Mechanism Reduction for the Formation of Secondary Organic Aerosol for Integration into a 3-D Air Quality Model

AdAm xiA

Diane Michelangeli

YORK UNIVERSITÉ UNIVERSITY
redefine THE POSSIBLE.

Paul Makar

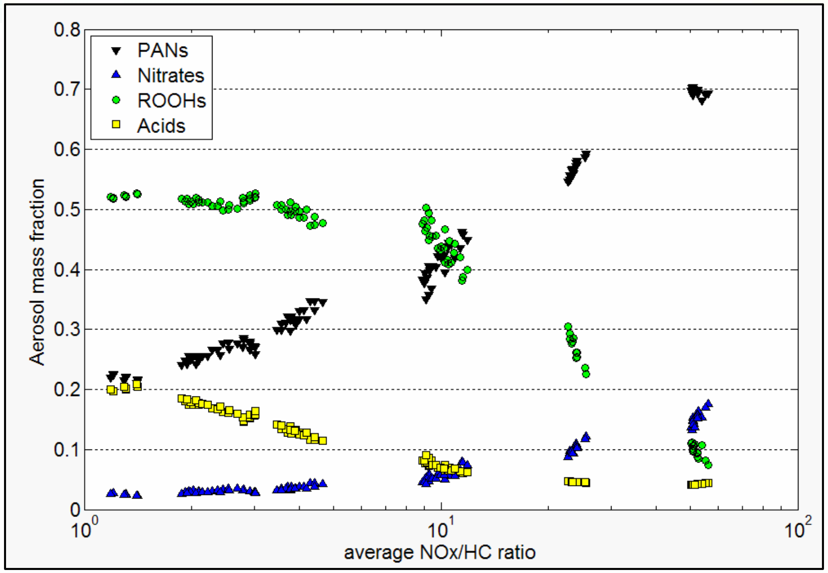
Environment Canada
Environnement Canada

Supported by NSERC

Objective

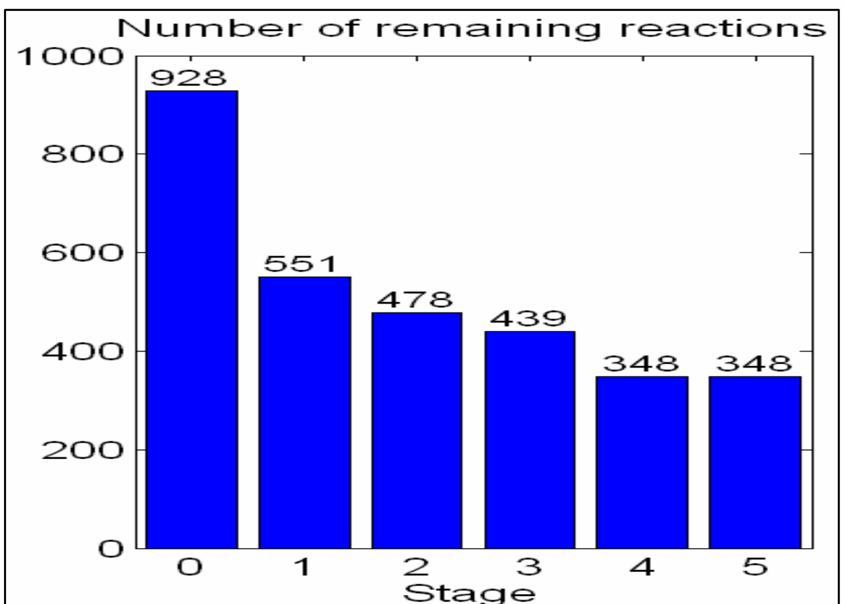
To obtain an **accurate & simple chemical mechanism** for the formation of secondary organic aerosol (SOA) and ozone in a 3D air quality model

Outline



Part I

Detailed mechanism (MCM)
for SOA formation



Part II

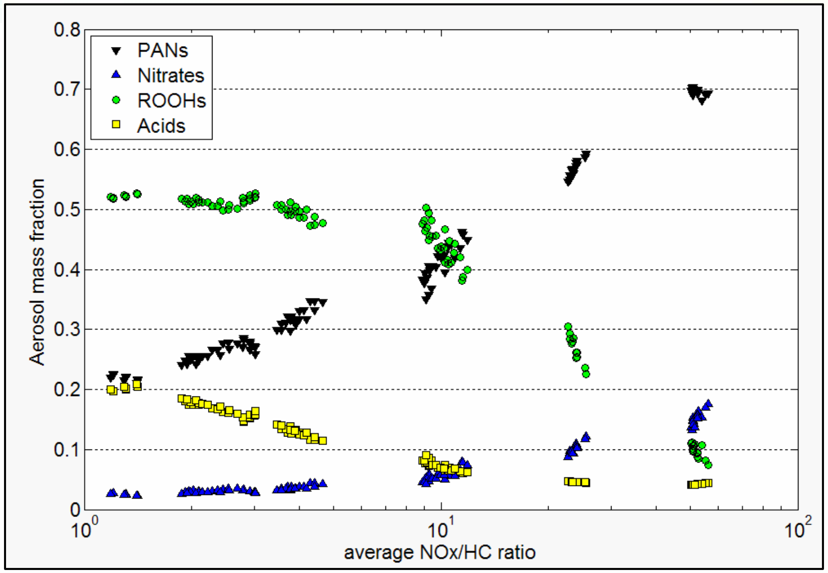
Systematic reduction of the <u>detailed mechanism</u>

Introduction

Chemical mechanisms for 3D Air Quality Models

- Most chemical mechanisms were developed primarily for ozone formation, not for SOA
- MCM can be a candidate, but too **expensive**
- Some simplified mechanisms for the SOA formation, such as MAM (Mainz Alpha-pinene Mechanism), are available, but no methodology
- **Systematic reduction techniques** are required to reduce the mechanism under a wide range of conditions.

Outline



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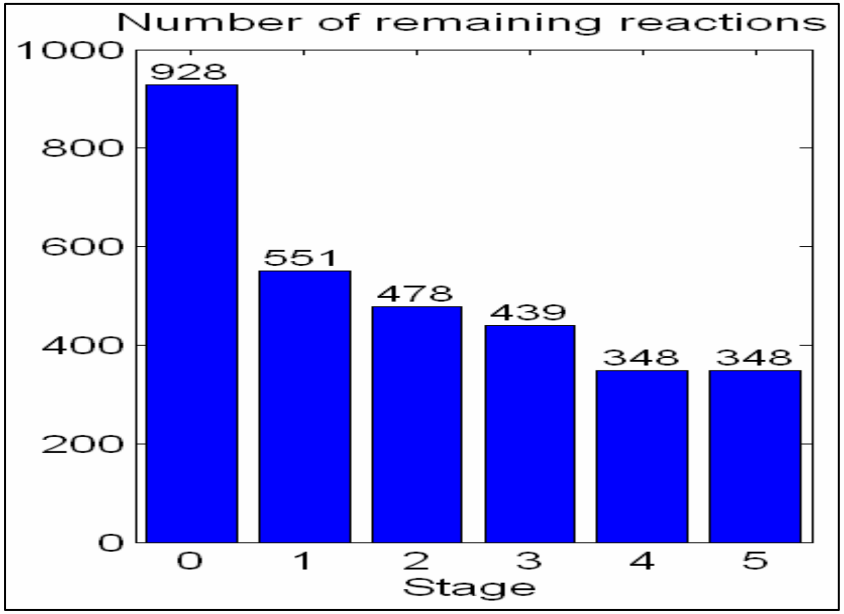


Part II

Systematic reduction of
the detailed mechanism

Model Settings for SOA formation

1. Chemistry (MCM v3.1 from http://mcm.leeds.ac.uk/MCM/)

α**-pinene** oxidation	Inorganic	**Organic**	Total
Number of species	21	**310**	331
Number of reactions	48	**928**	976

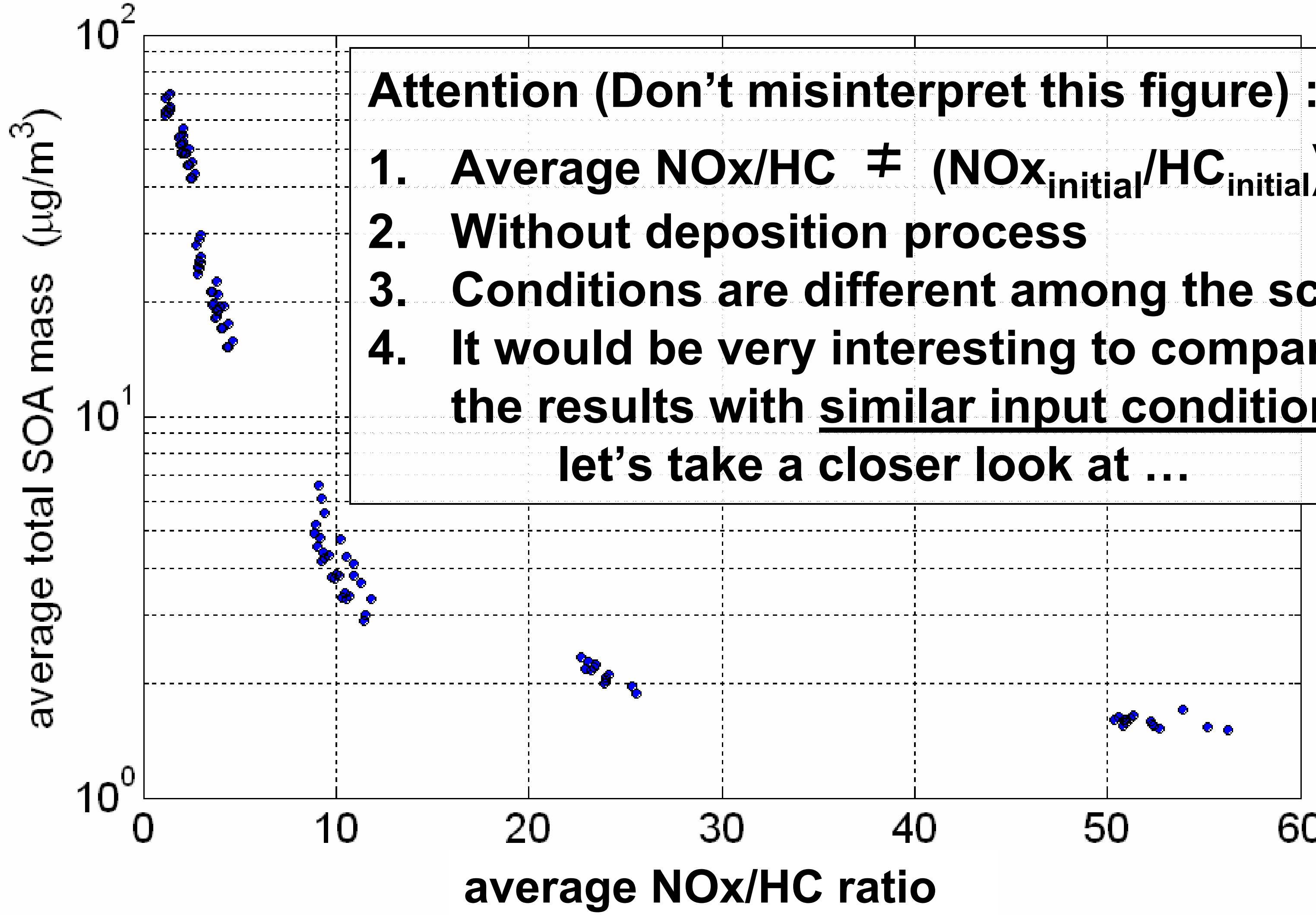
2. Model settings ***(108 selected scenarios—wide range of NOx/HC)***

- 0-D box model coupled with G/P partitioning process
- Different emission rates and initial concentrations
- Diurnal variations of temperature and RH
- Without deposition

3. Hourly data points from last two days (48 time points) are selected for data analysis

Model results of the full mechanism (1/3)

Summary of the 108 selected scenarios



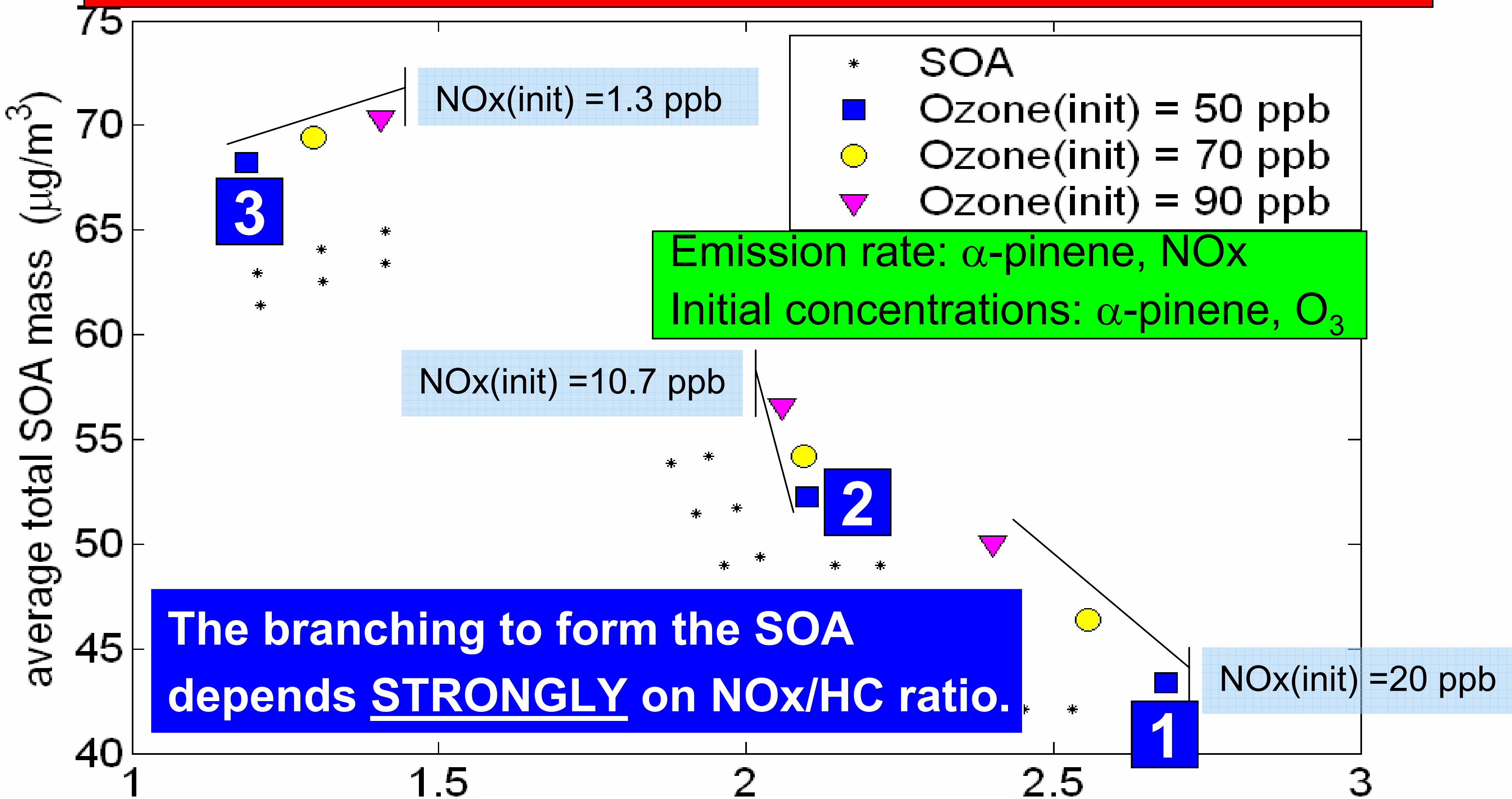
Attention (Don't misinterpret this figure) :

1. **Average NOx/HC ≠ ($NOx_{initial}/HC_{initial}$)**
2. **Without deposition process**
3. **Conditions are different among the scenarios**
4. **It would be very interesting to compare the results with <u>similar input conditions.</u>**

let's take a closer look at …

Model results of the full mechanism (1/2)

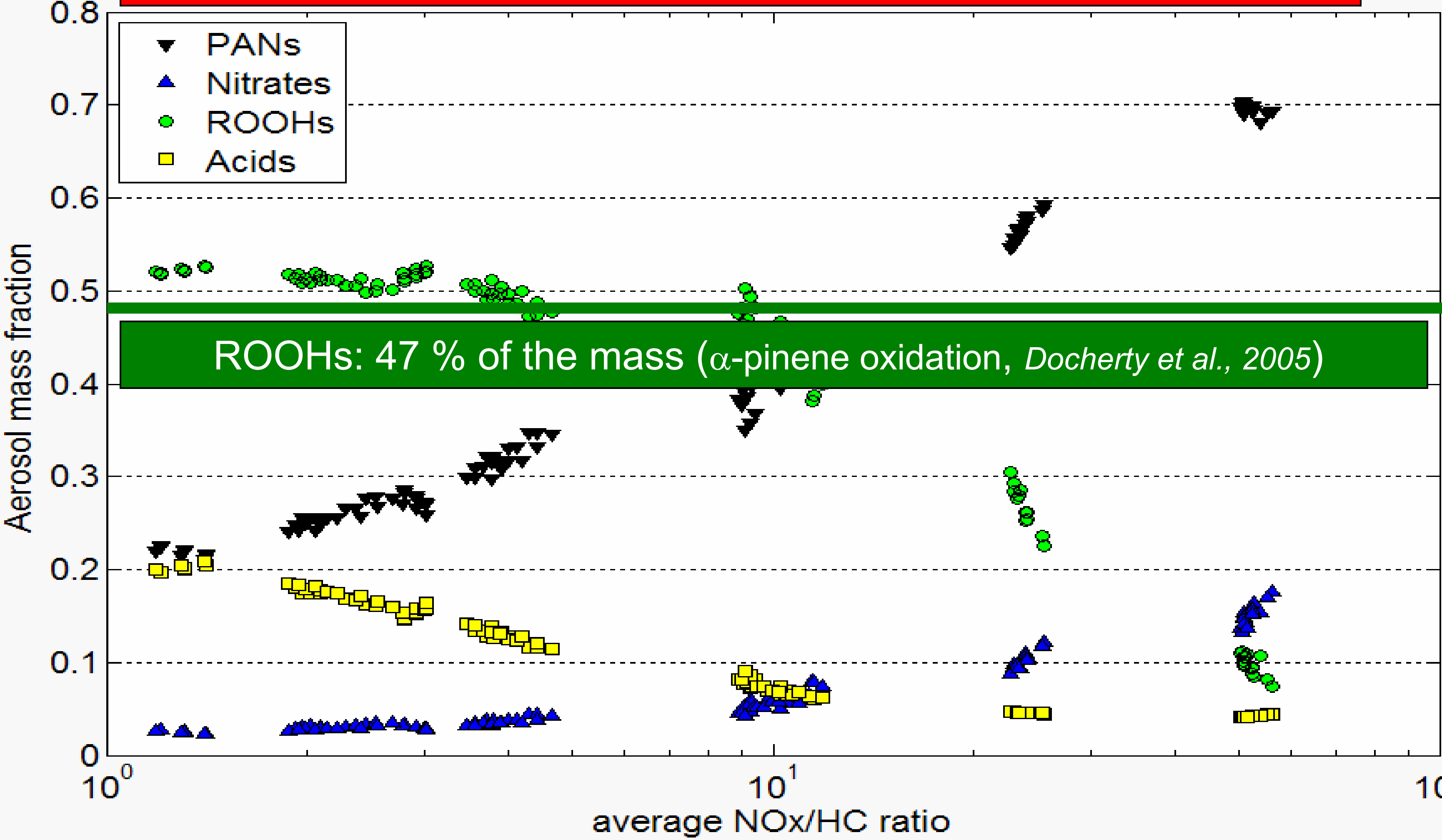
Total SOA mass changes with the NOx/HC



High NOx ⇨ products are more volatile ⇨ less SOA

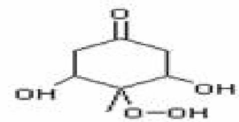
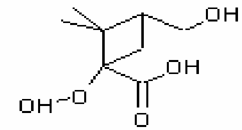
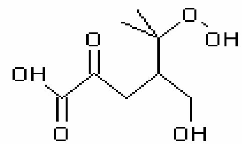
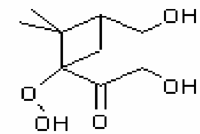
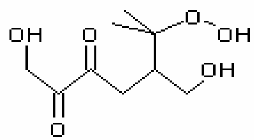
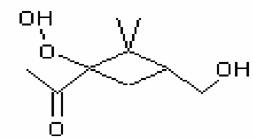
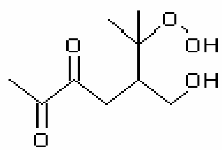
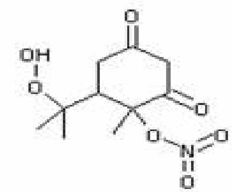
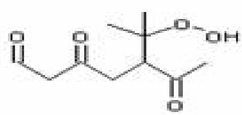
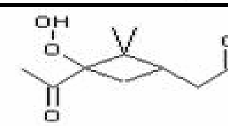
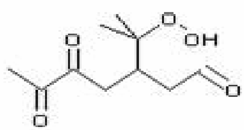
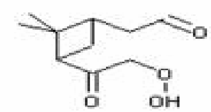
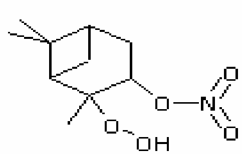
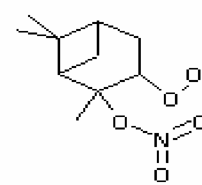
Model results of the full mechanism (2/2)

Organic aerosol mass compositions
change with the NOx/HC ratio



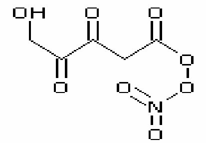
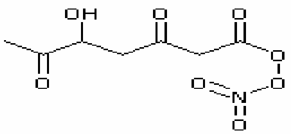
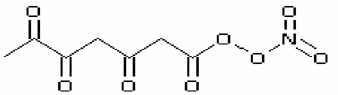
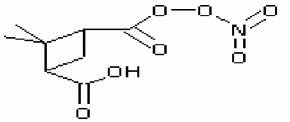
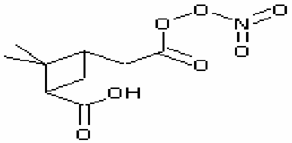
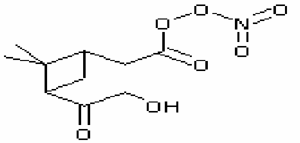
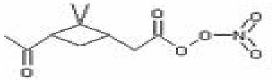
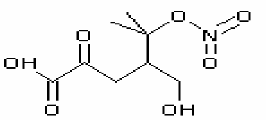
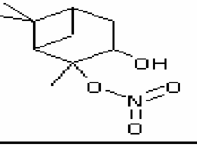
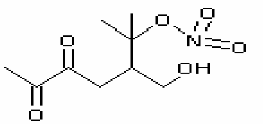
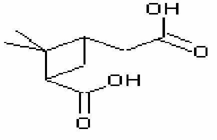
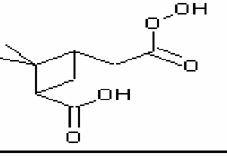
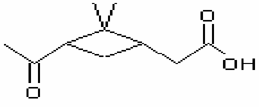
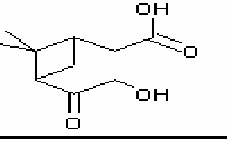
ROOHs: 47 % of the mass (α-pinene oxidation, *Docherty et al., 2005*)

28 important condensable compounds (1)

14 R-O-OH					
C719OOH		609	C812OOH		615
C813OOH		635	C921OOH		622
C922OOH		642	C97OOH		573
C98OOH		597	NC102OOH		643
C106OOH		594	C107OOH		570
C108OOH		594	C109OOH		577
NAPINAOOH		570	NAPINBOOH		570

Boiling point (K)

28 important condensable compounds (2)

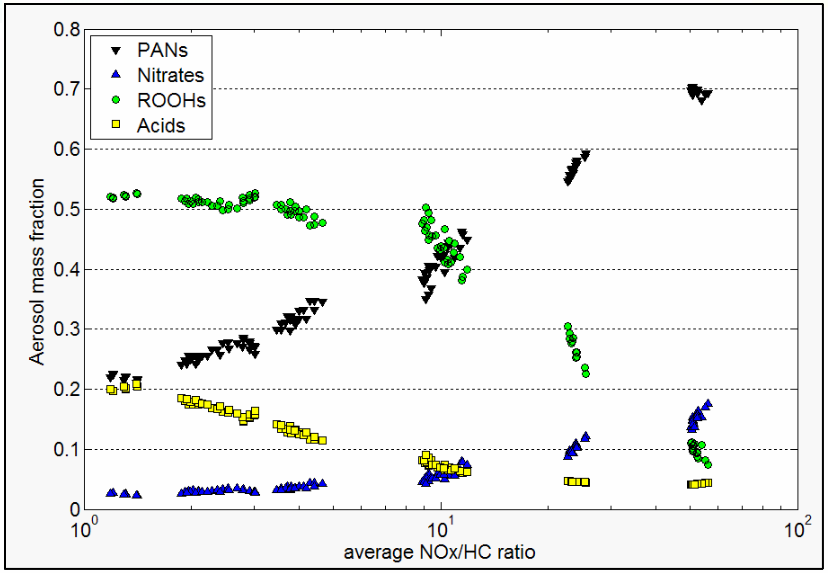
7 PAN					
H1C23C4PAN		601	H3C25C6PAN		615
C7PAN3		604	C721PAN		609
C811PAN		621	C920PAN		628
C10PAN2		580			
3 NO3					
C813NO3		640	APINANO3		559
C98NO3		603			
4 Acid					
PINIC		612	C811CO3H		602
PINONIC		569	HOPINONIC		619

Summary of SOA formation from MCM

1. Based on a detailed α**-pinene** oxidation scheme, **total SOA** formed is **NOx/HC dependent**, and **more SOA** is formed at **low NOx/HC**.

2. The **organic aerosol mass compositions** also change with the NOx/HC—the group of **ROOHs** is the **dominant** one at **low NOx/HC**.

Outline



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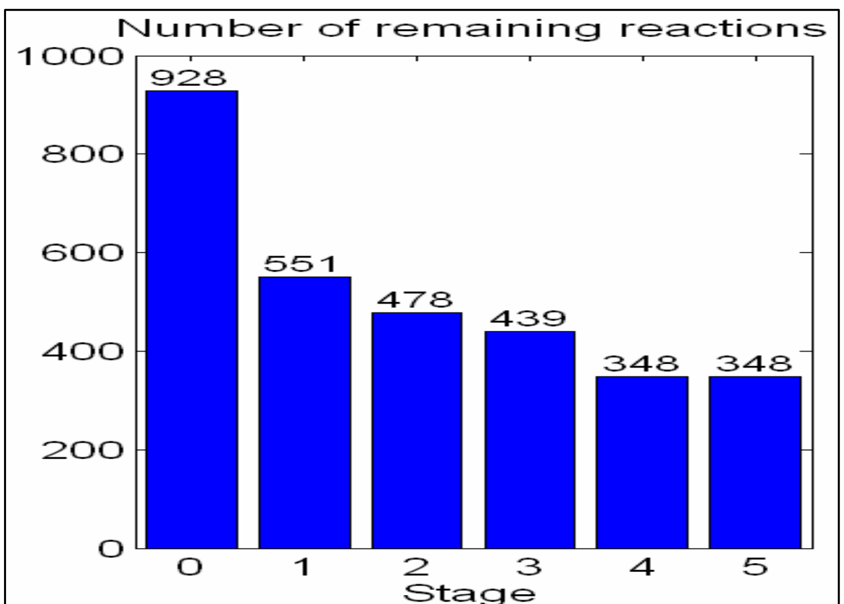


Part II

Systematic reduction of the detailed mechanism

Part II

Mechanism reduction techniques

Goal: remove unimportant species and reactions

Five stages:

1. DRG or DRGEP method ???
2. Principal component analysis (PCA)
3. Quasi-steady-state assumption (QSSA)
4. Iterative screening method (ISSA)
5. Linear lumping

Similar to rightsizing of a large company

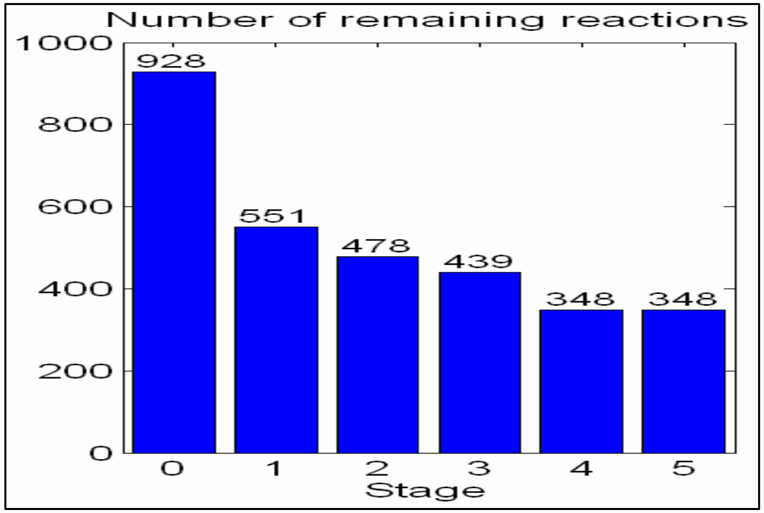
Rightsizing of a large company

Goal:
remove redundant people & departments/projects

Results:

People remained:
Important people
necessary people

Mechanism reduction



Goal:
remove redundant species & reactions

Major species

Species remained:
Important species
necessary species

1: Directed Relation Graph (DRG) *(Lu and Law 2005, 2006)*

Species contribution

Contribution coefficient (r_{AB})

$$r_{AB} \equiv \frac{\sum_{i=1,N} \left| \nu_{A,i} R_i \delta_{B,i} \right|}{\sum_{i=1,N} \left| \nu_{A,i} R_i \right|}$$

$\nu_{A,i}$: Stoich. coef. of ***A*** in ***i***th rxn

R_i : Reaction rate of ***i***th rxn

$\delta_{B,i}$ =1 if ***B*** is a reactant in ***i***th rxn

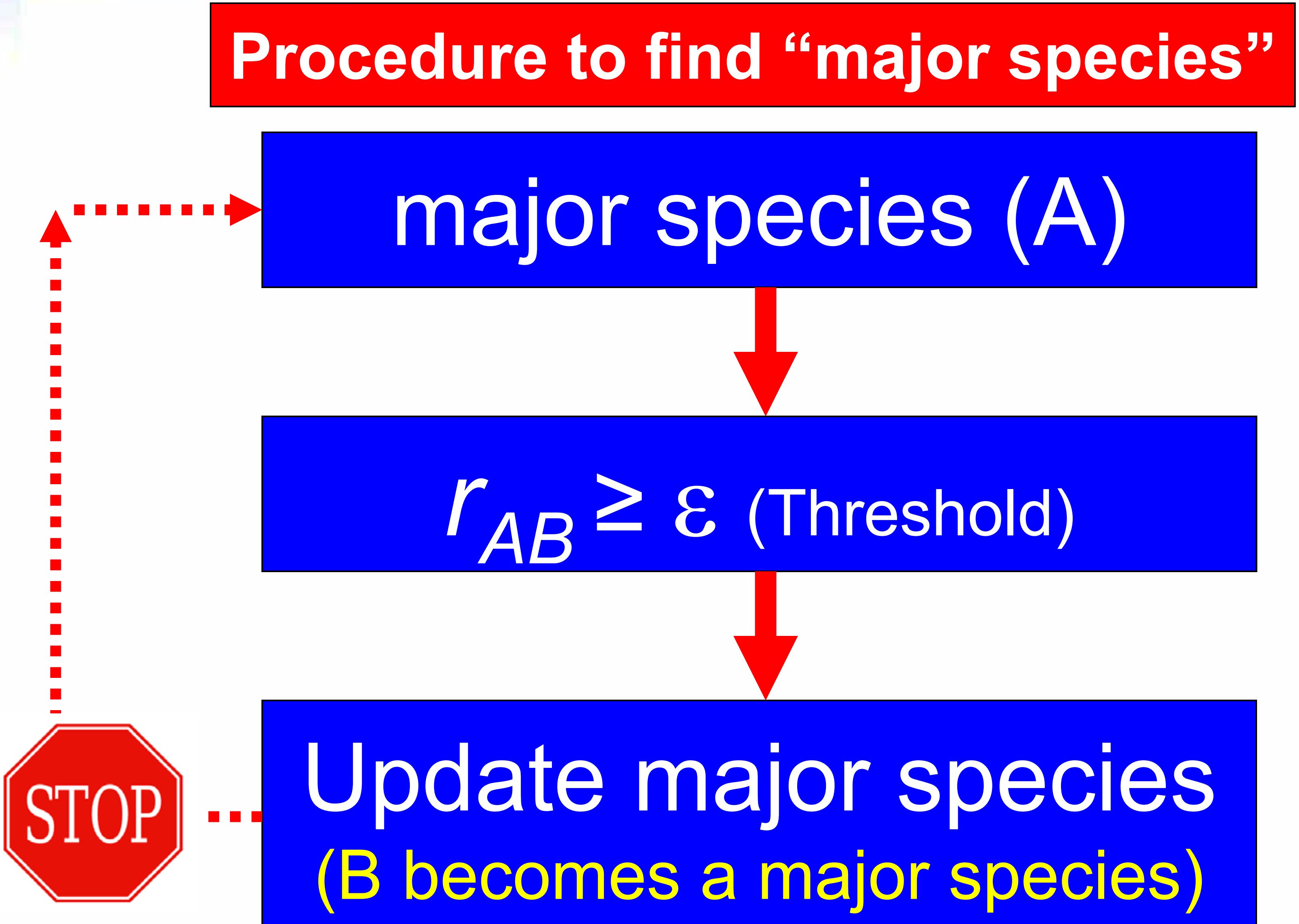
Example:

1) A + B => C	(k_1)	$R_1 = k_1 \times [A][B]$
2) A => B	(k_2)	$R_2 = k_2 \times [A]$
3) B => C	(k_3)	$R_3 = k_3 \times [B]$

Max(r_{AB})

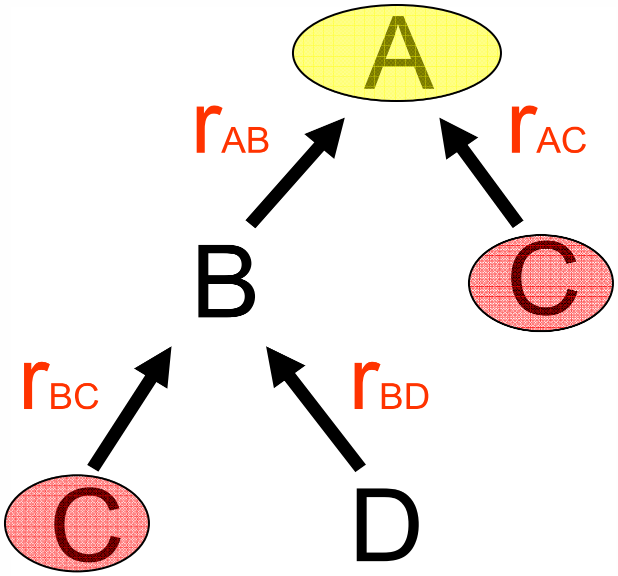
$$r_{AB} = \frac{\left|1 R_1 \times 1\right| + \left|1 R_2 \times 0\right| + \left|0 R_3 \times 1\right|}{\left|1 R_1\right| + \left|1 R_2\right| + \left|0 R_3\right|}$$

1: Directed Relation Graph (DRG)



1: DRG with error propagation (DRGEP)

(Pepiot and Pitsch, 2005)



Path-dependent coefficient:

Path #1: **C**→A $\quad r_{AC}$

Path #2: **C**→B→A $\quad r_{AB} \times r_{BC}$

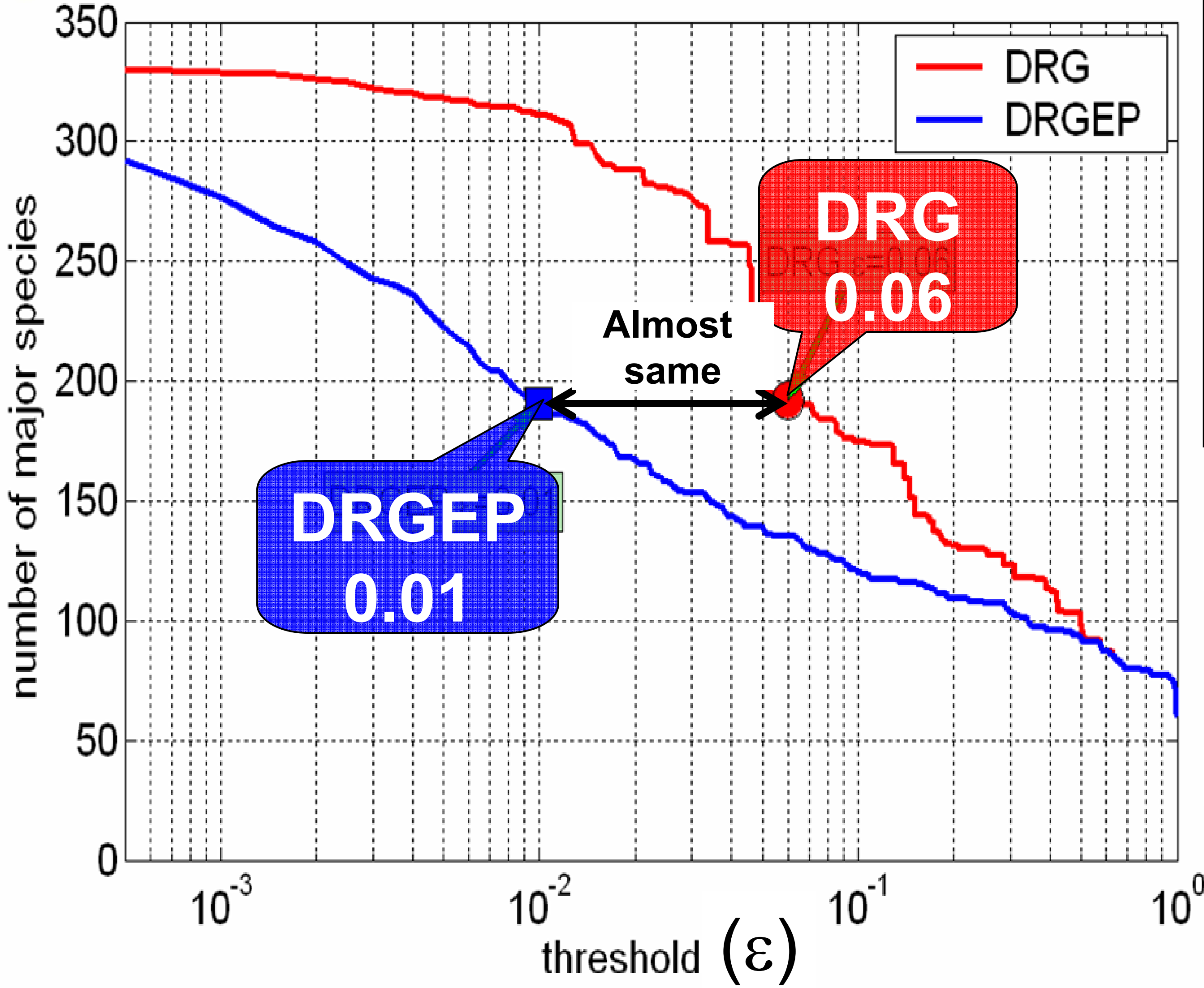
Generalized contribution coefficient

$$R_{AC} = \max\{r_{AB} \times r_{BC}, r_{AC}\}$$

In fact, R_{AC} is the ***maximum*** of **all Paths** from **C** to **A**.

Procedures: If $R_{AC} \geq \varepsilon$ (**given threshold**), then **C** is a *"major species" and* retained in the mechanism. **No Iteration.**

1:Comparison between DRG & DRGEP



39 important species:
- 1 α-pinene
- 28 condensable species
- 10 inorg. compounds
  - O_3 OH O^1D O
  - NO NO_2 NO_3
  - HNO_3 HO_2 H_2O_2

All inorganic species are kept

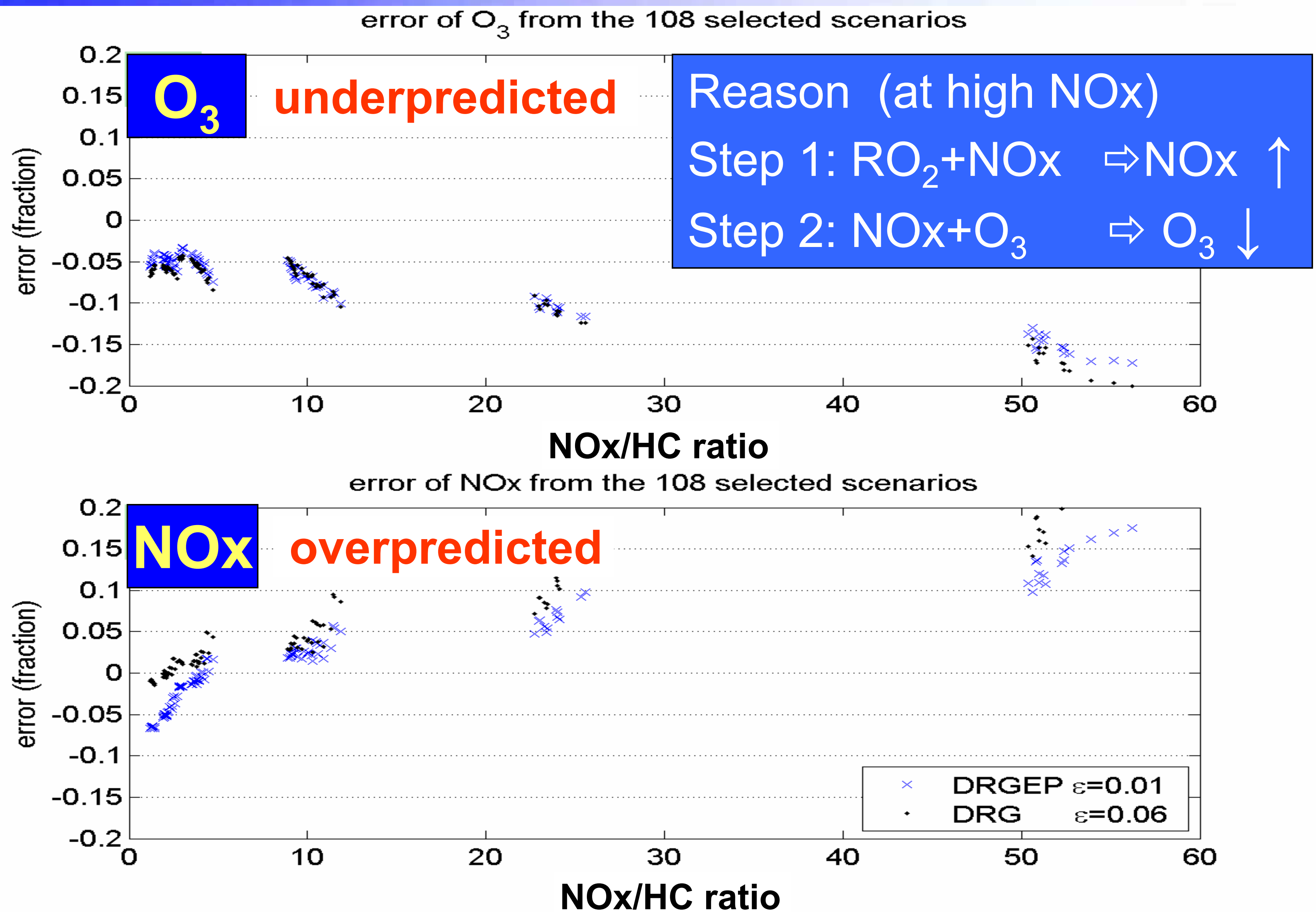
Species removed

DRG: 139
DRGEP: 140

Rxns removed

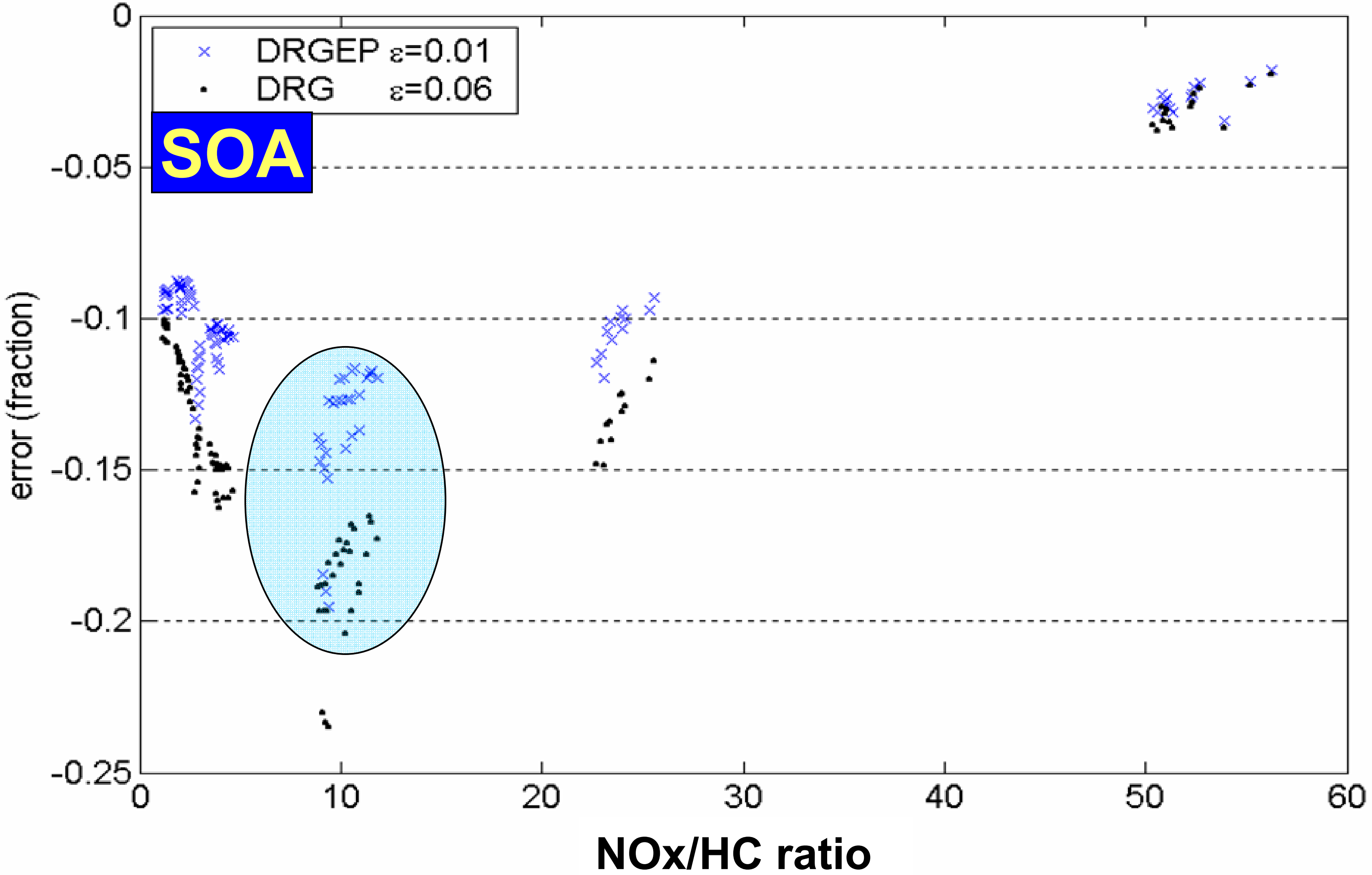
DRG: 387
DRGEP: 377

1:Comparison between DRG & DRGEP

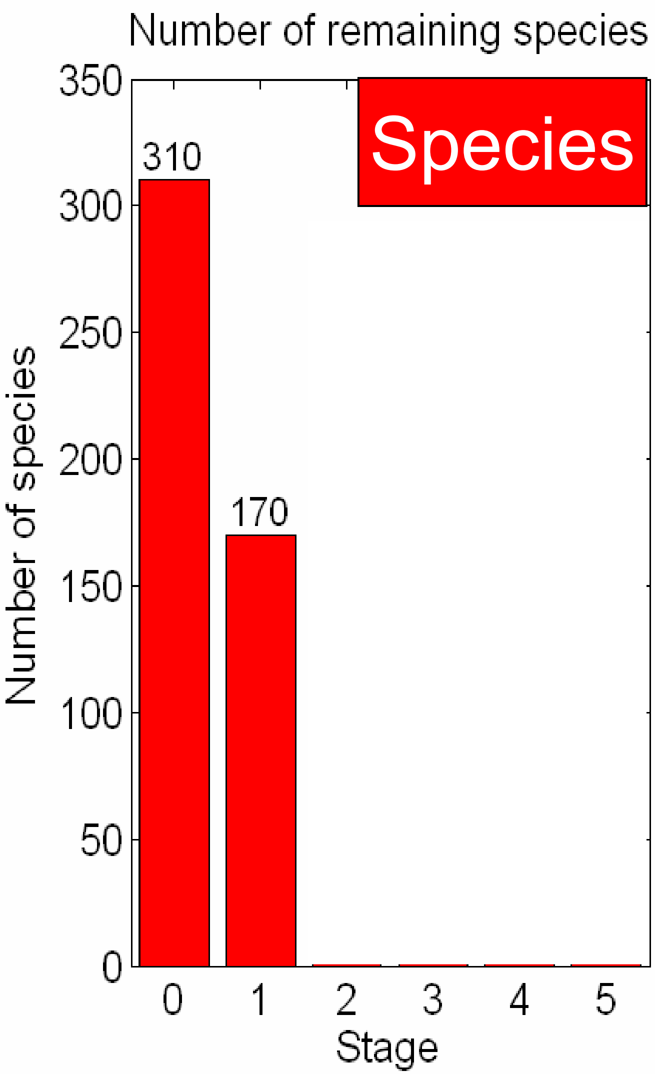


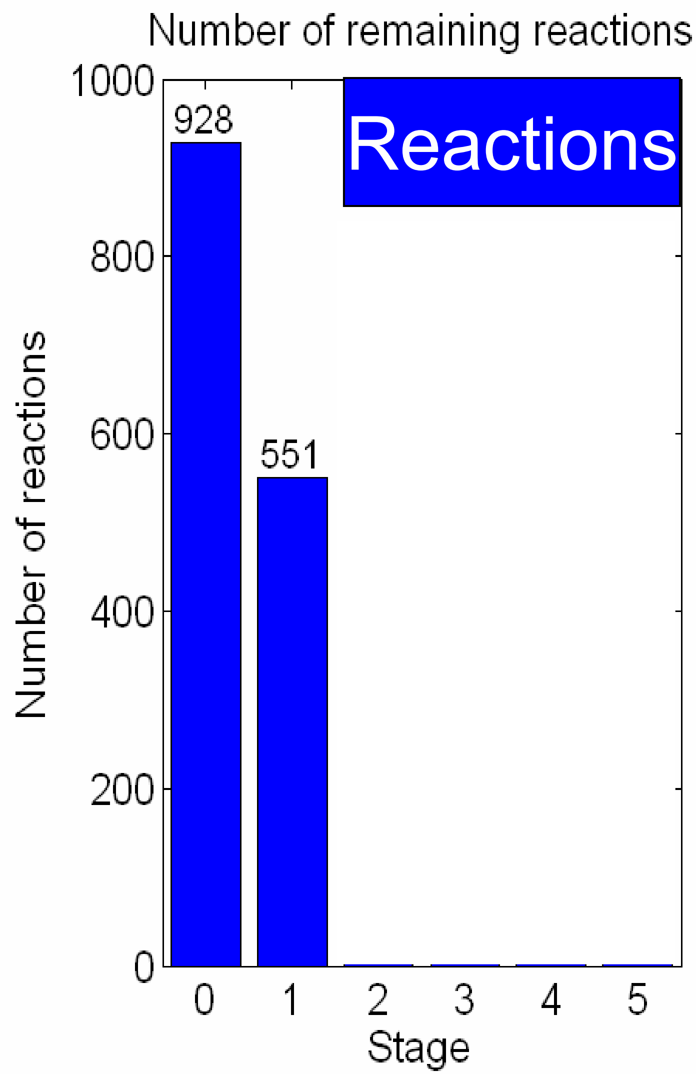
1:Comparison between DRG & DRGEP

DRGEP is better than DRG in predicting total SOA



Summary of model reduction (1)





Stages:
0) Full
1) DRGEP

Removed:
Species : 140
Reactions: 377

5:Linear lumping method

(This work)

Fixed fraction

1. Question

- To determine whether two species can be lumped

5:Linear lumping method

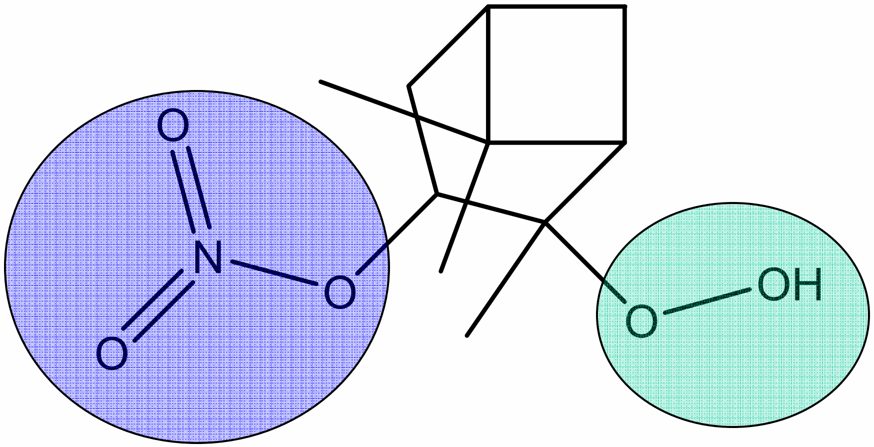
2. Analysis *(Huang et al. 2005)*

If **A1** and **A2** can be lumped, according to the linear lumping (**A=A1+A2**, **mixing ratio**), then

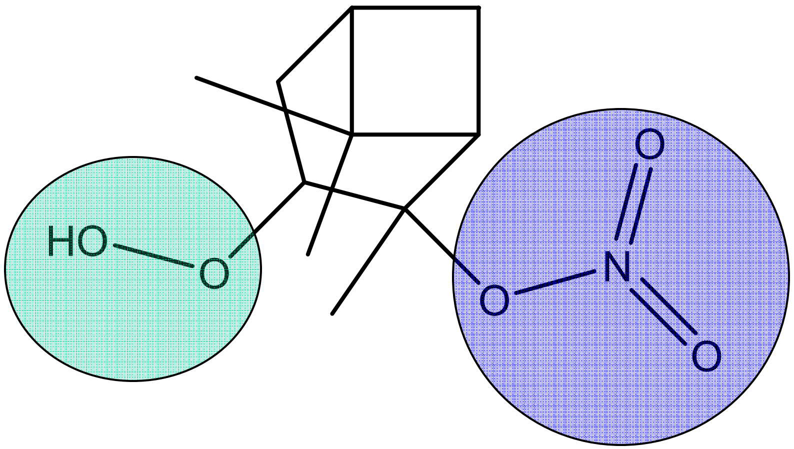
$$\begin{pmatrix} A1 \\ A2 \end{pmatrix} = (A1 + A2)\begin{pmatrix} \dfrac{A1}{A1+A2} \\ \\ \dfrac{A2}{A1+A2} \end{pmatrix} = A\begin{pmatrix} \dfrac{A1}{A1+A2} \\ \\ \dfrac{A2}{A1+A2} \end{pmatrix} = A\begin{pmatrix} x \\ 1-x \end{pmatrix}$$

If *x* is almost a **fixed value**, then the two species can be lumped. We need to determine the *X*.

5:Two selected compounds



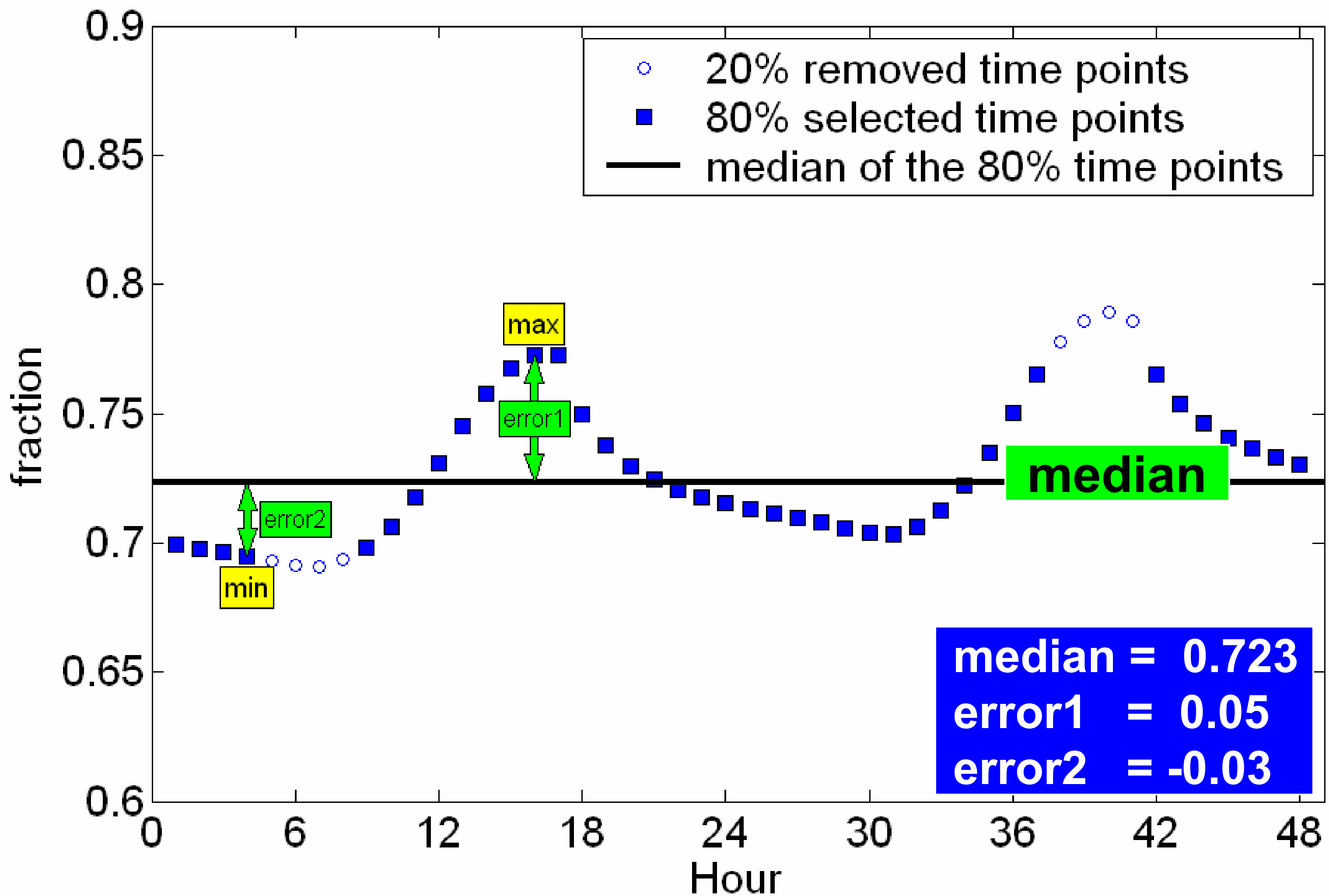
NAPINAOOH



NAPINBOOH

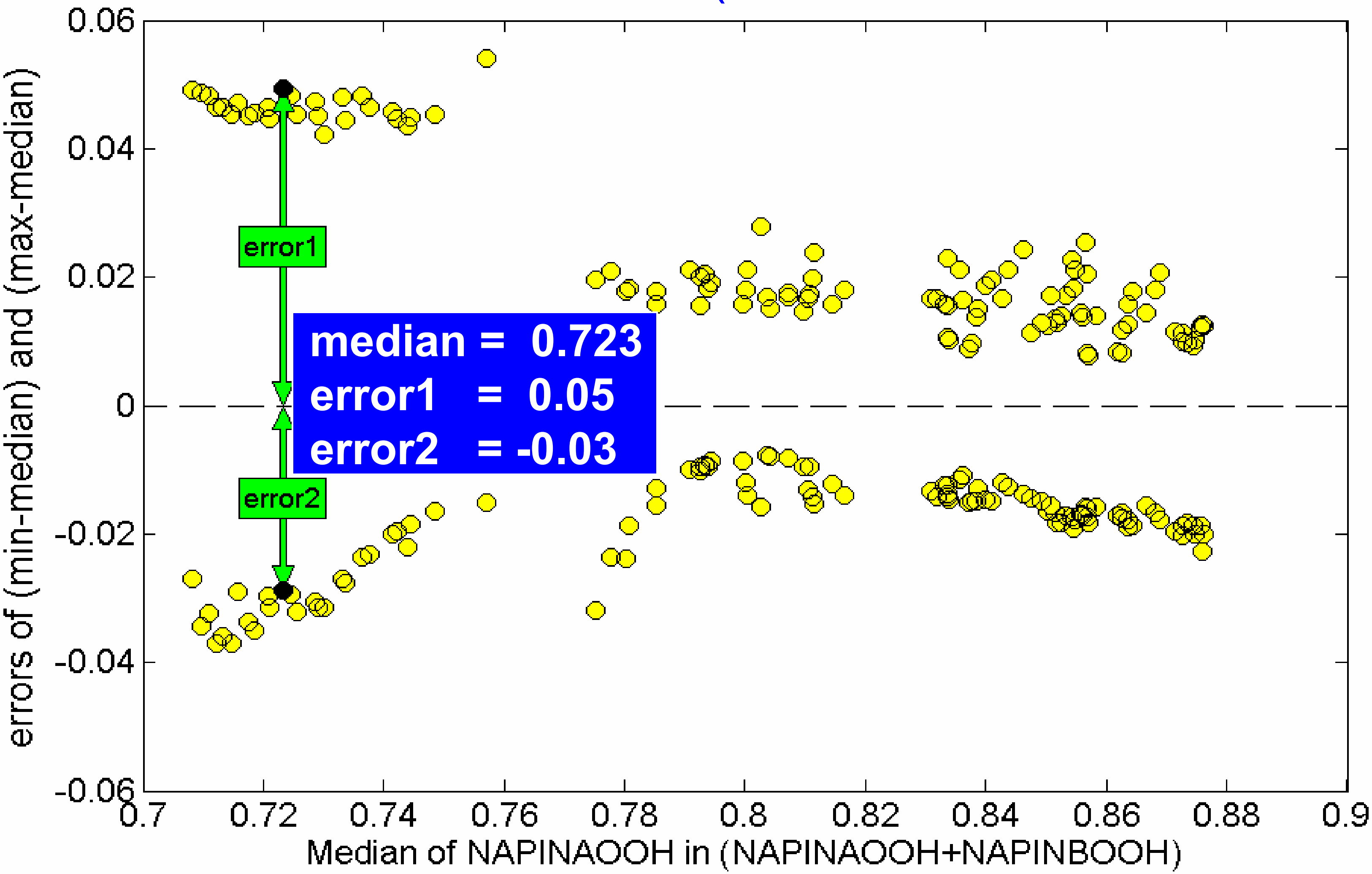
5: Fraction (gas phase) from one scenario

Fraction of ***NAPINAOOH*** in (***NAPINAOOH + NAPINBOOH***)



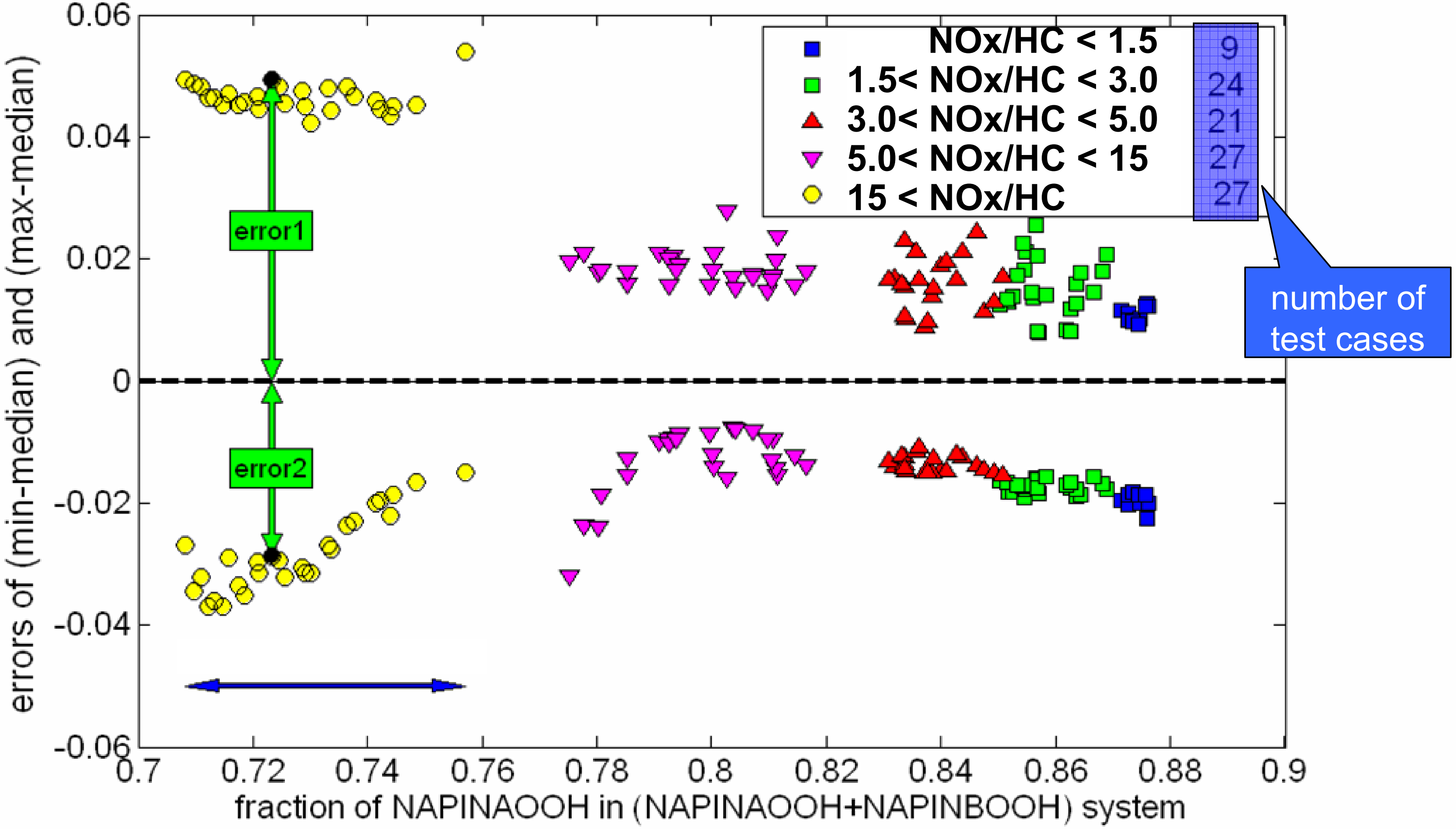
5: Fraction (gas phase) from 108 scenarios

Fraction of ***NAPINAOOH*** in (***NAPINAOOH + NAPINBOOH***)

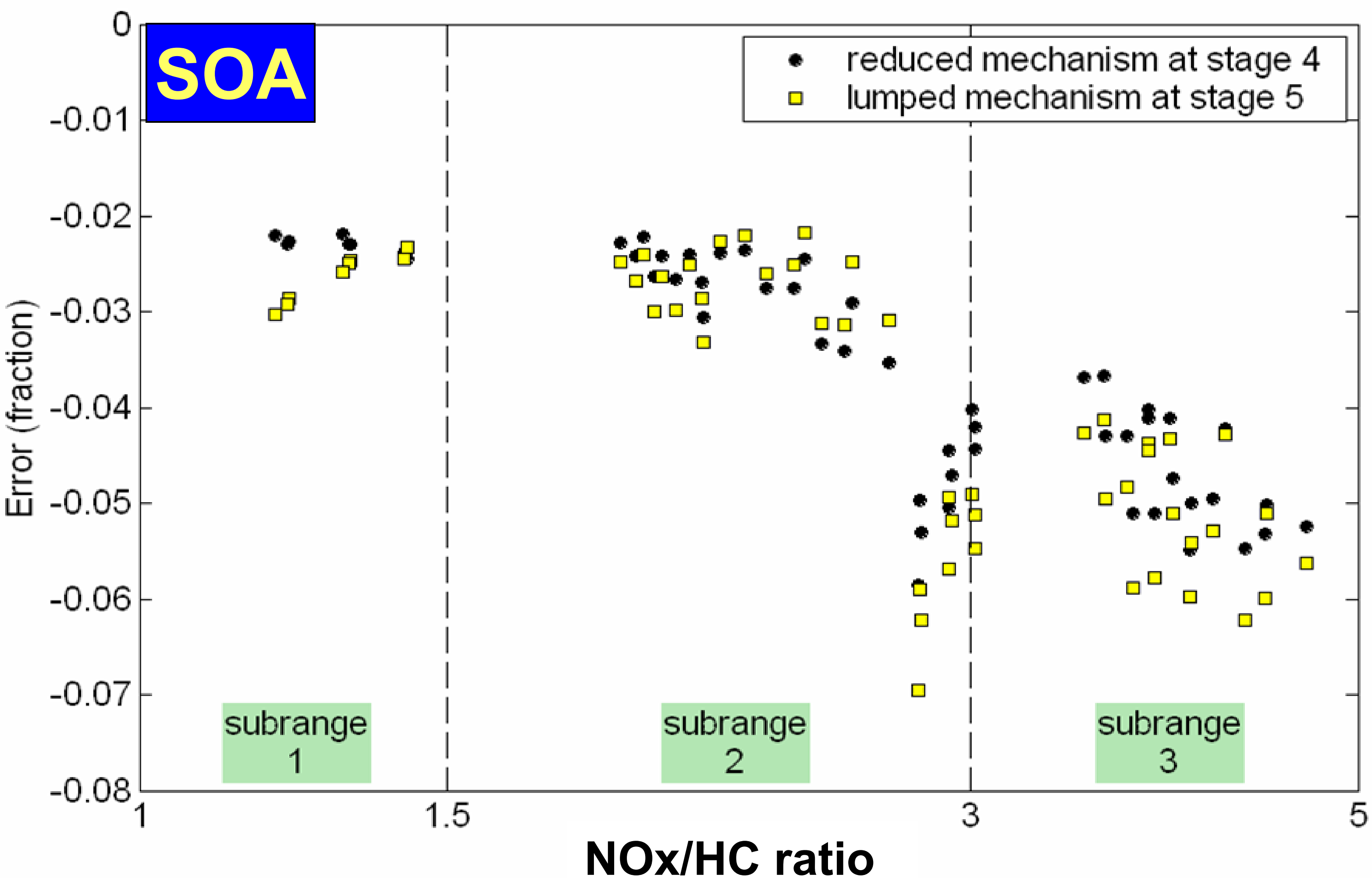


5: Fraction is NOx/HC dependent

$X_{each\ subrange} = \text{mean}(\text{fractions}_{each\ subrange})$

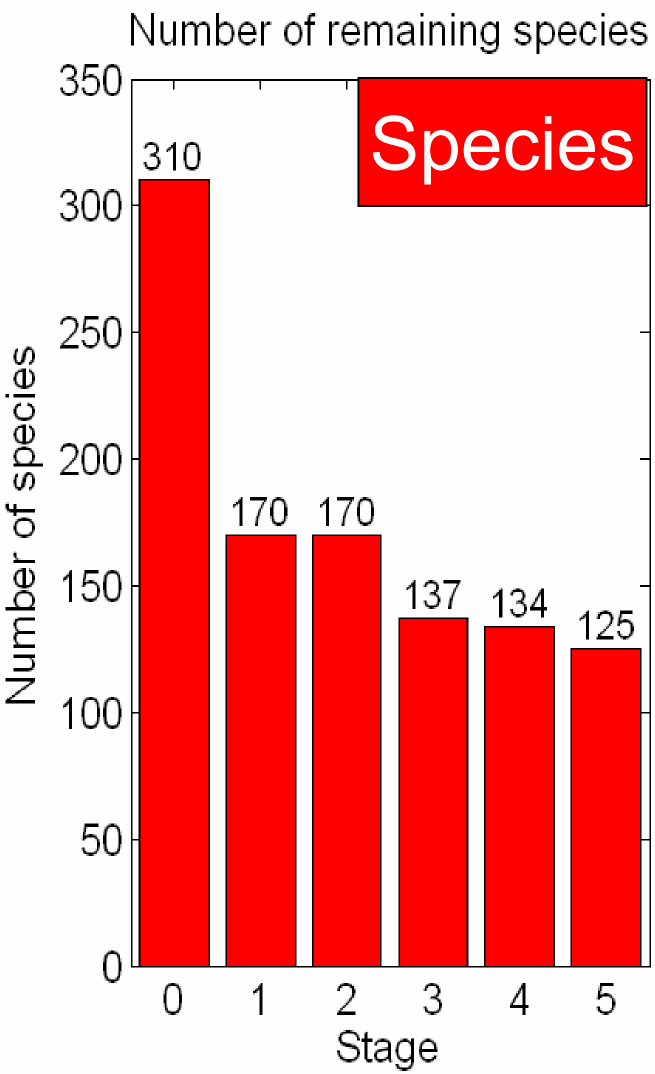


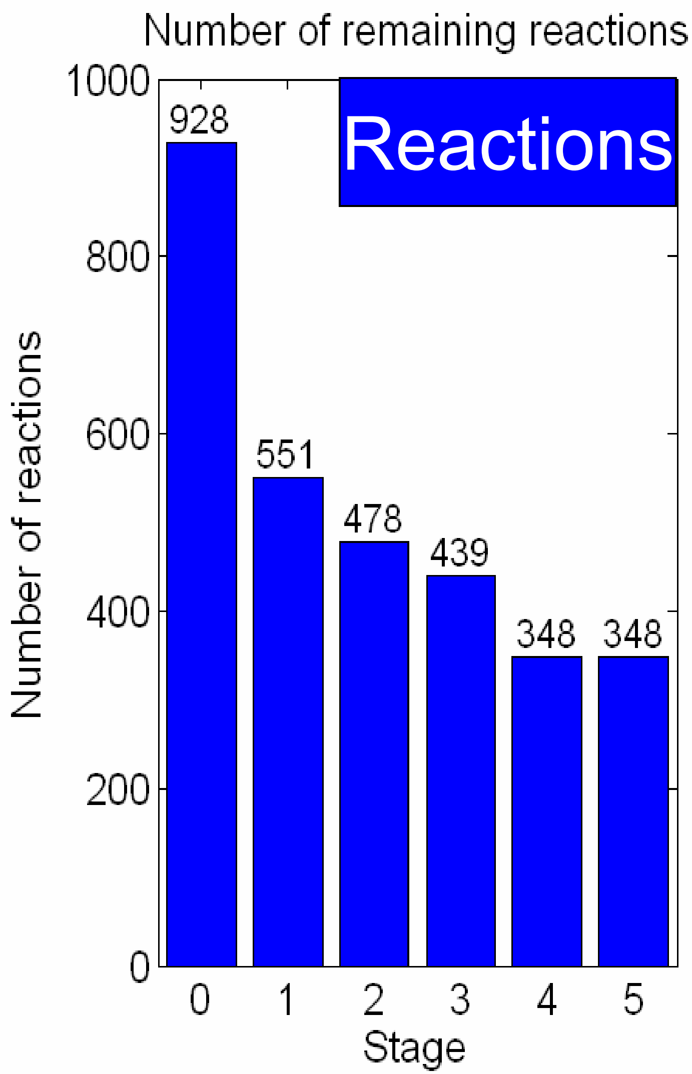
5:Lumped Mechanisms at stage 5



16 species have been lumped into 7 groups!

Summary of model reduction (5)



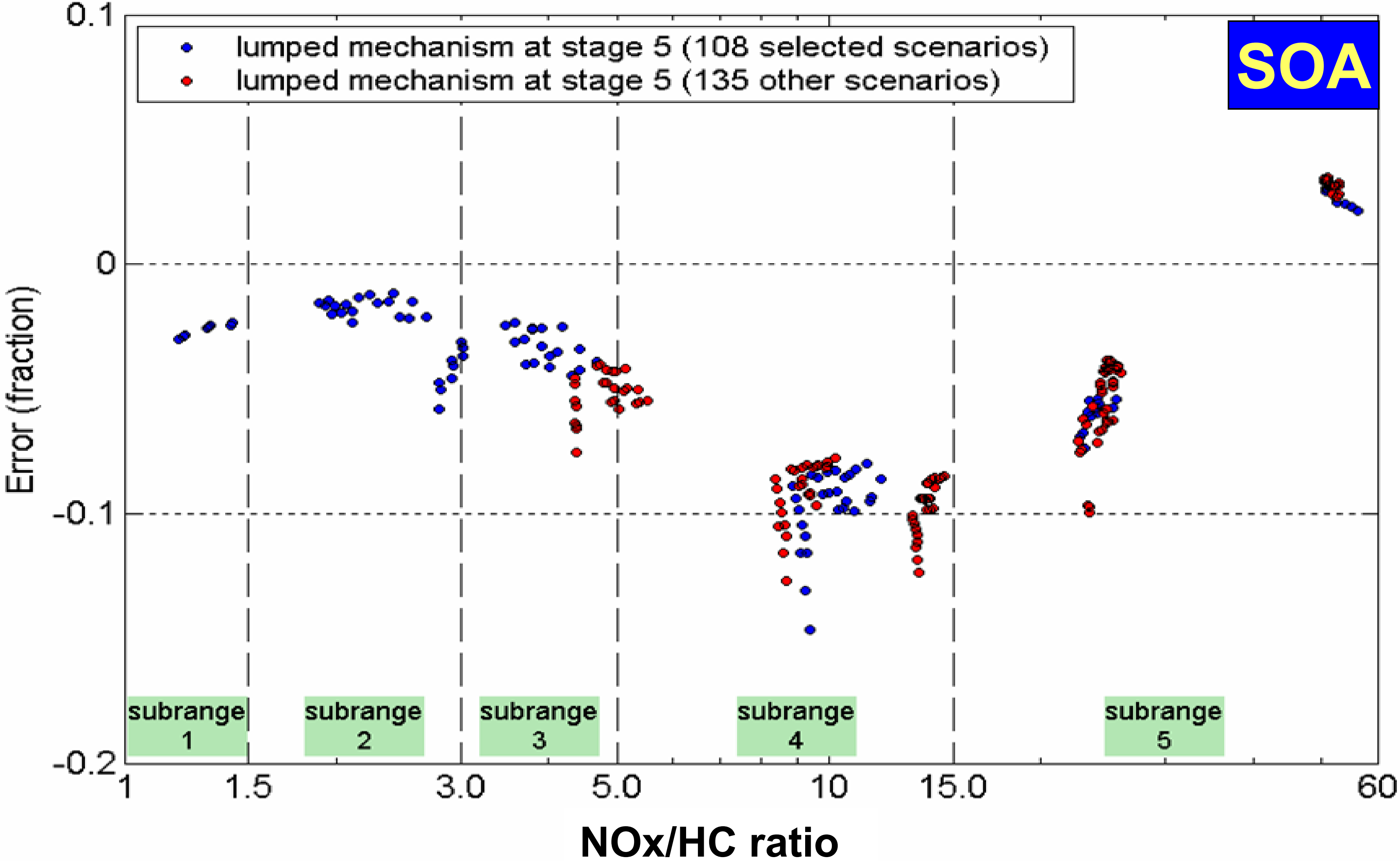


Stages:
0) Full
1) DRGEP
2) PCA
3) QSSA
4) ISSA
5) Lumping

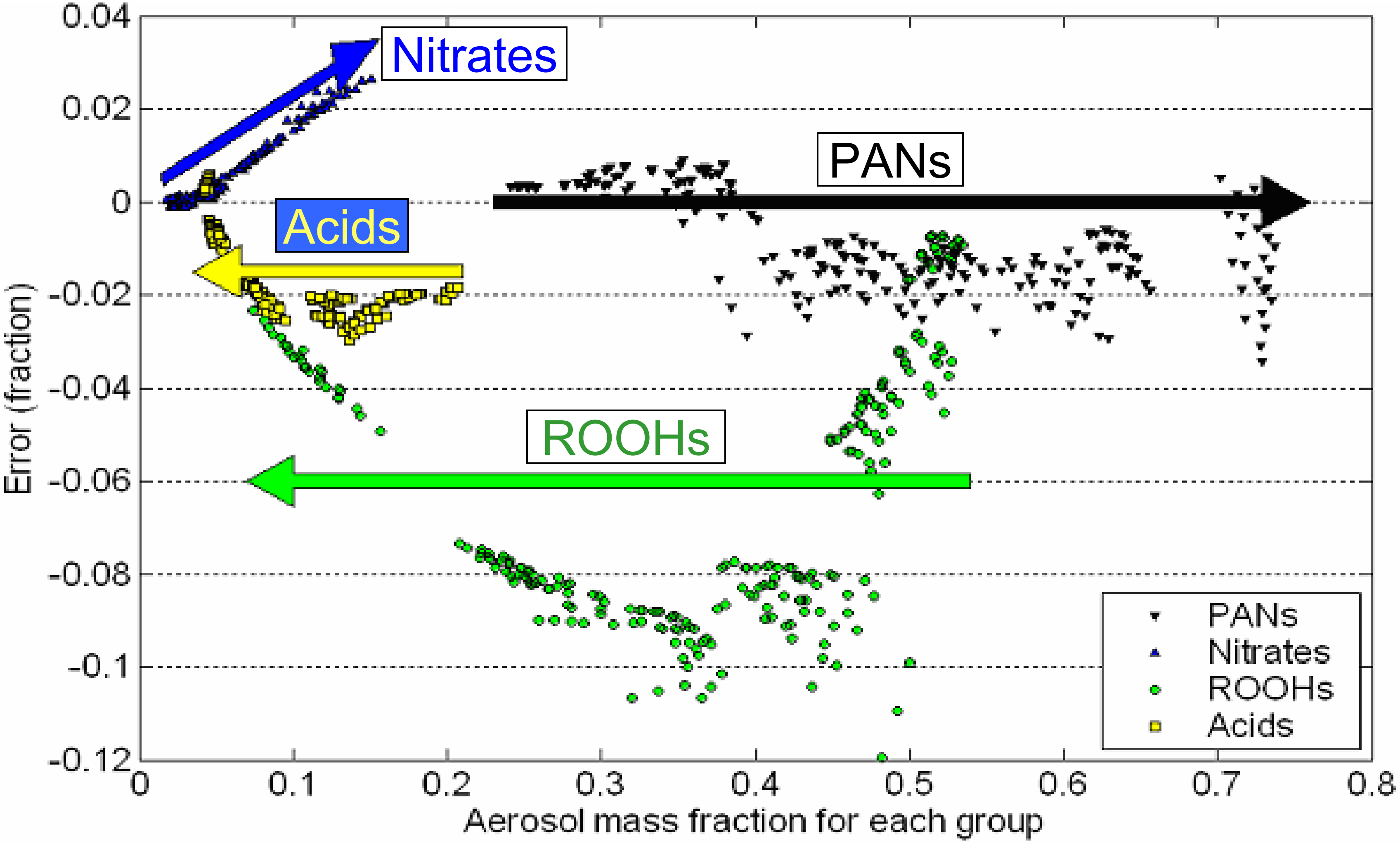
Removed:
Species : 9
Reactions: 0

Final evaluation

Reduced mechanism for total SOA formation under a **wider** range of NOx/HC (243 scenarios)



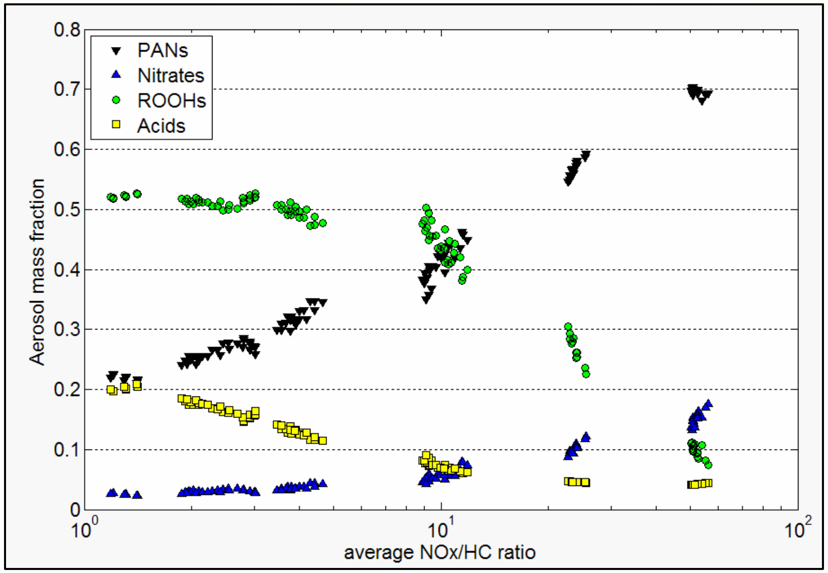
Final reduced mechanism could describe the SOA formation from each group under a wide range of NOx/HC



Summary mechanism reduction

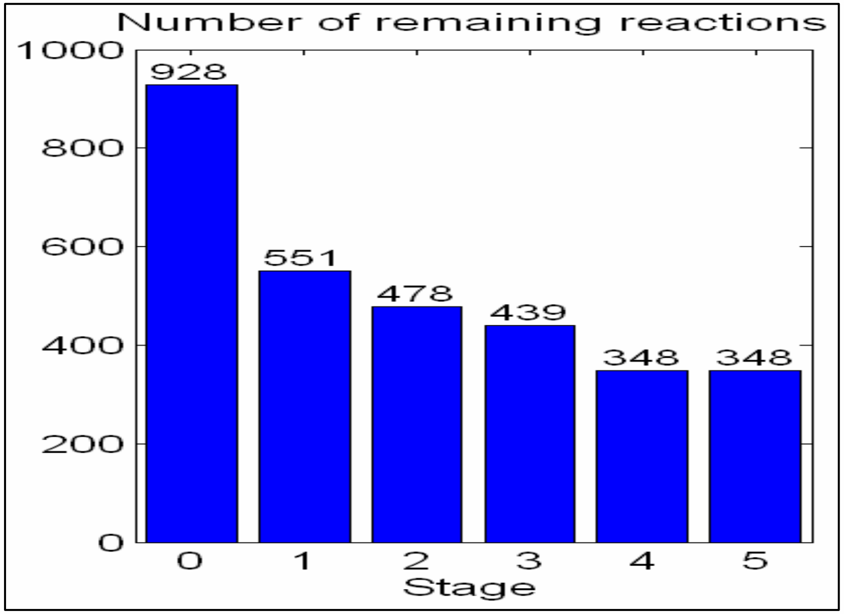
1. A **detailed α-pinene** oxidation mechanism has been **reduced systematically** by a factor of 2.5.
2. A **new lumping scheme** has been developed and applied to reduce the chemical mechanism.
3. SOA formation is **NOx/HC dependent**, therefore, the mechanism reduction is based on the NOx/HC (adaptive method).

Outline



Part I

Detailed mechanism (MCM) for SOA formation



Part II

Systematic reduction of the <u>detailed mechanism</u>

Conclusions

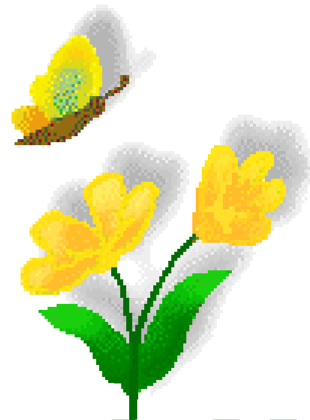
1. A **detailed chemical mechanism** shows that the **total SOA mass** and the **organic aerosol compositions** are **NOx/HC dependent**.

2. **Five systematic mechanism reduction methods** are used to reduce the large chemical mechanism.

Future studies

Mechanism reduction

1. **Automatic selection** of <u>**optimum threshold**</u> at each stage of mechanism reduction
2. Other mechanism reduction techniques.



Thank You

AdAm XiA

York University

Now at Environment Canada

AirQuality@Gmail.com


Thank you again !

Mechanism reduction
Stage 2 - 4

2:Principal Component Analysis

(Turanyi et al., 1989)

Remove redundant rxns

1. Rate sensitivity matrix **F**

$$F_{ij} = \frac{\partial \ln f_i}{\partial \ln k_j} = \frac{\upsilon_{ij} R_j}{f_i}$$

where

$$f_i(\mathrm{c},\mathrm{k}) = \frac{dc_i}{dt} = -\sum_{j=1}^{M} \nu_{ij} R_j$$

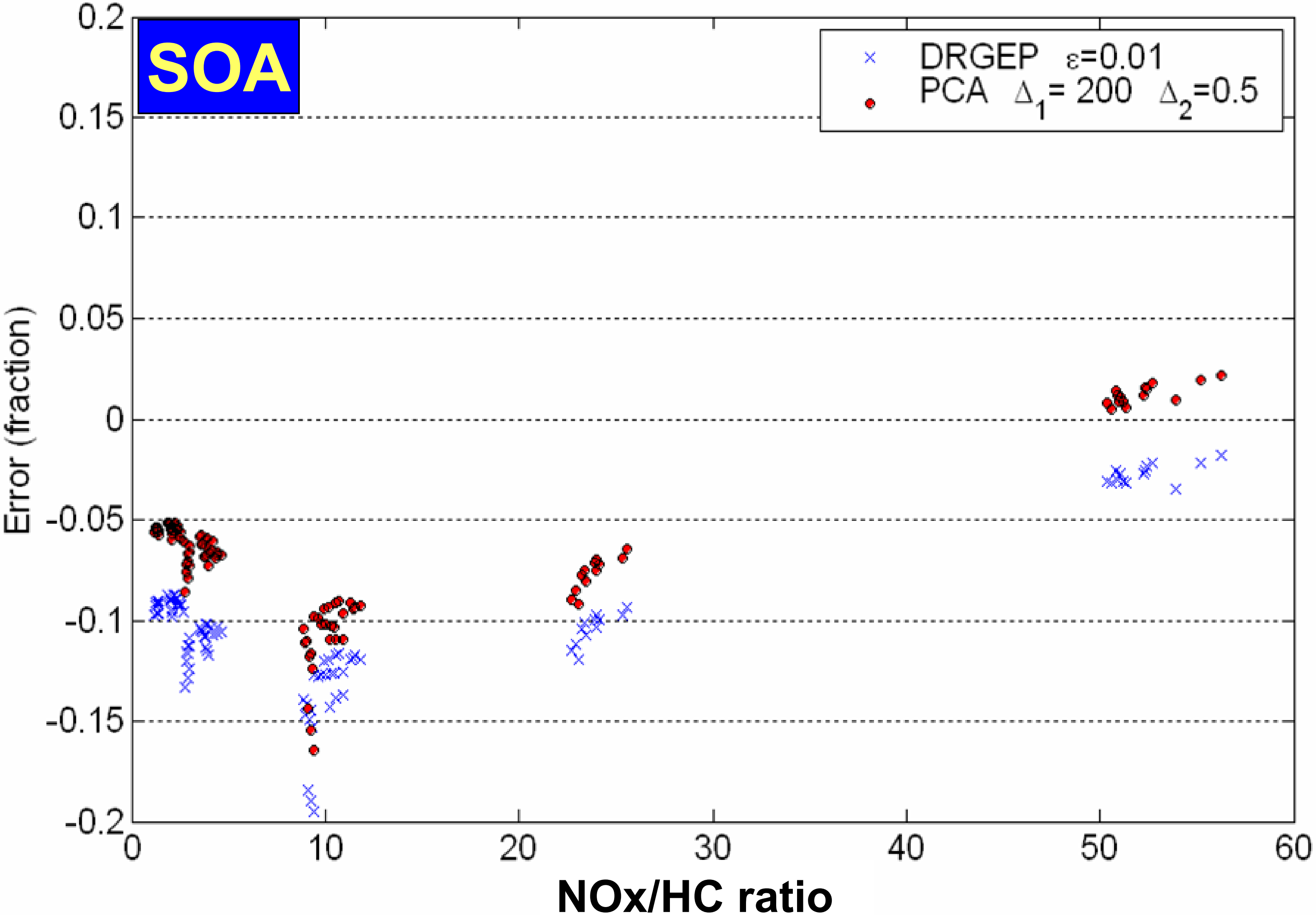
and k_j = rate constant for the reaction.

2. Principal Component Analysis (PCA) is the **eigenvalue-eigenvector** decomposition of the matrix $\mathbf{F}^T\mathbf{F}$.

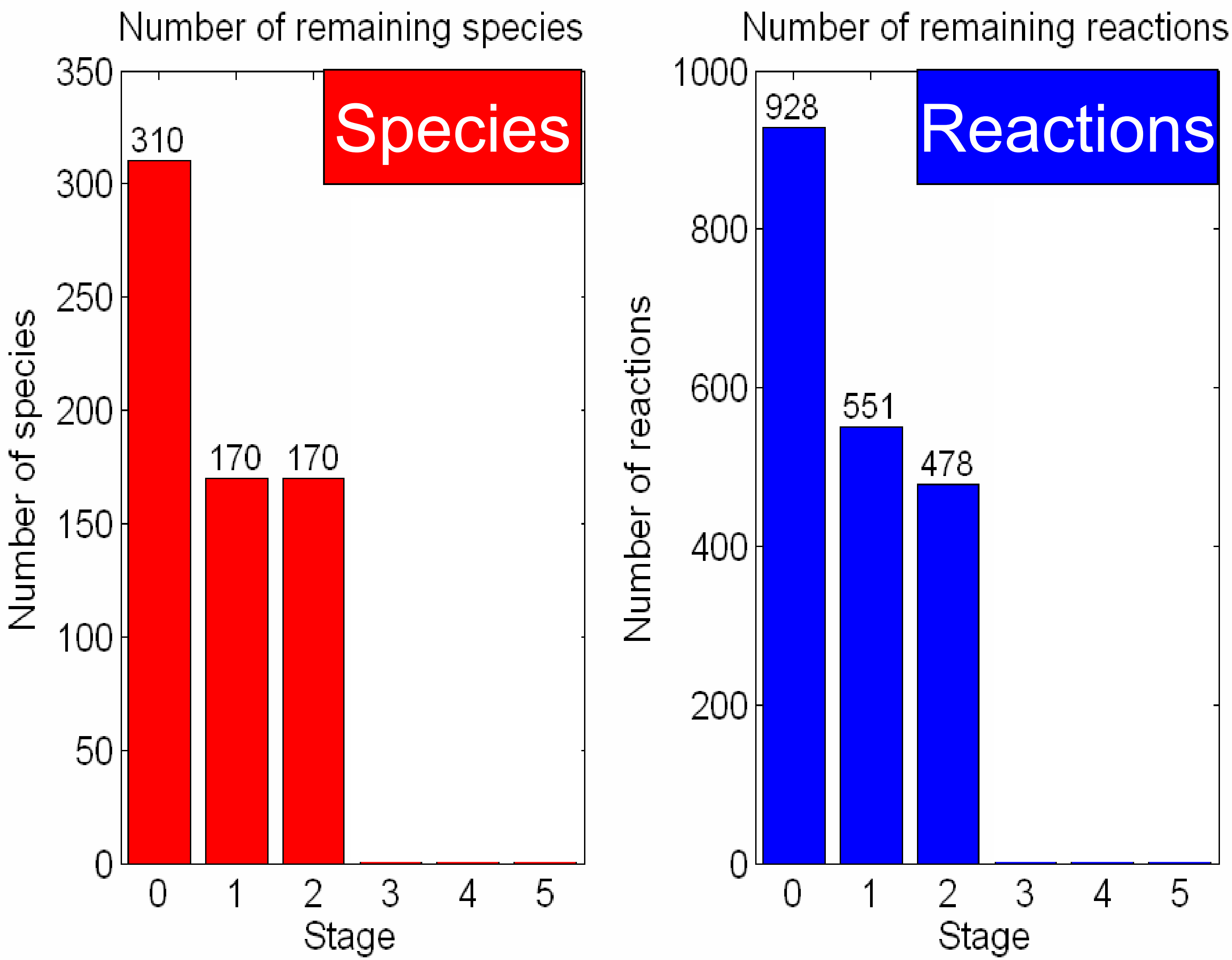
3. Reaction, corresponding to a **large eigenvector** and an associated **high eigenvalue,** is an **important reaction.**

4. As a result, 73 out of 551 reactions have been removed.
   (threshold for the eigenvalue is 200, threshold for the eigenvector is 0.5.)

2:Comparion between two stages



Summary of model reduction (2)



Stages:
0) Full
1) DRGEP
2) PCA

Removed:
Species : 0
Reactions: 73

3:Quasi-Steady-State species

(Turanyi et al., 1993)

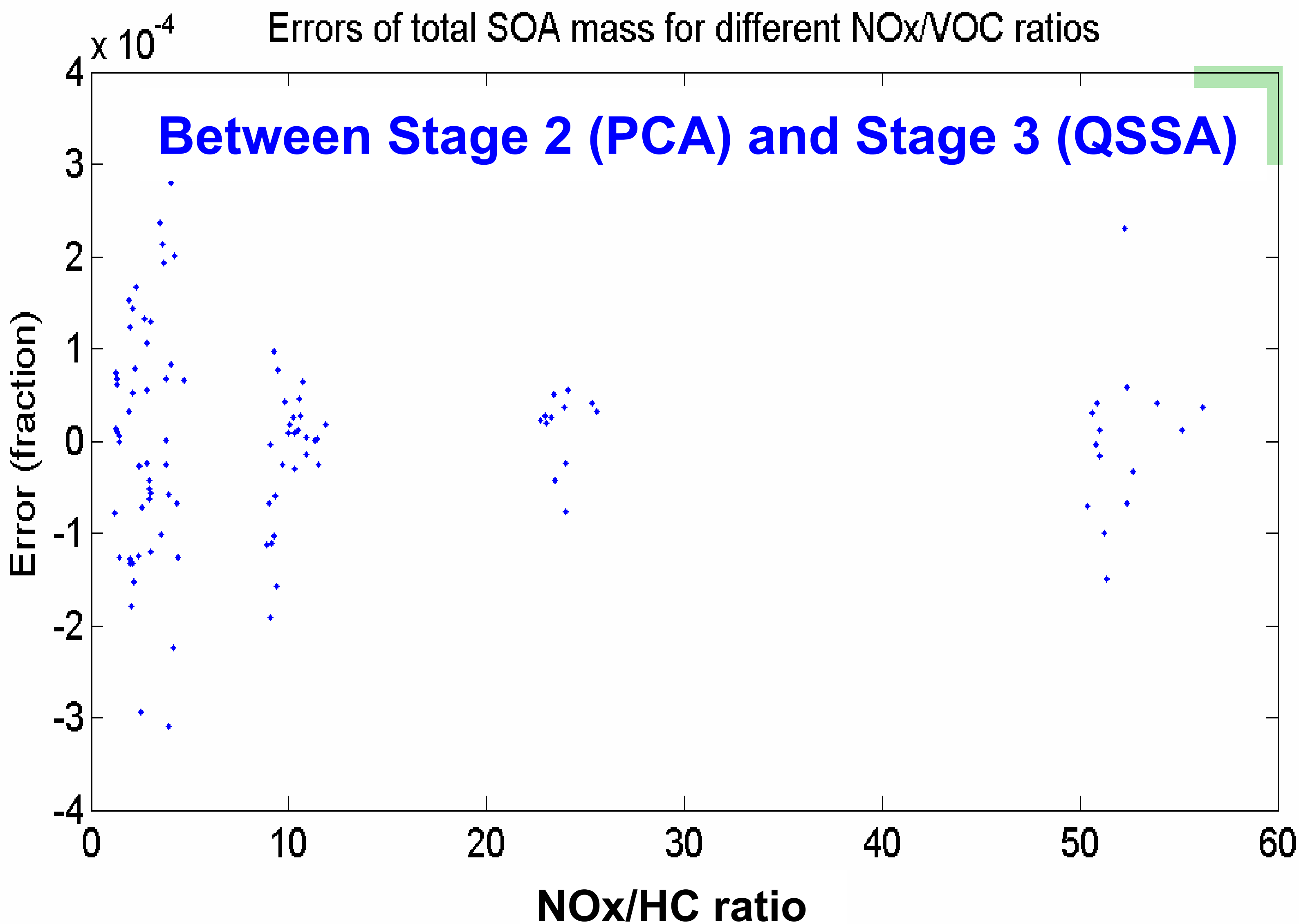
Remove QSS species

1 Species selected as QSS species, based on the instant error $\left(\frac{\Delta c_i}{c_i}\right)$, can be removed

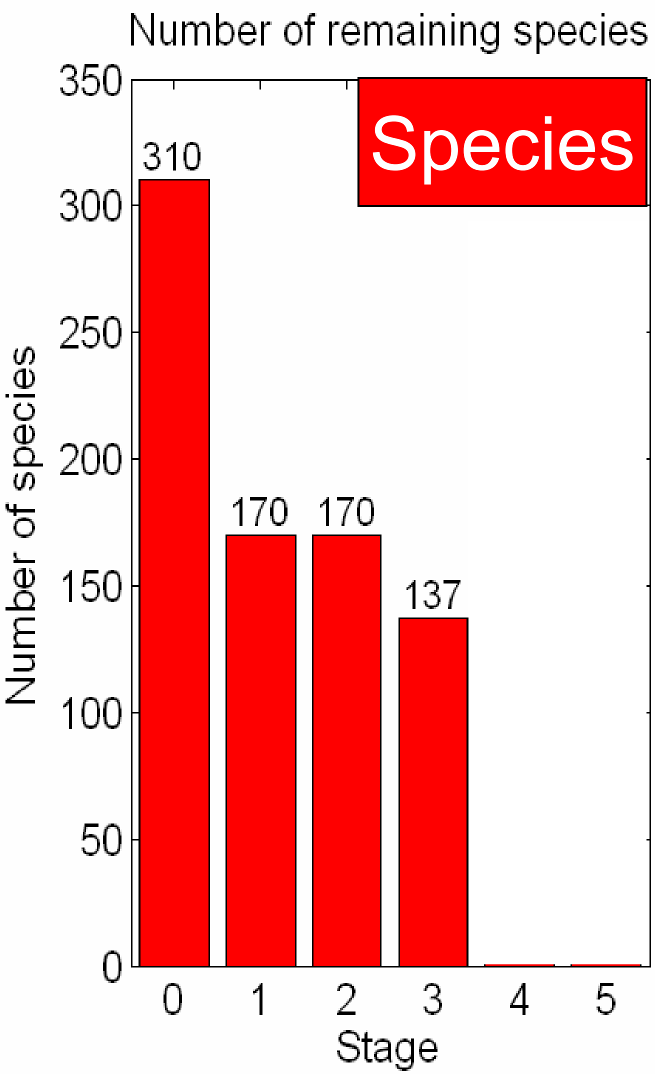
$$\frac{\Delta c_i}{c_i} \le 0.05$$ where $$\Delta c_i = \frac{1}{J_{ii}} \frac{dc_i}{dt}$$, $$J_{ii} = \frac{1}{\delta_{ij}} \frac{\partial}{\partial c_j}\left(\frac{dc_i}{dt}\right)$$

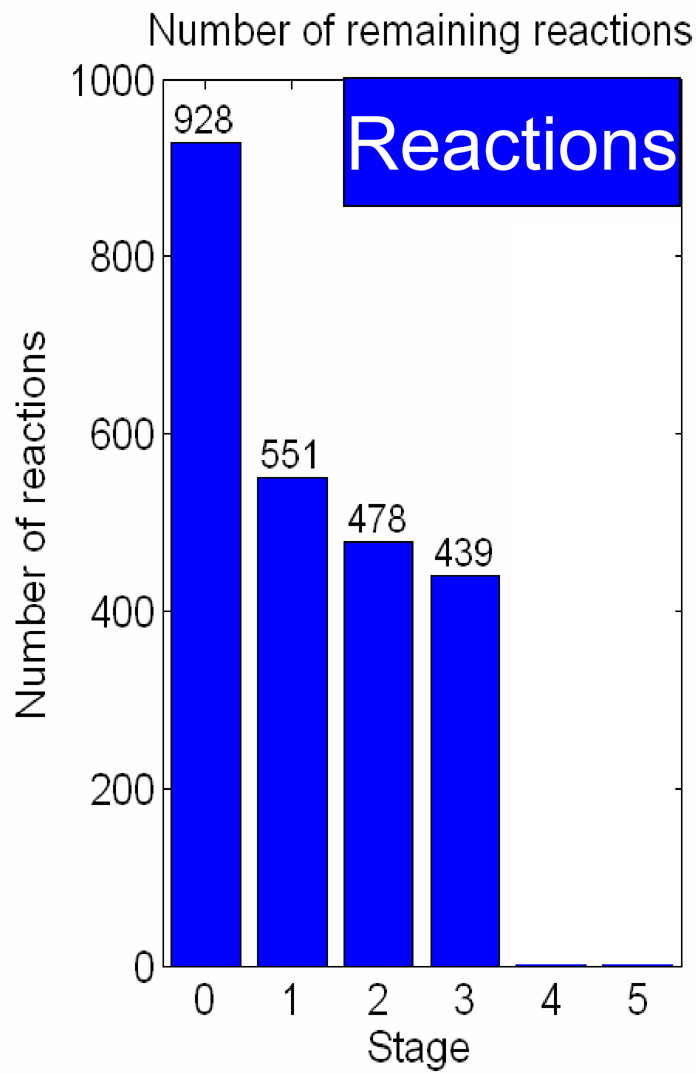
2. As a result of this method, 33 RO species have been removed.

3:Quasi-Steady-State species



Summary of model reduction (3)





Stages:
0) Full
1) DRGEP
2) PCA
3) QSSA

Removed:
Species : 33
Reactions: 39

4: Iterative screening method (ISSA)

(Mauersberger, 2005)

$$P_i - L_i = \sum_j \nu_{ij} R_j = \sum_j \nu_{ij}^{+} R_j - \sum_j \nu_{ij}^{-} R_j$$

Production	Loss
$f_{ij} = \dfrac{\nu_{ij}^{+} R_j}{P_i}$	$g_{ij} = \dfrac{\nu_{ij}^{-} R_j}{L_i}$

1) Major species → 2) Important rxns → 3) Species (updated)

i — species ***i*** (major species)

j — ***j***th rxn

R_j — reaction rate for the ***j***th rxn

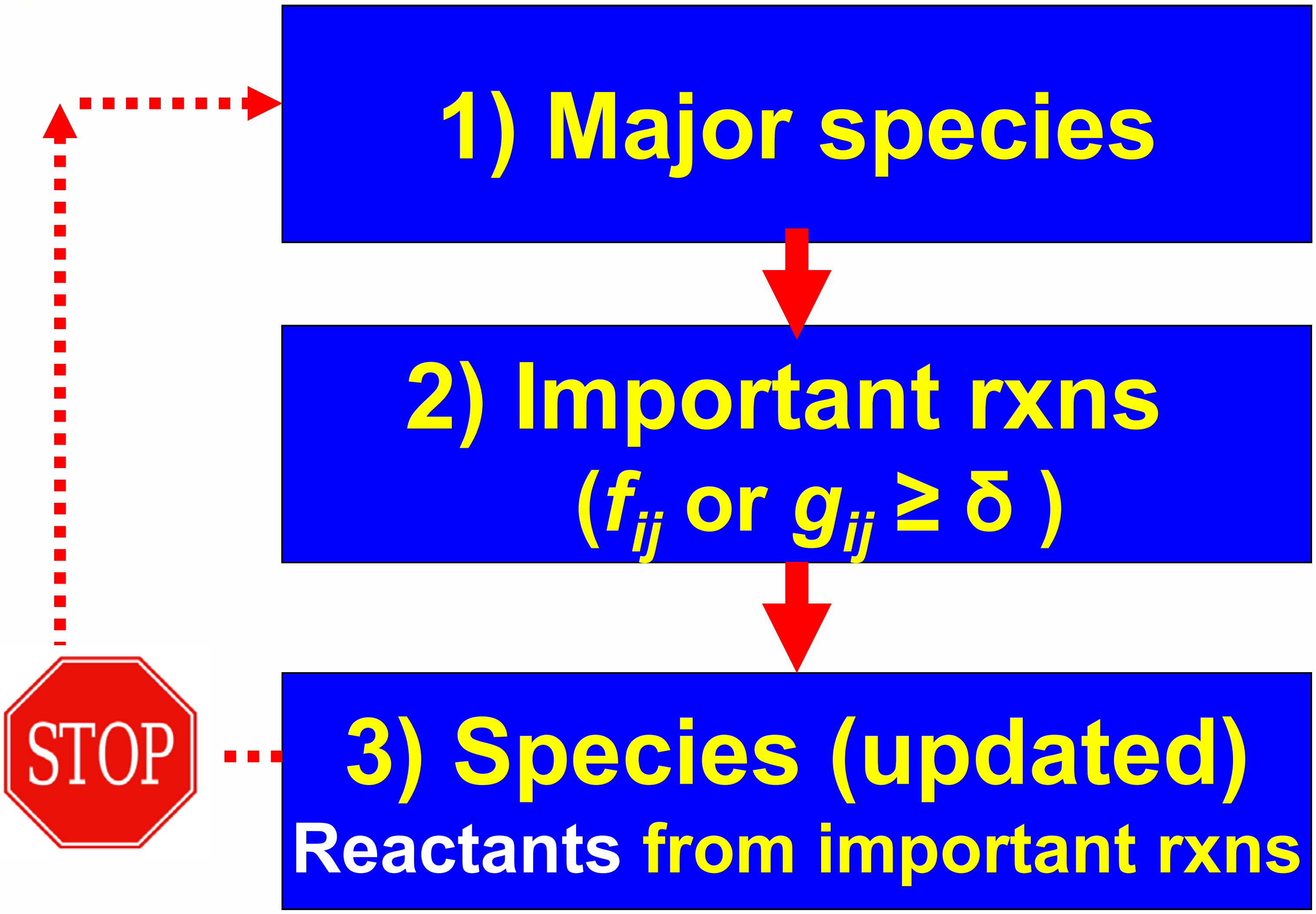
ν_{ij}^{+} —stoich. coeff. for species ***i*** in the ***j***th rxn as a **product**

f_{ij} —relative importance of the ***j***th rxn to the **production term** ***(P_i)*** for species ***i***

ν_{ij}^{-} —stoich. coeff. for species ***i*** in the ***j***th rxn as a **reactant**

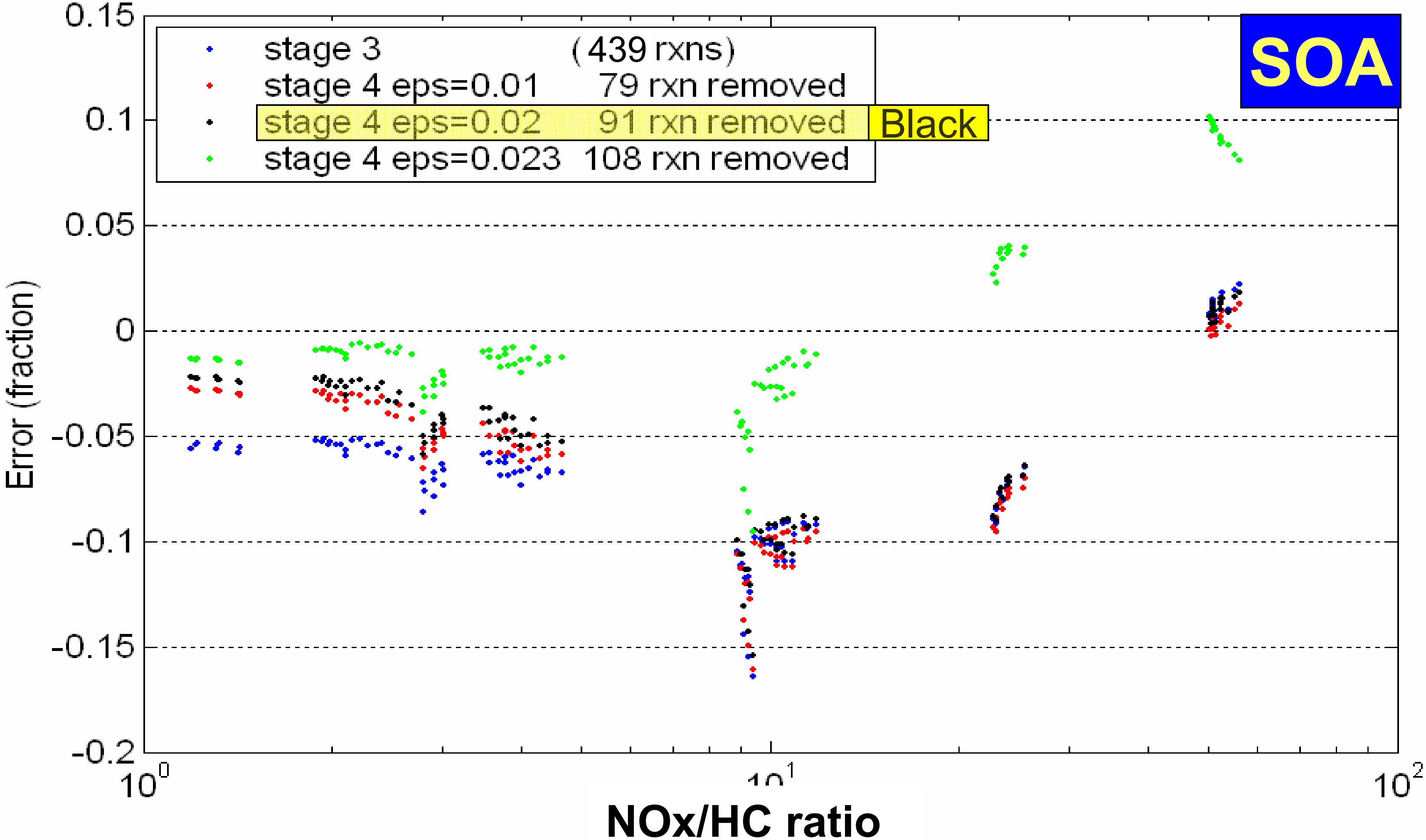
g_{ij} —relative importance of the ***j***th rxn to the **loss term** ***(L_i)*** for species ***i***

4: Procedure to find *"major species"* and "important reactions" by using ISSA

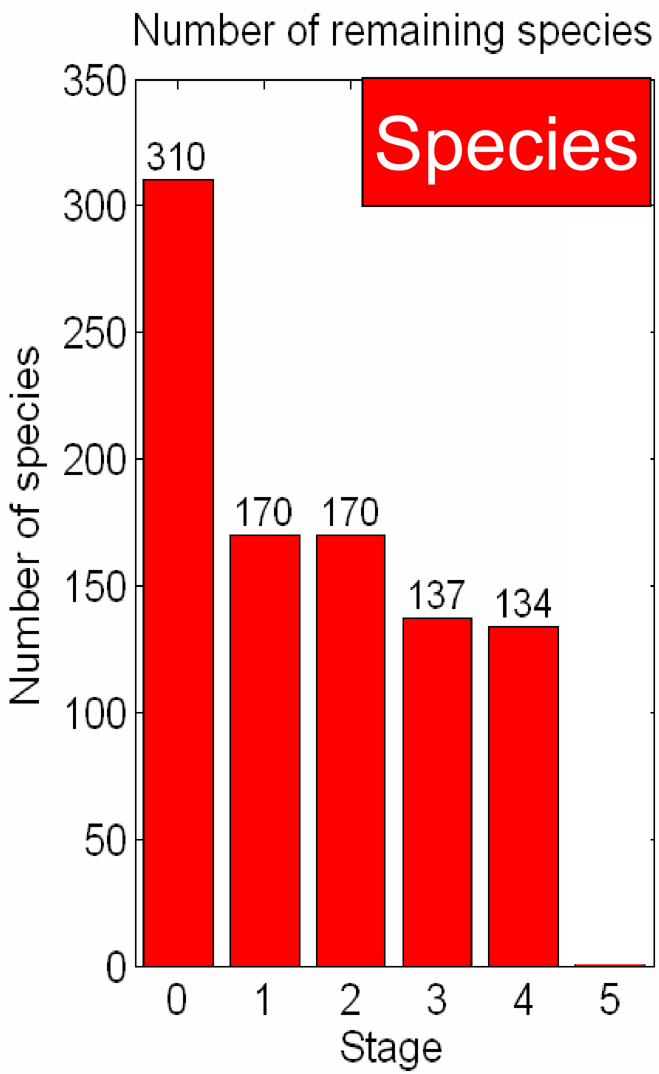


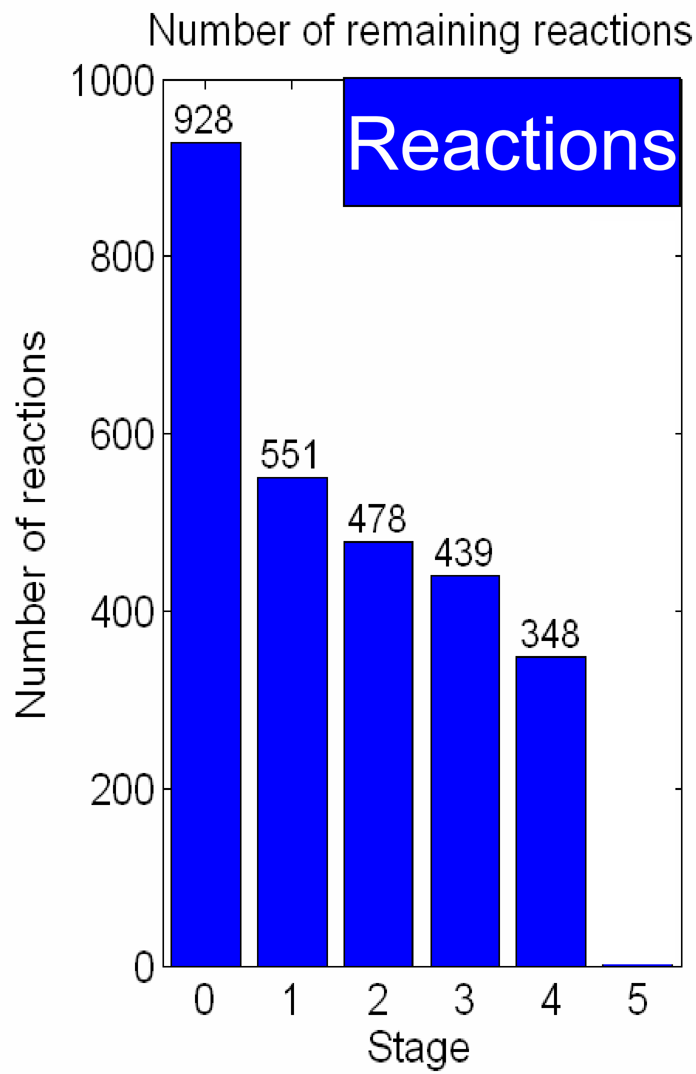
4: Evaluation of the ISSA method

Reduced mechanism is very sensitive to the selection of the threshold



Summary of model reduction (4)





Stages:
0) Full
1) DRGEP
2) PCA
3) QSSA
4) ISSA

Removed:
Species : 3
Reactions: 91