Modelling of Photochemical Smog

EH605 - Modelling of Earth System and Sustainability

PRESENTED BY

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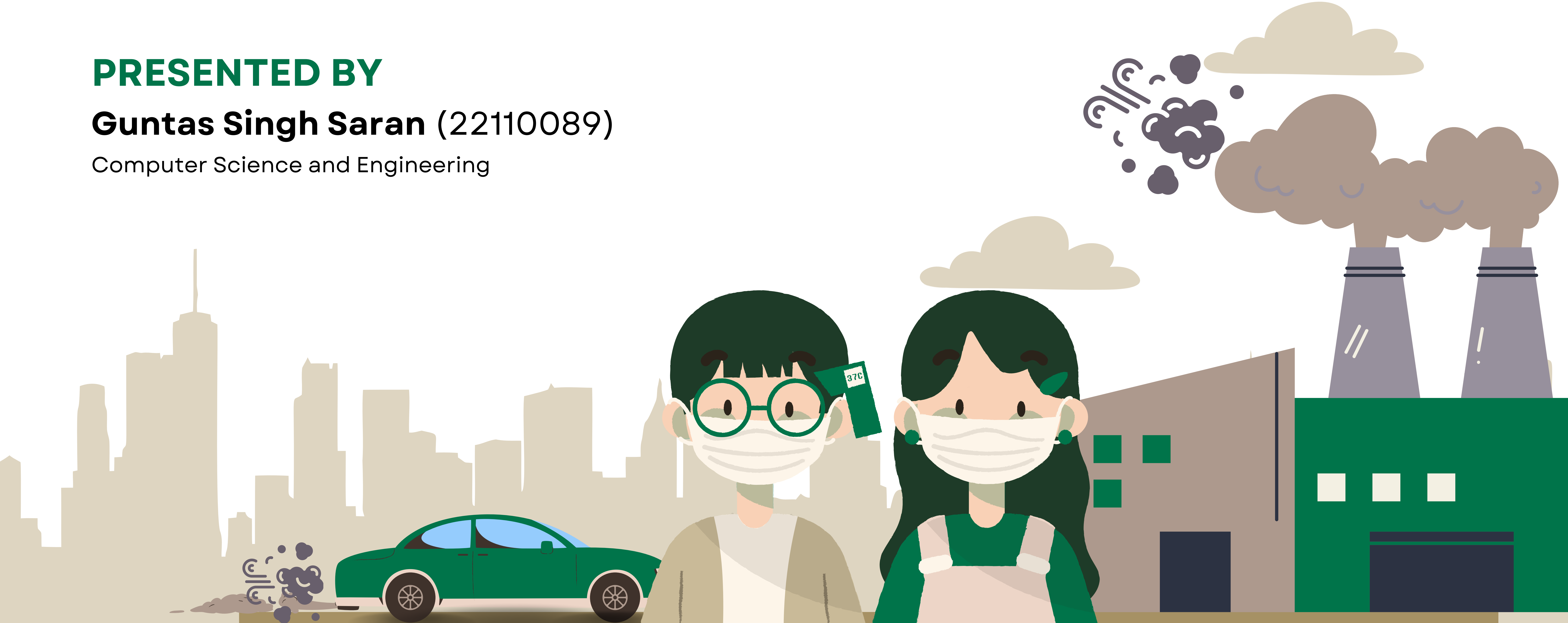
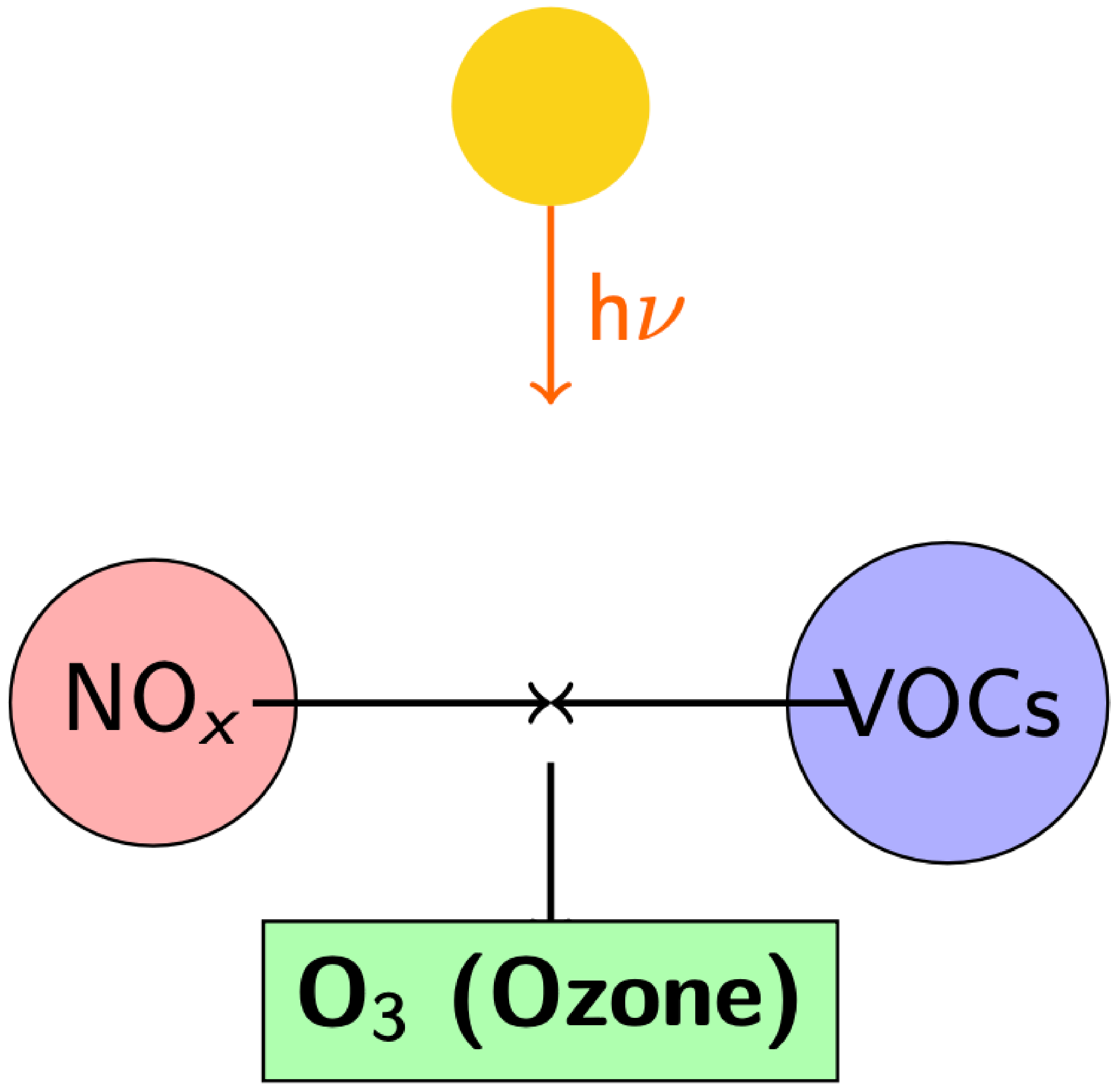
Computer Science and Engineering



Photochemical Smog

- Air pollution from sunlight-driven reactions
- First documented: Los Angeles, 1940s



- **Primary pollutants**: NOx , VOCs
- **Sunlight**: Energy source
- **Secondary pollutants**: O3, PAN, aldehydes

1. Photolysis of NO_2 and basic NO, NO_2, O_3 photolytic cycle

$$NO_2 + h\nu \xrightarrow{1} NO + O(^3P) \qquad k_1 = 0.508^{(1)}$$
$$O(^3P) + O_2 + M \xrightarrow{2} O_3 + M \qquad k_2 = 3.9 \times 10^{-6} \times exp(510/T)$$
$$O_3 + NO \xrightarrow{3} NO_2 + O_2 \qquad k_3 = 3.1 \times 10^3 \times exp(-1450/T)$$
$$NO_2 + O(^3P) \xrightarrow{4} NO + O_2 \qquad k_4 = 1.34 \times 10^4$$
$$NO + O(^3P) \xrightarrow{5} NO_2 \qquad k_5 = 5.6 \times 10^2 \times exp(584/T)$$

2. Chemistry of nitrogen trioxide: NO_3

$$NO_2 + O(^3P) \xrightarrow{6} NO_3 \qquad k_6 = 3.6 \times 10^3$$
$$O_3 + NO_2 \xrightarrow{7} O_2 + NO_3 \qquad k_7 = 1.74 \times 10^2 \times exp(-2450/T)$$
$$NO_3 + NO \xrightarrow{8} 2NO_2 \qquad k_8 = 2.7 \times 10^4$$

3. Nitrous acid and peroxy nitrous acid chemistry

$$NO + HO^* \xrightarrow{9} HONO \qquad k_9 = 1.7 \times 10^4$$

4. Photolysis of nitrous acid: $HONO$

$$HONO + h\nu \xrightarrow{10} HO^* + NO \qquad k_{10} = 0.0963^{(1)}$$

5. Nitrous acid chemistry

$$HO_2^* + NO_2 \xrightarrow{11} HONO + O_2 \qquad k_{11} = 5.82 \times 10^{-2} \times exp(1006/T)$$
$$HONO + HO^* \xrightarrow{12} NO_2 + H_2O \qquad k_{12} = 9.75 \times 10^3$$
$$NO_2 + HO_2^* \xrightarrow{13} HO_2NO_2 \qquad k_{13} = 58.2 \times exp(1006/T)$$
$$HO_2NO_2 \xrightarrow{14} NO_2 + HO_2^* \qquad k_{14} = 1.61 \times 10^{18} \times exp(-11575/T)$$

6. Conversion of NO to NO_2

$$HO_2^* + NO \xrightarrow{15} NO_2 + HO^* \qquad k_{15} = 1.2 \times 10^4$$
$$RO_2^* + NO \xrightarrow{16} NO_2 + RO^* \qquad k_{16} = 1.2 \times 10^4 \text{ (Estimated)}$$
$$RCO_3^* + NO \xrightarrow{17} NO_2 + RO_2^* + CO_2 \qquad k_{17} = 3.8 \times 10^3$$

7. Nitric acid formation: $HONO_2$

$$NO_2 + HO^* \xrightarrow{18} HONO_2 \qquad k_{18} = 1.477 \times 10^{15} \times 10^{-\left(\frac{11.6T}{17.4+T}\right)} \times \sqrt{\frac{280}{T}}$$

Source: https://doi.org/10.3390/pr13051384

processes

MDPI

Article

Mathematical Modeling of Photochemical and Chemical Interactions in Photochemical Smog Formation

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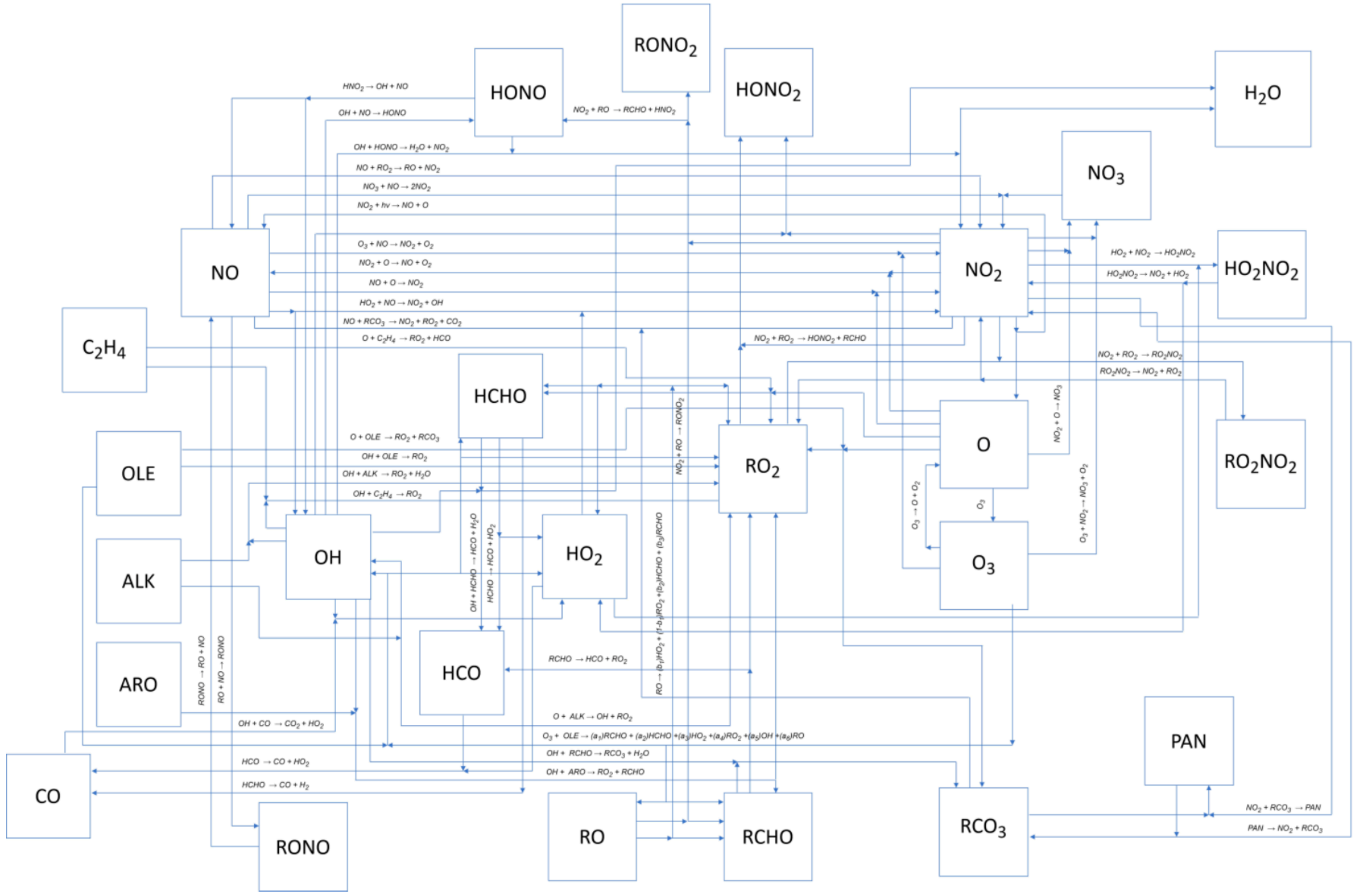


Objectives

Goal: Understand photochemical smog through progressive modelling

Model 1: Basic Photochemical Cycle

- 3-species: NO, NO_2, O_3
- 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, HO_2, RO_2)
- Success: Produces realistic ozone levels

Model1: 3-species

Chemical Reactions

$$NO_2 + h\nu \xrightarrow{k_1} NO + O_3$$

$$NO + O_3 \xrightarrow{k_3} NO_2 + O_2$$

Mass Balance

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

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

$$R_1 = k_1(t)[NO_2]$$

$$R_3 = k_3[O_3][NO]$$

Model1: 3-species

$$\mathrm{NO_2} + h\nu \xrightarrow{k_1} \mathrm{NO} + \mathrm{O_3}$$

$$\mathrm{NO} + \mathrm{O_3} \xrightarrow{k_3} \mathrm{NO_2} + \mathrm{O_2}$$

$$\frac{d[\mathrm{NO}]}{dt} = k_1[\mathrm{NO_2}] - k_3[\mathrm{NO}][\mathrm{O_3}] + E_{\mathrm{NO}}$$

$$\frac{d[\mathrm{NO_2}]}{dt} = -k_1[\mathrm{NO_2}] + k_3[\mathrm{NO}][\mathrm{O_3}] + E_{\mathrm{NO_2}}$$

$$\frac{d[\mathrm{O_3}]}{dt} = k_1[\mathrm{NO_2}] - k_3[\mathrm{NO}][\mathrm{O_3}]$$

$$\mathrm{NO_2} + h\nu \xrightarrow{k_1} \mathrm{NO} + \mathrm{O_3}$$

$$\mathrm{NO} + \mathrm{O_3} \xrightarrow{k_3} \mathrm{NO_2} + \mathrm{O_2}$$

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

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

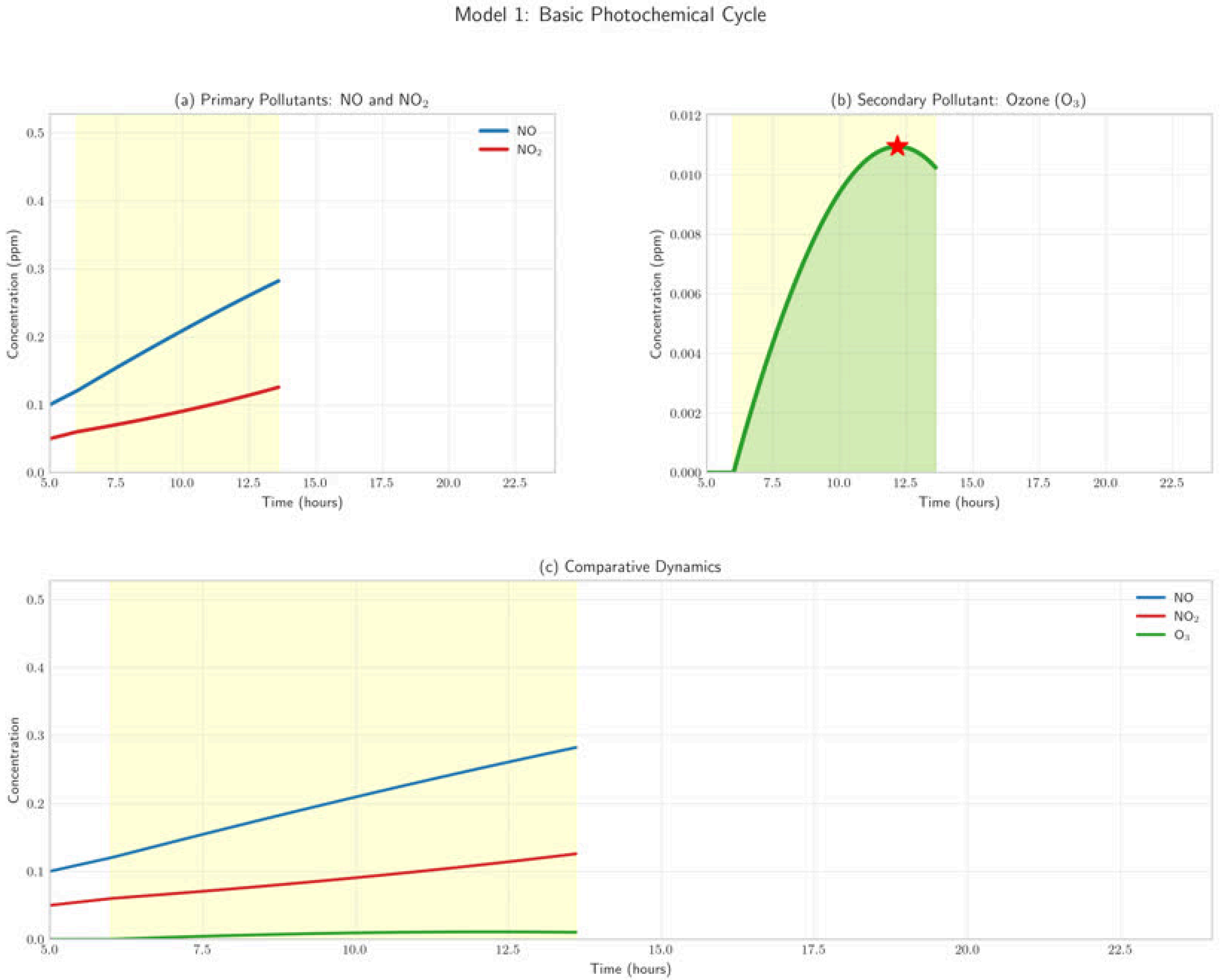
$$E_{\mathrm{NO_2}} = 0.01\ \mathrm{ppm/h}$$

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

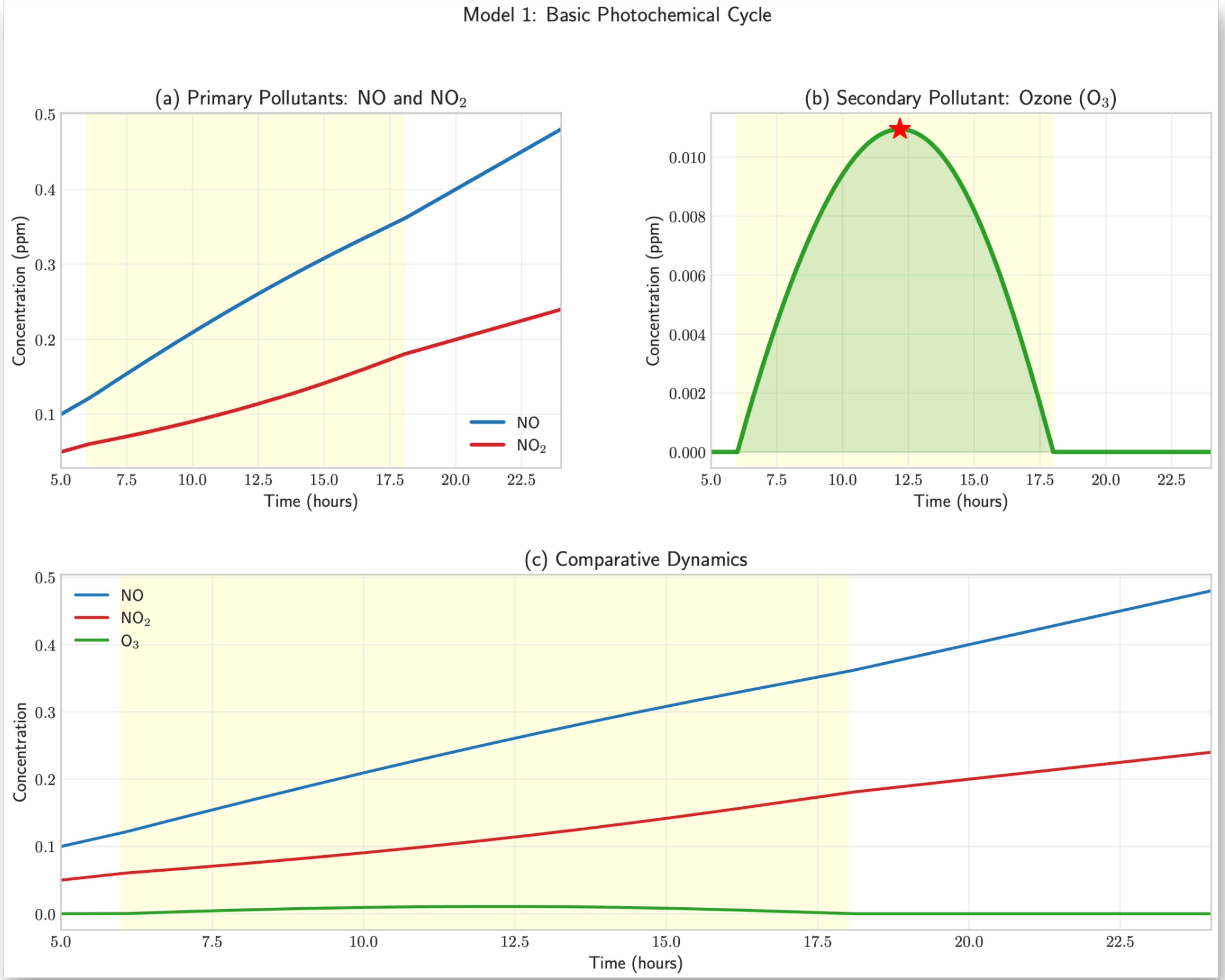
The Fundamental Problem

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

Source: https://doi.org/10.3390/pr13051384



Model 1: Basic Photochemical Cycle
(a) Primary Pollutants: NO and NO₂
NO
NO₂
Concentration (ppm)
Time (hours)
(b) Secondary Pollutant: Ozone (O₃)
Concentration (ppm)
Time (hours)
(c) Comparative Dynamics
NO
NO₂
O₃
Concentration
Time (hours)



Model 1: Basic Photochemical Cycle
(a) Primary Pollutants: NO and NO₂
Concentration (ppm)
Time (hours)
NO
NO₂
(b) Secondary Pollutant: Ozone (O₃)
Concentration (ppm)
Time (hours)
(c) Comparative Dynamics
NO
NO₂
O₃
Concentration
Time (hours)

Model1: 4-species

$$\mathrm{NO_2} + h\nu \xrightarrow{k_1} \mathrm{NO} + \mathrm{O}(^3\mathrm{P})$$

$$\mathrm{O}(^3\mathrm{P}) + \mathrm{O_2} + M \xrightarrow{k_2} \mathrm{O_3} + M$$

$$\mathrm{O_3} + \mathrm{NO} \xrightarrow{k_3} \mathrm{NO_2} + \mathrm{O_2}$$

$$\mathrm{NO_2} + \mathrm{O}(^3\mathrm{P}) \xrightarrow{k_4} \mathrm{NO} + \mathrm{O_2}$$

$$\mathrm{NO} + \mathrm{O}(^3\mathrm{P}) \xrightarrow{k_5} \mathrm{NO_2}$$

$$R_1 = k_1(t)[\mathrm{NO_2}]$$

$$R_2 = k_2[\mathrm{O}][\mathrm{O_2}]M$$

$$R_3 = k_3[\mathrm{O_3}][\mathrm{NO}]$$

$$R_4 = k_4[\mathrm{NO_2}][\mathrm{O}]$$

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

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

$$\frac{d[\mathrm{NO_2}]}{dt} = -R_1 + R_3 - R_4 + R_5 + E_{\mathrm{NO_2}}$$

$$\frac{d[\mathrm{O_3}]}{dt} = R_2 - R_3$$

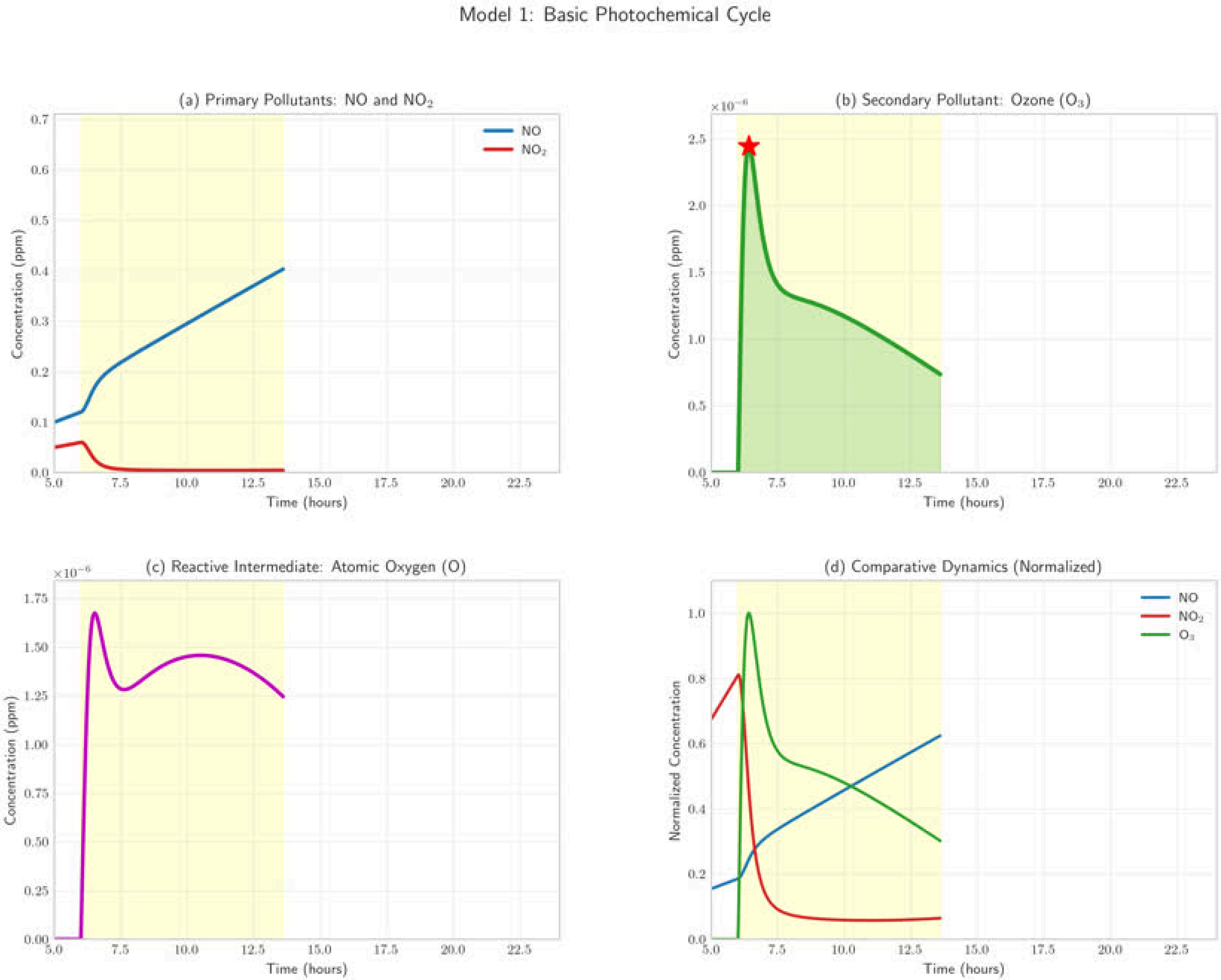
$$\frac{d[\mathrm{O}]}{dt} = R_1 - R_2 - R_4 - R_5$$

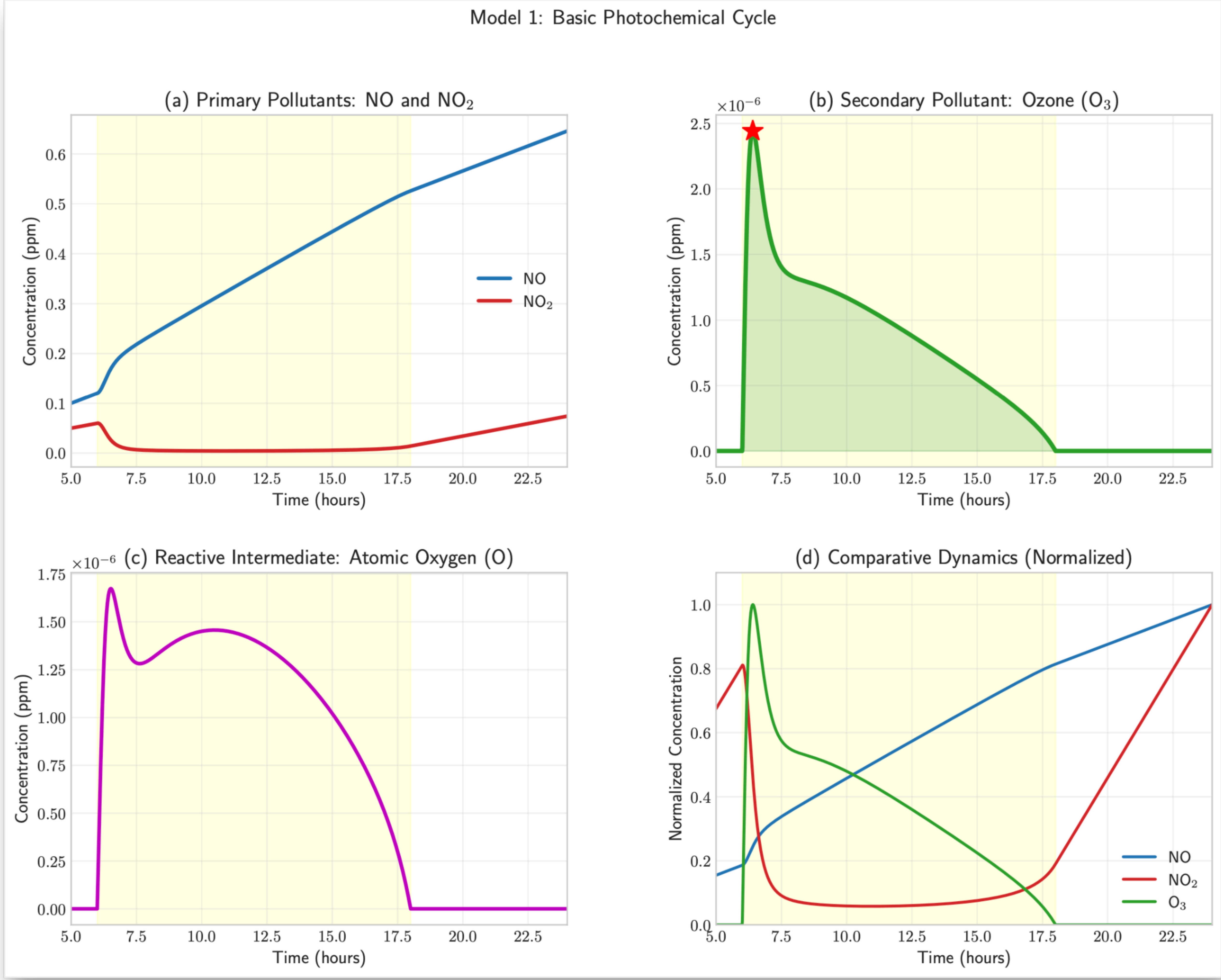
Table 2: Model 1 initial conditions (5:00 AM)

Species	Initial Concentration (ppm)
NO	0.100
NO_2	0.050
O_3	0.0
O	0.0

Parameter	Value	Units
$k_{1,\mathrm{max}}$	30.48	h^{-1}
k_2	1.44×10^{-3}	$\mathrm{ppm}^{-2}\ \mathrm{h}^{-1}$
k_3	1.20×10^{5}	$\mathrm{ppm}^{-1}\ \mathrm{h}^{-1}$
k_4	8.04×10^{5}	$\mathrm{ppm}^{-1}\ \mathrm{h}^{-1}$
k_5	1.99×10^{5}	$\mathrm{ppm}^{-1}\ \mathrm{h}^{-1}$
$[O_2]$ M	210,000	ppm
E_{NO}	0.02	$\mathrm{ppm}\ \mathrm{h}^{-1}$
$E_{\mathrm{NO_2}}$	0.01	$\mathrm{ppm}\ \mathrm{h}^{-1}$

Source: https://doi.org/10.3390/pr13051384


Model 1: Basic Photochemical Cycle
(a) Primary Pollutants: NO and NO$_2$
NO
NO$_2$
Concentration (ppm)
Time (hours)
(b) Secondary Pollutant: Ozone (O$_3$)
$\times 10^{-6}$
Concentration (ppm)
Time (hours)
(c) Reactive Intermediate: Atomic Oxygen (O)
$\times 10^{-6}$
Concentration (ppm)
Time (hours)
(d) Comparative Dynamics (Normalized)
NO
NO$_2$
O$_3$
Normalized Concentration
Time (hours)



Model 1: Basic Photochemical Cycle
(a) Primary Pollutants: NO and NO₂
Concentration (ppm)
Time (hours)
NO
NO₂
(b) Secondary Pollutant: Ozone (O₃)
×10⁻⁶
Concentration (ppm)
Time (hours)
(c) Reactive Intermediate: Atomic Oxygen (O)
×10⁻⁶
Concentration (ppm)
Time (hours)
(d) Comparative Dynamics (Normalized)
Normalized Concentration
Time (hours)
NO
NO₂
O₃

Key Findings

Critical Finding

Peak O_3 = 0.003 ppb at 8:00 AM

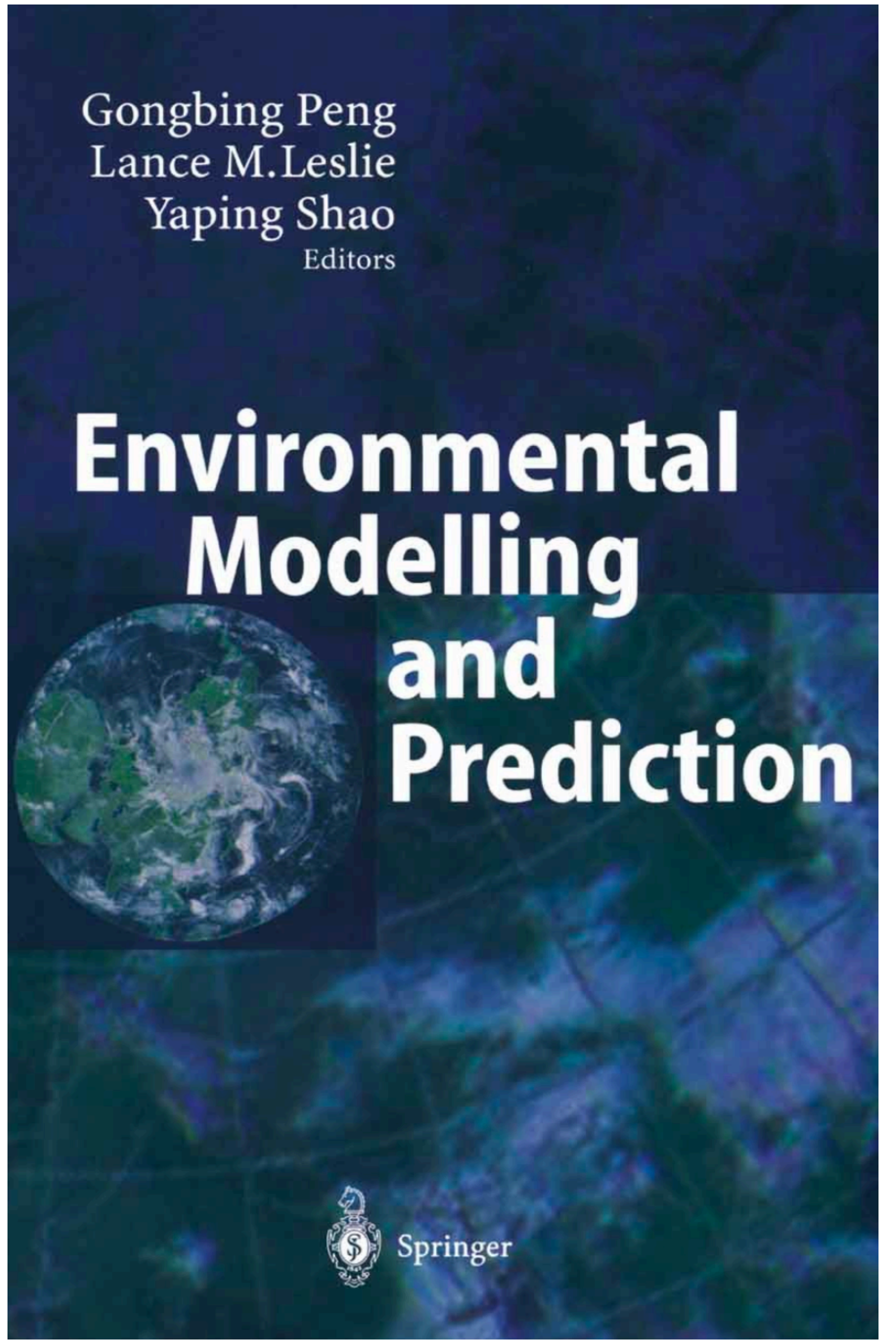
Observations:

- **Minimal ozone**: Far below air quality standard (0.07 ppm = 70 ppb)
- **Rapid titration**: NO immediately reacts with any O_3 formed
- **NO/NO_2 cycling**: Interconversion without net oxidation
- **Atomic oxygen**: Very low ($\sim 10^{-6}$ ppm) due to fast O_2 reaction

Fundamental Limitation

No mechanism to convert NO to NO_2 without consuming O_3

- Missing: VOC chemistry
- Missing: Radical pathways (OH, HO_2, RO_2)
- 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:

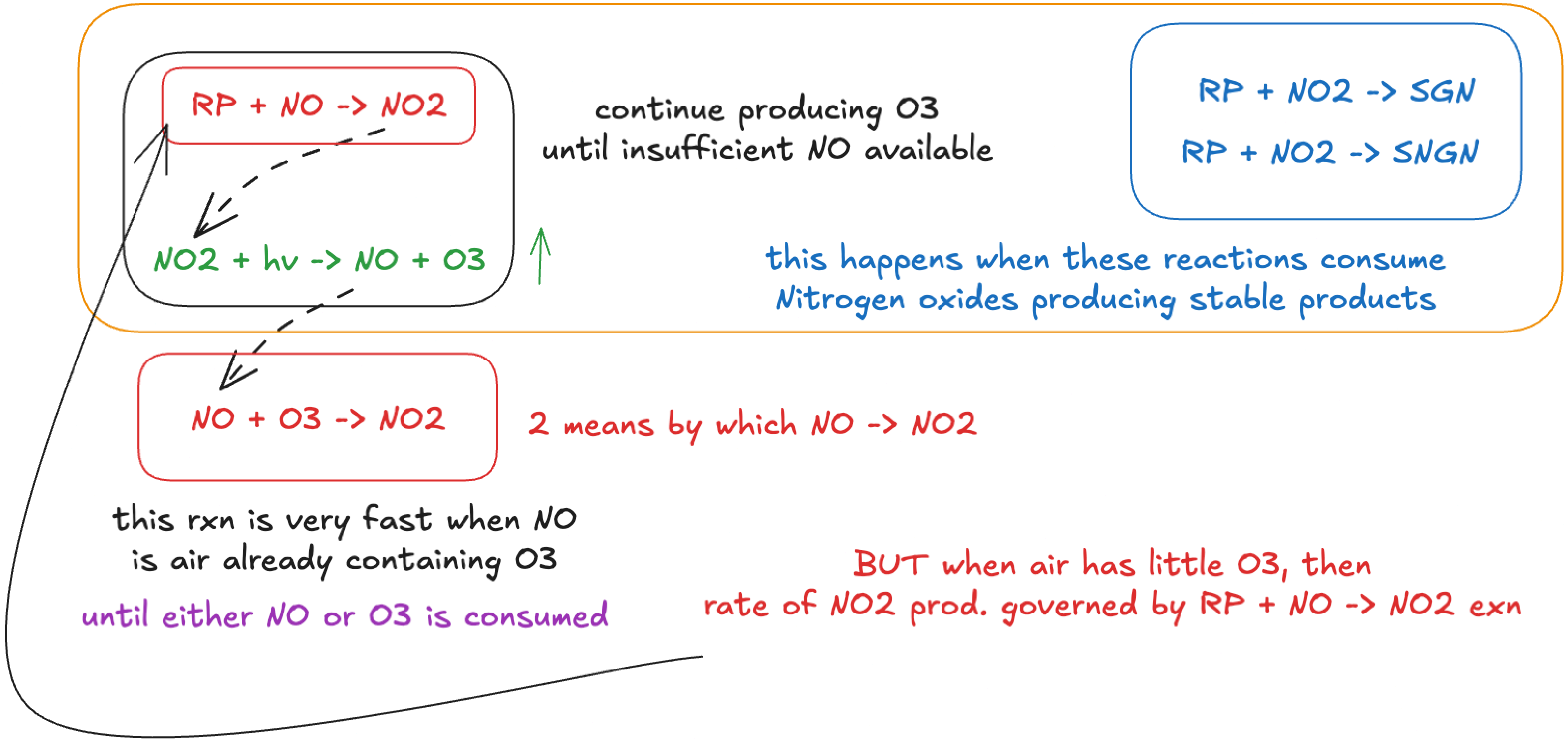
$$
\begin{aligned}
&\mathrm{ROC+hv} \longrightarrow \mathrm{RP+ROC}\\
&\mathrm{RP+NO} \longrightarrow \mathrm{NO_2}\\
&\mathrm{NO_2+hv} \longrightarrow \mathrm{NO+O_3}\\
&\mathrm{NO+O} \longrightarrow \mathrm{NO_2}\\
&\mathrm{RP+RP} \longrightarrow \mathrm{RP}\\
&\mathrm{RP+NO_2} \longrightarrow \mathrm{SGN}\\
&\mathrm{RP+NO_2} \longrightarrow \mathrm{SNGN}
\end{aligned}
$$

Source: https://doi.org/10.1007/978-3-662-04868-9_10

Generic Reaction Set (GRS) Mechanism

r1 = k1(t) [ROC]	ROC + hv -> RP + ROC
r2 = k2 [RP][NO]	RP + NO -> NO2
r3 = k3(t) [NO2]	NO2 + hv -> NO + O3
r4 = k4 [NO][O3]	NO + O3 -> NO2
r5 = k5 [RP][RP]	RP + RP -> RP
r6 = k6 [RP][NO2]	RP + NO2 -> SGN
r7 = k7 [RP][NO2]	RP + NO2 -> SNGN

ROC = Reactive Organic Compound
RP = Radical Pool
SGN = Stable Gaseous Product
SNGN = Stable Non-Gaseous Product
NO
O3
NO2



Source: https://doi.org/10.1007/978-3-662-04868-9_10

Model2: 11-species

Added Species (7 new):

VOCs:

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

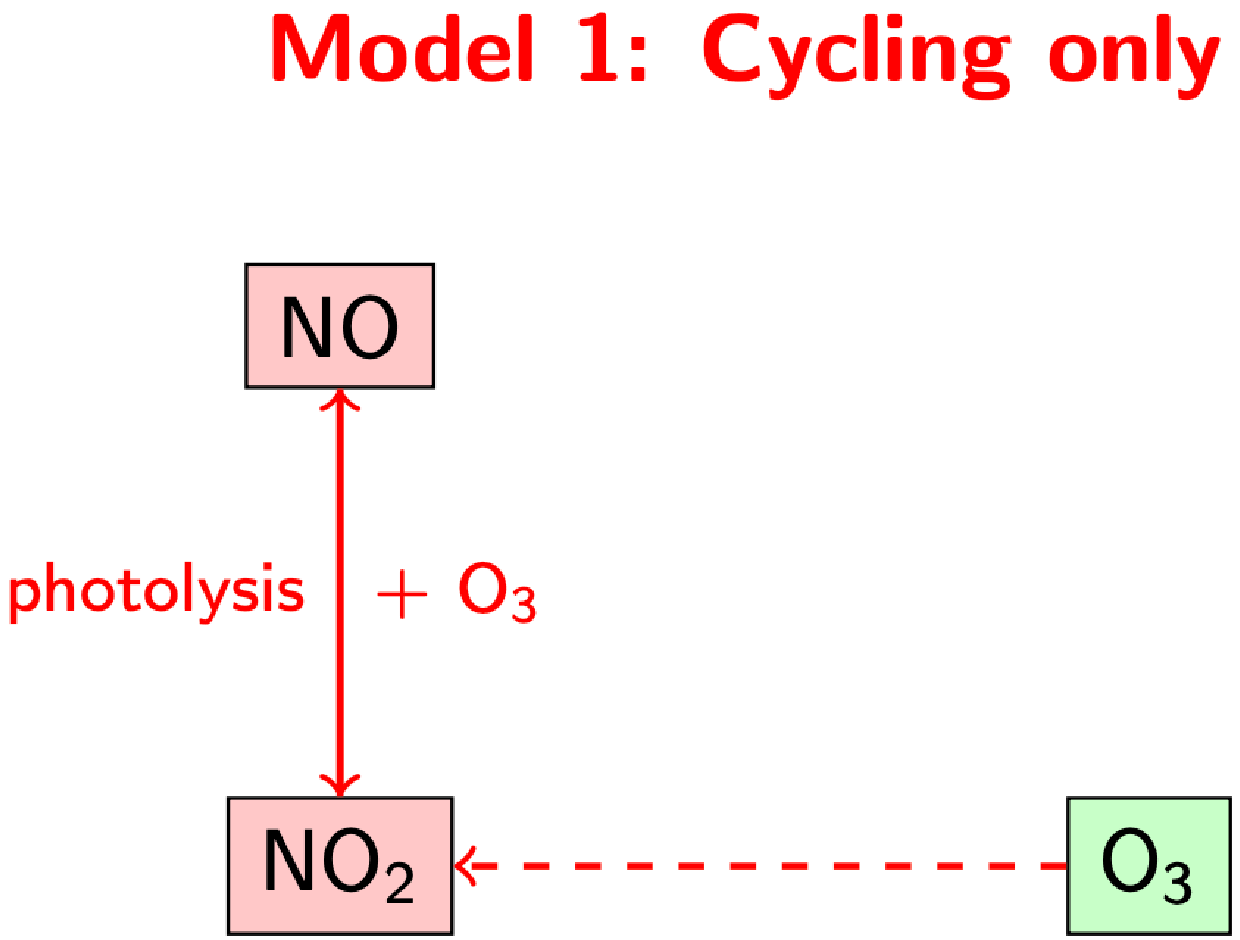
Radicals:

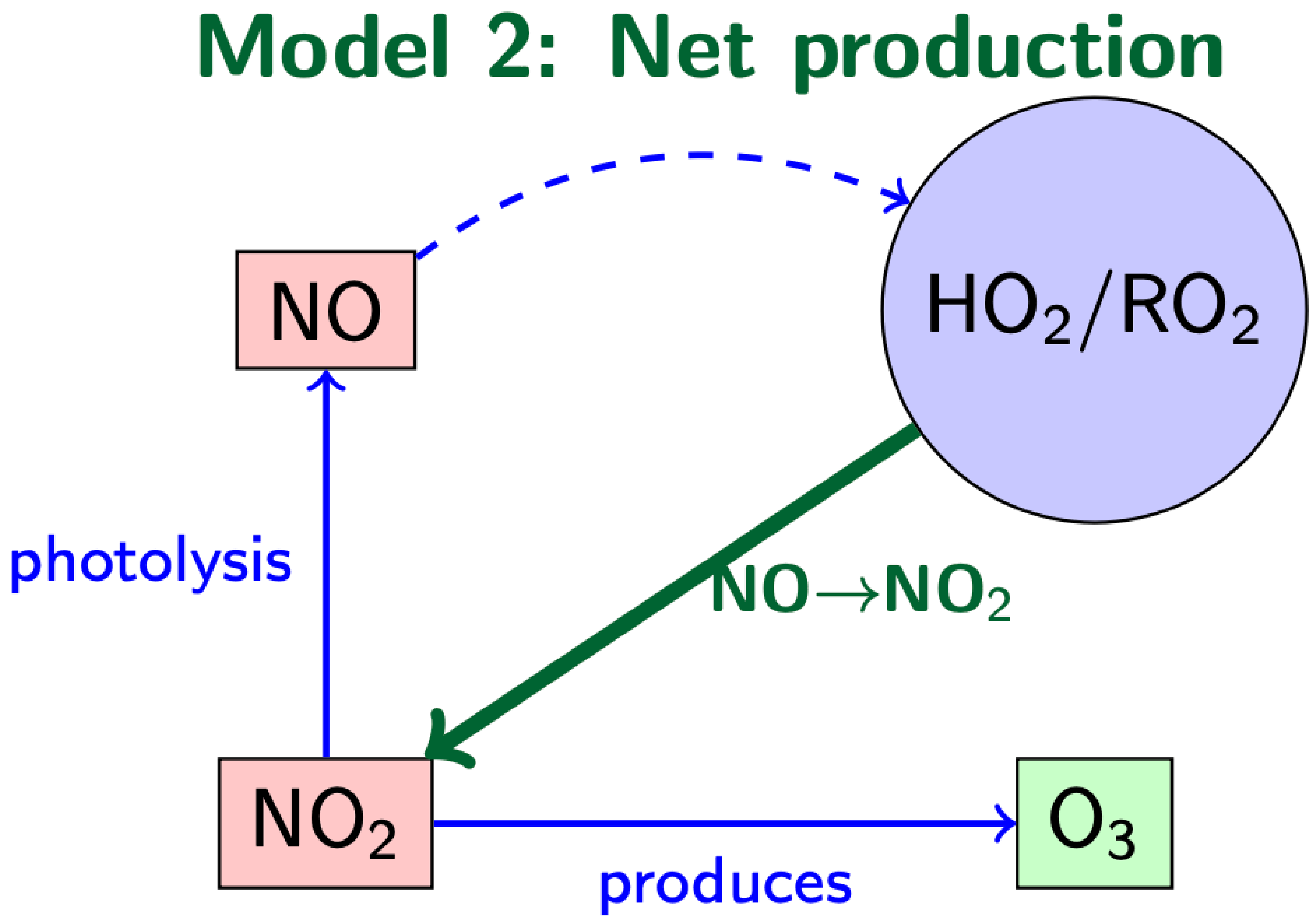
- OH (hydroxyl radical)
- HO_2 (hydroperoxyl radical)
- RO_2 (organic peroxy radicals)

Total System

- **11 species**: NO, NO_2, O_3, O, CO, HCHO, ALK, OLE, OH, HO_2, RO_2
- **15 reactions**: 5 from Model 1 + 10 new

Model2: 11-species





Reactions

$$O_3 + h\nu \xrightarrow{k_4} O(^1D) + O_2$$

$$O(^1D) + H_2O \xrightarrow{k_5} 2OH$$

$$CO + OH \xrightarrow{k_6} HO_2 + CO_2$$

$$HCHO + h\nu \xrightarrow{k_7} 2HO_2 + CO$$

$$HCHO + OH \xrightarrow{k_8} HO_2 + CO + H_2O$$

$$ALK + OH \xrightarrow{k_9} RO_2$$

$$OLE + OH \xrightarrow{k_{10}} RO_2$$

$$OLE + O_3 \xrightarrow{k_{11}} 0.5HCHO + \text{products}$$

$$HO_2 + NO \xrightarrow{k_{12}} NO_2 + OH \quad \textbf{(Key!)}$$

$$RO_2 + NO \xrightarrow{k_{13}} NO_2 + HO_2 \quad \textbf{(Key!)}$$

$$HO_2 + HO_2 \xrightarrow{k_{14}} H_2O_2 + O_2$$

$$OH + NO_2 \xrightarrow{k_{15}} HNO_3$$

OH Production

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \rightarrow 2OH$$

VOC Oxidation

$$CO + OH \rightarrow HO_2 + CO_2$$
$$HCHO + h\nu \rightarrow 2HO_2 + CO$$
$$HCHO + OH \rightarrow HO_2 + CO$$
$$ALK + OH \rightarrow RO_2$$
$$OLE + OH \rightarrow RO_2$$

The Catalytic Cycle:

1. **Initiation**: $O_3 + h\nu \rightarrow O(^1D) \xrightarrow{H_2O} 2OH$
2. **Propagation**:
   - OH attacks VOCs: $VOC + OH \rightarrow RO_2/HO_2$
   - Radicals oxidize NO: $HO_2/RO_2 + NO \rightarrow NO_2 + OH/HO_2$
   - NO_2 photolyzes: $NO_2 + h\nu \rightarrow NO + O_3$
3. **Termination**:
   - $HO_2 + HO_2 \rightarrow H_2O_2$
   - $OH + NO_2 \rightarrow HNO_3$

Key Addition

Key Innovation: NO Oxidation WITHOUT O_3 Consumption

$$HO_2 + NO \rightarrow NO_2 + OH \tag{R12}$$
$$RO_2 + NO \rightarrow NO_2 + HO_2 \tag{R13}$$

Why this matters:

- Converts NO to NO_2 **without consuming O_3**
- NO_2 then photolyzes: $NO_2 + h\nu \rightarrow NO + O_3$
- **Net result: O_3 production!**

Formulation

For Model 2 with 11 species and 15 reactions:

1. **Nitric Oxide (NO):**

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

2. **Nitrogen Dioxide (NO_2):**

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

3. **Ozone (O_3):**

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

4. **Atomic Oxygen (O):**

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

5. **Carbon Monoxide (CO):**

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

6. **Formaldehyde (HCHO):**

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

7. **Alkanes (ALK):**

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

8. **Olefins (OLE):**

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

9. **Hydroxyl Radical (OH):**

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

10. **Hydroperoxyl Radical (HO_2):**

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

11. **Organic Peroxy Radical (RO_2):**

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

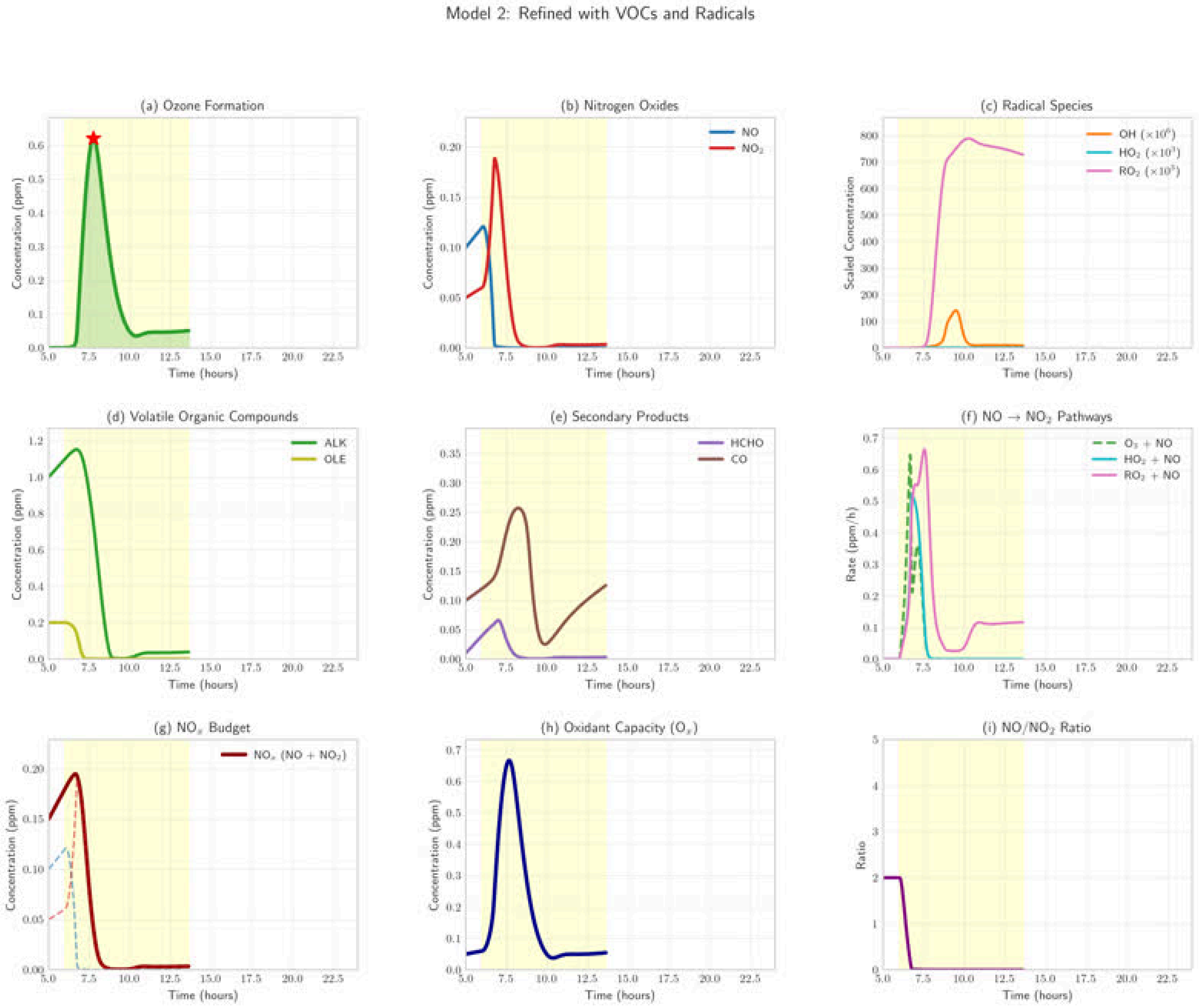
Parameters

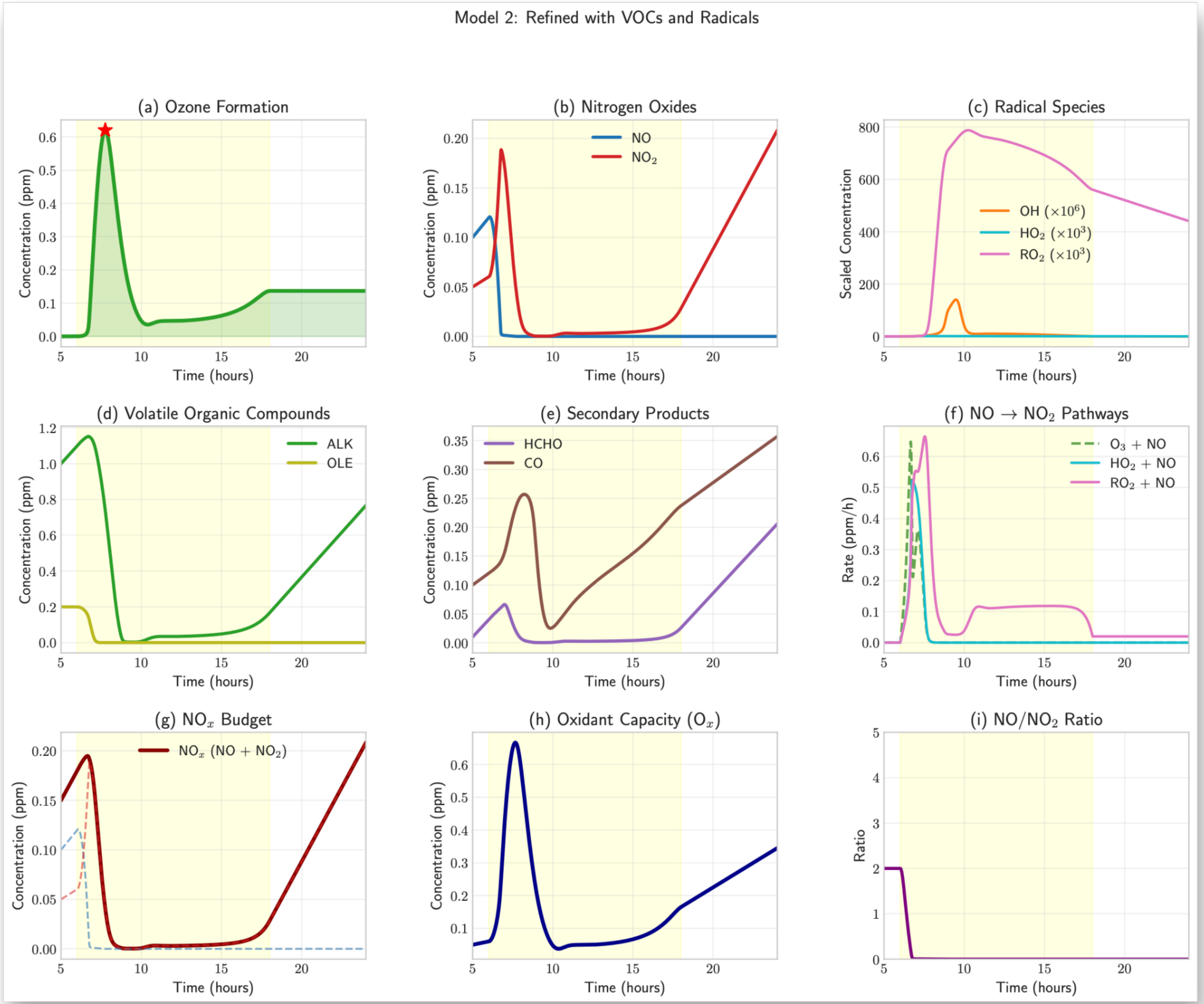
$R_1 = k_1(t)[NO_2]$	(NO_2 photolysis)
$R_2 = k_2[O][O_2]$	(O_3 formation)
$R_3 = k_3[O_3][NO]$	(NO oxidation by O_3)
$R_4 = k_4(t)[O_3]$	(O_3 photolysis)
$R_5 = k_5[O(^1D)][H_2O]$	(OH formation)
$R_6 = k_6[CO][OH]$	(CO oxidation)
$R_7 = k_7(t)[HCHO]$	(HCHO photolysis)
$R_8 = k_8[HCHO][OH]$	(HCHO oxidation)
$R_9 = k_9[ALK][OH]$	(Alkane oxidation)
$R_{10} = k_{10}[OLE][OH]$	(Olefin oxidation by OH)
$R_{11} = k_{11}[OLE][O_3]$	(Olefin ozonolysis)
$R_{12} = k_{12}[HO_2][NO]$	**(Key: $NO \to NO_2$ via HO_2)**
$R_{13} = k_{13}[RO_2][NO]$	**(Key: $NO \to NO_2$ via RO_2)**
$R_{14} = k_{14}[HO_2]^2$	(HO_2 termination)
$R_{15} = k_{15}[OH][NO_2]$	(HNO_3 formation)

Reaction	Rate Constant	Units
k_4 (O_3 photolysis)	1.968	h^{-1}
k_5 ($O(^1D) + H_2O$)	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

Source: https://doi.org/10.3390/pr13051384


Model 2: Refined with VOCs and Radicals
(a) Ozone Formation
(b) Nitrogen Oxides
NO
NO2
(c) Radical Species
OH (×10^6)
HO2 (×10^3)
RO2 (×10^3)
Scaled Concentration
(d) Volatile Organic Compounds
ALK
OLE
(e) Secondary Products
HCHO
CO
(f) NO → NO2 Pathways
O3 + NO
HO2 + NO
RO2 + NO
Rate (ppm/h)
(g) NOx Budget
NOx (NO + NO2)
(h) Oxidant Capacity (Ox)
(i) NO/NO2 Ratio
Ratio
Concentration (ppm)
Time (hours)



Model 2: Refined with VOCs and Radicals
(a) Ozone Formation
Concentration (ppm)
Time (hours)
(b) Nitrogen Oxides
NO
NO2
(c) Radical Species
Scaled Concentration
OH (×10^6)
HO2 (×10^3)
RO2 (×10^3)
(d) Volatile Organic Compounds
ALK
OLE
(e) Secondary Products
HCHO
CO
(f) NO → NO2 Pathways
Rate (ppm/h)
O3 + NO
HO2 + NO
RO2 + NO
(g) NOx Budget
NOx (NO + NO2)
(h) Oxidant Capacity (Ox)
(i) NO/NO2 Ratio
Ratio

Key Findings

Success!

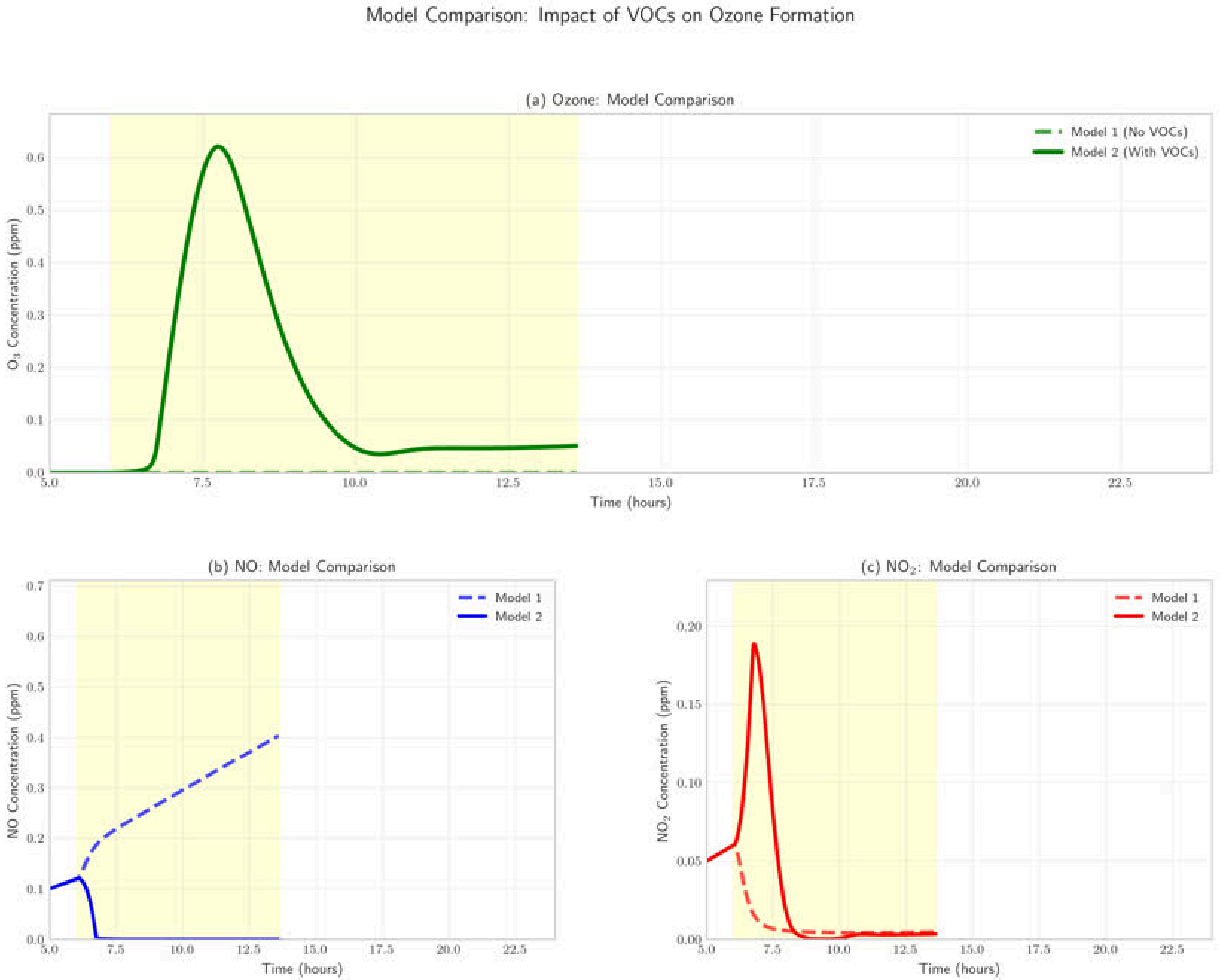
Peak O_3 = **0.6 ppm** at 8:30

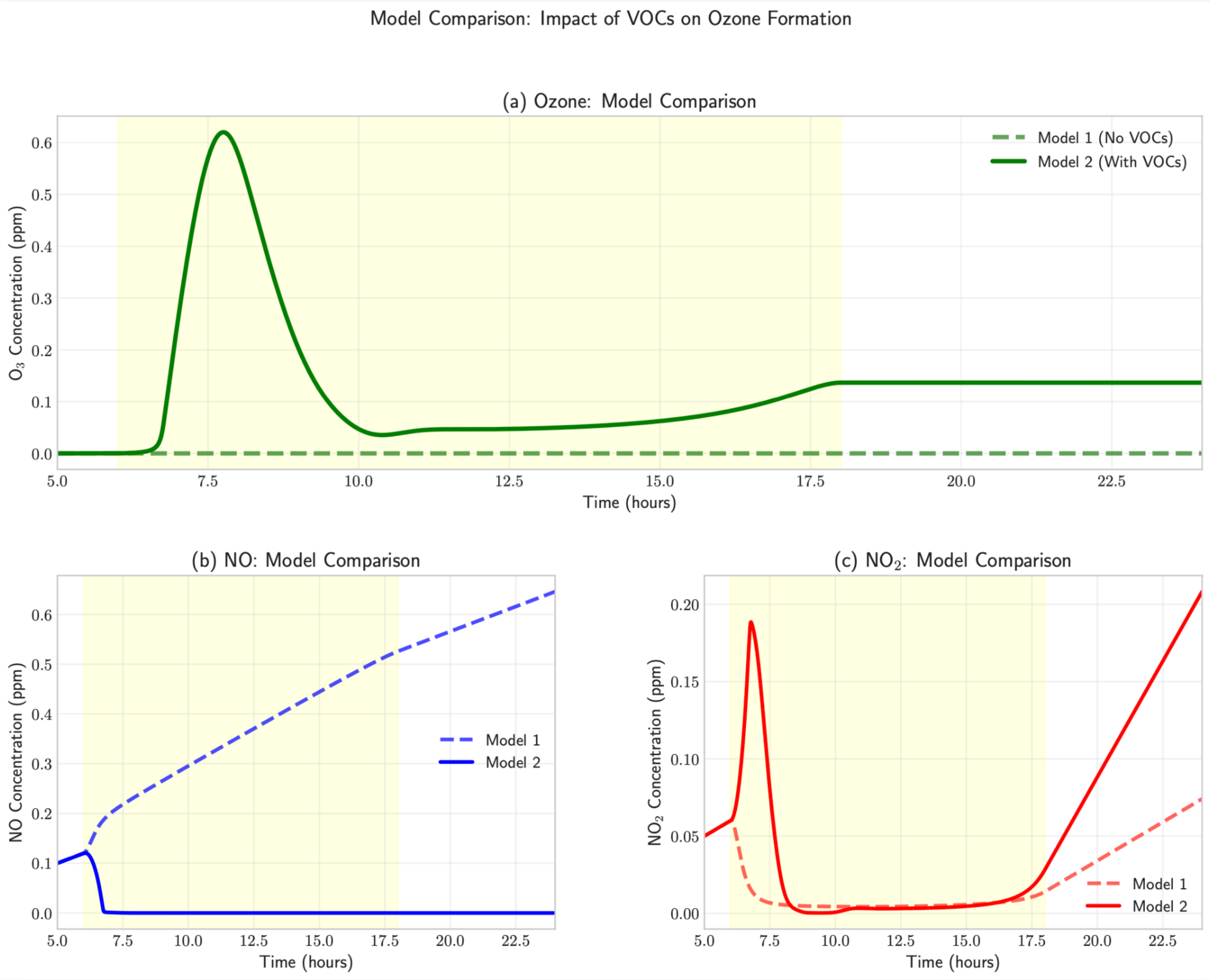
Detailed Findings:

1. **Radical dynamics**: OH, HO_2, RO_2 peak at noon (10^{-6}-10^{-3} ppm)
2. **VOC consumption**: ALK $\downarrow$ 27%, OLE $\downarrow$ 100% (fully depleted)
3. **Pathway dominance at peak O_3**:
   - RO_2 + NO: 94.5%
   - HO_2 + NO: 2.9%
   - O_3 titration: only 2.6%
4. **NO_x budget**: Decreases 0.15 $\rightarrow$ 0.08 ppm (HNO_3 formation)
5. **Catalytic amplification**: Trace OH (10^{-6} ppm) produces substantial O_3

Comparison

Metric	**Model 1**	**Model 2**
Species	4	11
Reactions	5	15
Peak O_3 (ppm)	3×10^{-6}	0.6
Peak time	11:00	13:30
Enhancement	1x	$200,000\times$
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
(a) Ozone: Model Comparison
Model 1 (No VOCs)
Model 2 (With VOCs)
O3 Concentration (ppm)
Time (hours)
(b) NO: Model Comparison
Model 1
Model 2
NO Concentration (ppm)
Time (hours)
(c) NO2: Model Comparison
Model 1
Model 2
NO2 Concentration (ppm)
Time (hours)


Model Comparison: Impact of VOCs on Ozone Formation
(a) Ozone: Model Comparison
Model 1 (No VOCs)
Model 2 (With VOCs)
O_3 Concentration (ppm)
Time (hours)
(b) NO: Model Comparison
Model 1
Model 2
NO Concentration (ppm)
Time (hours)
(c) NO_2: Model Comparison
Model 1
Model 2
NO_2 Concentration (ppm)
Time (hours)

THANK YOU

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