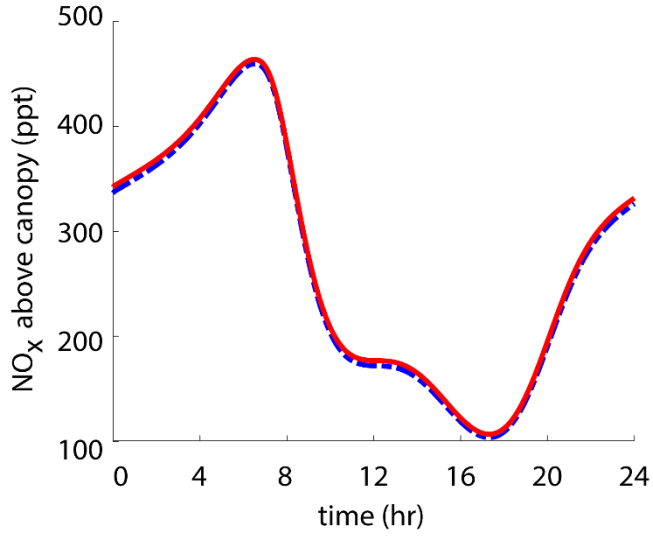
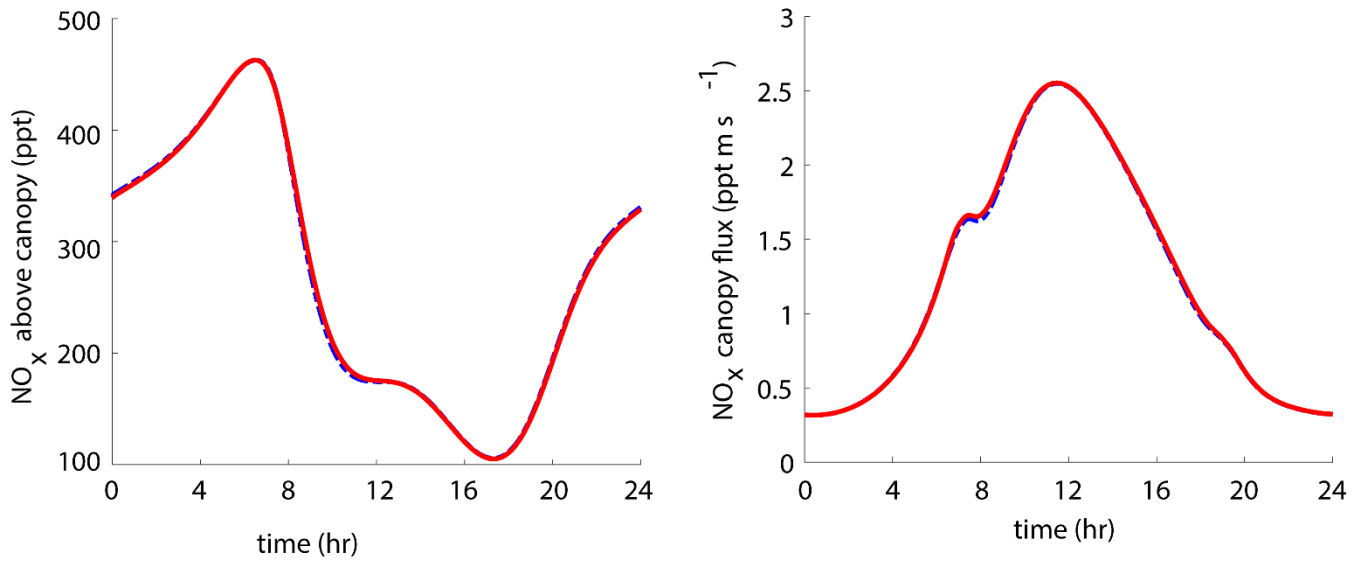


Figure S4: Model predictions for the above canopy  $\text{NO}_x$  mixing ratios (a) and fluxes (b) for  $\tau/T_L = 8$  (blue dash) and  $\tau/T_L = 1.2$  (red solid).

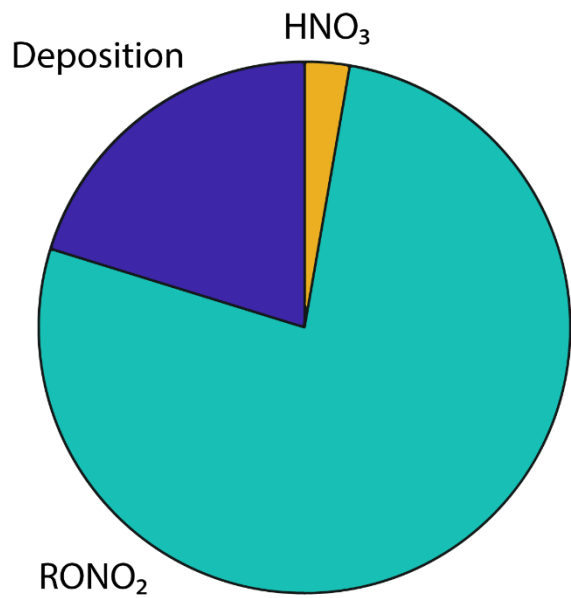


**Figure S5: Model predictions for the above canopy NO<sub>x</sub> mixing ratios (a) and fluxes (b) for an  $l_w$  scaling factor of 0.1 (blue dash) and 2 (red solid).**

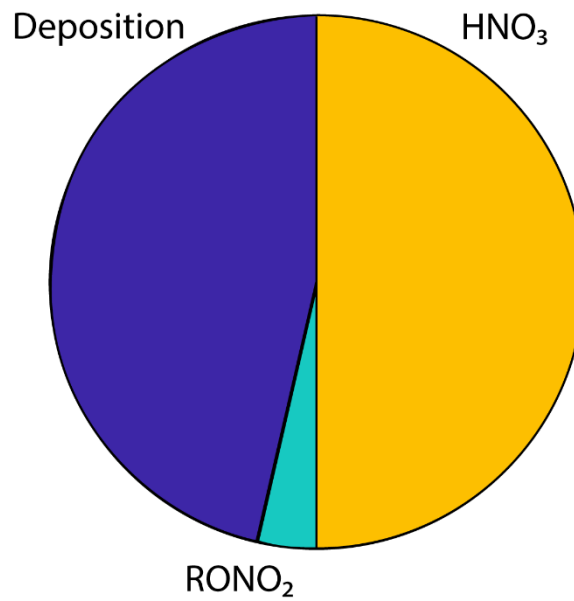


**Figure S6: Model predictions for the above canopy  $\text{NO}_x$  mixing ratios (a) and fluxes (b) for  $k_{\text{rad}} = 0.6$  (blue dash) and  $k_{\text{rad}} = 0$  (red solid).**

a)



b)



**Figure S7: Multi-box model prediction of the average daily fraction of NO<sub>x</sub> lost to nitric acid formation, alkyl nitrate formation, and deposition in an environment with 0.1-0.2 ppb NO<sub>x</sub> (a) and 20-30 ppb NO<sub>x</sub> (b).**

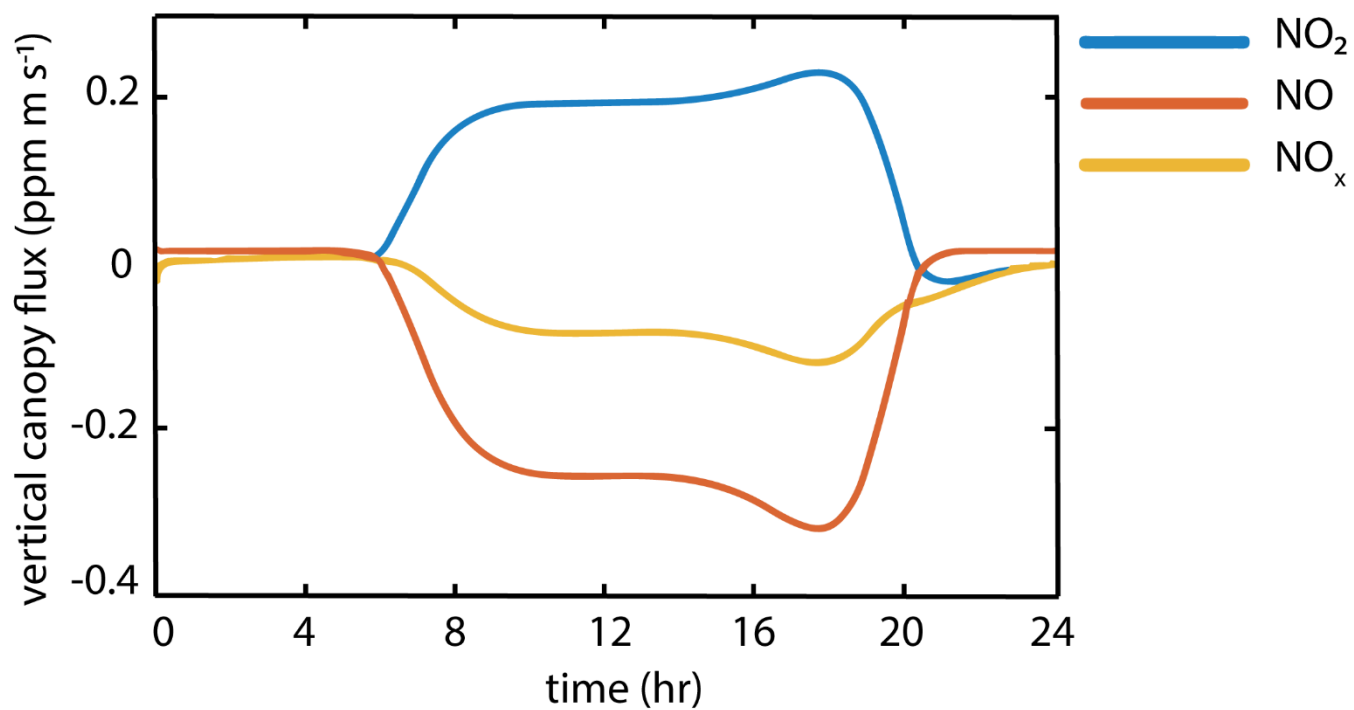


Figure S8: Multi-box model prediction of the diurnal canopy flux in an environment with daily minimum NO<sub>x</sub> concentrations of 20 ppb during the day and maximum concentrations of 50 ppb at night. Model was run using parameters for Blogett Forest.

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**Figure S9: Satellite image of east San Francisco Bay Area**

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