

Supporting information

5

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

Species ^a	UMBS (ppb)	BEARPEX-2009 (ppb)
NO ₂	0.7	0.4 ^b
O ₃	30	50
CH ₂ O	1	1
CH ₃ 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_x plumes from near-by Sacramento in the afternoon.

15

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

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

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

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

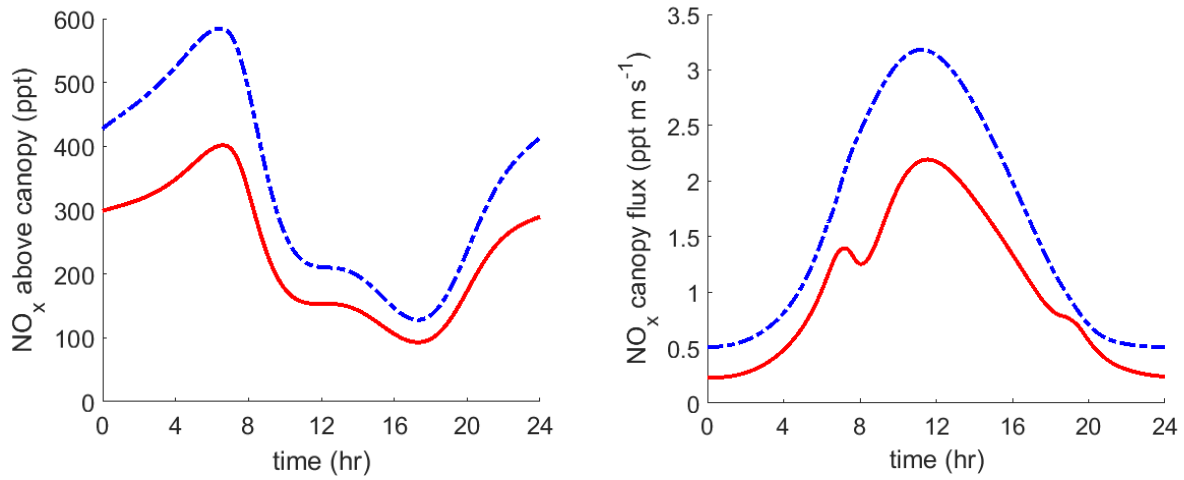


Figure S1: Above canopy NO_x mixing ratios (a) and fluxes (b) for a LAI scaling factor of 0.25 (blue dash) and 1.5 (red solid).

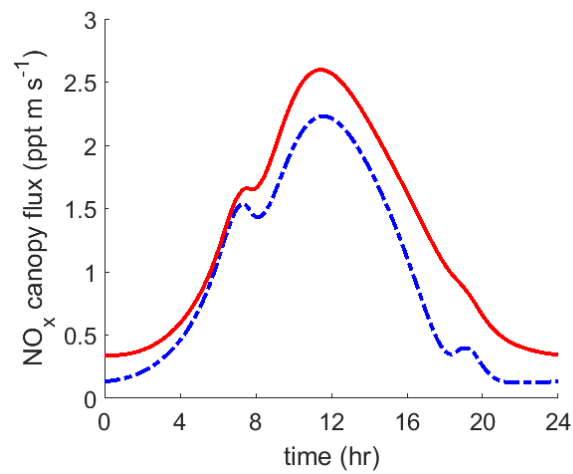
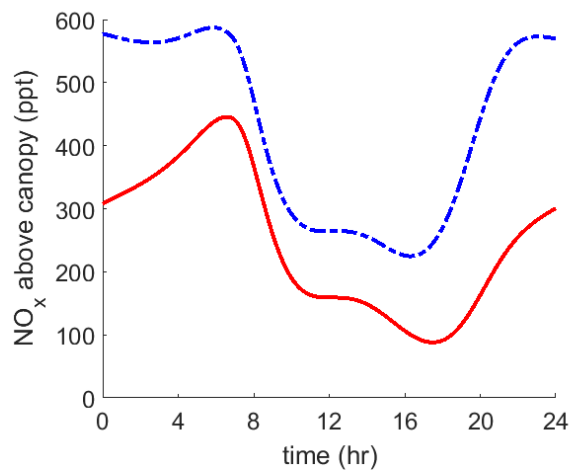


Figure S2: Above canopy NO_x mixing ratios (a) and fluxes (b) for $\alpha = 0.01$ (blue dash) and $\alpha = 0.1$ (red solid).

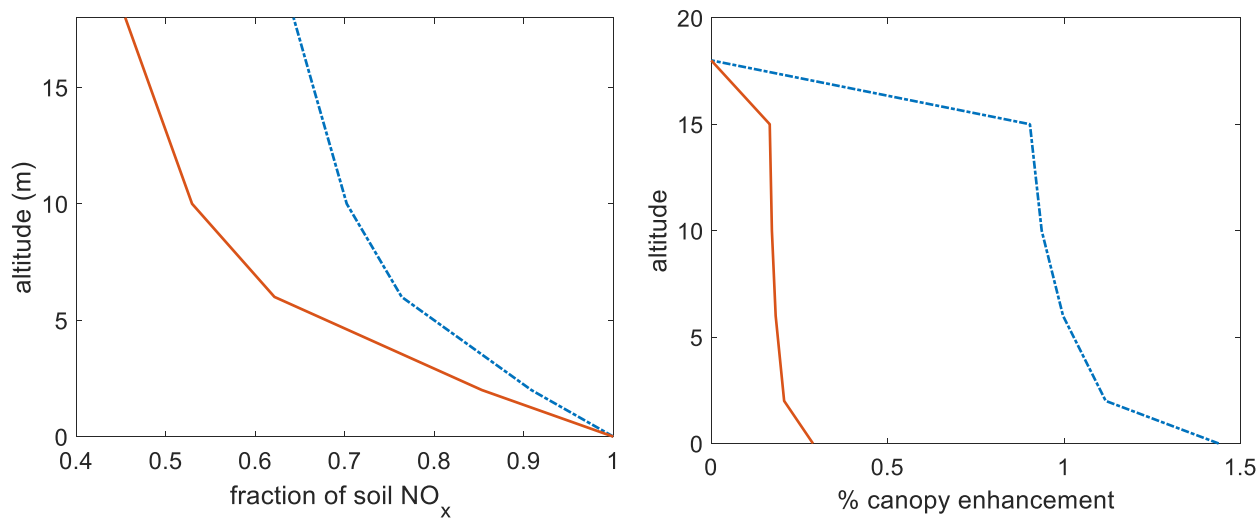


Figure S3: Fraction of soil NO_x ventilated vertically (a) percent of NO_x within the canopy relative to above-canopy concentrations (b) for an NO emission rate of 10 ppt m s⁻¹ (blue dash) and 1 ppt m s⁻¹ (red solid).

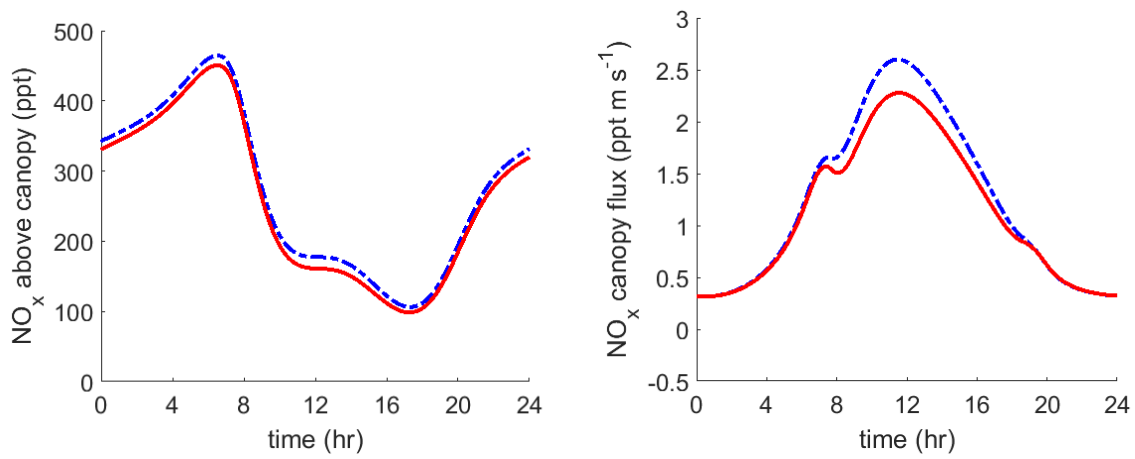


Figure S4: Above canopy NO_x mixing ratios (a) and fluxes (b) for $\tau/T_L = 8$ (blue dash) and $\tau/T_L = 1.2$ (red solid).

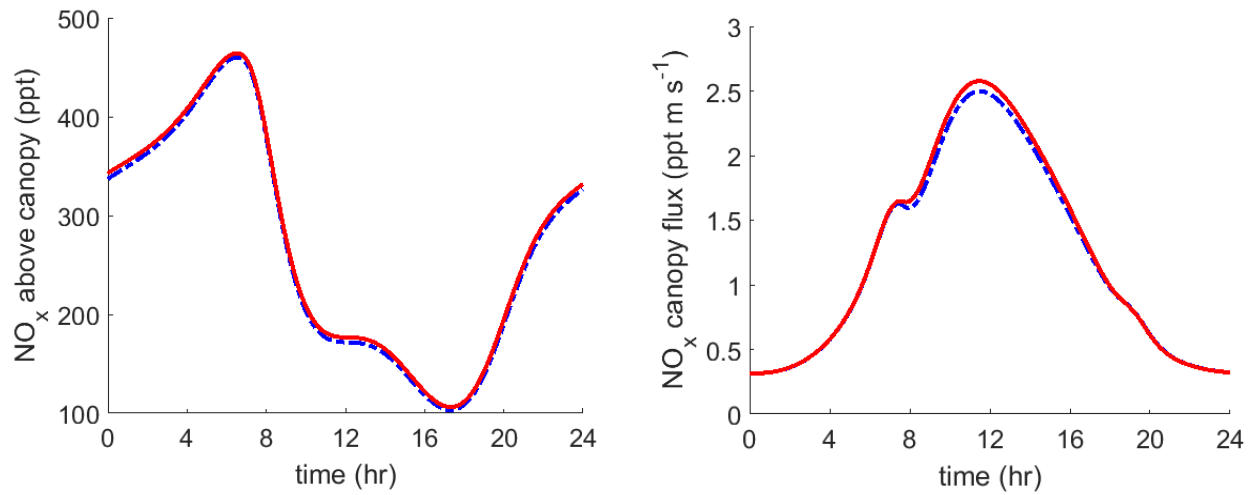


Figure S5: Above canopy NO_x mixing ratios (a) and fluxes (b) for an l_w scaling factor of 0.1 (blue dash) and 2 (red solid).

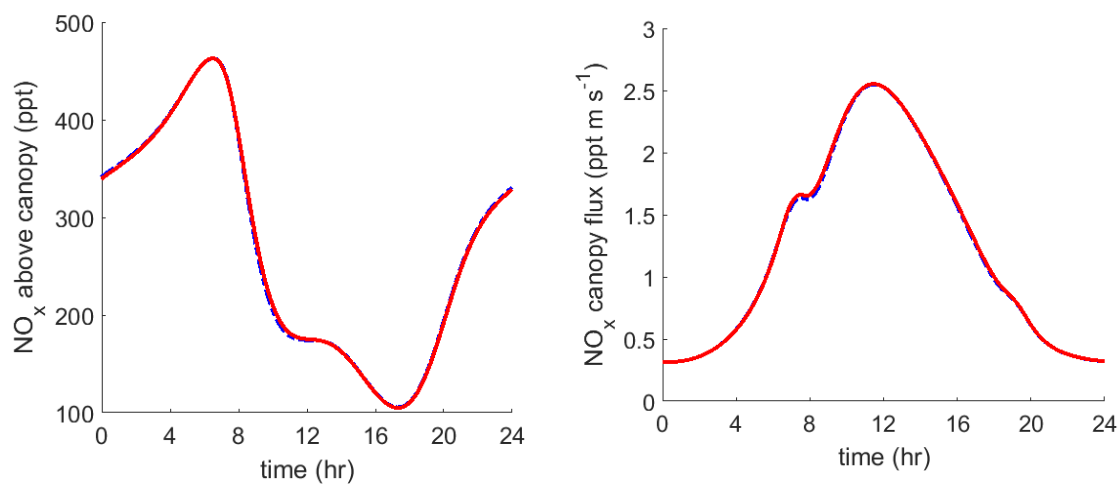


Figure S6: Above canopy NO_x mixing ratios (a) and fluxes (b) for $k_{\text{rad}} = 0.6$ (blue dash) and $k_{\text{rad}} = 0$ (red solid).

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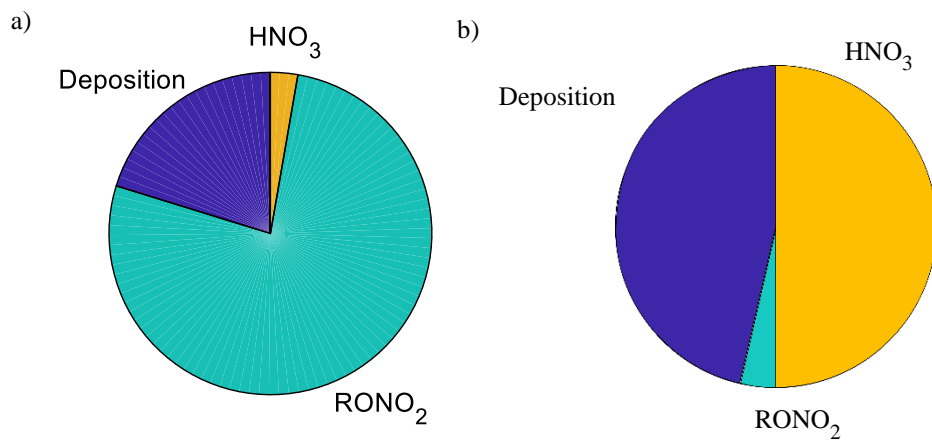


Figure S7: Multi-box model prediction of the average daily fraction of NO_x lost to nitric acid formation, alkyl nitrate formation, and deposition in an environment with 0.1-0.2 ppb NO_x (a) and 20-30 ppb NO_x (b).

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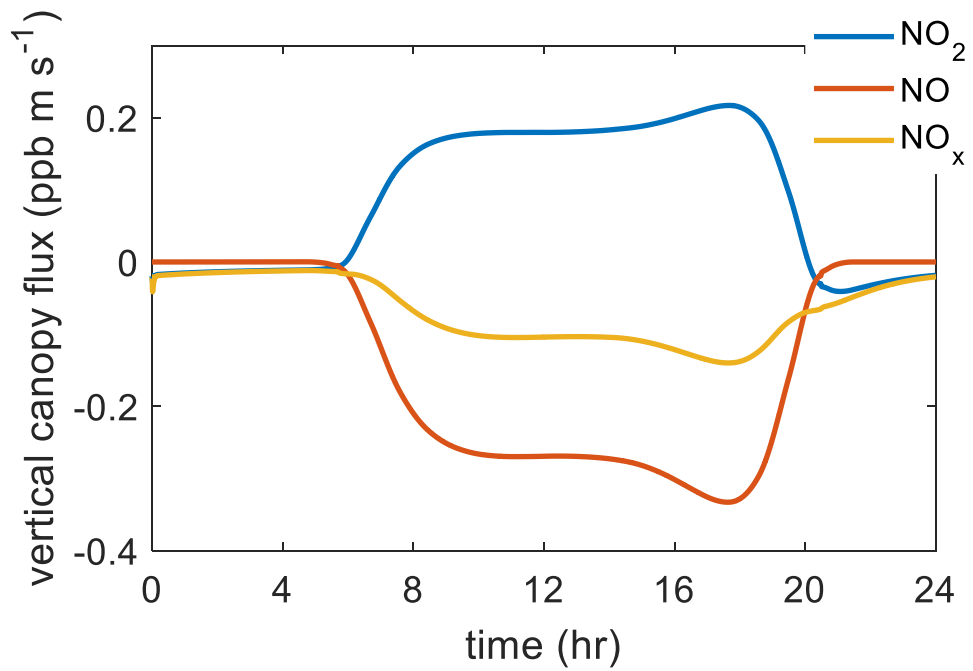


Figure S8: Multi-box model prediction of the diurnal canopy flux in an environment with daily minimum NO_x concentrations of 20 ppb during the day and maximum concentrations of 50 ppb at night.

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Figure S9: Satellite image of east San Francisco Bay Area

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