



Modelling of Photochemical Smog

EH605 - Modelling of Earth System and Sustainability

PRESENTED BY

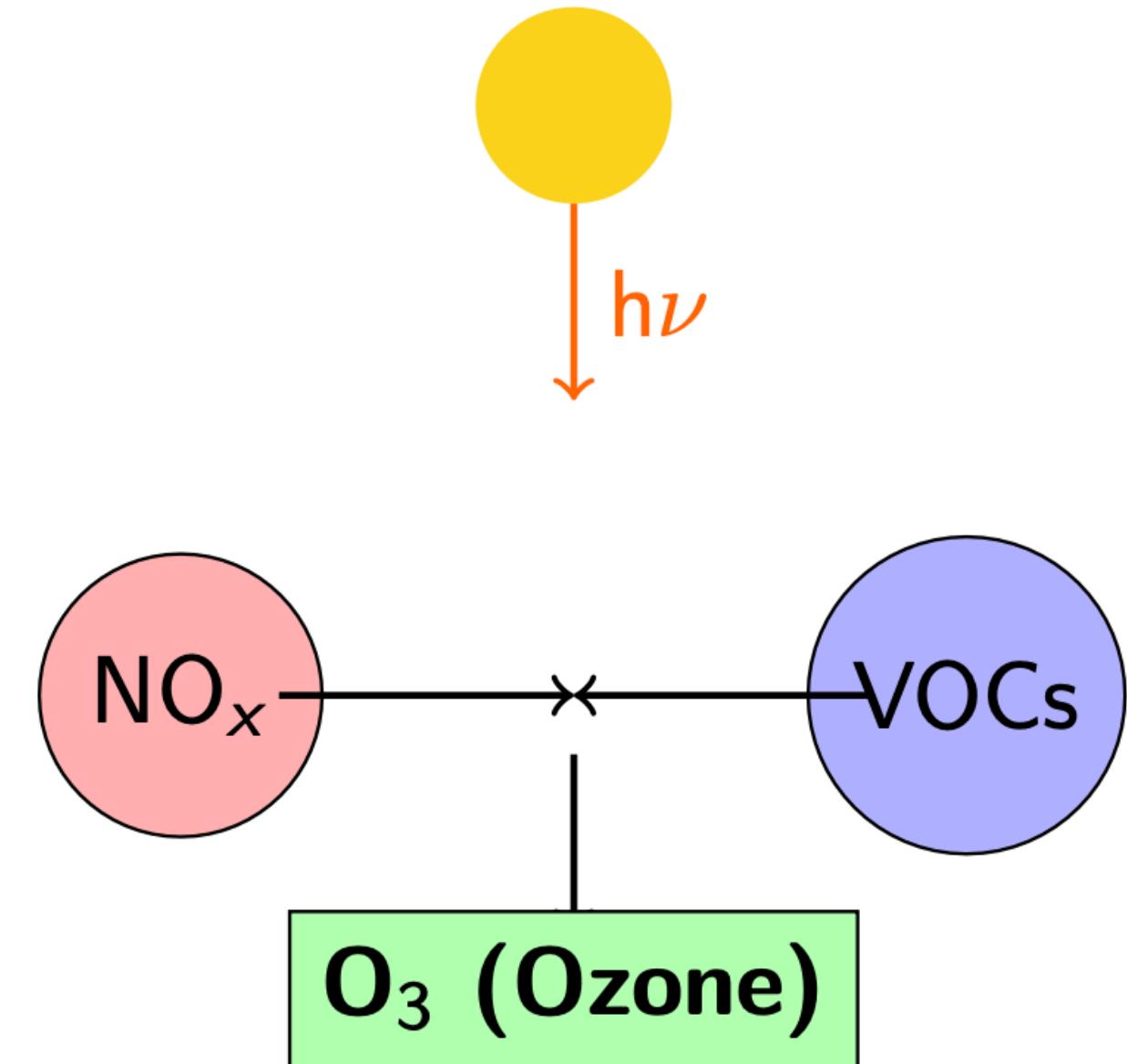
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Computer Science and Engineering



Photochemical Smog

- Air pollution from sunlight-driven reactions
- First documented: Los Angeles, 1940s
- **Primary pollutants:** NO_x, VOCs
- **Sunlight:** Energy source
- **Secondary pollutants:** O₃, PAN, aldehydes



The Problem

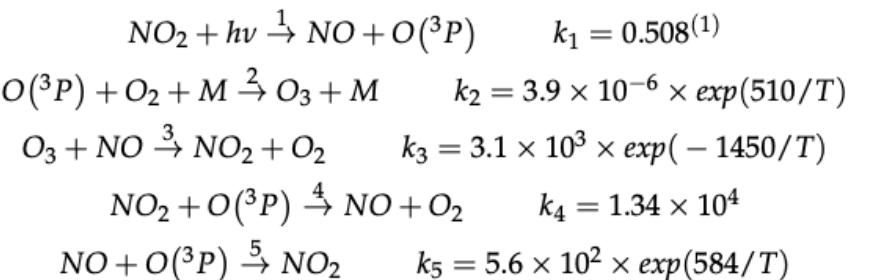
Health and Environmental Impacts

- **Health:** Respiratory diseases, cardiovascular problems
- **Agriculture:** Crop damage (10-30% yield loss)
- **Ecosystems:** Vegetation damage, forest decline
- **Standards:** $O_3 > 0.07 \text{ ppm}$ is hazardous

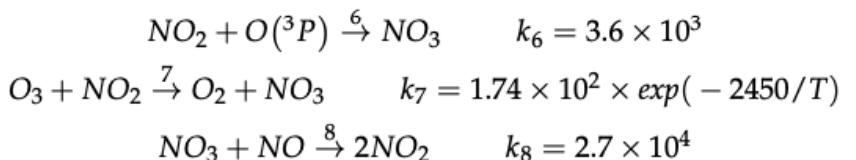
The Challenge

- Complex nonlinear chemistry (100s of reactions)
- Multiple timescales (seconds to hours)
- **Question:** How does chemistry produce net ozone?

1. Photolysis of NO_2 and basic $\text{NO}, \text{NO}_2, \text{O}_3$ photolytic cycle



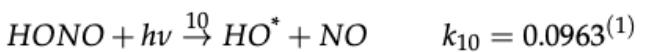
2. Chemistry of nitrogen trioxide: NO_3



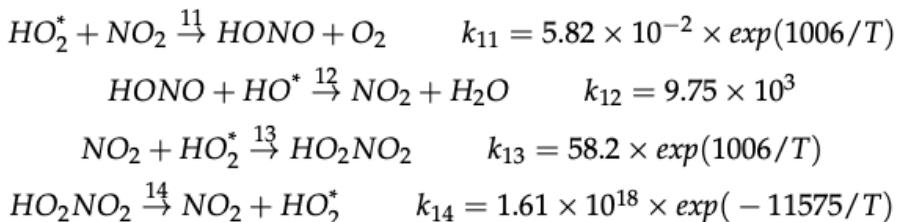
3. Nitrous acid and peroxy nitrous acid chemistry



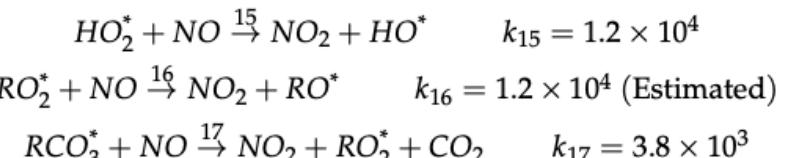
4. Photolysis of nitrous acid: *HONO*



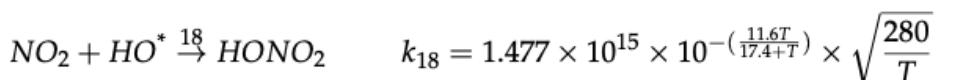
5. Nitrous acid chemistry



6. Conversion of NO to NO_2



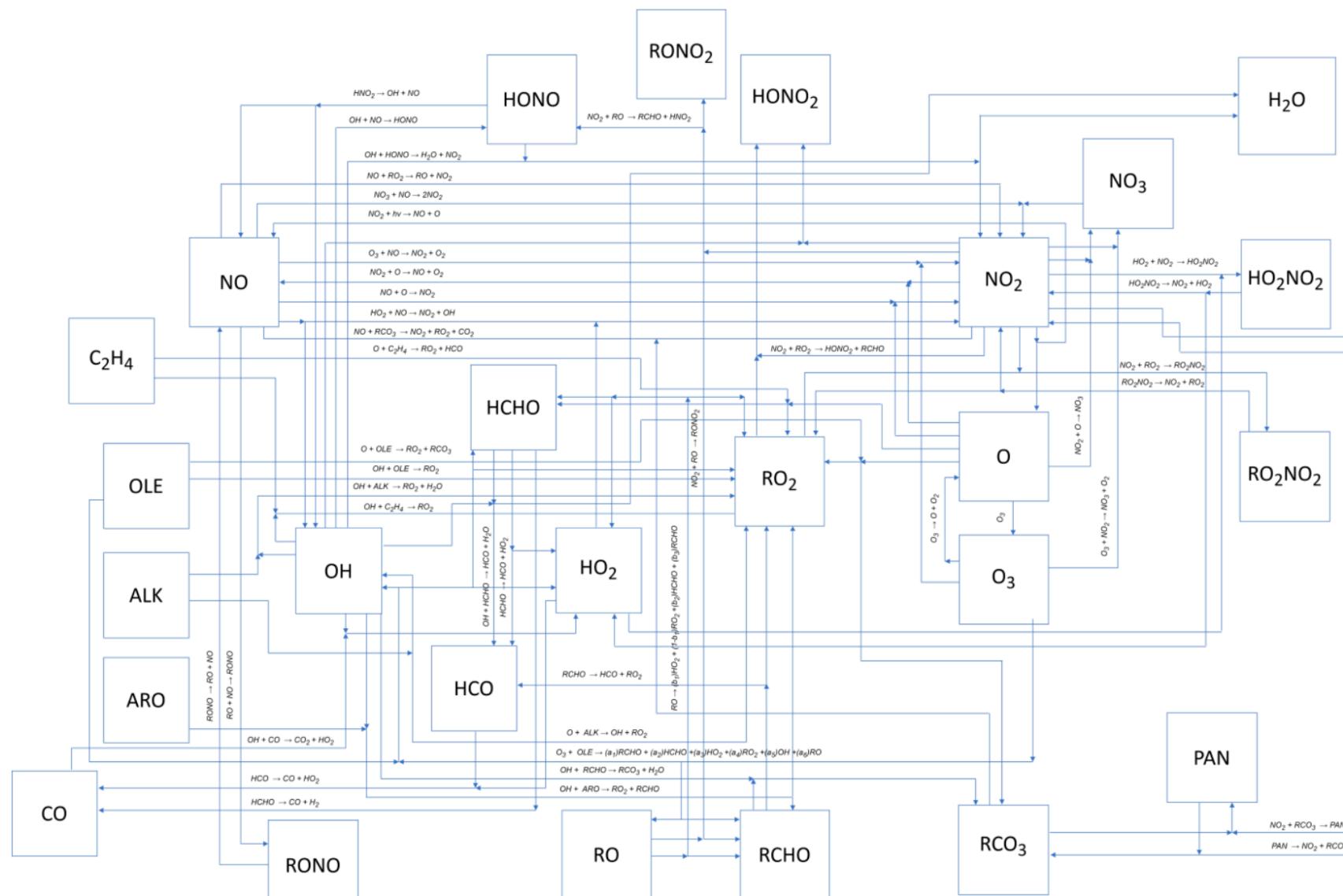
7. Nitric acid formation: $HONO_2$



Article

Mathematical Modeling of Photochemical and Chemical Interactions in Photochemical Smog Formation

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Objectives

Goal: Understand photochemical smog through progressive modelling

Model 1: Basic Photochemical Cycle

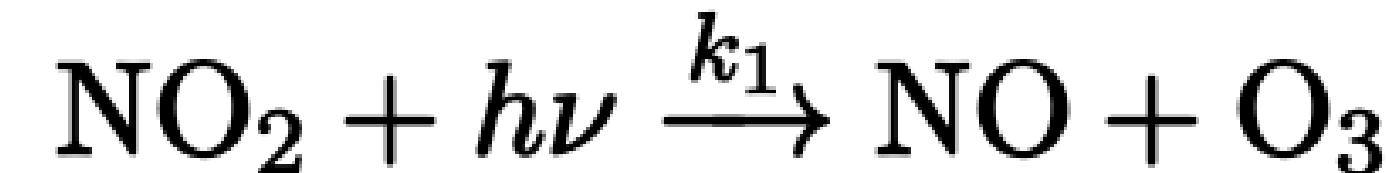
- 3-species: NO, NO₂, O₃
- 4-species: Add atomic oxygen (O)
- Capture photostationary state
- **Limitation:** Cannot produce net ozone

Model 2: Extended with VOCs and Radicals

- 11 species, 15 reactions
- Include VOC oxidation chemistry
- Add radical pathways (OH, HO₂, RO₂)
- **Success:** Produces realistic ozone levels

Model1: 3-species

Chemical Reactions



Mass Balance

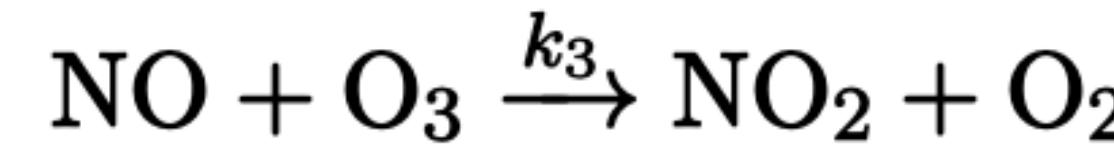
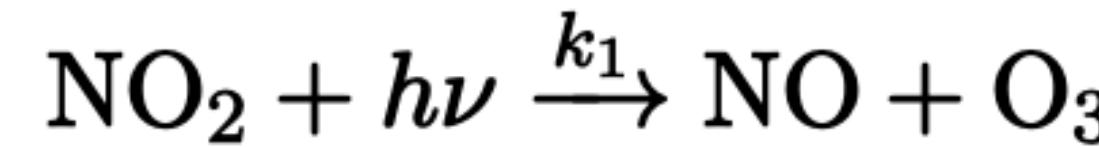
$$\frac{dC_i}{dt} = r_i + E_i = \sum_{j=1}^{N_{\text{rxn}}} \nu_{ij} R_j + E_i$$

where: $R_j = k_j \prod_i [C_i]^{\nu_{ij}}$ (reaction rate)

$$R_1 = k_1(t) [\text{NO}_2]$$

$$R_3 = k_3 [\text{O}_3] [\text{NO}]$$

Model1: 3-species



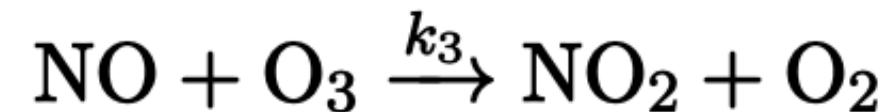
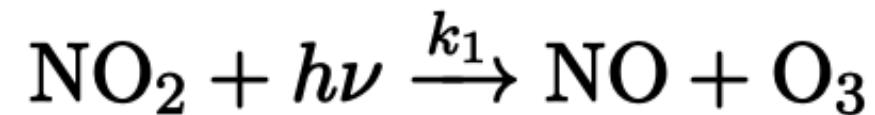
$$\frac{d[\text{NO}]}{dt} = k_1[\text{NO}_2] - k_3[\text{NO}][\text{O}_3] + E_{\text{NO}}$$

$$\frac{d[\text{NO}_2]}{dt} = -k_1[\text{NO}_2] + k_3[\text{NO}][\text{O}_3] + E_{\text{NO}_2}$$

$$\frac{d[\text{O}_3]}{dt} = k_1[\text{NO}_2] - k_3[\text{NO}][\text{O}_3]$$

$$E_{\text{NO}} = 0.02 \text{ ppm/h}$$

$$E_{\text{NO}_2} = 0.01 \text{ ppm/h}$$



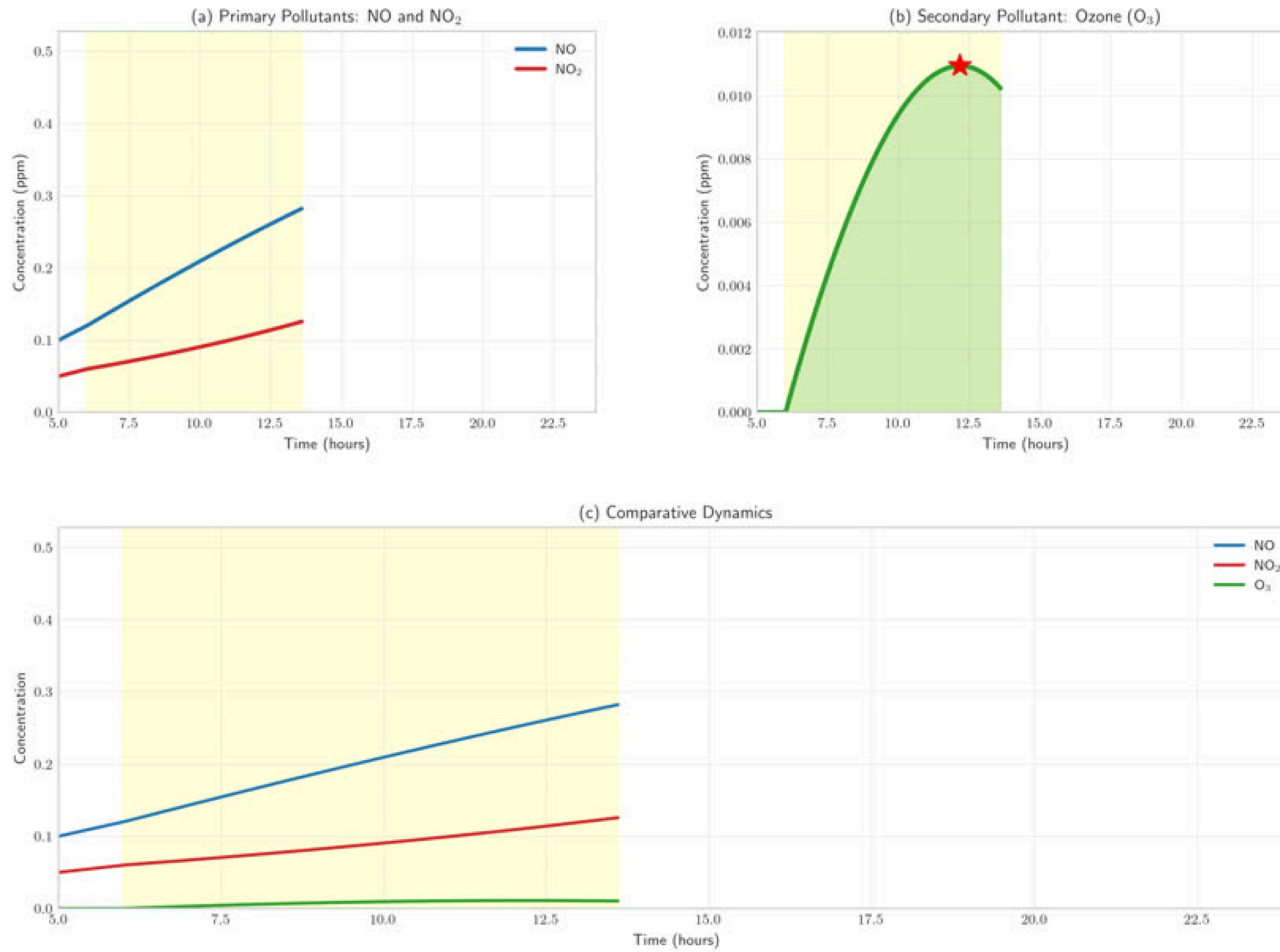
Parameter	Value	Units
$k_{1,\max}$	30.48	h^{-1}
k_3	1.20×10^5	$\text{ppm}^{-1} \text{ h}^{-1}$

$$k_1(t) = \begin{cases} k_{1,\max} \sin\left(\frac{\pi(t_{\text{clock}}-6)}{12}\right) & \text{if } 6 \leq t_{\text{clock}} \leq 18 \\ 0 & \text{otherwise} \end{cases}$$

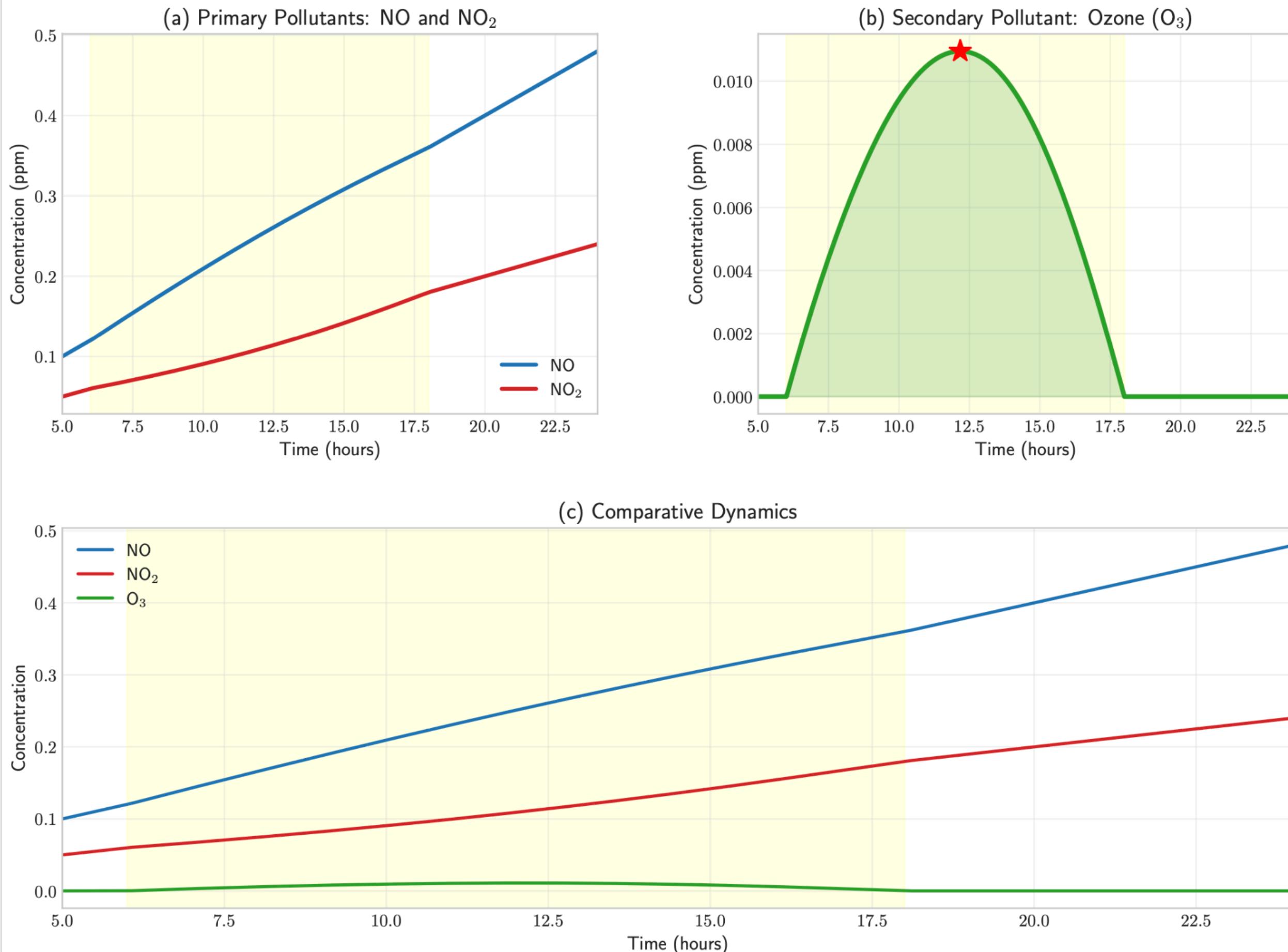
The Fundamental Problem

Every O_3 molecule created by NO_2 photolysis is consumed by reaction with NO. The system cycles but doesn't accumulate ozone.

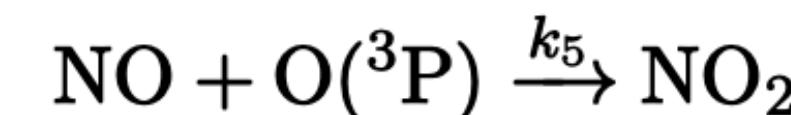
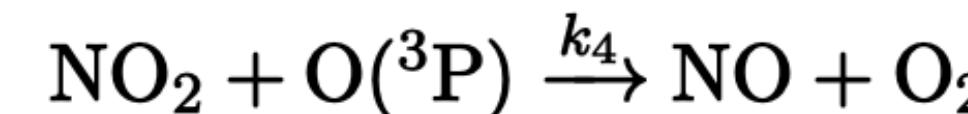
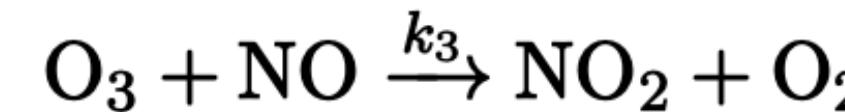
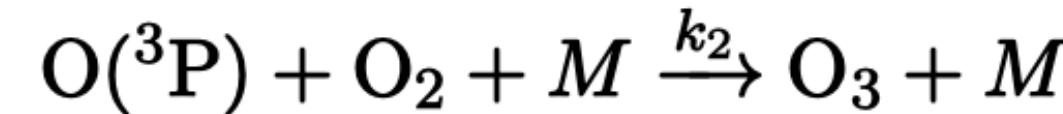
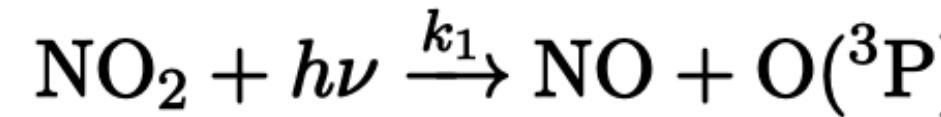
Model 1: Basic Photochemical Cycle



Model 1: Basic Photochemical Cycle



Model1: 4-species



$$R_1 = k_1(t)[\text{NO}_2]$$

$$R_2 = k_2[\text{O}][\text{O}_2]M$$

$$R_3 = k_3[\text{O}_3][\text{NO}]$$

$$R_4 = k_4[\text{NO}_2][\text{O}]$$

$$R_5 = k_5[\text{NO}][\text{O}]$$

$$\frac{d[\text{NO}]}{dt} = R_1 - R_3 + R_4 - R_5 + E_{\text{NO}}$$

$$\frac{d[\text{NO}_2]}{dt} = -R_1 + R_3 - R_4 + R_5 + E_{\text{NO}_2}$$

$$\frac{d[\text{O}_3]}{dt} = R_2 - R_3$$

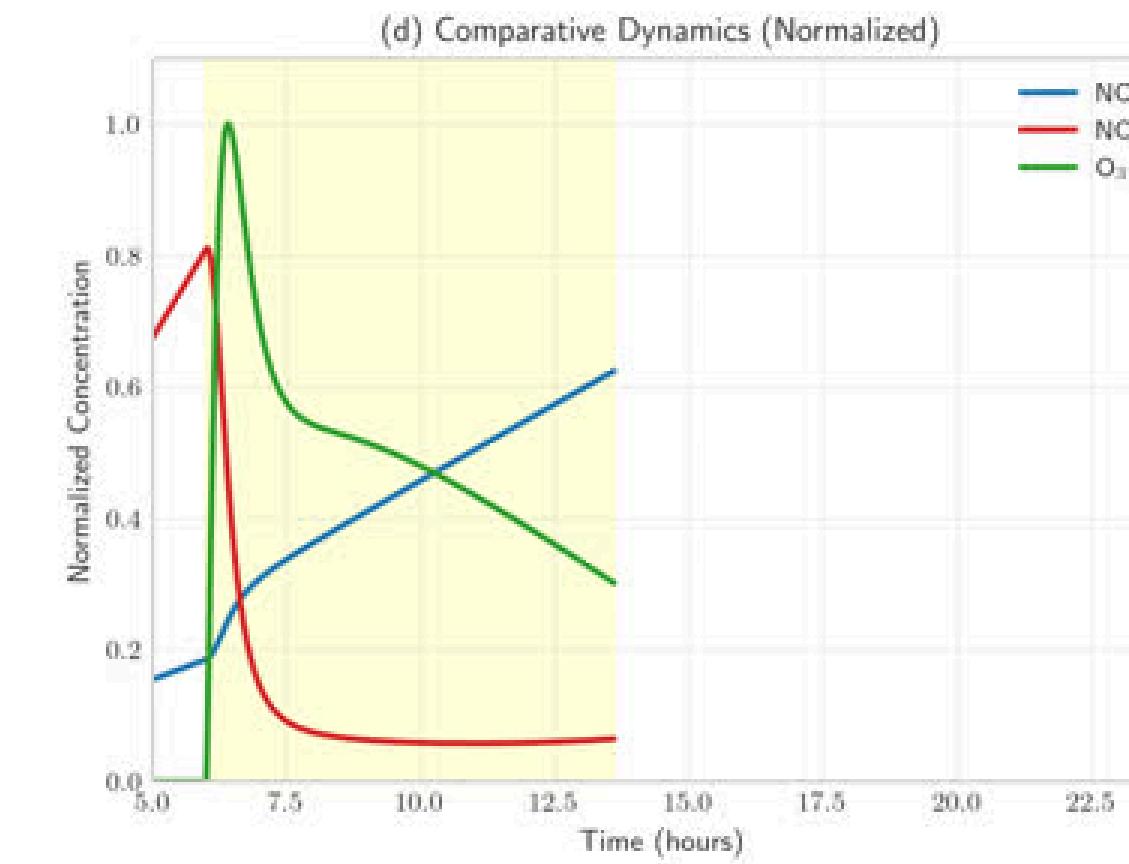
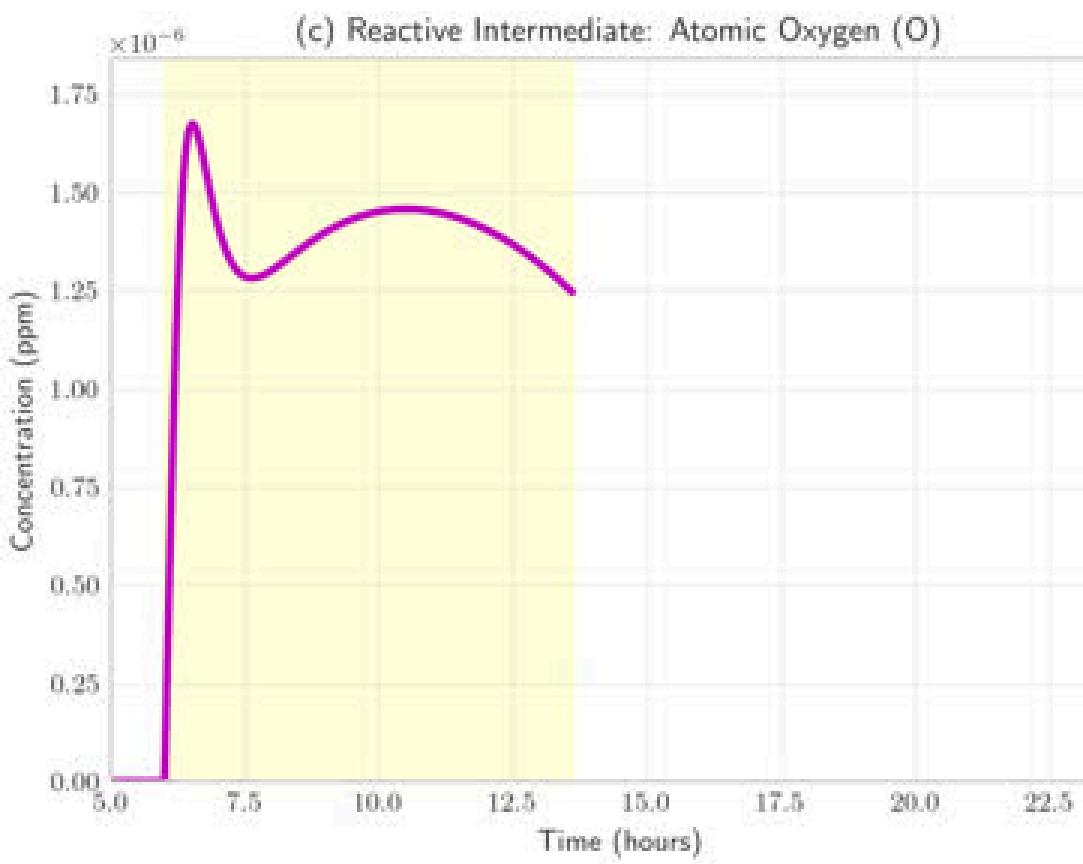
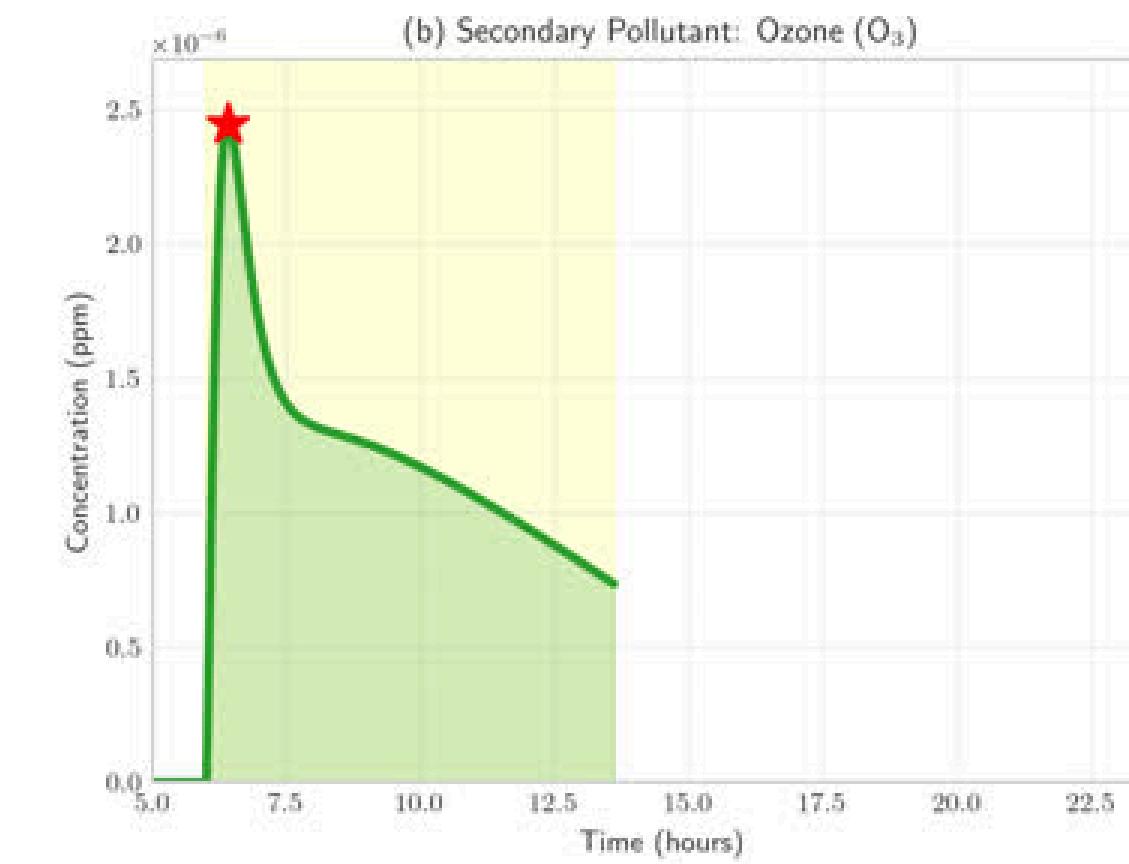
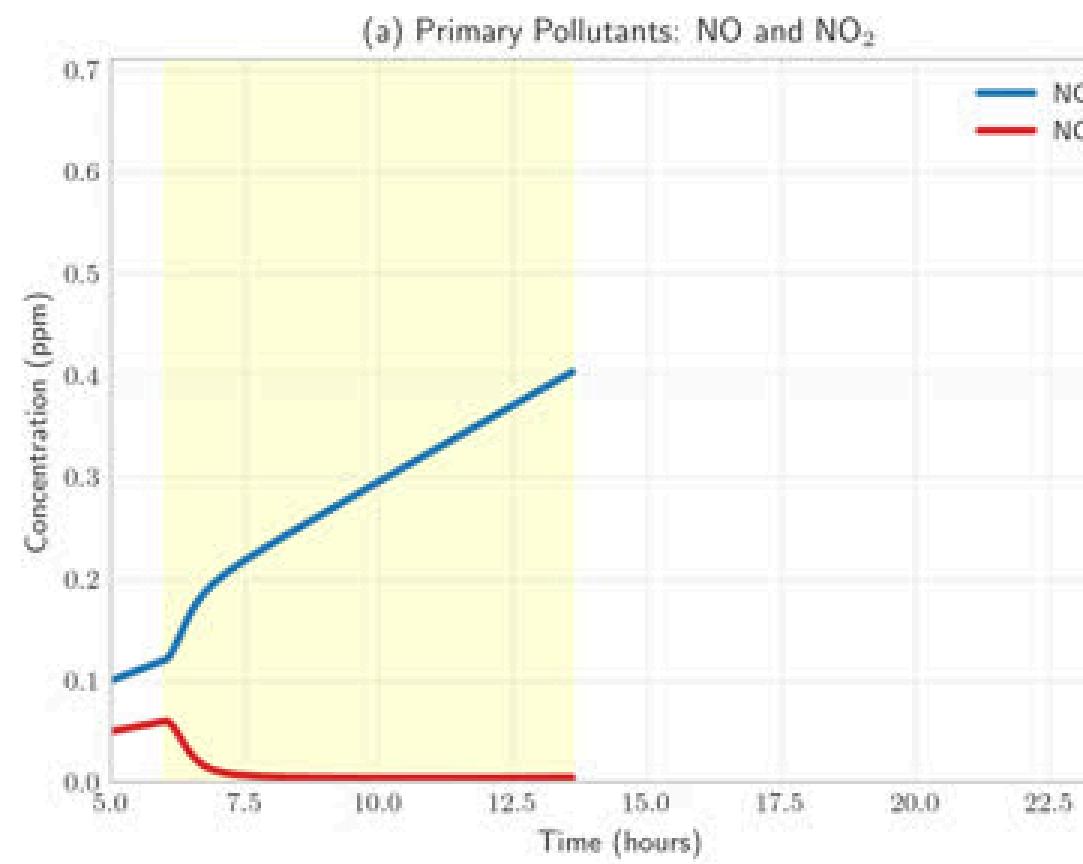
$$\frac{d[\text{O}]}{dt} = R_1 - R_2 - R_4 - R_5$$

Table 2: Model 1 initial conditions (5:00 AM)

Species	Initial Concentration (ppm)
NO	0.100
NO ₂	0.050
O ₃	0.0
O	0.0

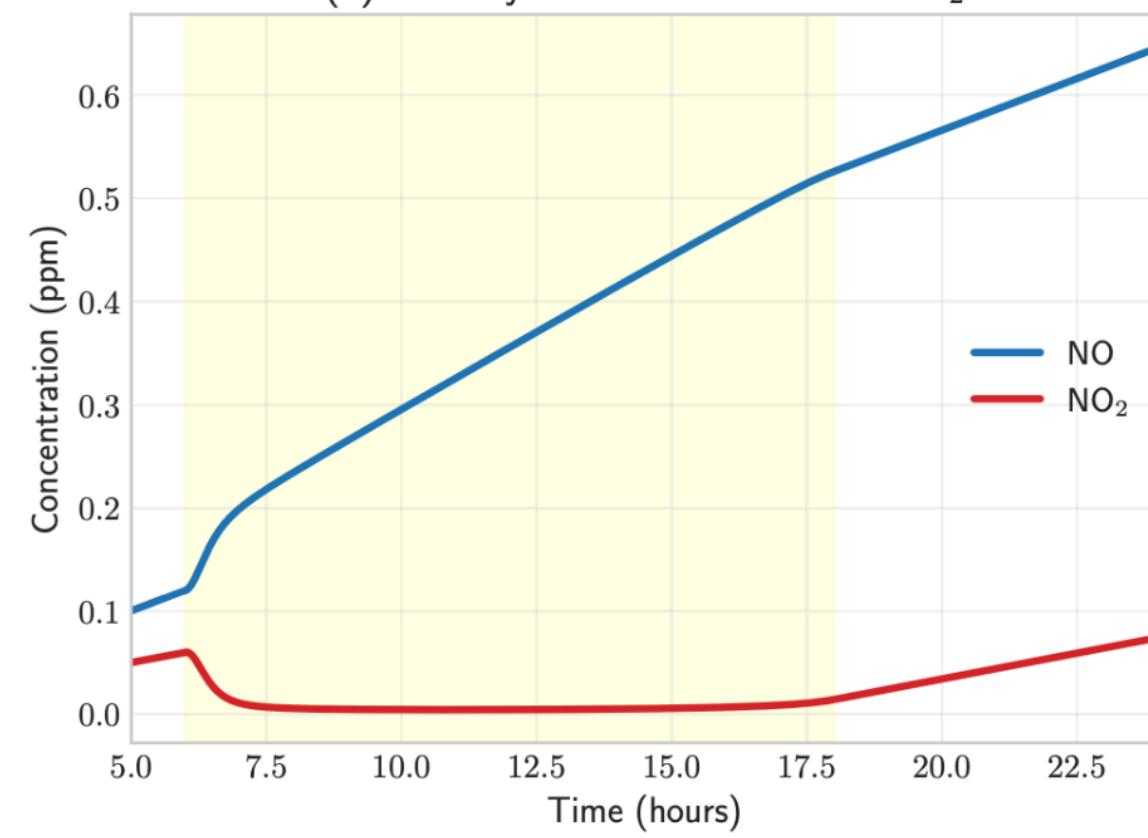
Parameter	Value	Units
$k_{1,\text{max}}$	30.48	h^{-1}
k_2	1.44×10^{-3}	$\text{ppm}^{-2} \text{ h}^{-1}$
k_3	1.20×10^5	$\text{ppm}^{-1} \text{ h}^{-1}$
k_4	8.04×10^5	$\text{ppm}^{-1} \text{ h}^{-1}$
k_5	1.99×10^5	$\text{ppm}^{-1} \text{ h}^{-1}$
[O ₂] M	210,000	ppm
E_{NO}	0.02	ppm h^{-1}
E_{NO_2}	0.01	ppm h^{-1}

Model 1: Basic Photochemical Cycle

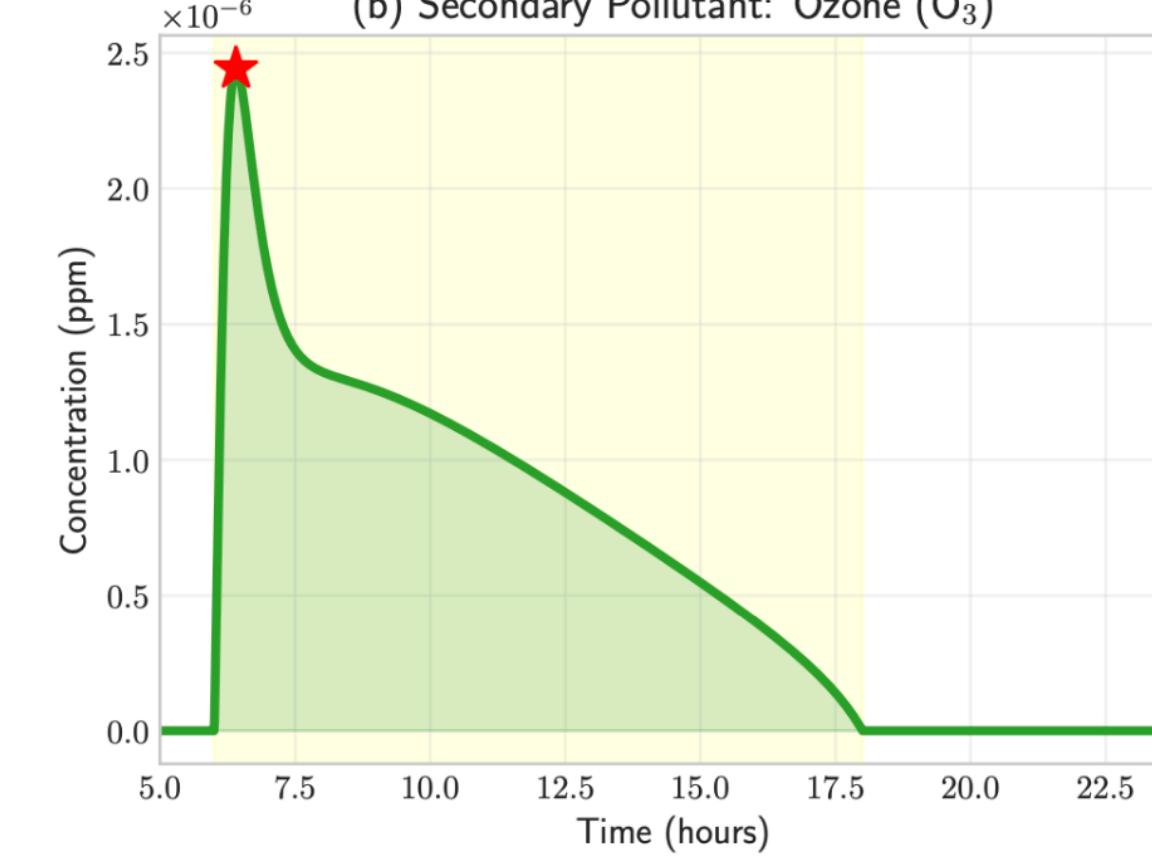


Model 1: Basic Photochemical Cycle

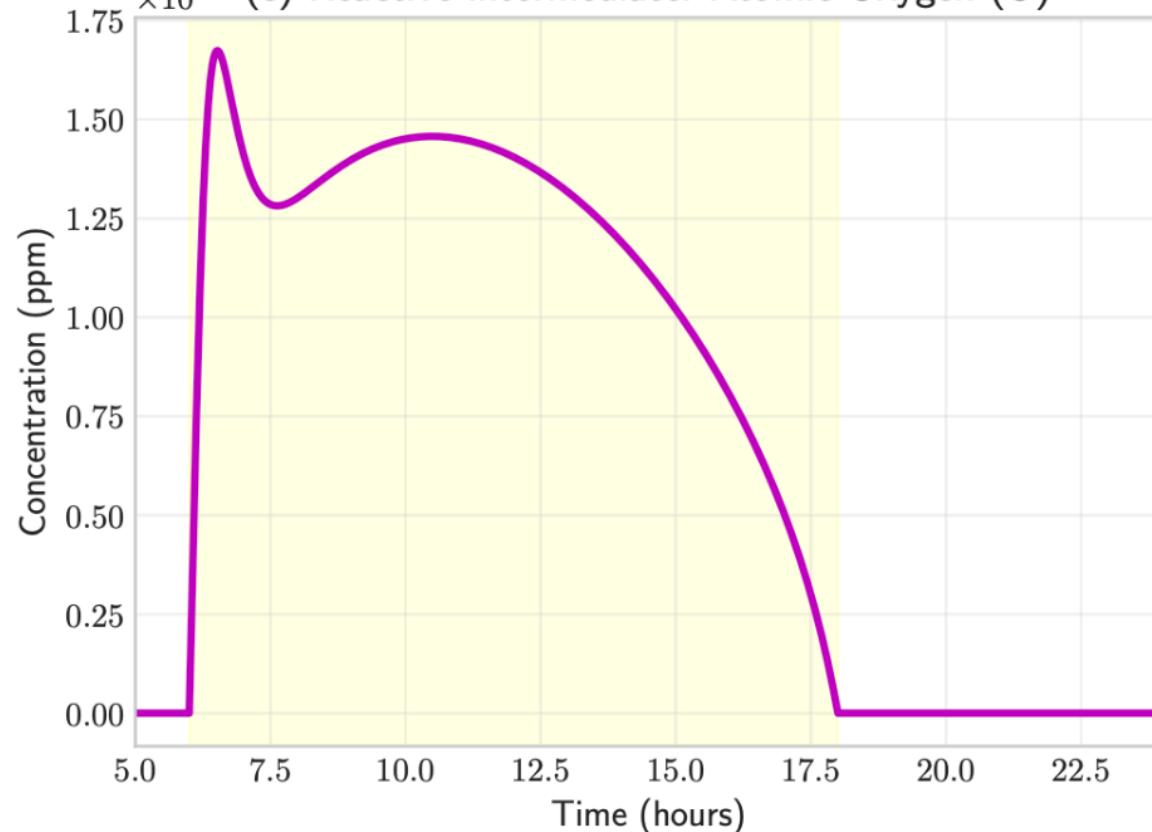
(a) Primary Pollutants: NO and NO₂



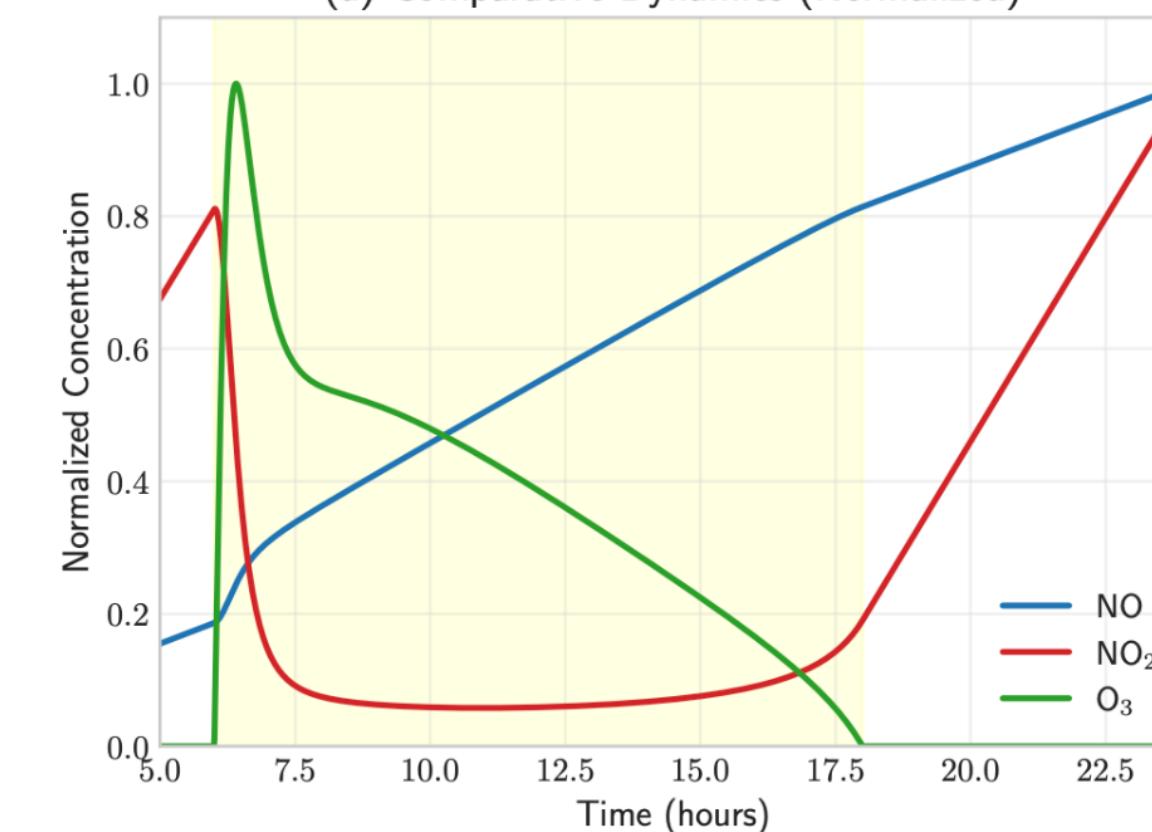
(b) Secondary Pollutant: Ozone (O₃)



(c) Reactive Intermediate: Atomic Oxygen (O)



(d) Comparative Dynamics (Normalized)



Key Findings

Critical Finding

Peak O₃ = 0.003 ppb at 8:00 AM

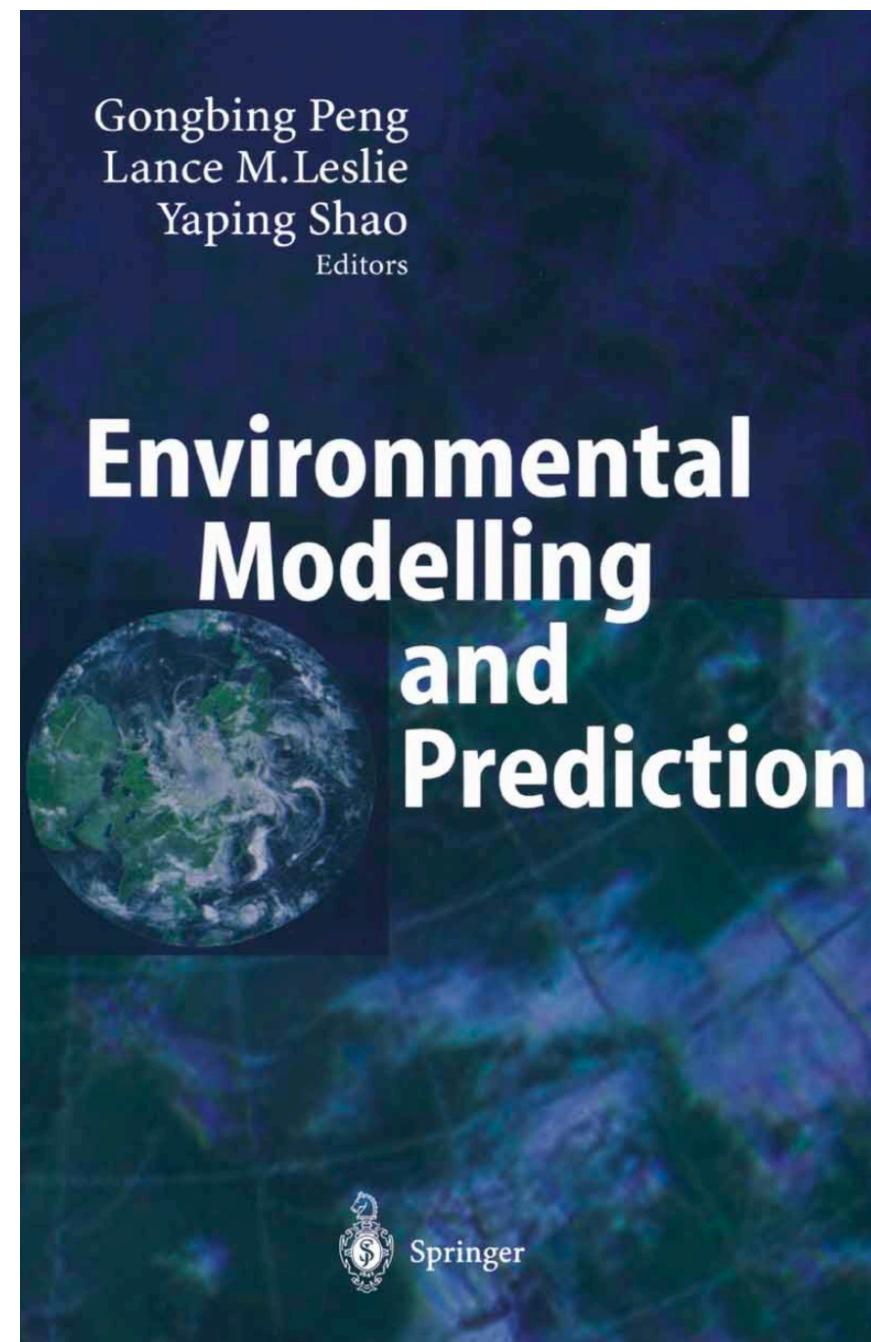
Observations:

- **Minimal ozone:** Far below air quality standard (0.07 ppm = 70 ppb)
- **Rapid titration:** NO immediately reacts with any O₃ formed
- **NO/NO₂ cycling:** Interconversion without net oxidation
- **Atomic oxygen:** Very low ($\sim 10^{-6}$ ppm) due to fast O₂ reaction

Fundamental Limitation

No mechanism to convert NO to NO₂ without consuming O₃

- Missing: VOC chemistry
- Missing: Radical pathways (OH, HO₂, RO₂)
- Cannot explain real urban smog episodes

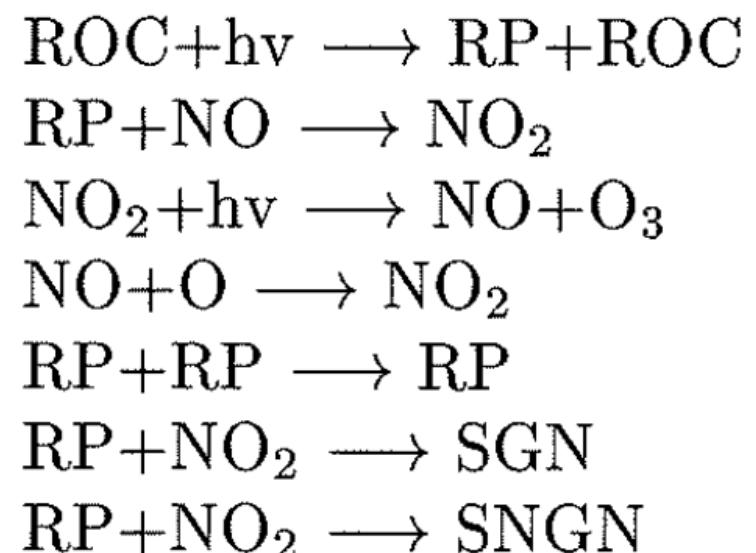


10. Modelling of Photochemical Smog

Hiep Duc, Vo Anh and Merched Azzi

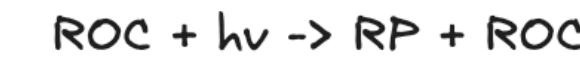
10.2.4 The GRS Mechanism

The chemistry component of f_i of the above equation is based on the GRS mechanism, which consists of the following reactions:



Generic Reaction Set (GRS) Mechanism

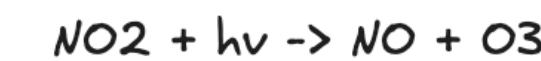
$$r_1 = k_1(t) [ROC]$$



$$r_2 = k_2 [RP][NO]$$



$$r_3 = k_3(t) [NO_2]$$



$$r_4 = k_4 [NO][O_3]$$



$$r_5 = k_5 [RP][RP]$$



$$r_6 = k_6 [RP][NO_2]$$



$$r_7 = k_7 [RP][NO_2]$$



ROC = Reactive Organic Compound

RP = Radical Pool

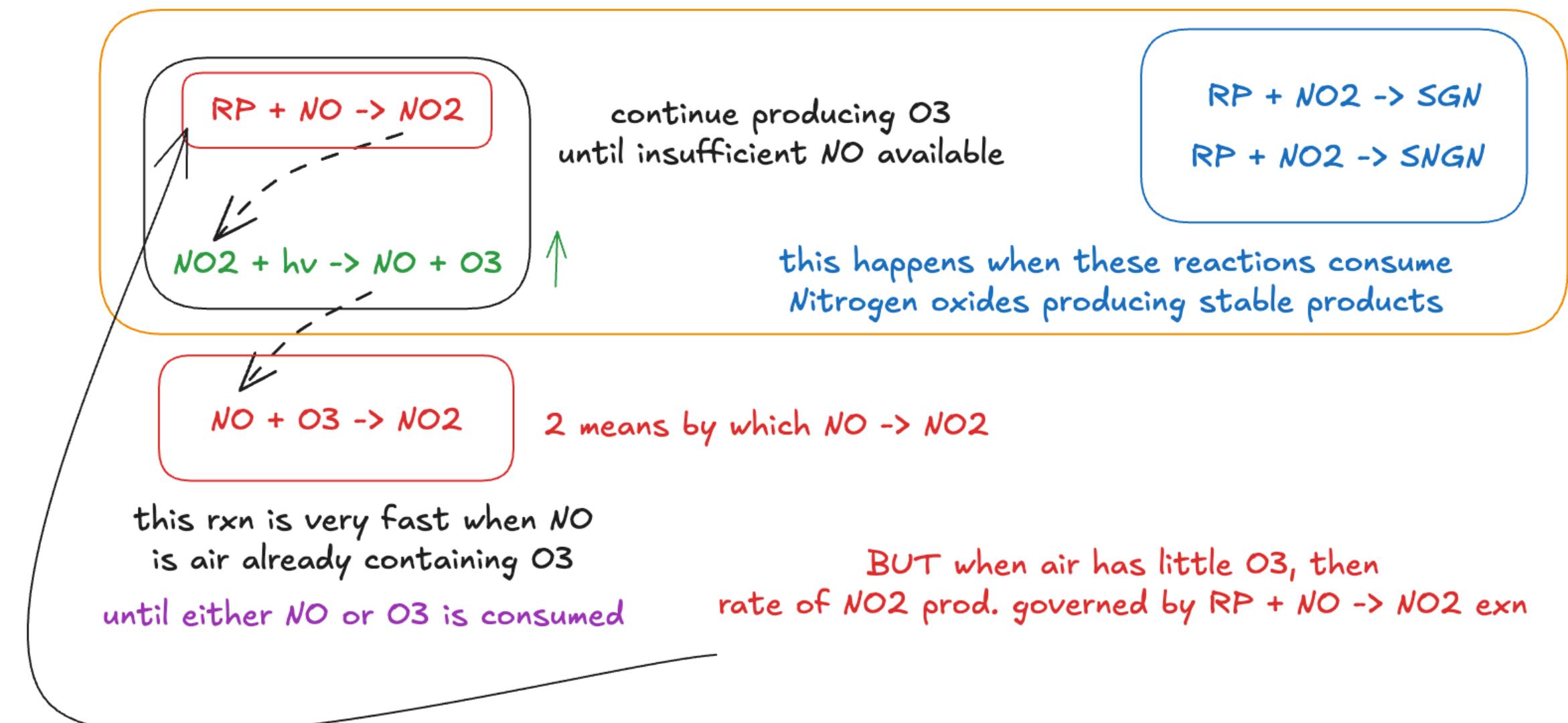
SGN = Stable Gaseous Product

SNGN = Stable Non-Gaseous Product

NO

O₃

NO₂



Model2: 11-species

Added Species (7 new):

VOCs:

- CO (carbon monoxide)
- HCHO (formaldehyde)
- ALK (lumped alkanes)
- OLE (lumped olefins)

Radicals:

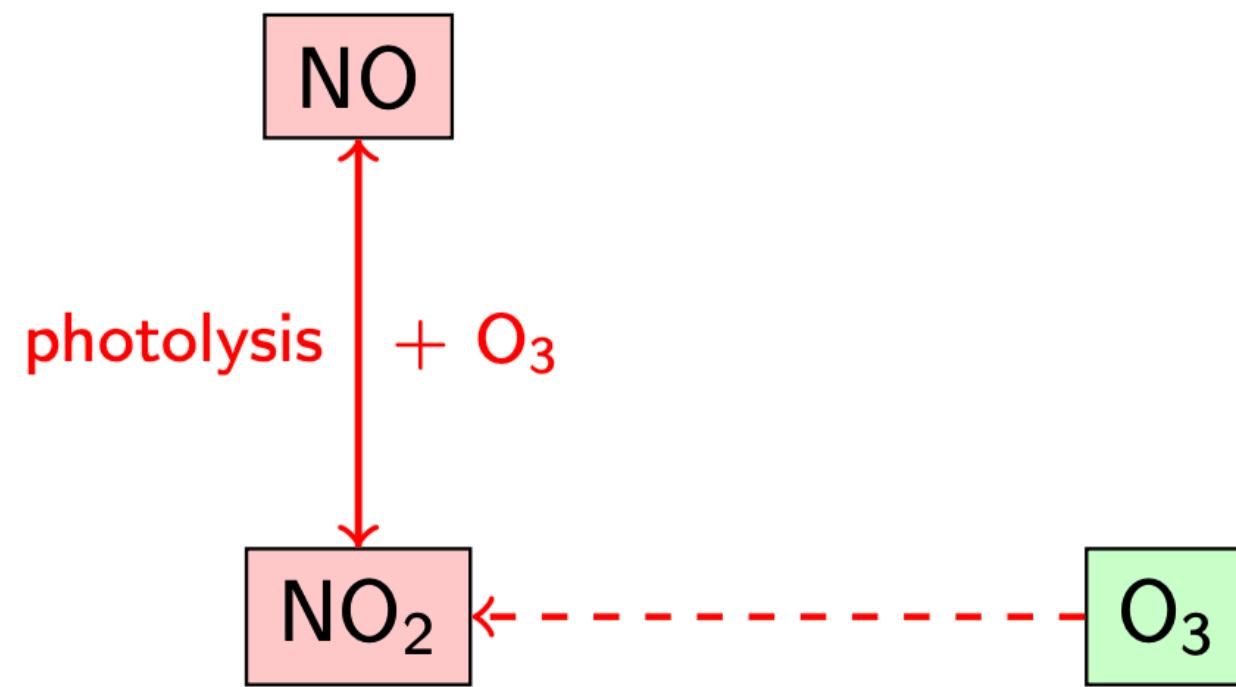
- OH (hydroxyl radical)
- HO₂ (hydroperoxyl radical)
- RO₂ (organic peroxy radicals)

Total System

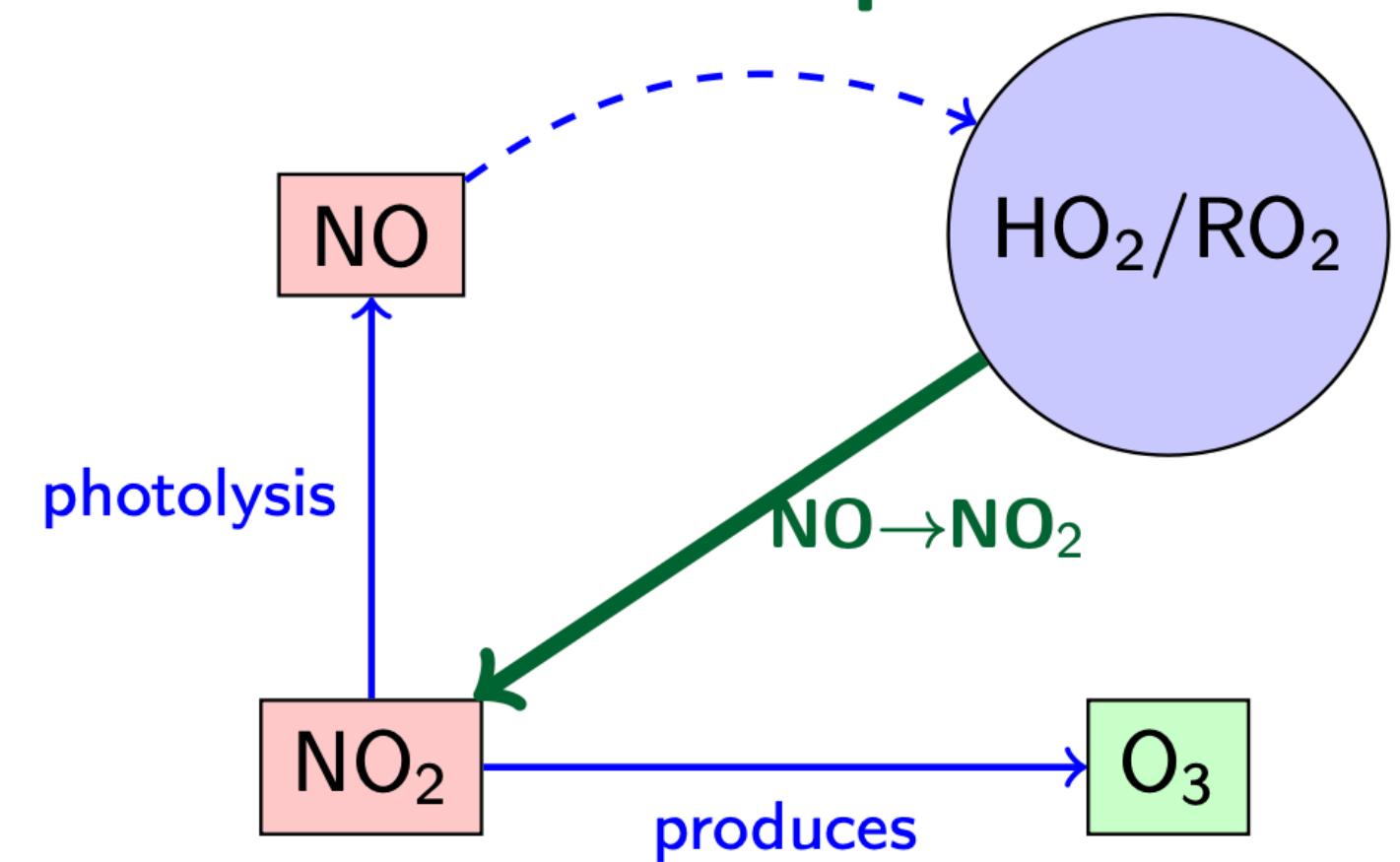
- **11 species:** NO, NO₂, O₃, O, CO, HCHO, ALK, OLE, OH, HO₂, RO₂
- **15 reactions:** 5 from Model 1 + 10 new

Model2: 11-species

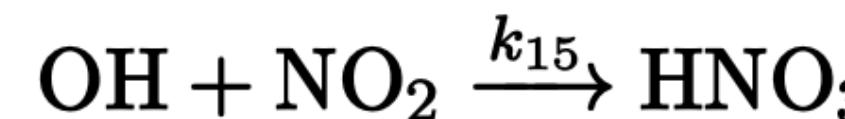
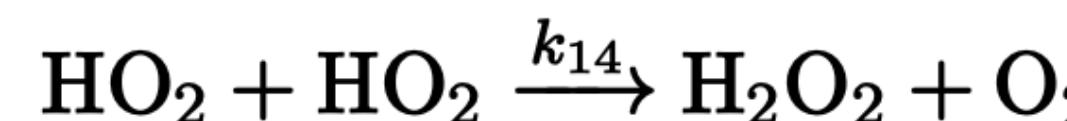
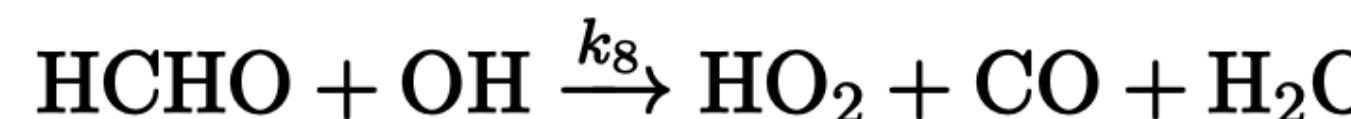
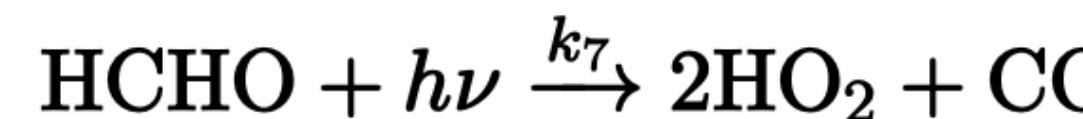
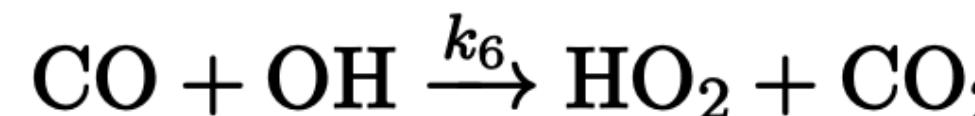
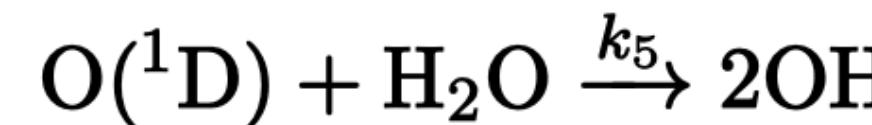
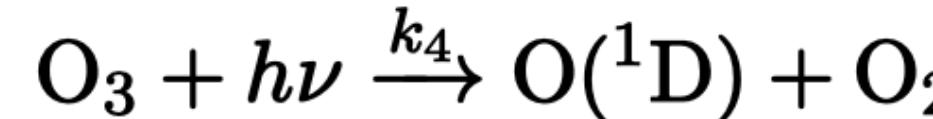
Model 1: Cycling only



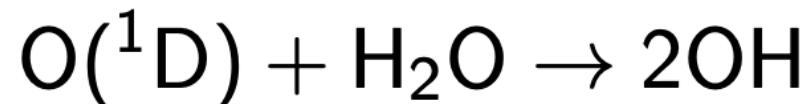
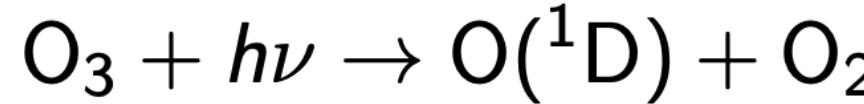
Model 2: Net production



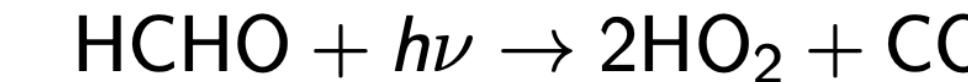
Reactions



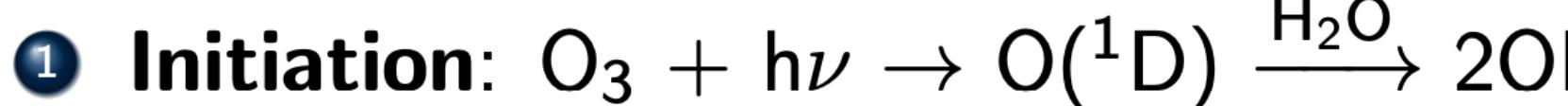
OH Production



VOC Oxidation



The Catalytic Cycle:

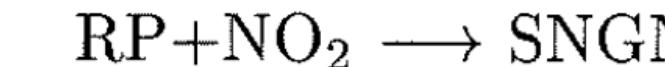
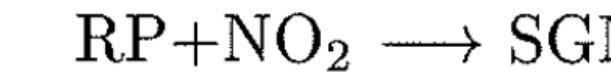


② **Propagation:**

- OH attacks VOCs: $\text{VOC} + \text{OH} \rightarrow \text{RO}_2/\text{HO}_2$
- Radicals oxidize NO: $\text{HO}_2/\text{RO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}/\text{HO}_2$
- NO_2 photolyzes: $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}_3$

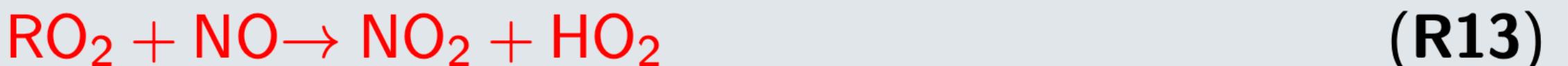
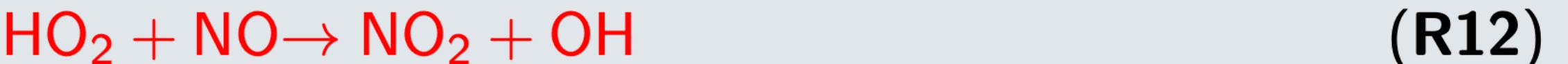
③ **Termination:**

- $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$
- $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$



Key Addition

Key Innovation: NO Oxidation WITHOUT O₃ Consumption



Why this matters:

- Converts NO to NO₂ **without consuming O₃**
- NO₂ then photolyzes: NO₂ + hν → NO + O₃
- **Net result: O₃ production!**

For Model 2 with 11 species and 15 reactions:

1. Nitric Oxide (NO):

$$\begin{aligned}\frac{d[NO]}{dt} &= R_1 - R_3 - R_{12} - R_{13} + E_{NO} \\ &= k_1[NO_2] - k_3[O_3][NO] - k_{12}[HO_2][NO] \\ &\quad - k_{13}[RO_2][NO] + E_{NO}\end{aligned}\tag{35}$$

2. Nitrogen Dioxide (NO₂):

$$\begin{aligned}\frac{d[NO_2]}{dt} &= -R_1 + R_3 + R_{12} + R_{13} - R_{15} + E_{NO_2} \\ &= -k_1[NO_2] + k_3[O_3][NO] + k_{12}[HO_2][NO] \\ &\quad + k_{13}[RO_2][NO] - k_{15}[OH][NO_2] + E_{NO_2}\end{aligned}\tag{36}$$

3. Ozone (O₃):

$$\begin{aligned}\frac{d[O_3]}{dt} &= R_2 - R_3 - R_4 - R_{11} \\ &= k_2[O][O_2] - k_3[O_3][NO] - k_4[O_3] - k_{11}[OLE][O_3]\end{aligned}\tag{37}$$

4. Atomic Oxygen (O):

$$\begin{aligned}\frac{d[O]}{dt} &= R_1 - R_2 \\ &= k_1[NO_2] - k_2[O][O_2]\end{aligned}\tag{38}$$

5. Carbon Monoxide (CO):

$$\begin{aligned}\frac{d[CO]}{dt} &= -R_6 + R_7 + R_8 + E_{CO} \\ &= -k_6[CO][OH] + k_7[HCHO] + k_8[HCHO][OH] + E_{CO}\end{aligned}\tag{39}$$

6. Formaldehyde (HCHO):

$$\begin{aligned}\frac{d[HCHO]}{dt} &= 0.5R_{11} - R_7 - R_8 + E_{HCHO} \\ &= 0.5k_{11}[OLE][O_3] - k_7[HCHO] - k_8[HCHO][OH] \\ &\quad + E_{HCHO}\end{aligned}\tag{40}$$

7. Alkanes (ALK):

$$\begin{aligned}\frac{d[ALK]}{dt} &= -R_9 + E_{ALK} \\ &= -k_9[ALK][OH] + E_{ALK}\end{aligned}\tag{41}$$

Formulation

8. Olefins (OLE):

$$\begin{aligned}\frac{d[OLE]}{dt} &= -R_{10} - R_{11} + E_{OLE} \\ &= -k_{10}[OLE][OH] - k_{11}[OLE][O_3] + E_{OLE}\end{aligned}\tag{42}$$

9. Hydroxyl Radical (OH):

$$\begin{aligned}\frac{d[OH]}{dt} &= 2R_5 - R_6 - R_8 - R_9 - R_{10} - R_{15} + R_{12} \\ &= 2k_5[O(^1D)][H_2O] - k_6[CO][OH] - k_8[HCHO][OH] \\ &\quad - k_9[ALK][OH] - k_{10}[OLE][OH] - k_{15}[OH][NO_2] \\ &\quad + k_{12}[HO_2][NO]\end{aligned}\tag{43}$$

10. Hydroperoxyl Radical (HO₂):

$$\begin{aligned}\frac{d[HO_2]}{dt} &= R_6 + 2R_7 + R_8 + 0.5R_{11} + R_{13} - R_{12} - 2R_{14} \\ &= k_6[CO][OH] + 2k_7[HCHO] + k_8[HCHO][OH] \\ &\quad + 0.5k_{11}[OLE][O_3] + k_{13}[RO_2][NO] \\ &\quad - k_{12}[HO_2][NO] - 2k_{14}[HO_2]^2\end{aligned}\tag{44}$$

11. Organic Peroxy Radical (RO₂):

$$\begin{aligned}\frac{d[RO_2]}{dt} &= R_9 + R_{10} + 0.5R_{11} - R_{13} \\ &= k_9[ALK][OH] + k_{10}[OLE][OH] + 0.5k_{11}[OLE][O_3] \\ &\quad - k_{13}[RO_2][NO]\end{aligned}\tag{45}$$

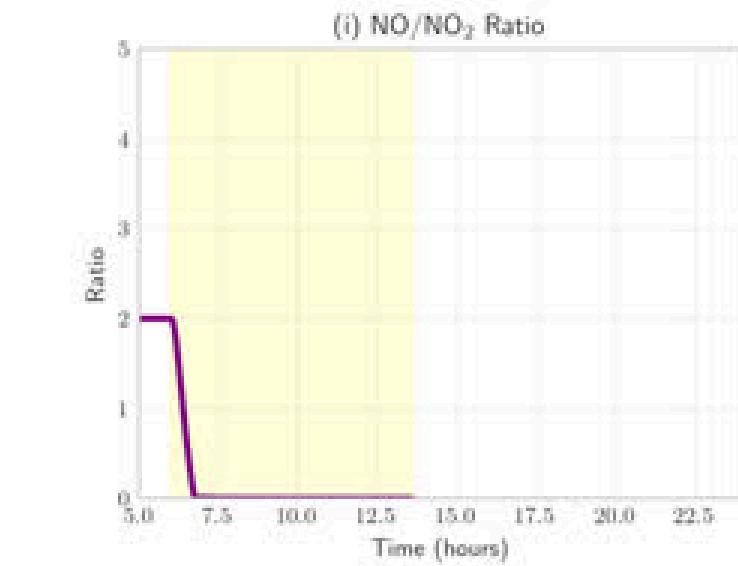
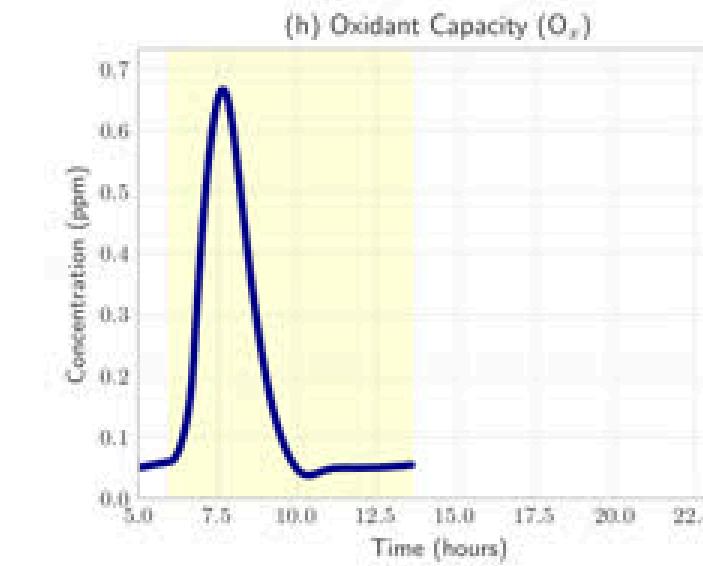
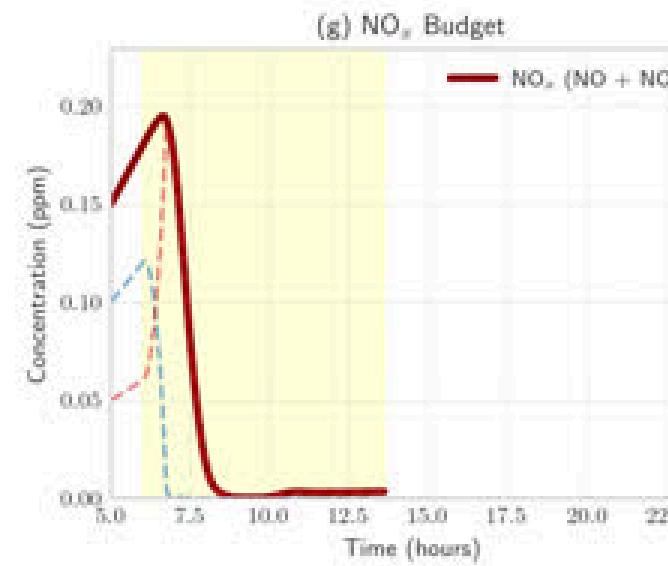
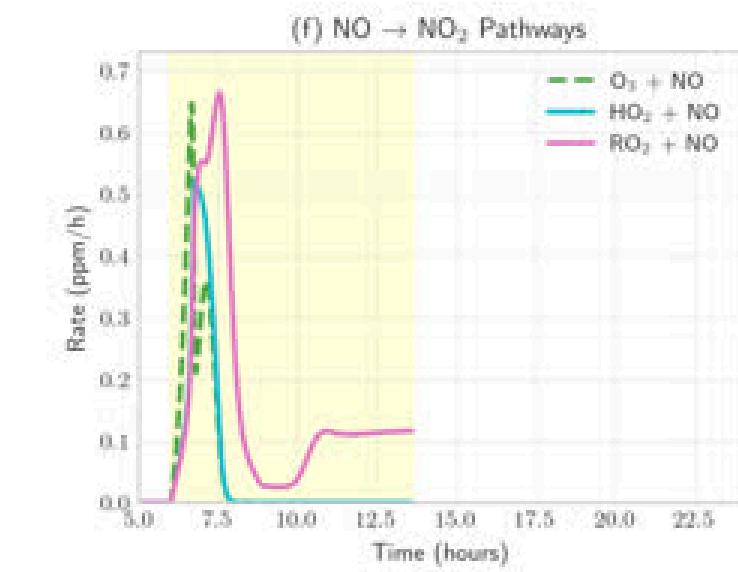
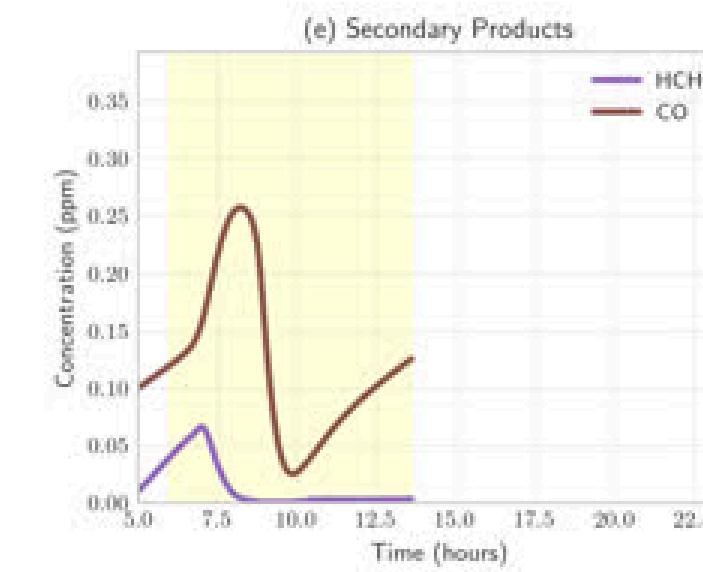
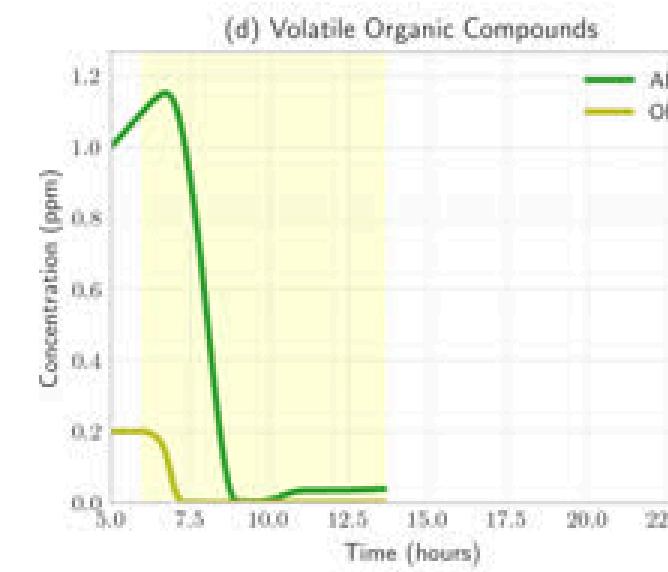
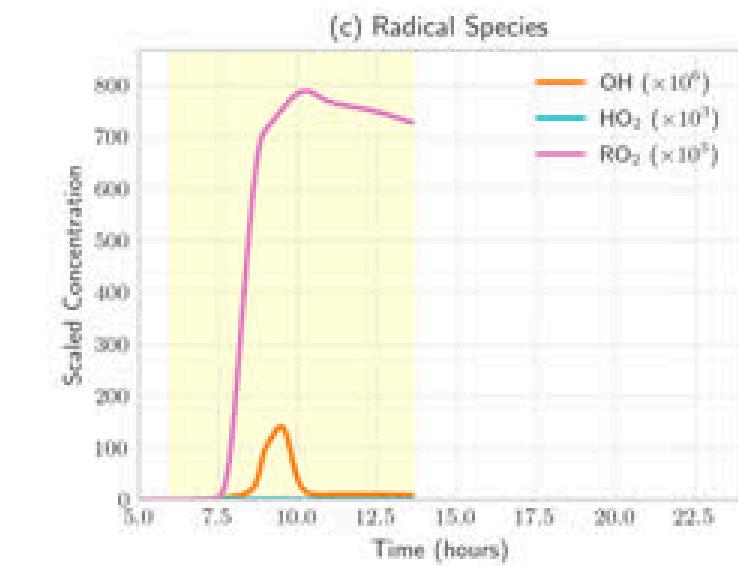
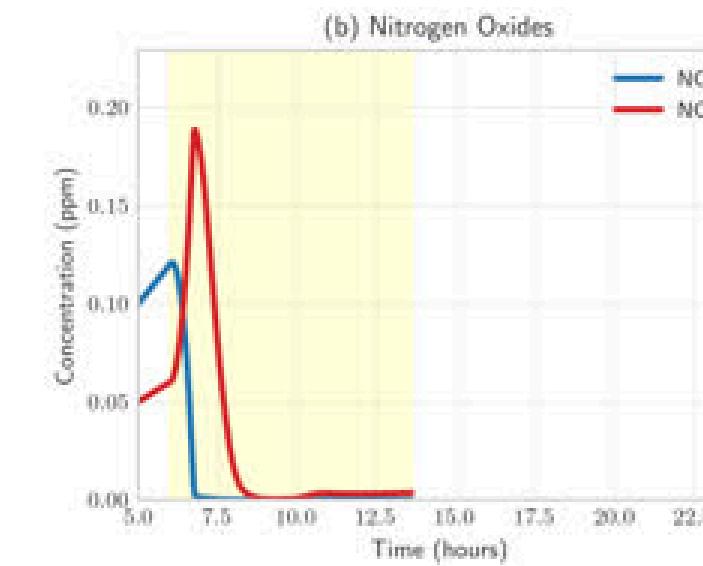
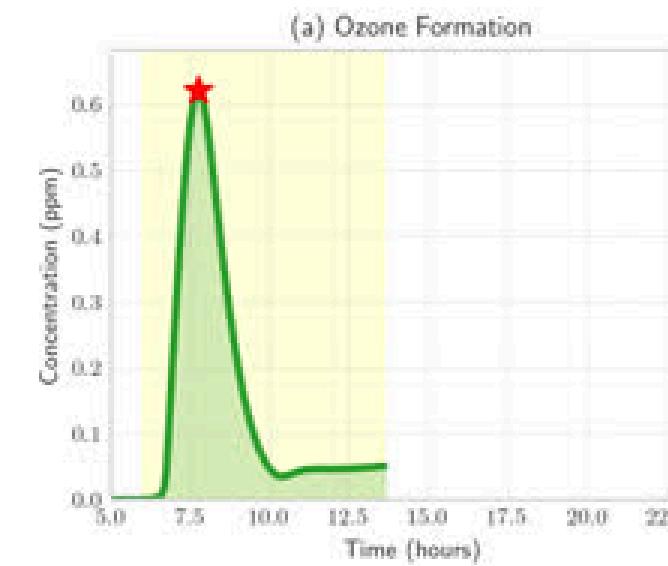
Parameters

$R_1 = k_1(t)[\text{NO}_2]$	(NO ₂ photolysis)
$R_2 = k_2[\text{O}][\text{O}_2]$	(O ₃ formation)
$R_3 = k_3[\text{O}_3][\text{NO}]$	(NO oxidation by O ₃)
$R_4 = k_4(t)[\text{O}_3]$	(O ₃ photolysis)
$R_5 = k_5[\text{O}(\text{¹D})][\text{H}_2\text{O}]$	(OH formation)
$R_6 = k_6[\text{CO}][\text{OH}]$	(CO oxidation)
$R_7 = k_7(t)[\text{HCHO}]$	(HCHO photolysis)
$R_8 = k_8[\text{HCHO}][\text{OH}]$	(HCHO oxidation)
$R_9 = k_9[\text{ALK}][\text{OH}]$	(Alkane oxidation)
$R_{10} = k_{10}[\text{OLE}][\text{OH}]$	(Olefin oxidation by OH)
$R_{11} = k_{11}[\text{OLE}][\text{O}_3]$	(Olefin ozonolysis)
$R_{12} = k_{12}[\text{HO}_2][\text{NO}]$	(Key: NO → NO ₂ via HO ₂)
$R_{13} = k_{13}[\text{RO}_2][\text{NO}]$	(Key: NO → NO ₂ via RO ₂)
$R_{14} = k_{14}[\text{HO}_2]^2$	(HO ₂ termination)
$R_{15} = k_{15}[\text{OH}][\text{NO}_2]$	(HNO ₃ formation)

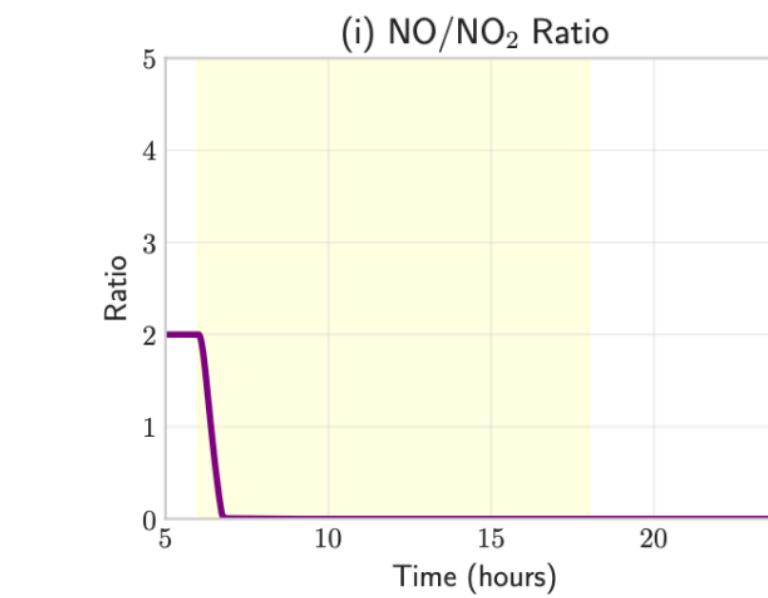
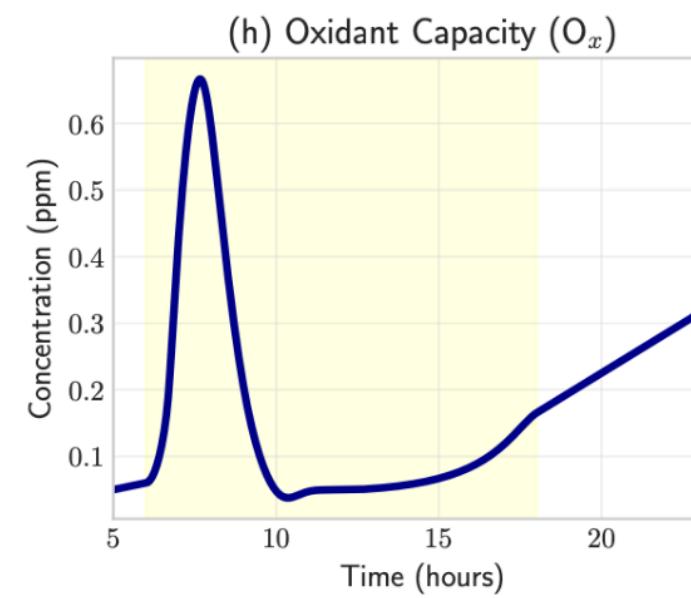
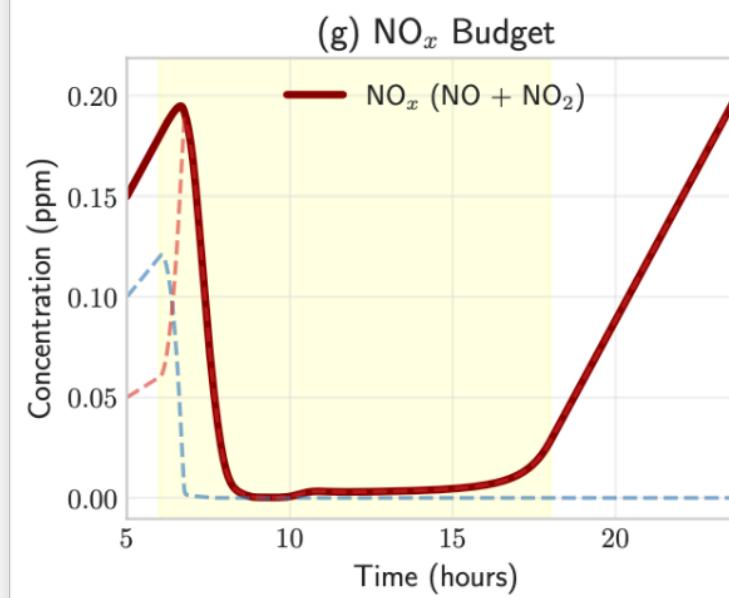
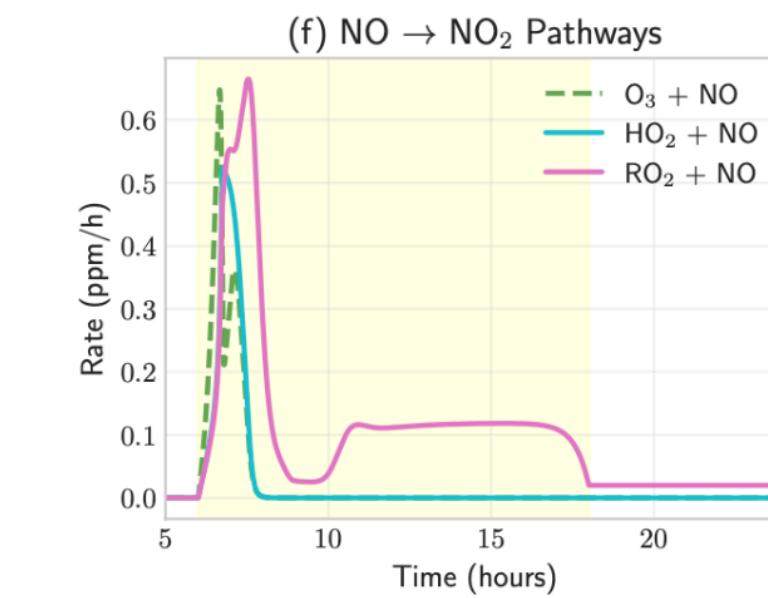
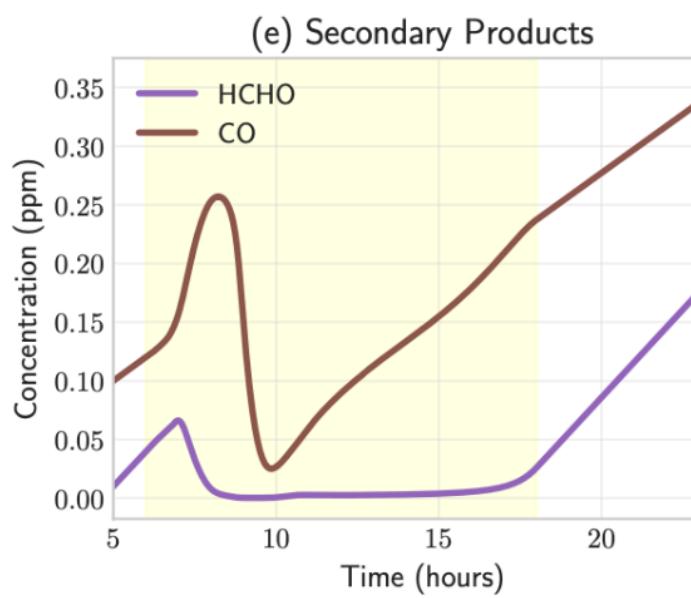
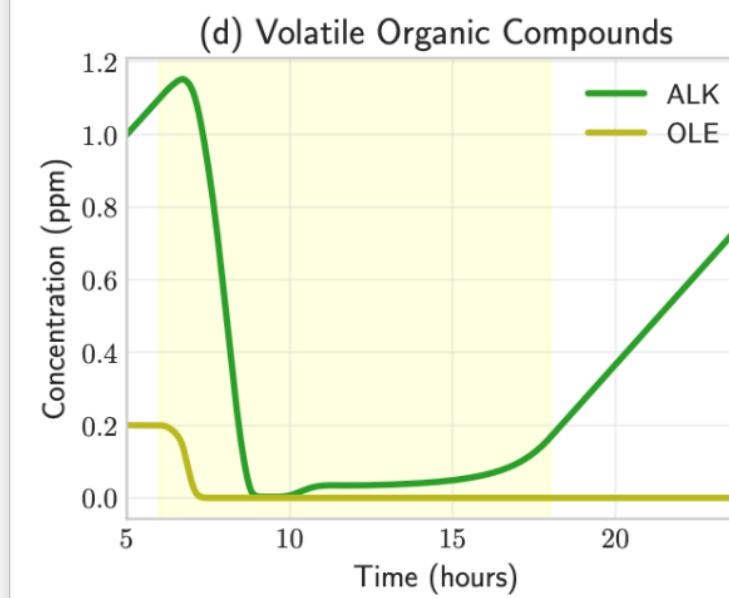
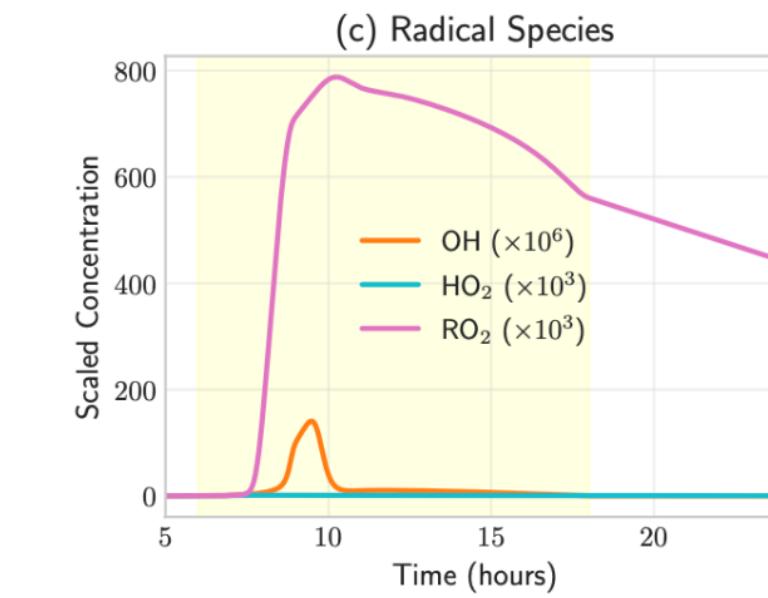
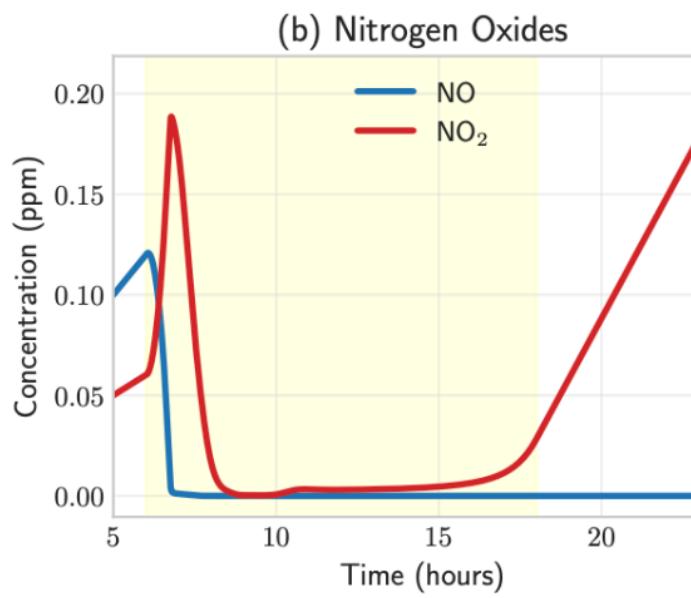
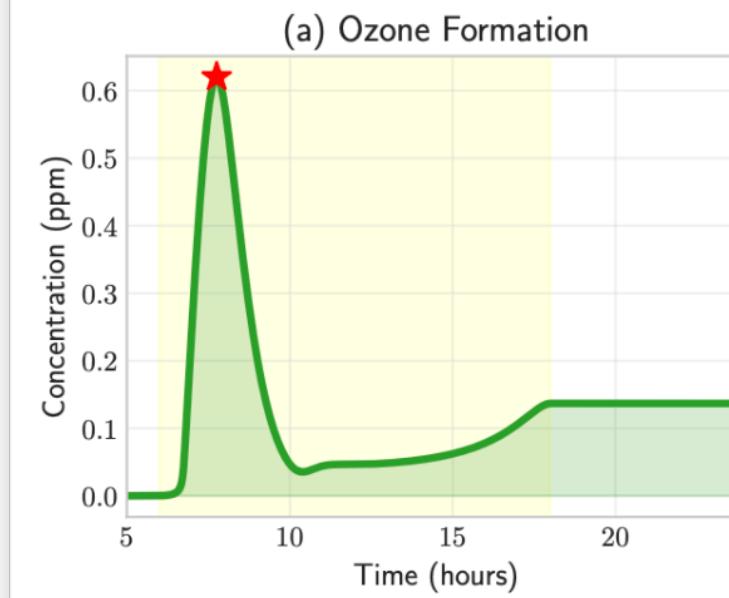
Reaction	Rate Constant	Units
k_4 (O ₃ photolysis)	1.968	h ⁻¹
k_5 (O(¹D) + H ₂ O)	6.0×10^6	ppm ⁻¹ h ⁻¹
k_6 (CO + OH)	2.64×10^4	ppm ⁻¹ h ⁻¹
k_7 (HCHO photolysis)	0.170	h ⁻¹
k_8 (HCHO + OH)	1.152×10^6	ppm ⁻¹ h ⁻¹
k_9 (ALK + OH)	2.82×10^5	ppm ⁻¹ h ⁻¹
k_{10} (OLE + OH)	5.349×10^6	ppm ⁻¹ h ⁻¹
k_{11} (OLE + O ₃)	8.16	ppm ⁻¹ h ⁻¹
k_{12} (HO ₂ + NO)	7.2×10^5	ppm ⁻¹ h ⁻¹
k_{13} (RO ₂ + NO)	7.2×10^5	ppm ⁻¹ h ⁻¹
k_{14} (HO ₂ + HO ₂)	2.22×10^5	ppm ⁻¹ h ⁻¹
k_{15} (OH + NO ₂)	Complex T-dep.	ppm ⁻¹ h ⁻¹

Species	Initial (ppm)	Emission (ppm h ⁻¹)
NO	0.100	0.02
NO ₂	0.050	0.01
CO	0.100	0.02
HCHO	0.010	0.03
ALK	1.000	0.10
OLE	0.200	0.0
OH	0	0
HO ₂	0	0
RO ₂	0	0

Model 2: Refined with VOCs and Radicals



Model 2: Refined with VOCs and Radicals



Key Findings

Success!

Peak O₃ = **0.6 ppm** at 8:30

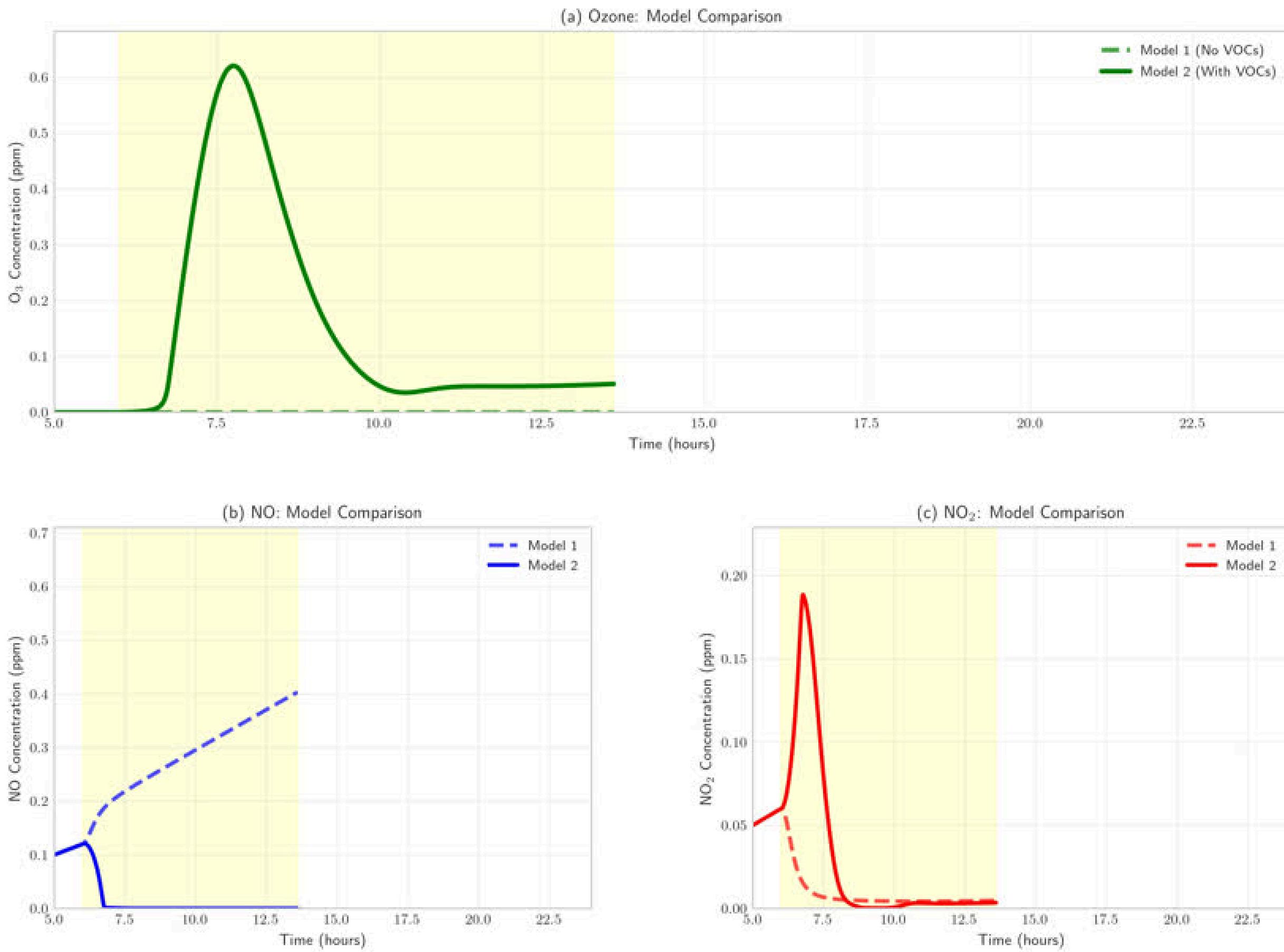
Detailed Findings:

- ① **Radical dynamics:** OH, HO₂, RO₂ peak at noon (10^{-6} - 10^{-3} ppm)
- ② **VOC consumption:** ALK ↓ 27%, OLE ↓ 100% (fully depleted)
- ③ **Pathway dominance at peak O₃:**
 - RO₂ + NO: **94.5%**
 - HO₂ + NO: 2.9%
 - O₃ titration: only 2.6%
- ④ **NO_x budget:** Decreases 0.15 → 0.08 ppm (HNO₃ formation)
- ⑤ **Catalytic amplification:** Trace OH (10^{-6} ppm) produces substantial O₃

Comparison

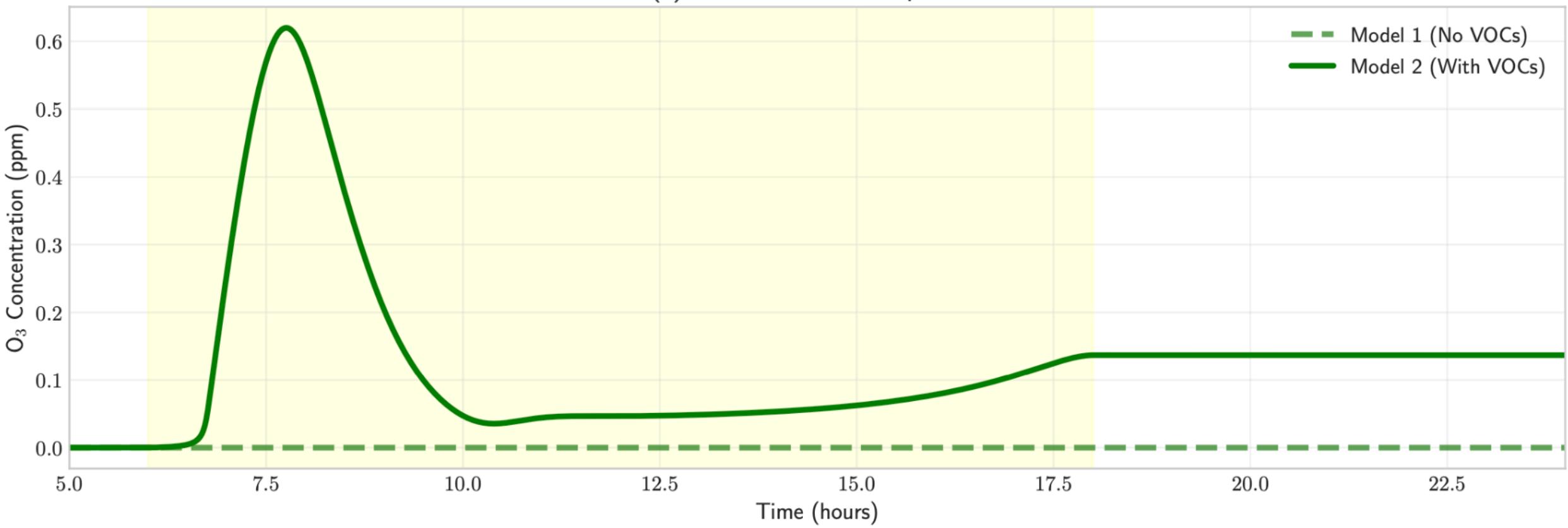
Metric	Model 1	Model 2
Species	4	11
Reactions	5	15
Peak O₃ (ppm)	3×10^{-6}	0.6
Peak time	11:00	13:30
Enhancement	1x	200,000x
Min NO (ppm)	0.029	0.0003
VOC chemistry	No	Yes
Net O ₃ production	No	Yes

Model Comparison: Impact of VOCs on Ozone Formation

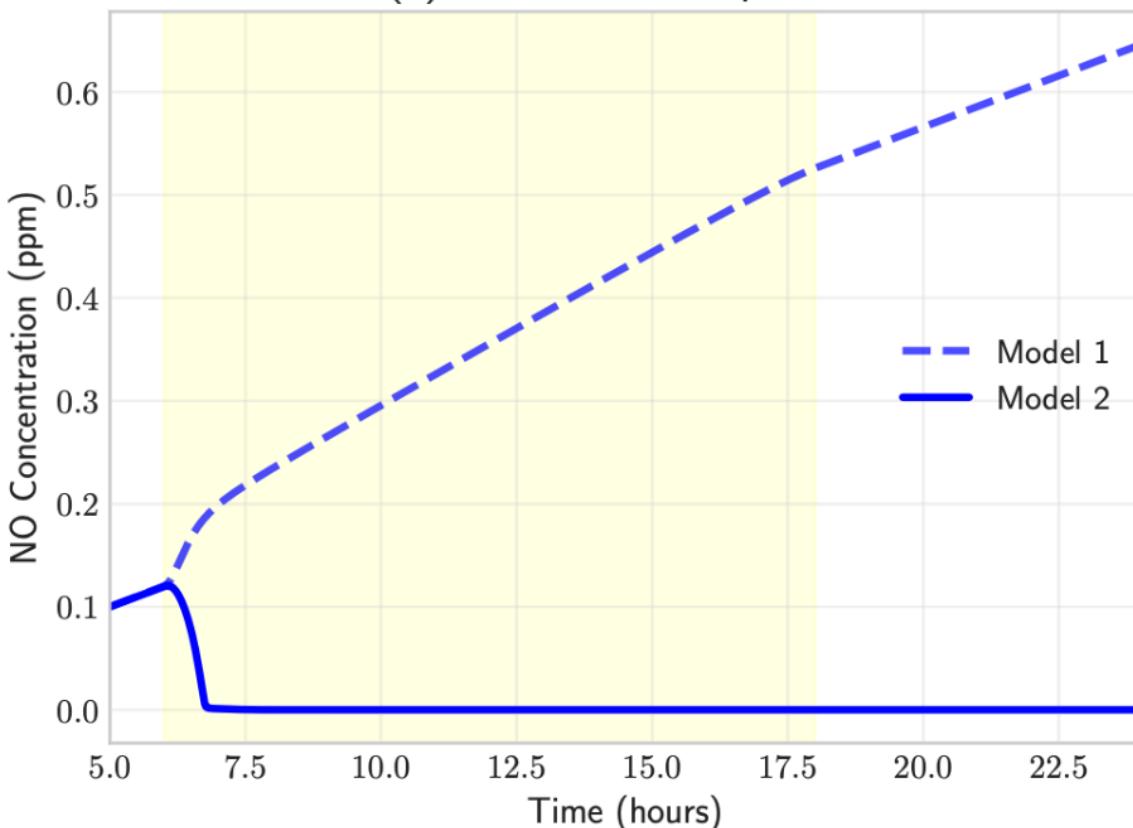


Model Comparison: Impact of VOCs on Ozone Formation

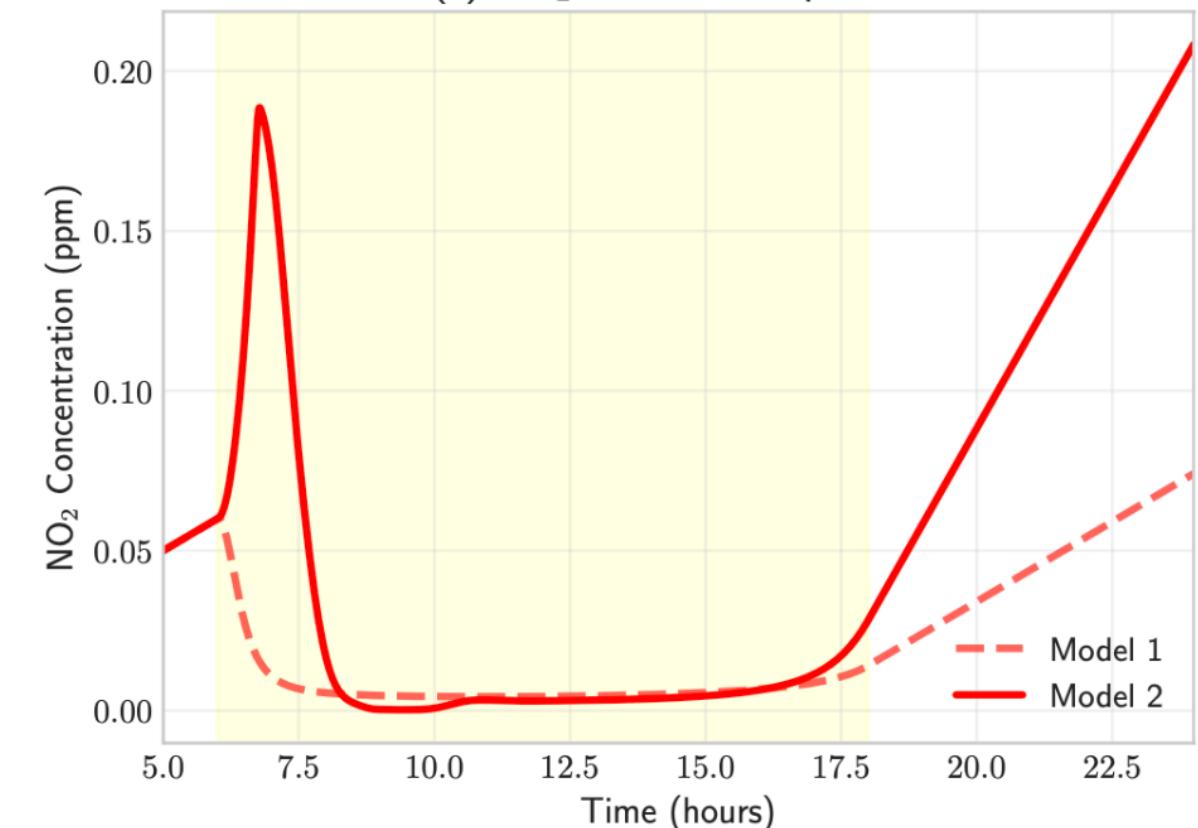
(a) Ozone: Model Comparison



(b) NO: Model Comparison



(c) NO₂: Model Comparison





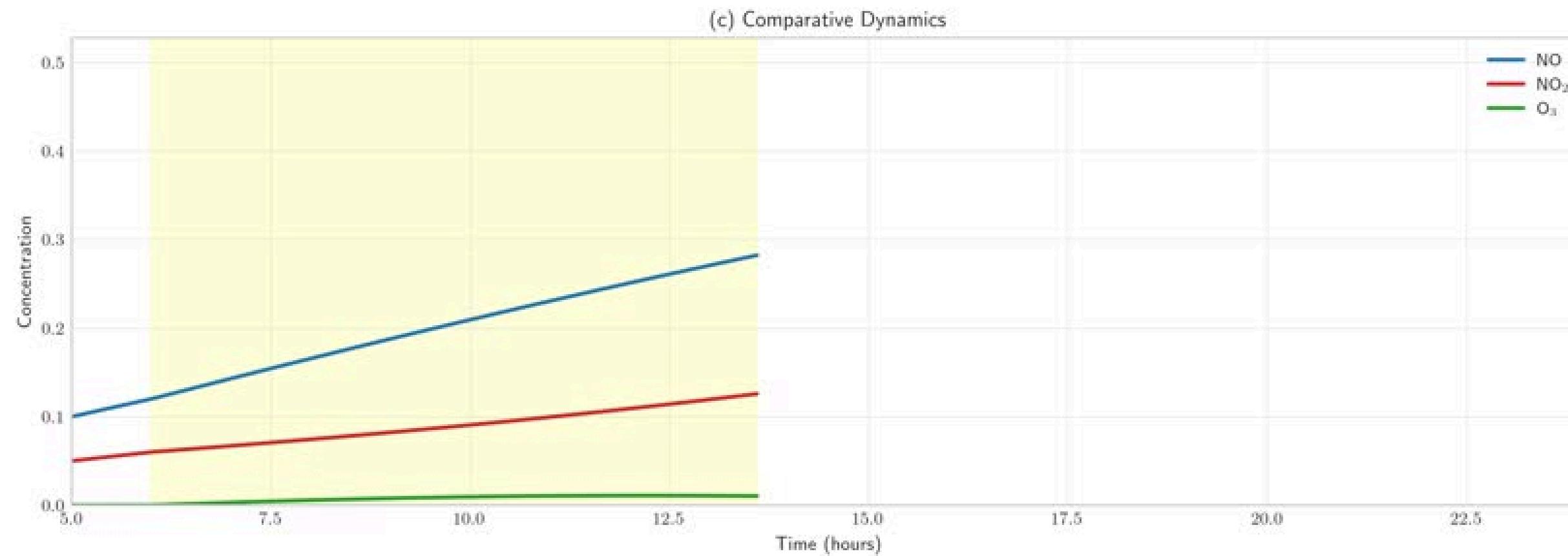
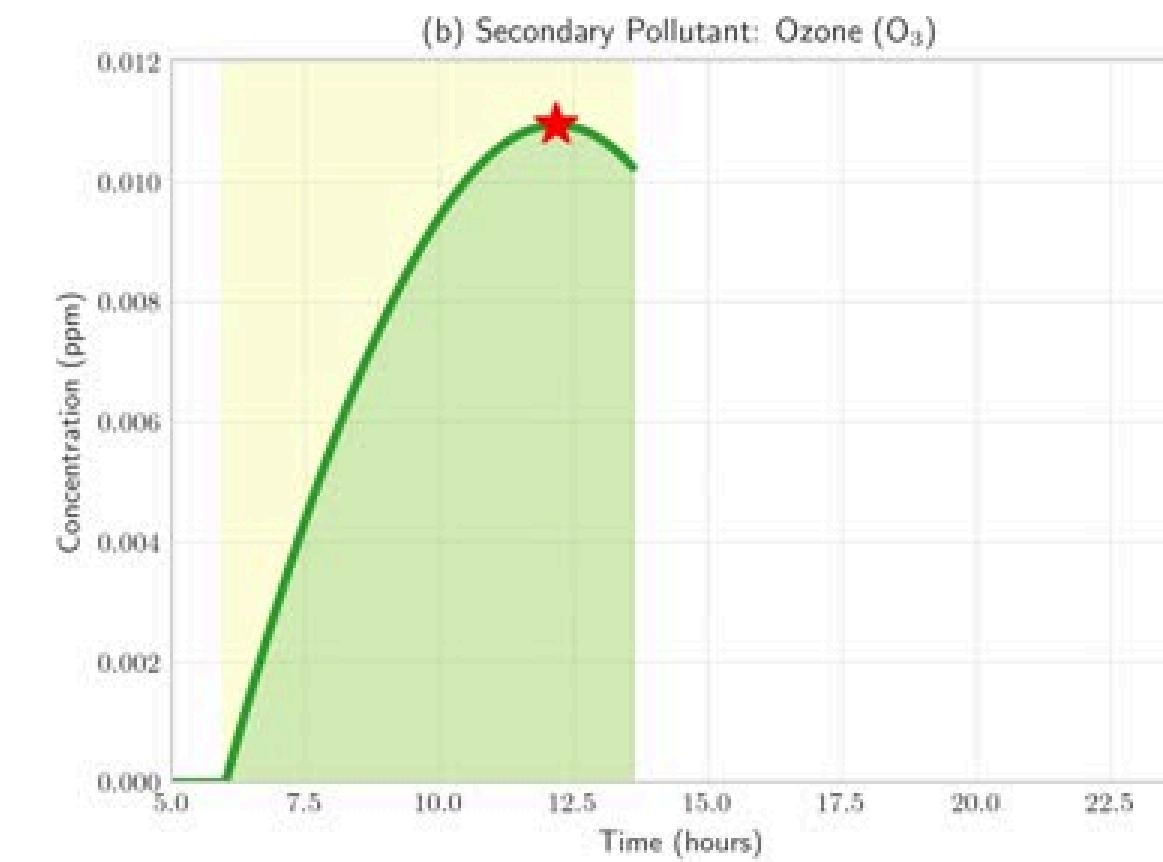
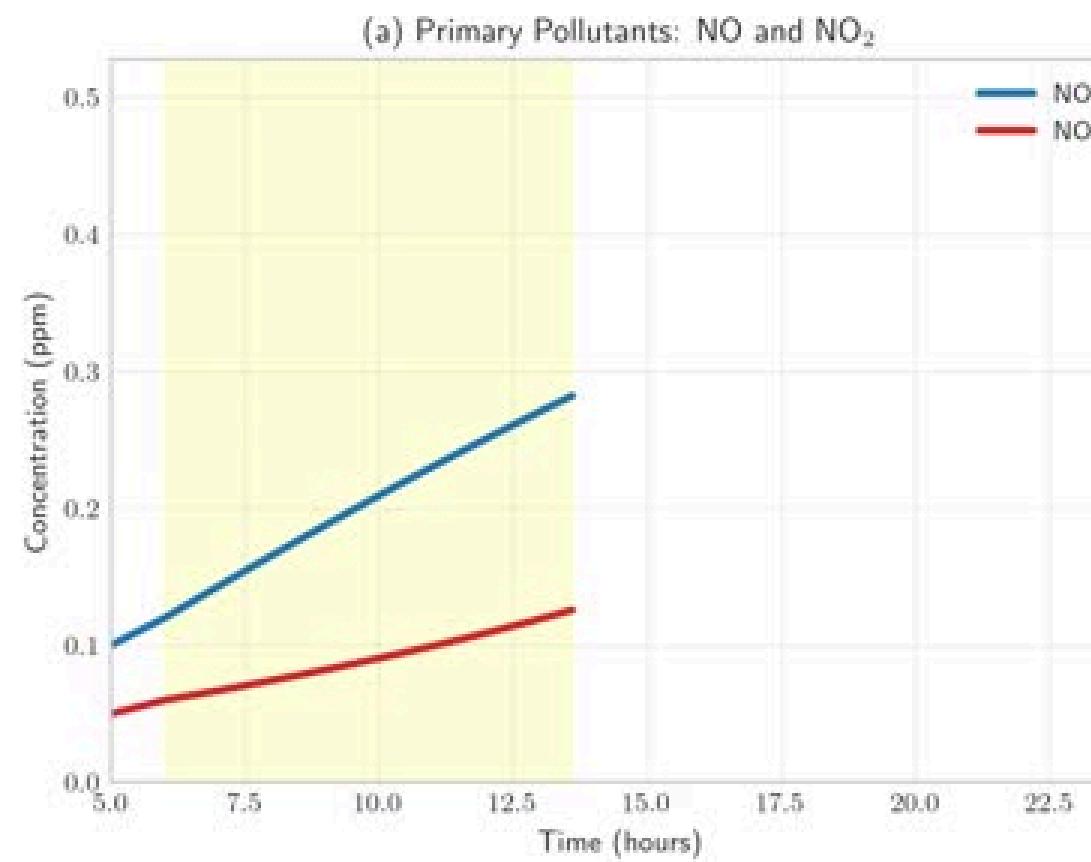
THANK YOU

Guntas Singh Saran
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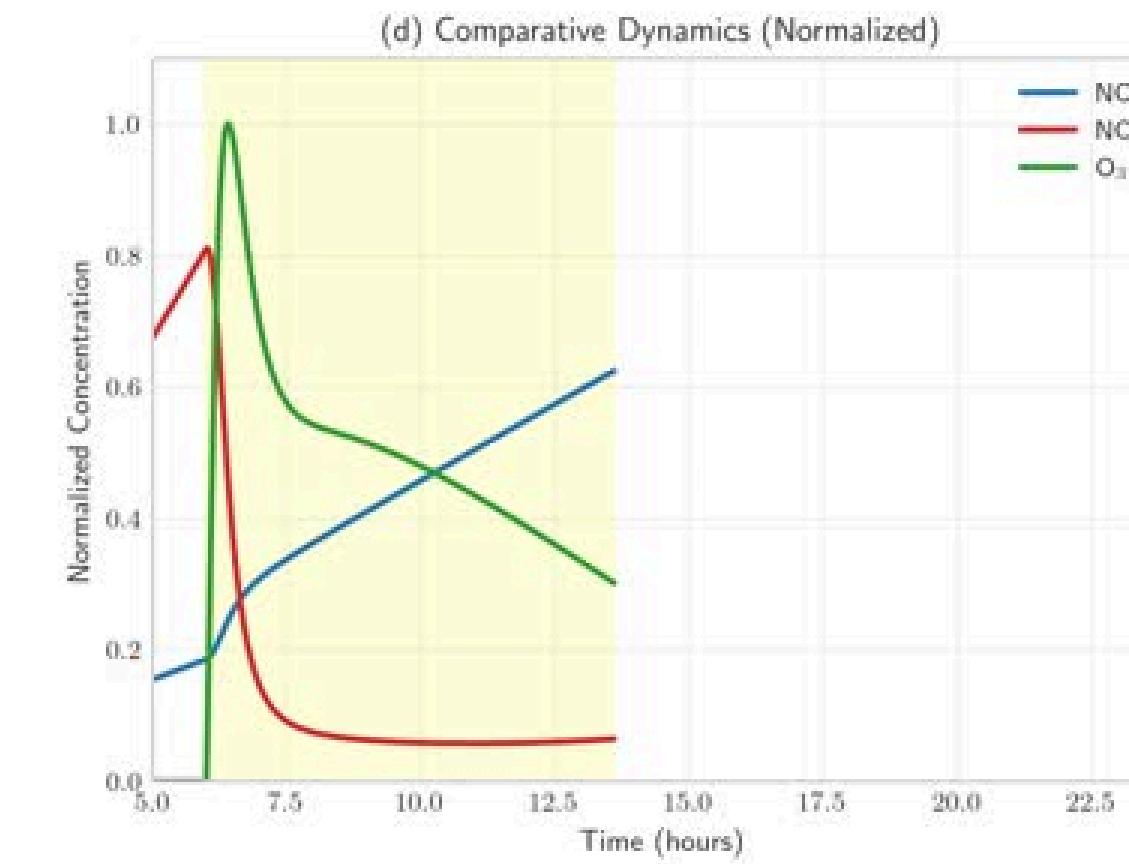
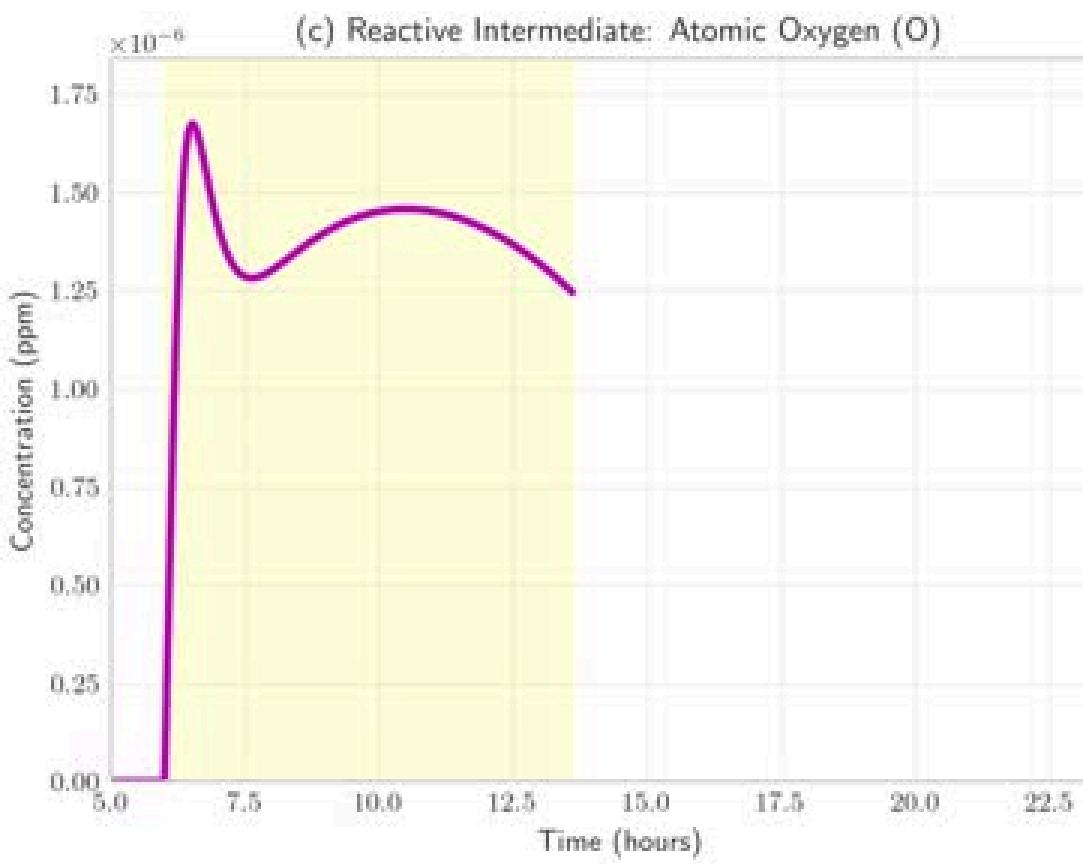
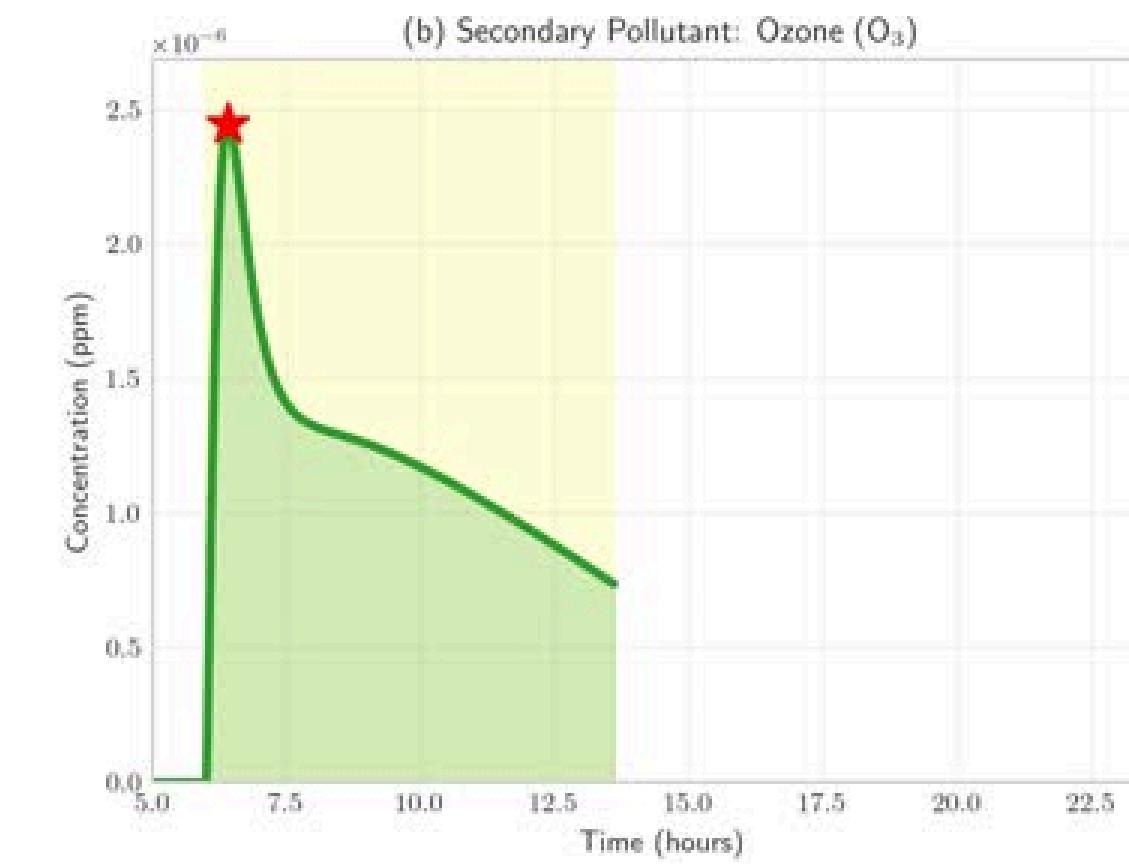
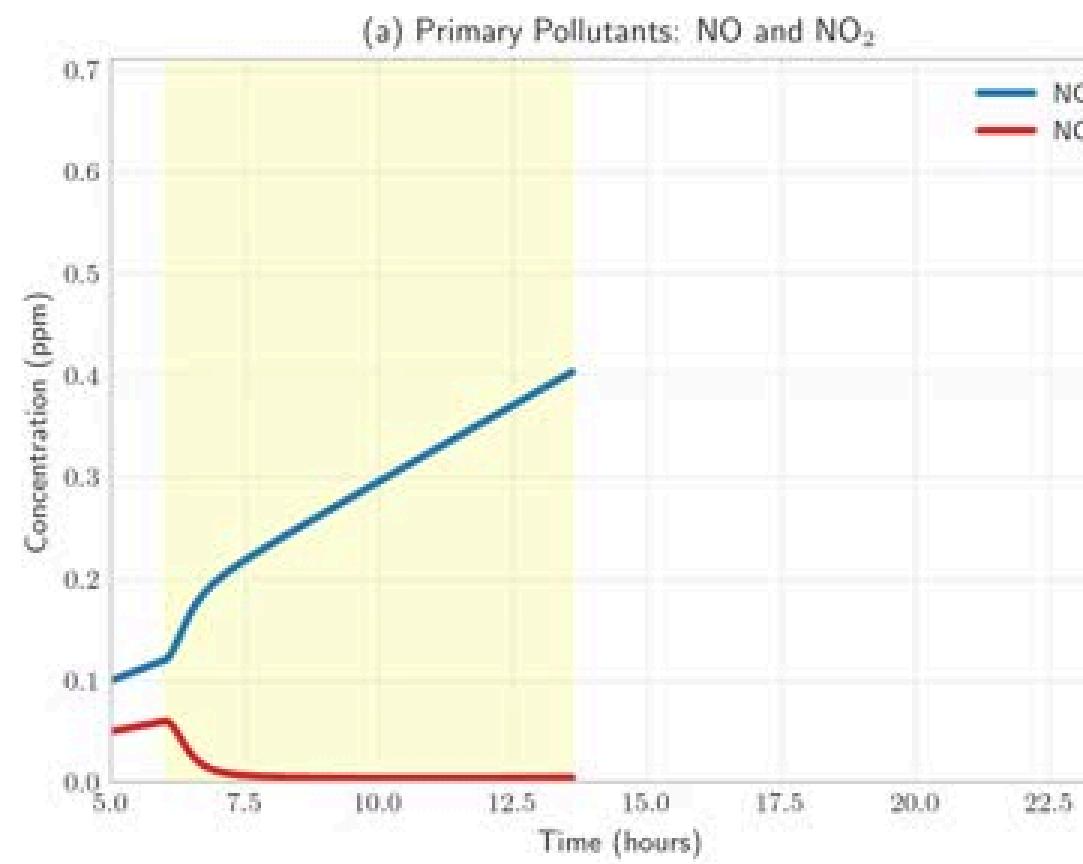
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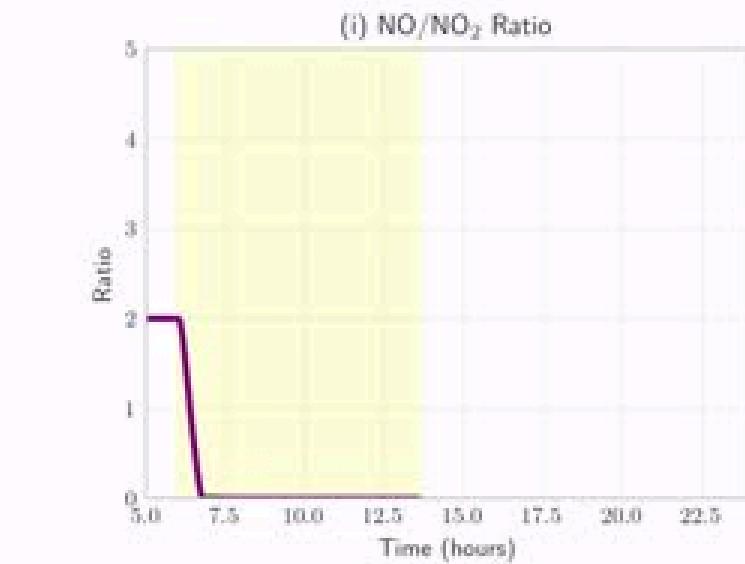
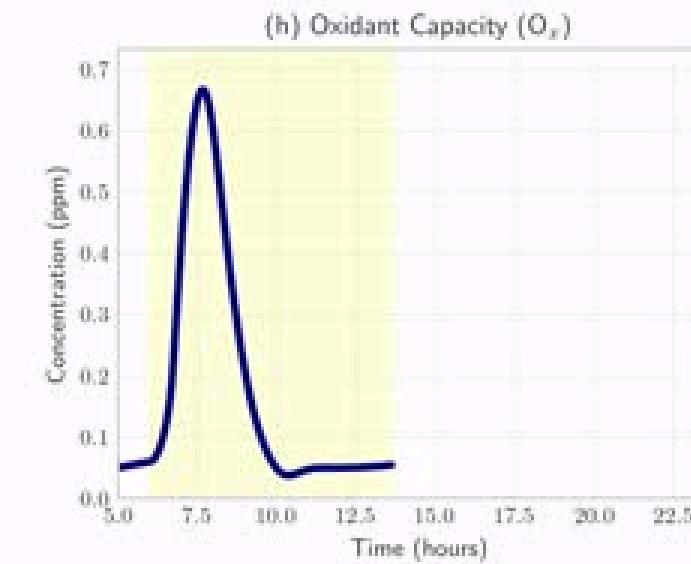
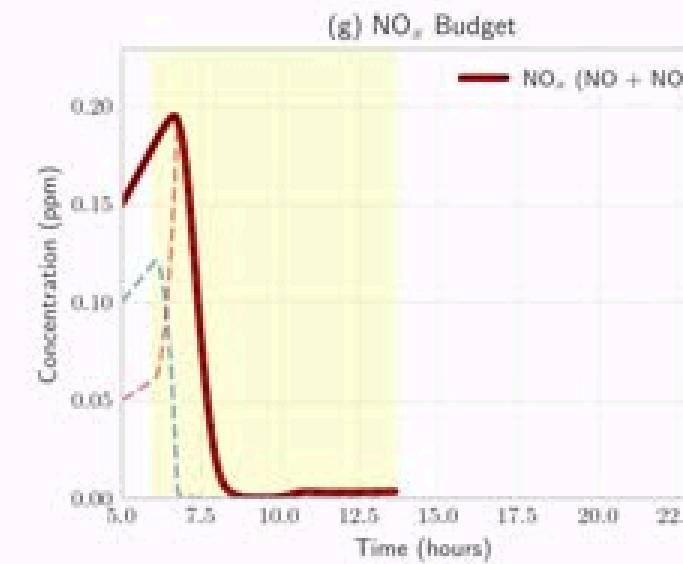
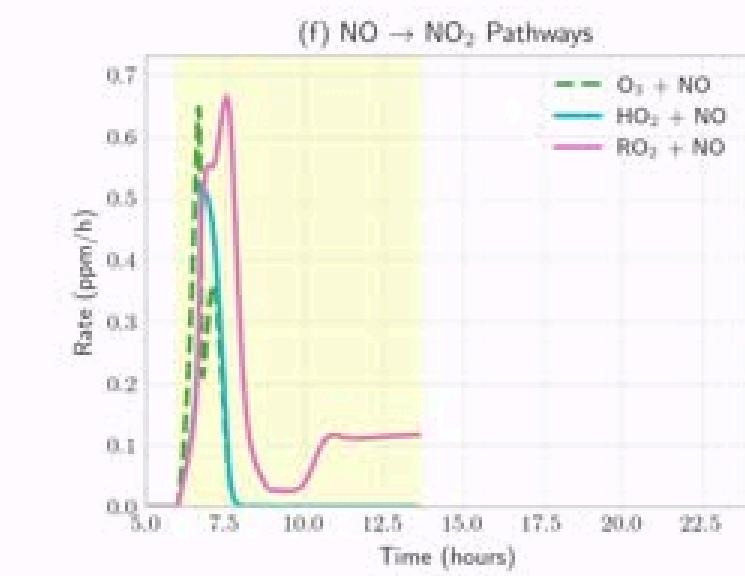
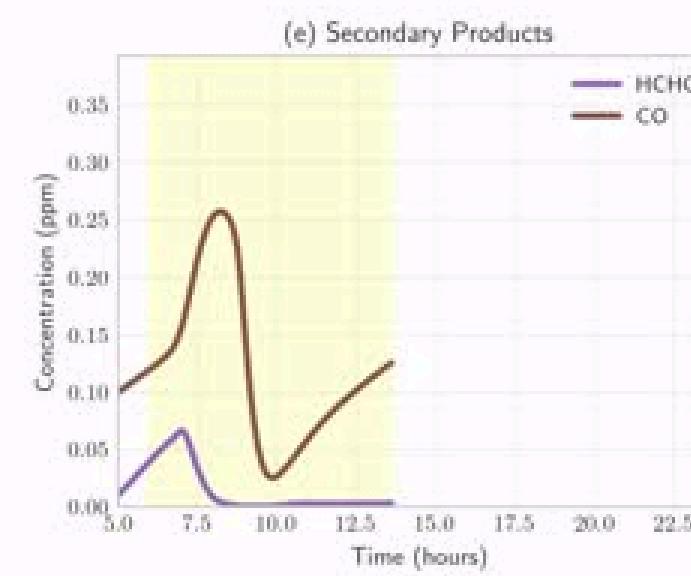
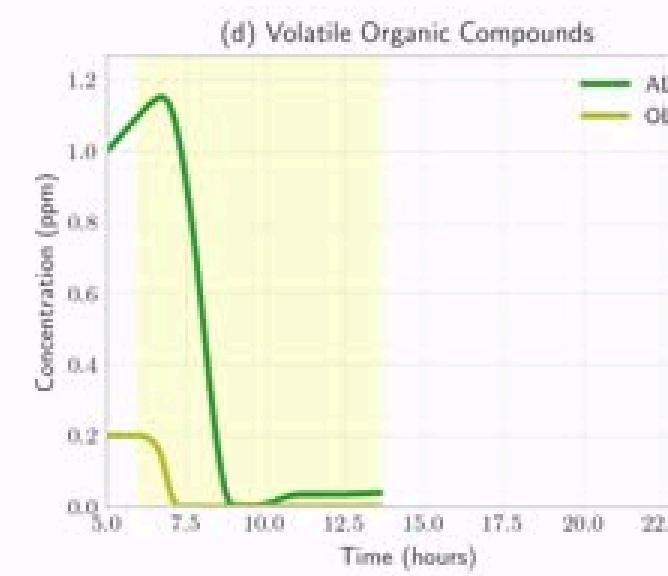
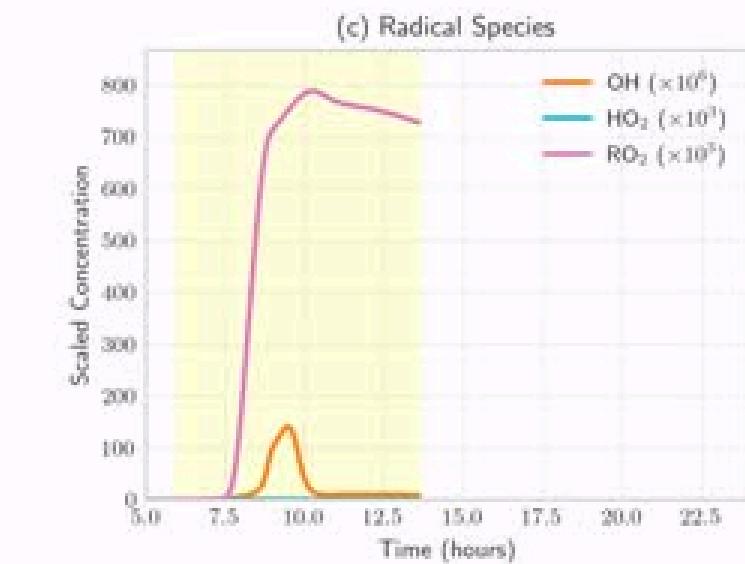
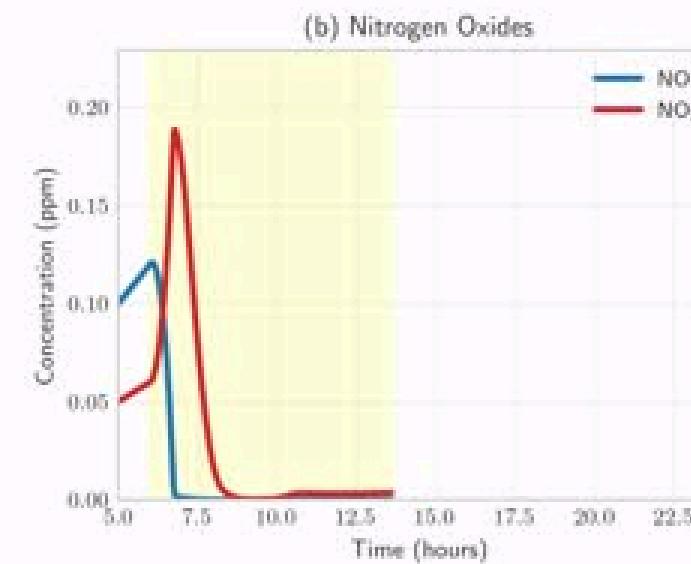
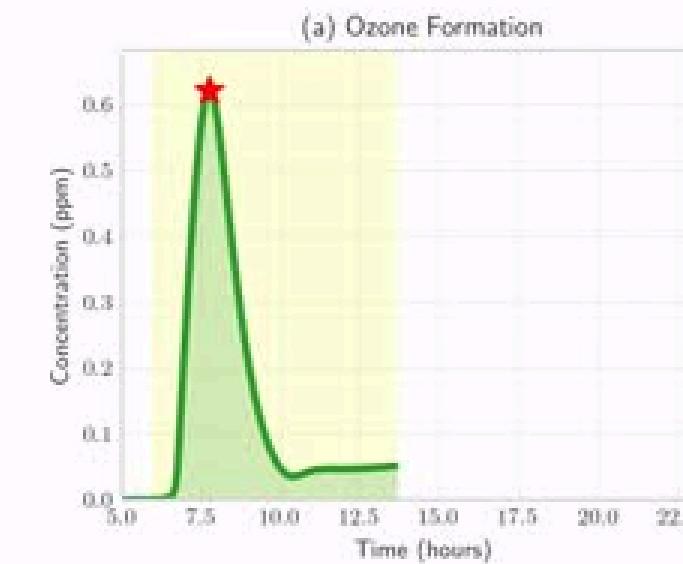
Model 1: Basic Photochemical Cycle



Model 1: Basic Photochemical Cycle



Model 2: Refined with VOCs and Radicals



Model Comparison: Impact of VOCs on Ozone Formation

