Capstone Project Final Presentation

Automated Model Reduction for Atmospheric Chemical Mechanisms (AMORE Project)

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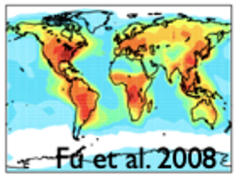
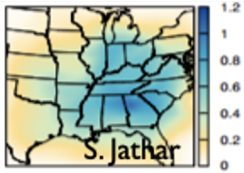
Atmospheric Chemistry Modeling: Bridging Scales

GLOBAL



REGIONAL



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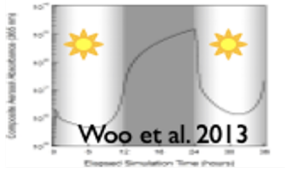
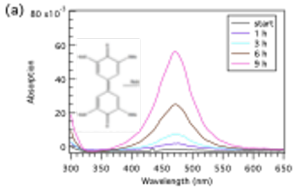


MOLECULAR

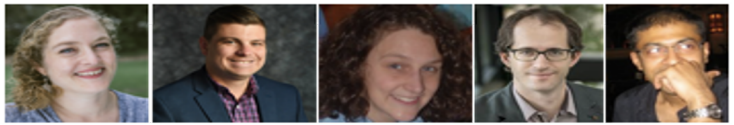


Length Scale

Computational expense

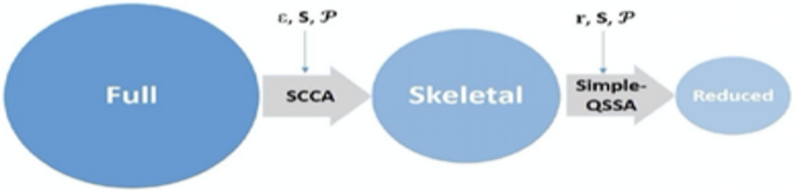
'Size' of chemical mechanism

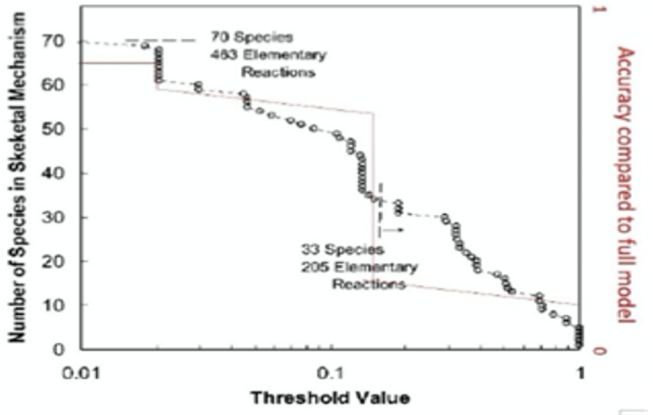
AMORE (Atmospheric Chemistry MOdel REduction)



An automated tool for flexibly generating accurate reduced chemical mechanisms for use in atmospheric chemistry and air quality models.

Two-step model reduction: graph theory-based strongly-connected component analysis followed by simplified quasi-steady state analysis





Introduction

Objective

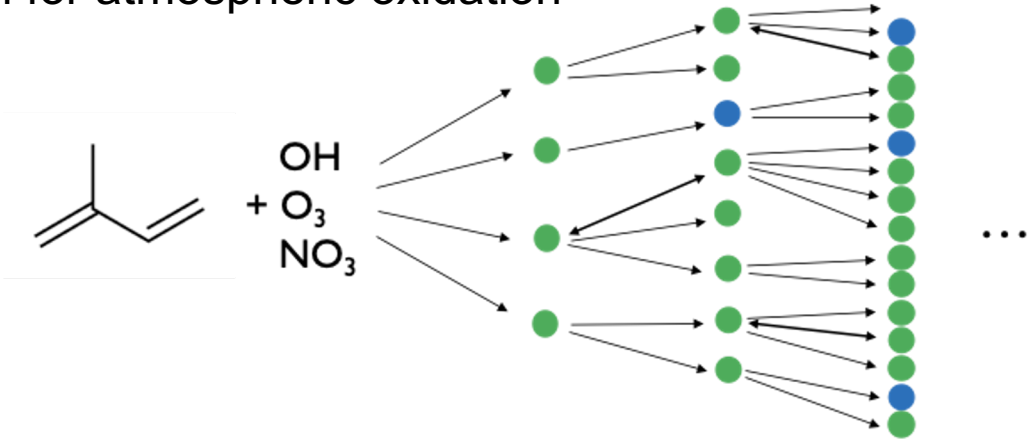
- Develop and implement a graph-based algorithm to automatically generate reduced gas-phase chemical mechanisms.
- Improve accuracy and efficiency of large-scaled atmospheric chemistry models.

Why it is meaningful?

- Enable the improved, sustained and consistent development of chemical mechanisms for air quality forecasting, research, and policy analysis.
- Understand the air quality, especially how air pollutants move in the atmosphere.
- Limitation of the computational complexity
- The chemical stiffness in the detailed chemical mechanisms

Dataset Overview

Isoprene: Fuel for atmospheric oxidation



Isoprene Mechanisms	Number of species	Number of reactions
MCM v.3.3.1	602	1926
CB05	18	9
CB6r2	38	22
GEOS-Chem v11.02c	106	335
GFDL-AM3	23	12
GISS ModelE	15	3
Paulot 2009 (high and low NOx, reduced)	45	28
Wennberg 2018 (full)	385	810

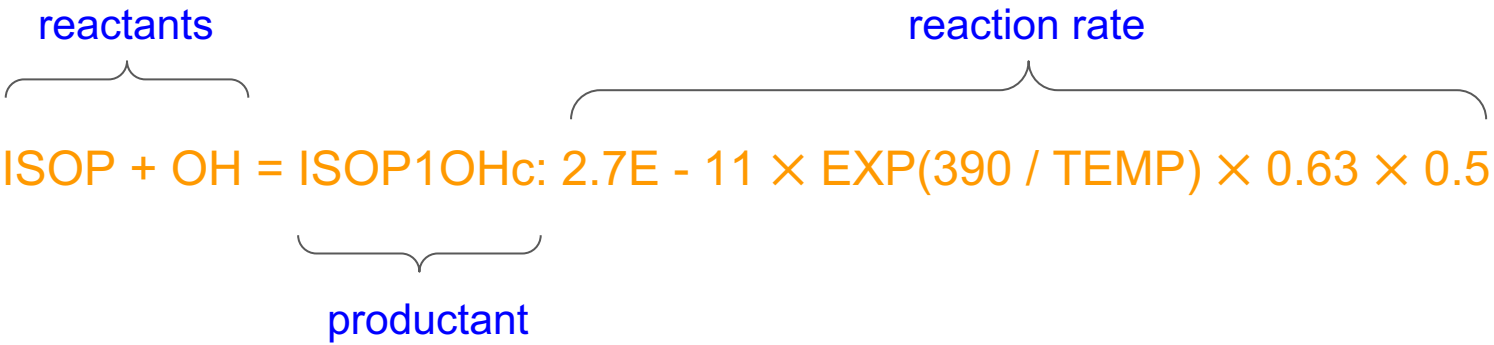
Dataset Format: **Kinetic Preprocessor (KPP) format**

- A file of chemical reactions in the full mechanism.
- A file of species involved in the full mechanism.
- A file contains editable input parameters and initial values of included species, temperature, etc.

Procedure

Data Preprocessing

An Example of Chemical Reaction



- A list of tuple with reaction and reaction rate formula

  (‘ISOP + OH = ISOP1OHc’, 2.7E - 11 × EXP(390 / TEMP) × 0.63 × 0.5)

Procedure

Data Preprocessing

ISOP + OH = ISOP1OHc: 2.7E - 11 × EXP(390 / TEMP) × 0.63 × 0.5

The weight of the reaction for the product

$$R_A = \sum_{i=1,I} v_{A,i} w_i$$

$v_{A,i}$: the stoichiometric of species A

w_i : the production rate

$$\begin{aligned} r_{ISOP1OHc} &= v_{ISOP1OHc,i} \times w_i \\ &= v_{ISOP1OHc,i} \times k \times c[ISOP] \times c[OH] \\ &= 1 \times 2.7E-11 \times EXP(390/TEMP) \times 0.63 \times 0.5 \times c[ISOP] \times c[OH] \end{aligned}$$

- k : the reaction rate for this particular reaction (equation)
- c[ISOP] and c[OH] are the initial concentration values of ISOP and OH respectively

Procedure

Data Preprocessing

How to measure the influence of one species on another?

$$r_{AB} = \frac{\sum |v_{A,i} w_i \delta_{Bi}|}{\sum |v_{A,i} w_i|}$$

Normalized contribution of species B to the production rate of species A

$$\delta_{Bi} = \begin{cases} 1, & \text{if the ith elementary reaction involves species B} \\ 0, & \text{otherwise} \end{cases}$$

Procedure

Graph Construction

Directed Relation Graph (DRG)

- Node: a species in the detailed mechanism
- Edge from A to B: A is dependent on B (the removal of B would directly induce significant error to the production rate of A)

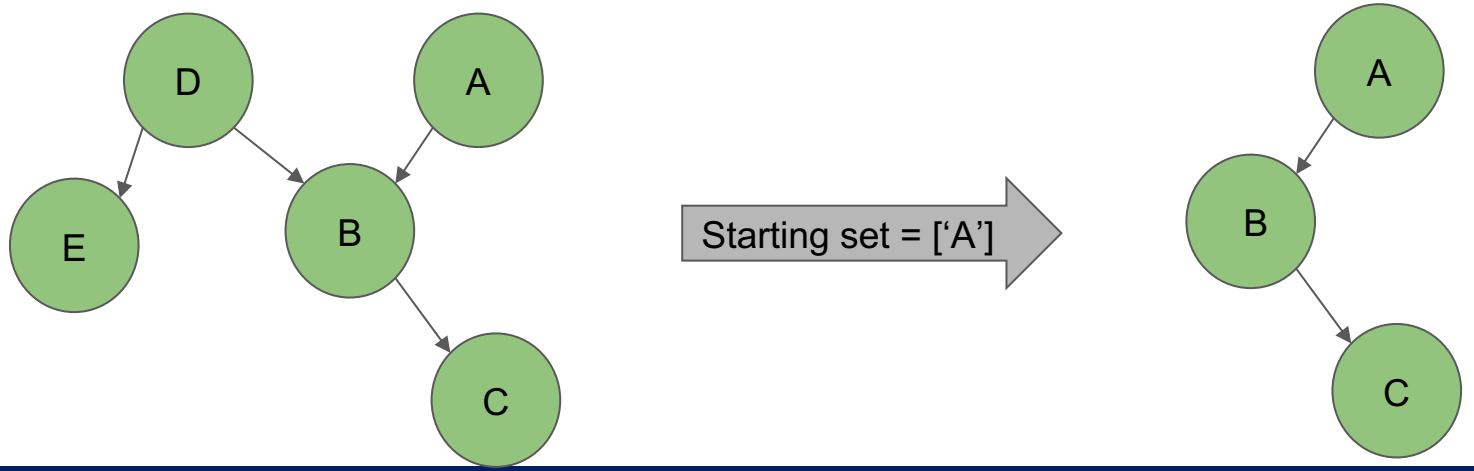
ISOP + OH = ISOP1OHc: 2.7E - 11 × EXP(390 / TEMP) × 0.63 × 0.5

Procedure

Graph Construction

Directed Relation Graph (DRG)

- Perform a depth first search starting from the ‘starting sets’ and obtain a skeleton graph
- We used organic species as starting sets while treating others as background species.

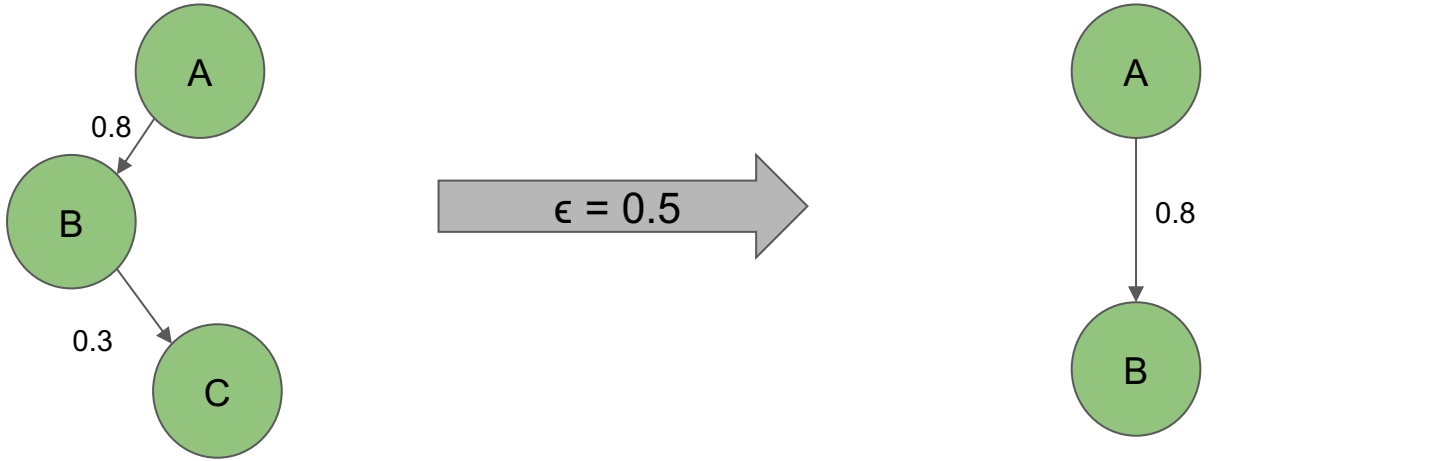


Procedure

Graph Reduction

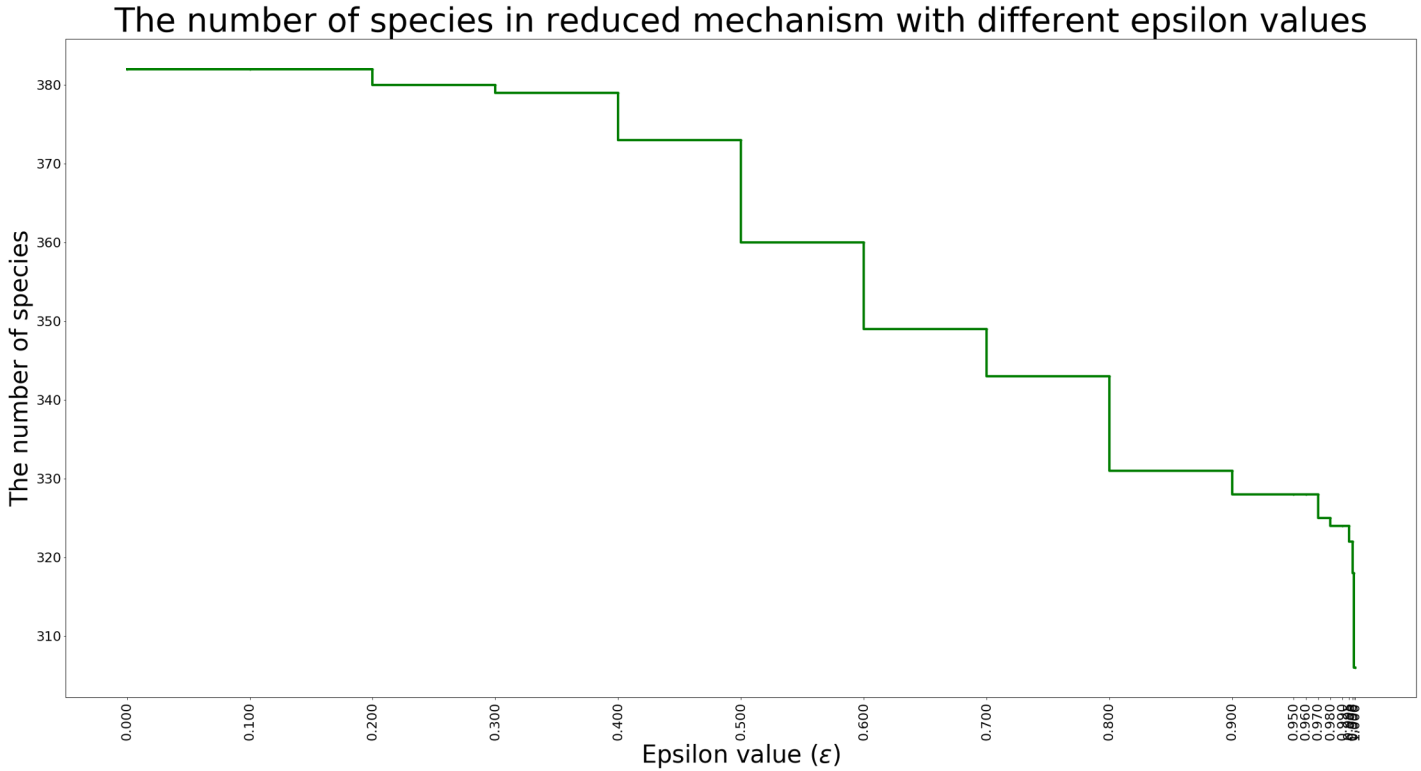
Method:

- Define a threshold value ϵ
- Only keep the paths that all the edges has a weight greater than ϵ such that $r_{AB} \geq \epsilon$



Results

The number of Species for various threshold values



Product

Python Package Chem_graph

We created a python package called chem_graph accessible on Github. Our product contains following functionalities:

- Read and parse the raw file, and construct the graph accordingly
- Given threshold value and starting set, compute the reduced graph and dependent set
- Visualize the graph

Product

Algorithm 1 Original DFS Approach

Given r_{AB} dictionary, list of ϵ E. starting set S
Create graph g based on r_{AB}
for *each* ϵ *in* E **do**
    create visited set v
    create stack s, push S into s
    while s *not empty* **do**
        pop one element e from s
        for *each neighbor* n *of* e **do**
            if the edge weight smaller than ϵ, continue
            if n visited, continue
            push n to v and s
        end
    end
    output v for ϵ
end

Algorithm 2 Modified DFS Approach

Given r_{AB} dictionary, list of ϵ E. starting set S
Sort r_{AB} dictionary based on the edge weight from high to low;
Sort E from high to low;
create visited set v
create set c to keep track of graph
for *each* ϵ *in* E **do**
    include new edges with value smaller than last ϵ_0 but larger than current ϵ
    for *each new edge* **do**
        if the destination node of the new edge is not visited, continue
        DFS from the destination node, push the newly visited to v
    end
    output current v for current ϵ
end

Running time: O(n(V+E))

Running time: O(nlog(n) + V+E)

Product

Sample Usage

```
from chem_graph import *
demo_graph = ChemGraph()
priority_species = ['ISOP1CO4OOHc']
demo_graph.construct(path='isoprene_full_v5', starting_set=priority_species, must_contain=['ISOP'])
```

File path

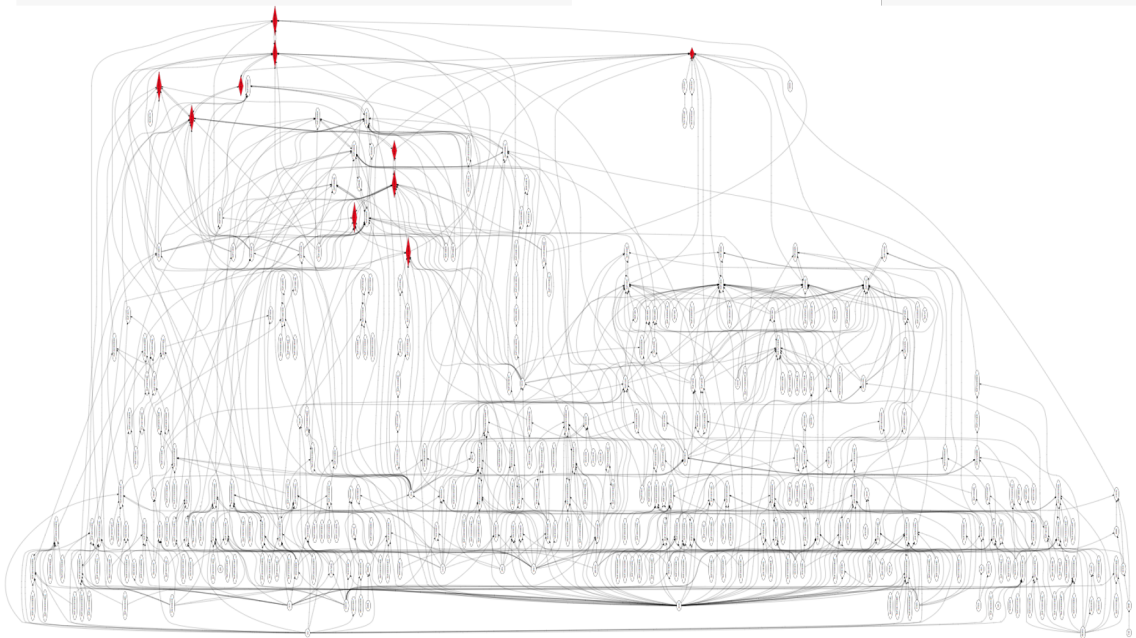
Starting set

Must contain

Product

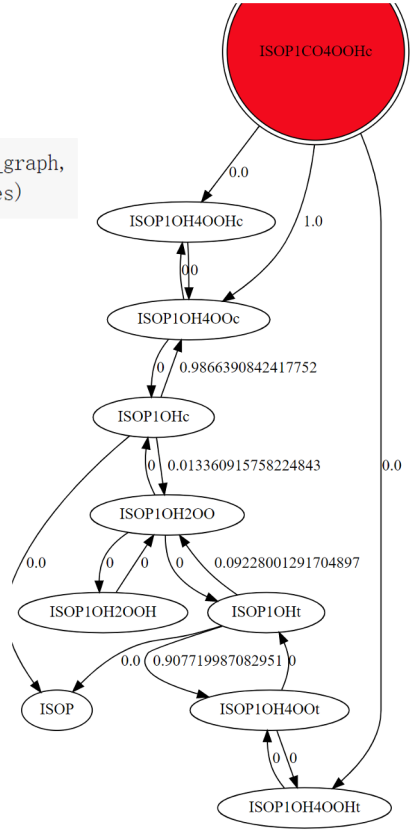
Sample Usage

```
visualize_graph(graph=demo_graph.whole_graph,
                highlight=priority_species)
```



Whole Graph

```
visualize_graph(graph=demo_graph.reduced_graph,
                highlight=priority_species)
```



Skeleton Graph

Future Direction

- Evaluation on the reduce mechanism
- Evaluation on the generated graph

References

[1] Lu, Tianfeng, and Chung K. Law.A directed relation graph method for mechanism reduction. Proceedings of the Combustion Institute 30.1 (2005) : 1333-1341.
[2] Sun, Wenting, et al. "A path flux analysis method for the reduction of detailed chemical kinetic mechanisms." Combustion and Flame 157.7 (2010): 1298-1307.
[3] V. Damian,et al. “The Kinetic PreProcessor KPP – A Software Environment for Solving Chemical Kinetics”, Computers and Chemical Engineering, Vol. 26, No. 11, p. 1567-1579, 2002
[4] Paulot, F, et al. “Isoprene photooxidation: new insights into the production of acids and organic nitrates”. Atmos. Chem. Phys. 9 (2009)
[5] Graphviz API Reference. https://graphviz.readthedocs.io/en/stable/api.html

Thank You!