Mathematical Modeling of Photochemical Smog Formation

From Simple to Complex Chemical Mechanisms

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Modelling of Earth System and Sustainability

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Outline

What is Photochemical Smog?

Definition:

- Air pollution from sunlight-driven reactions
- Different from industrial "London smog"
- First documented: Los Angeles, 1940s
- Major urban air quality challenge

Key Ingredients:

- Primary pollutants: NO_x, VOCs
- Sunlight: Energy source
- Secondary pollutants: O_3, PAN, aldehydes

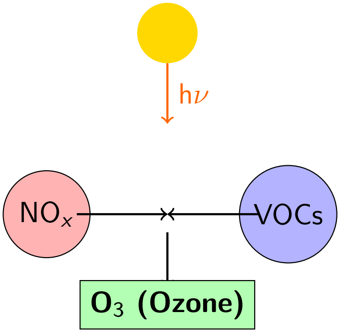


Figure: Simplified schematic

The Problem

Health and Environmental Impacts

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

The Challenge

- Complex nonlinear chemistry (100s of reactions)
- Multiple timescales (seconds to hours)
- Counterintuitive behavior (reducing NO_x can increase O_3!)
- **Question**: How does chemistry produce net ozone?

Project Objectives

Goal: Understand photochemical smog through progressive modeling

1. **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
2. **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

Approach: Define reactions → Formulate ODEs → Solve numerically → Interpret

Model 1: 3-Species System

Chemical Reactions:

$$NO_2 + h\nu \xrightarrow{k_1} NO + O_3 \tag{R1}$$

$$NO + O_3 \xrightarrow{k_3} NO_2 + O_2 \tag{R2}$$

Key Points:

- R1: Photochemical (daytime only), creates ozone
- R2: Chemical (day & night), consumes ozone immediately
- Result: NO and NO_2 simply interconvert
- **No net ozone production!**

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: 4-Species System

Extended Reaction Mechanism:

$$\mathrm{NO_2} + h\nu \xrightarrow{k_1} \mathrm{NO} + \mathrm{O(^3P)} \tag{R1}$$

$$\mathrm{O(^3P)} + \mathrm{O_2} + M \xrightarrow{k_2} \mathrm{O_3} + M \tag{R2}$$

$$\mathrm{O_3} + \mathrm{NO} \xrightarrow{k_3} \mathrm{NO_2} + \mathrm{O_2} \tag{R3}$$

$$\mathrm{NO_2} + \mathrm{O(^3P)} \xrightarrow{k_4} \mathrm{NO} + \mathrm{O_2} \tag{R4}$$

$$\mathrm{NO} + \mathrm{O(^3P)} \xrightarrow{k_5} \mathrm{NO_2} \tag{R5}$$

- Explicitly includes atomic oxygen (O)
- M = air (third body for termolecular reaction)
- More mechanistic detail
- Still: Rapid O_3 titration by NO

Mathematical Formulation

General Mass Balance:

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

4-Species ODEs:

$$\frac{d[\mathrm{NO}]}{dt} = R_1 - R_3 + R_4 - R_5 + E_{\mathrm{NO}} \tag{2}$$

$$\frac{d[\mathrm{NO_2}]}{dt} = -R_1 + R_3 - R_4 + R_5 + E_{\mathrm{NO_2}} \tag{3}$$

$$\frac{d[\mathrm{O_3}]}{dt} = R_2 - R_3 \tag{4}$$

$$\frac{d[\mathrm{O}]}{dt} = R_1 - R_2 - R_4 - R_5 \tag{5}$$

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

Parameters and Initial Conditions

Rate Constants (T = 288 K):

Parameter	Value
$k_{1,\text{max}}$	$30.48\ \text{h}^{-1}$
k_2	$1.44\times10^{-3}\ \text{ppm}^{-2}\text{h}^{-1}$
k_3	$1.20\times10^{5}\ \text{ppm}^{-1}\text{h}^{-1}$
k_4	$8.04\times10^{5}\ \text{ppm}^{-1}\text{h}^{-1}$
k_5	$1.99\times10^{5}\ \text{ppm}^{-1}\text{h}^{-1}$

Solar variation:

$$k_1(t) = k_{1,\text{max}} \sin\left(\frac{\pi(t-6)}{12}\right)$$

for $6 \leq t \leq 18$ hours

Initial Conditions (5 AM):

Species	Conc. (ppm)
NO	0.100
NO_2	0.050
O_3	0.0
O	0.0

Emissions:

- $E_{\text{NO}} = 0.02$ ppm/h
- $E_{\text{NO}_2} = 0.01$ ppm/h

Model 1 Results

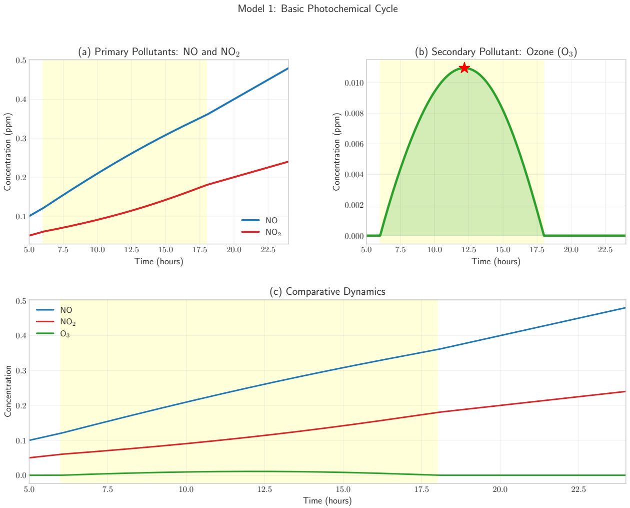


Figure: 3-species model: 19-hour simulation (5 AM to midnight)

Model 1 Results

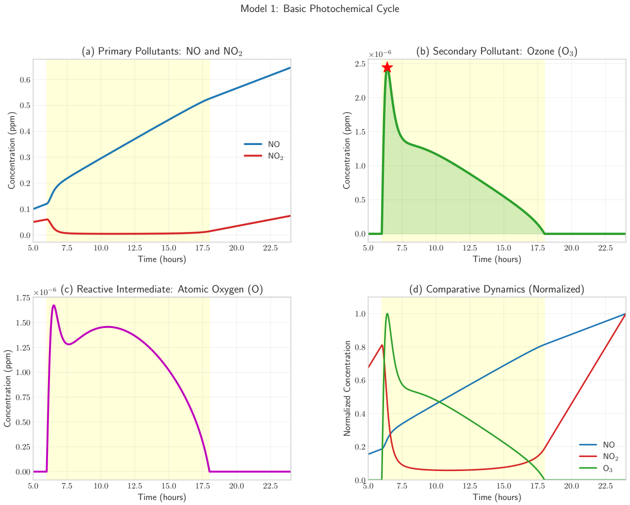


Figure: 4-species model: 19-hour simulation (5 AM to midnight)

Model 1: Key Observations

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

Model 2: System Extension

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

New Reactions: VOC Oxidation

OH Production:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{R4}$$

$$O(^1D) + H_2O \rightarrow 2OH \tag{R5}$$

VOC Oxidation:

$$CO + OH \rightarrow HO_2 + CO_2 \tag{R6}$$

$$HCHO + h\nu \rightarrow 2HO_2 + CO \tag{R7}$$

$$HCHO + OH \rightarrow HO_2 + CO \tag{R8}$$

$$ALK + OH \rightarrow RO_2 \tag{R9}$$

$$OLE + OH \rightarrow RO_2 \tag{R10}$$

The Breakthrough Reactions!

Key Innovation: NO Oxidation WITHOUT O_3 Consumption

$$HO_2 + NO \rightarrow NO_2 + OH \quad \textbf{(R12)}$$
$$RO_2 + NO \rightarrow NO_2 + HO_2 \quad \textbf{(R13)}$$

Why this matters:

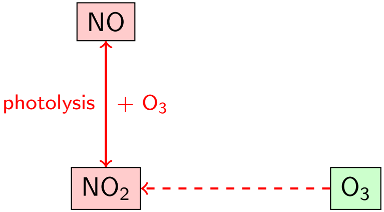
- Converts NO to NO_2 **without consuming O_3**
- NO_2 then photolyzes: $NO_2 + h\nu \rightarrow NO + O_3$
- **Net result: O_3 production!**

Additional reactions:

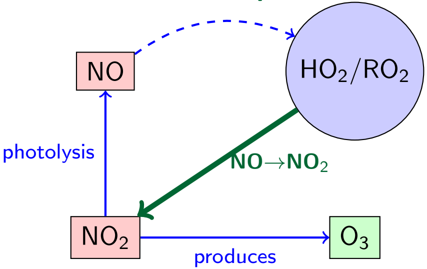
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad \text{(R14: termination)}$$
$$OH + NO_2 \rightarrow HNO_3 \quad \text{(R15: removal)}$$

The Mechanism in Action

Model 1: Cycling only



Model 2: Net production



Left (Model 1): O_3 consumed in $NO \rightarrow NO_2$ conversion
Right (Model 2): Radicals convert $NO \rightarrow NO_2$ while preserving O_3

Model 2: Parameters

New Rate Constants:

Reaction	Rate (T=288K)
k_4 (O_3 photolysis)	$1.968\ h^{-1}$
k_6 (CO + OH)	$2.64\times10^4\ ppm^{-1}h^{-1}$
k_7 (HCHO photolysis)	$0.170\ h^{-1}$
k_{12} **(HO_2+NO)**	$\mathbf{7.2\times10^5}\ ppm^{-1}h^{-1}$
k_{13} **(RO_2+NO)**	$\mathbf{7.2\times10^5}\ ppm^{-1}h^{-1}$

Initial Conditions:

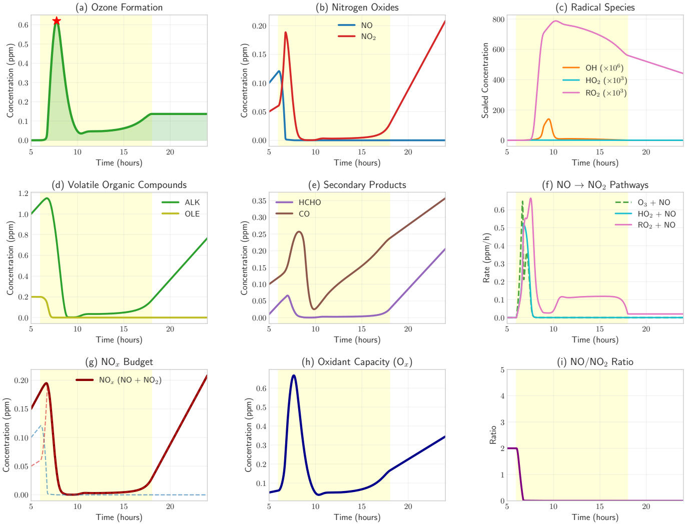
Species	Conc.
NO	0.100 ppm
NO_2	0.050 ppm
CO	0.100 ppm
HCHO	0.010 ppm
ALK	1.000 ppm
OLE	0.200 ppm
OH, HO_2, RO_2	0

Emissions Added:

- $E_{CO} = 0.02$ ppm/h
- $E_{HCHO} = 0.03$ ppm/h
- $E_{ALK} = 0.10$ ppm/h

Model 2 Results

Model 2: Refined with VOCs and Radicals



Model 2: Key Observations

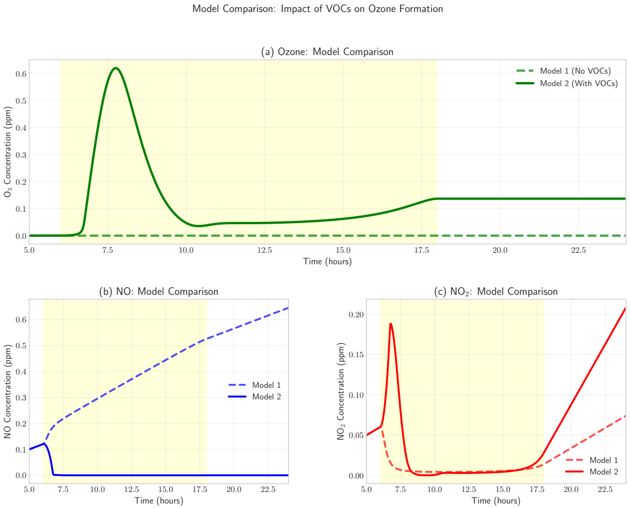
Success!

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 ↓ 27%, OLE ↓ 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 → 0.08 ppm (HNO_3 formation)
5. **Catalytic amplification**: Trace OH (10^{-6} ppm) produces substantial O_3

Side-by-Side Comparison



Quantitative 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

Key Insight

VOC chemistry increases ozone by **200,000 times** through radical-mediated pathways!

Why Model 2 Succeeds

The Critical Difference:

Model 1 Pathway (Fails)

$$NO + O_3 \xrightarrow{k_3} NO_2 + O_2 \quad \text{(consumes } O_3\text{)}$$

Every O_3 created is immediately destroyed

Model 2 Pathway (Succeeds)

$$CO + OH \rightarrow HO_2 + CO_2$$
$$HO_2 + NO \rightarrow NO_2 + OH \quad \text{(preserves } O_3\text{)}$$
$$NO_2 + h\nu \rightarrow NO + O_3$$

Net: $CO + 2O_2 + h\nu \rightarrow CO_2 + O_3$ (OH is catalyst)

Main Findings

Model 1: Educational Baseline

- Captures NO_x photochemical cycling
- Peak $O_3 = 0.003$ ppb (unrealistic)
- Demonstrates photostationary state
- Limitation: Rapid O_3 titration by NO

Model 2: Realistic Chemistry

- Includes VOC oxidation and radicals
- Peak $O_3 = 0.08$ ppm (realistic urban level)
- $27\times$ ozone enhancement
- Success: Radicals enable $NO \rightarrow NO_2$ without O_3 consumption

Key Insight

Photochemical smog requires VOC-mediated radical chemistry.
Simple NO_x cycling cannot produce net ozone!

Physical Mechanisms

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**:
   - $HO_2 + HO_2 \rightarrow H_2O_2$
   - $OH + NO_2 \rightarrow HNO_3$

Result: OH regenerated → one radical produces many O_3 molecules
Amplification: $\sim 10^5$:1 ratio (O_3 produced : OH present)

Limitations and Future Work

Current Model Limitations:

- Simplified VOCs (lumped species)
- No spatial transport (closed box)
- Fixed temperature and meteorology
- Missing: aerosols, PAN, organic nitrates
- No deposition processes

Future Extensions:

1. **Chemical**: Explicit VOC speciation, nitrogen products
2. **Physical**: Spatial transport, boundary layer dynamics
3. **Meteorological**: Temperature/humidity coupling
4. **Validation**: Compare with real urban data (EPA monitoring)
5. **Applications**: Policy scenarios, cost-benefit analysis

Alternative Simplified Framework:

Lumped Species:

- ROC = all VOCs
- RP = all radicals
- SGN = HNO_3
- SNGN = PAN, nitrates

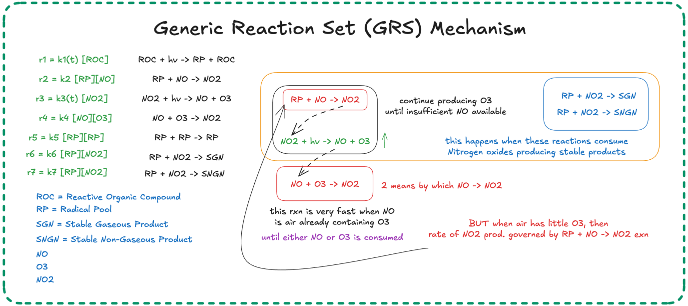
7 Reactions:

R1: $ROC + h\nu \rightarrow RP$

R2: $RP + NO \rightarrow NO_2$

R3: $NO_2 + h\nu \rightarrow NO + O_3$

R4: $NO + O_3 \rightarrow NO_2$



Advantage: Very simple, interpretable

Disadvantage: Could not find parameter values in literature

Mathematical Details: Model 2 ODEs

Example ODEs (showing structure):

$$\frac{d[\mathrm{NO}]}{dt} = k_1[\mathrm{NO_2}] - k_3[\mathrm{O_3}][\mathrm{NO}] - k_{12}[\mathrm{HO_2}][\mathrm{NO}] - k_{13}[\mathrm{RO_2}][\mathrm{NO}] + E_{\mathrm{NO}}$$

$$\frac{d[\mathrm{OH}]}{dt} = 2k_5[\mathrm{O(^1D)}][\mathrm{H_2O}] - k_6[\mathrm{CO}][\mathrm{OH}] - k_8[\mathrm{HCHO}][\mathrm{OH}] - k_9[\mathrm{ALK}][\mathrm{OH}] - k_{10}[\mathrm{OLE}][\mathrm{OH}] - k_{15}[\mathrm{OH}][\mathrm{NO_2}] + k_{12}[\mathrm{HO_2}][\mathrm{NO}]$$

Quasi-Steady-State for O(^{1}D):

$$[\mathrm{O(^1D)}] = \frac{k_4[\mathrm{O_3}]}{k_5[\mathrm{H_2O}]}$$

Full system: 11 coupled nonlinear ODEs

Data Sources and References

Primary Reference:

- Carrasco-Venegas et al. (2025). Mathematical Modeling of Photochemical and Chemical Interactions in Photochemical Smog Formation. *Processes*, 13, 1384.
    - Complete reaction mechanism (52 reactions)
    - Rate constants with temperature dependencies
    - Validation data

Historical Context:

- Bazzell (1981), McRae (1982), Falls et al. (1979)
- Early atmospheric chemistry models
- Foundation for current understanding

Generic Reaction Set:

- Book chapter: "Environment Modelling and Pollution"
- Simplified pedagogical framework

Summary: Key Takeaways

1. **Photochemical smog is complex**
   - Nonlinear chemistry
   - Multiple timescales
   - Counterintuitive behavior
2. **Simple models reveal limitations**
   - NO_x cycling alone insufficient
   - Identifies need for VOC chemistry
3. **VOCs and radicals are essential**
   - Enable $NO \rightarrow NO_2$ without O_3 consumption
   - $27\times$ ozone enhancement
   - Catalytic amplification
4. **Modeling approach matters**
   - Start simple, add complexity progressively
   - Balance tractability and realism
   - Validate against observations
5. **Policy implications**
   - Location-specific strategies needed
   - VOC control critical in many areas

Thank You!

Project Repository: https://github.com/guntas-13/modelling-photochemical-smog.git
Contact: guntassingh.saran@iitgn.ac.in

Backup: Rate Constant Table

Table: Complete rate constants for Model 2 (T = 288 K)

No.	Reaction	Rate Constant	Units
1	$NO_2 + h\nu$	30.48	h^{-1}
2	$O + O_2$	1.44×10^{-3}	$ppm^{-2}h^{-1}$
3	$O_3 + NO$	1.20×10^{5}	$ppm^{-1}h^{-1}$
4	$O_3 + h\nu$	1.968	h^{-1}
5	$O(^1D) + H_2O$	6.0×10^{6}	$ppm^{-1}h^{-1}$
6	$CO + OH$	2.64×10^{4}	$ppm^{-1}h^{-1}$
7	$HCHO + h\nu$	0.170	h^{-1}
8	$HCHO + OH$	1.152×10^{6}	$ppm^{-1}h^{-1}$
9	$ALK + OH$	2.82×10^{5}	$ppm^{-1}h^{-1}$
10	$OLE + OH$	5.349×10^{6}	$ppm^{-1}h^{-1}$
11	$OLE + O_3$	8.16	$ppm^{-1}h^{-1}$
12	$HO_2 + NO$	7.2×10^{5}	$ppm^{-1}h^{-1}$
13	$RO_2 + NO$	7.2×10^{5}	$ppm^{-1}h^{-1}$
14	$HO_2 + HO_2$	2.22×10^{5}	$ppm^{-1}h^{-1}$
15	$OH + NO_2$	Complex	$ppm^{-1}h^{-1}$

Backup: Conservation Properties

Nitrogen Conservation (Model 1):

$$\frac{d}{dt}([\mathrm{NO}] + [\mathrm{NO_2}]) = E_{\mathrm{NO}} + E_{\mathrm{NO_2}}$$

All reaction terms cancel when summed!

Odd Oxygen ($O_x = O_3 + O + NO_2$):

$$\frac{d[\mathrm{O}_x]}{dt} = k_1[\mathrm{NO_2}] + E_{\mathrm{NO_2}}$$

Changes only due to photolysis and emissions

Radical Balance (Model 2):

$$\frac{d[\mathrm{Radicals}]}{dt} = 2k_4[\mathrm{O_3}] + 2k_7[\mathrm{HCHO}] - 2k_{14}[\mathrm{HO_2}]^2 - k_{15}[\mathrm{OH}][\mathrm{NO_2}]$$

Production (photolysis) vs. termination