Structure-activity relationships for the development of MCM/GECKOA mechanisms

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Atmospheric Chemical Services

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University of York

Camille Mouchel-Vallon, Sasha Madronich, John Orlando
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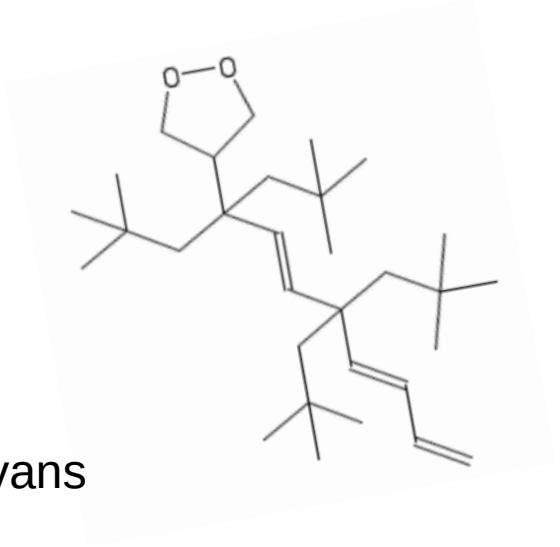

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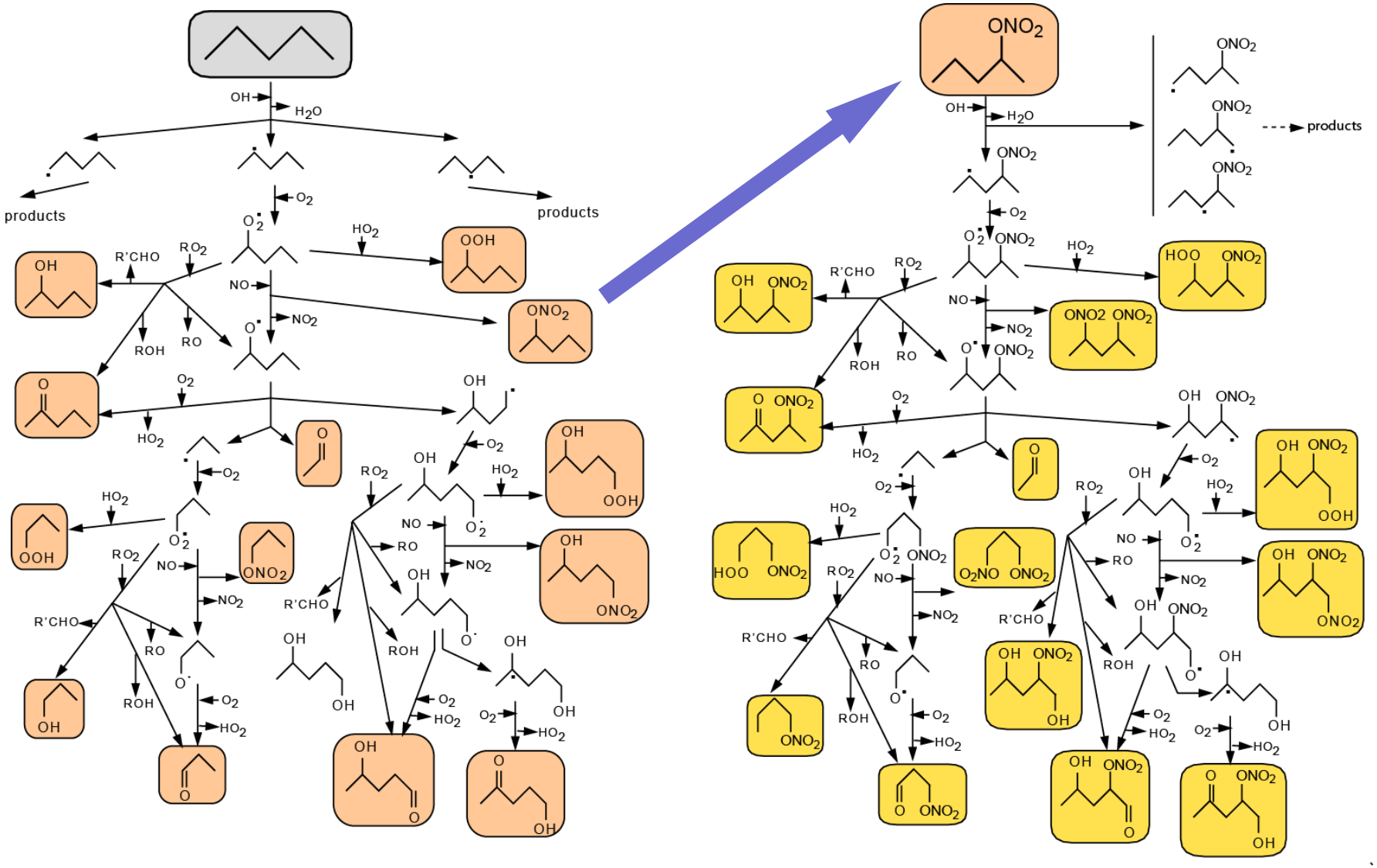
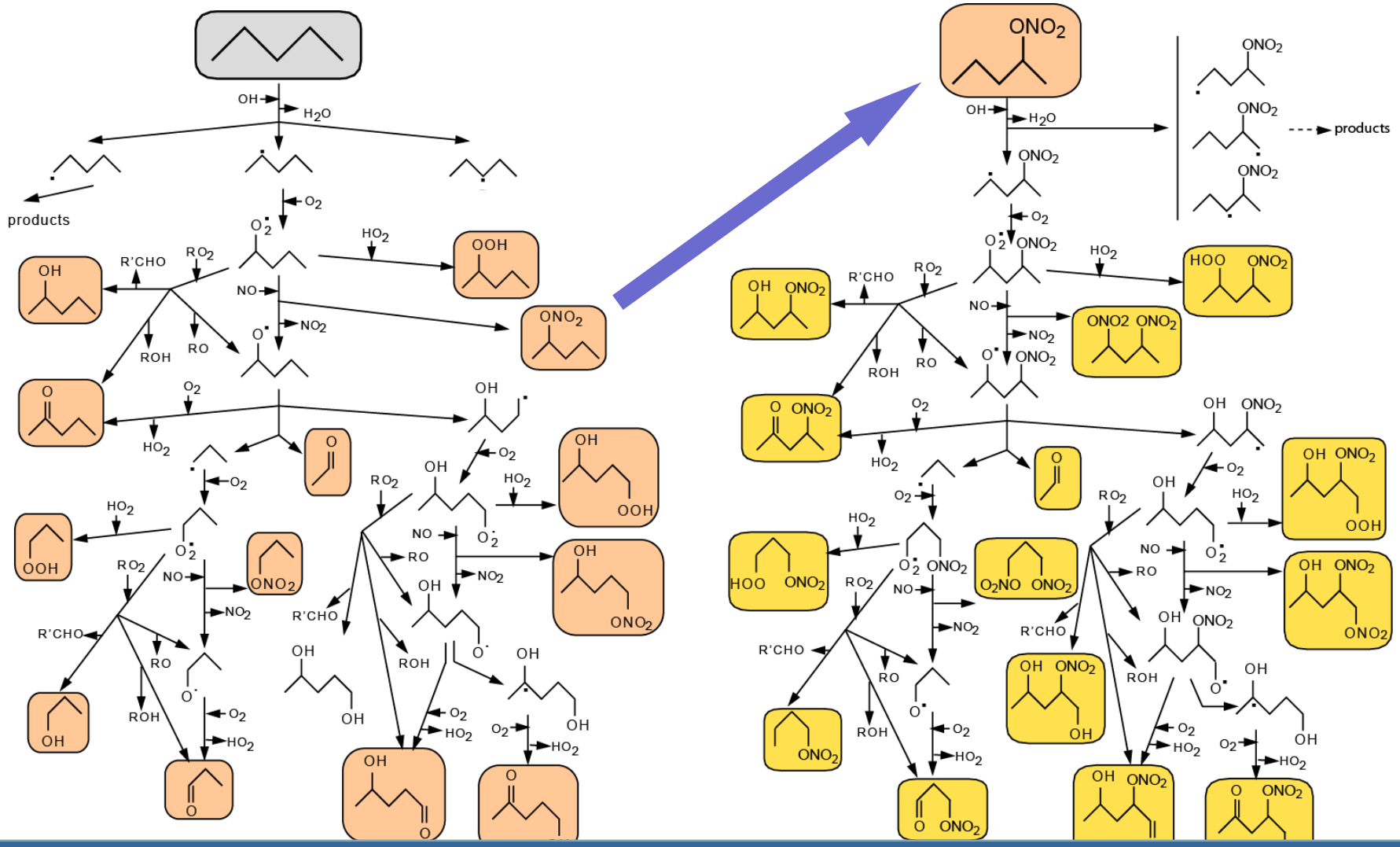
Why explicit organic chemical mechanisms ?



Why explicit organic chemical mechanisms ?

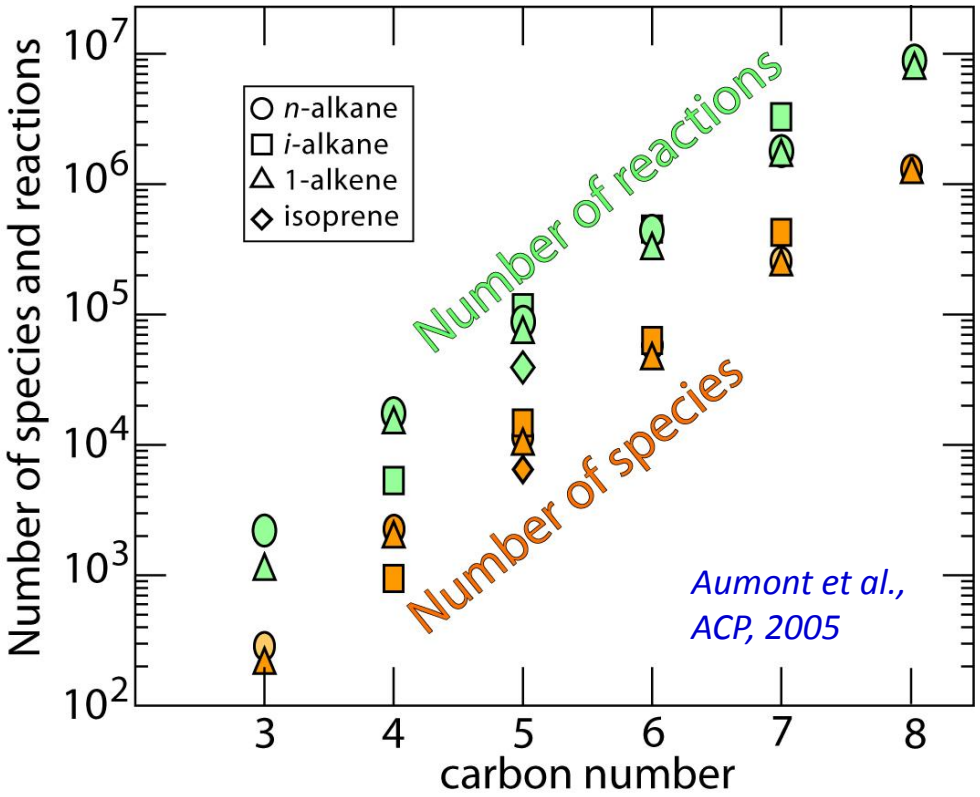


- Fundamental understanding of the HOx/NOx/Ox chemistry, SOA formation …
- Reference scheme to examine the reliability of simplified (reduced) schemes.
- Objective tools to explore our ignorance through comparisons with observations

How big are explicit chemical schemes ?

Two problems :

- Explicit schemes are too large to be reasonably written by hand
- The quantity of physical and chemical data needed to develop explicit schemes is far in excess of available experimental data.



Data processing tools are required to:

- Assimilate all the data provided by laboratory studies
- Codify the various estimation methods
- Generate consistent and comprehensive multiphase oxidation schemes on a systematic basis

→ Development of *GECKO-A*

Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere

The chemical scheme generator

precursors

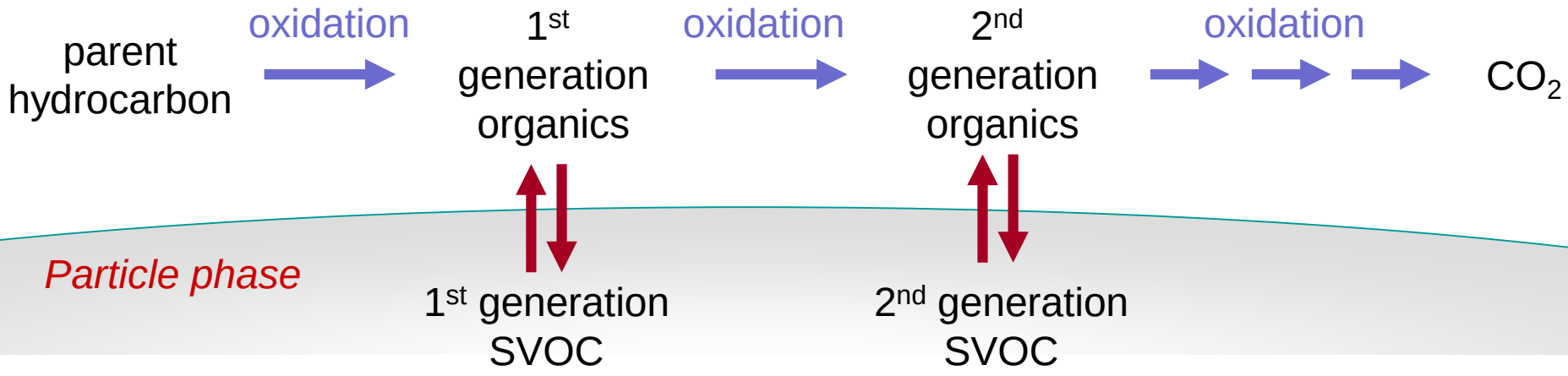
Experimental data & estimation methods (SAR)

GECKO-A

Computing code:
generate detailed mechanism (reactions, mass transfer …)

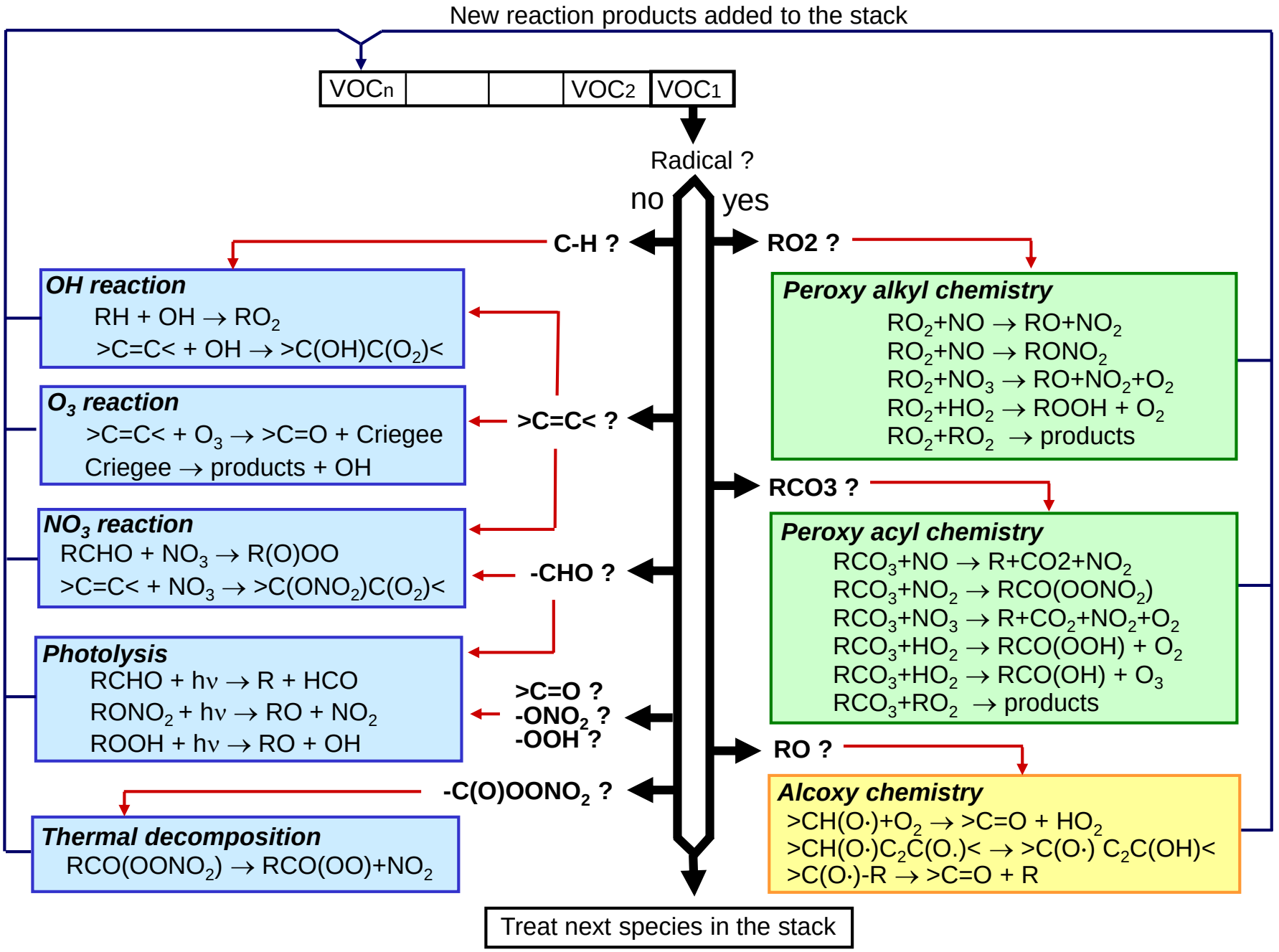
Protocol:
select chemical pathways
provide kinetic & thermodynamic data

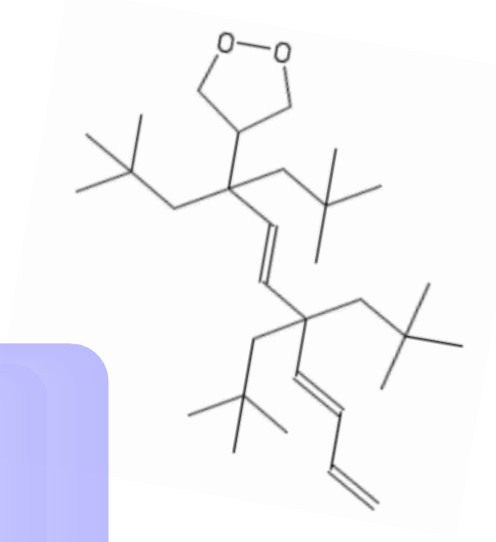
Explicit chemical schemes + properties (Psat, H, ...)



- Condensed phase assumed to behave as an ideal well mixed liquid homogeneous phase.
- P^{vap} estimated for each intermediate using structure/properties relationship.

Flow diagram of the generator





The Magnify Project

Mechanisms for Atmospheric chemistry: GeneratioN, Interpretation and Fidelity

Objective:
Provide state-of-the science atmospheric chemical mechanisms based on a sustainable approach

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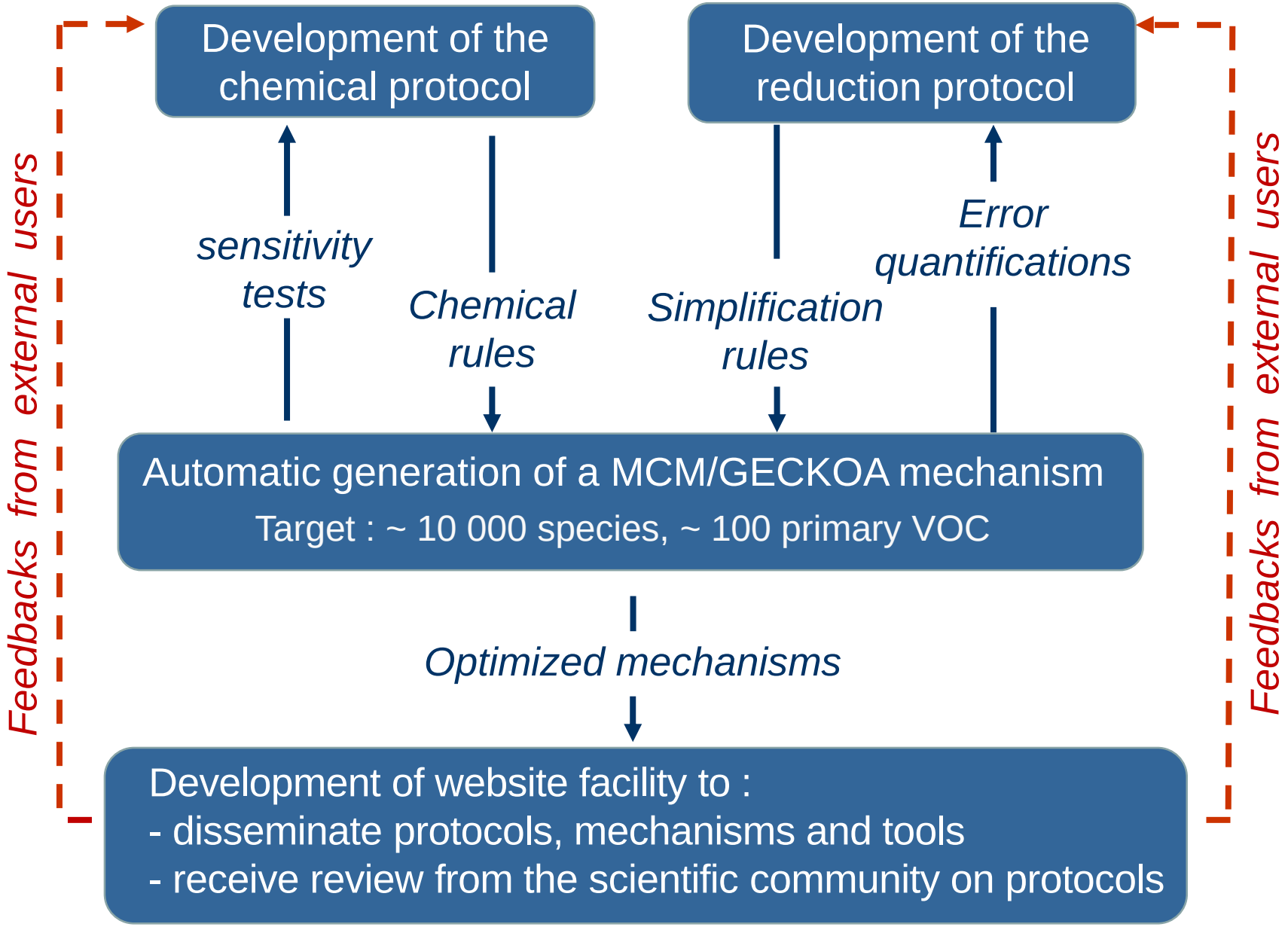
ANR

project ANR-14-CE01-001

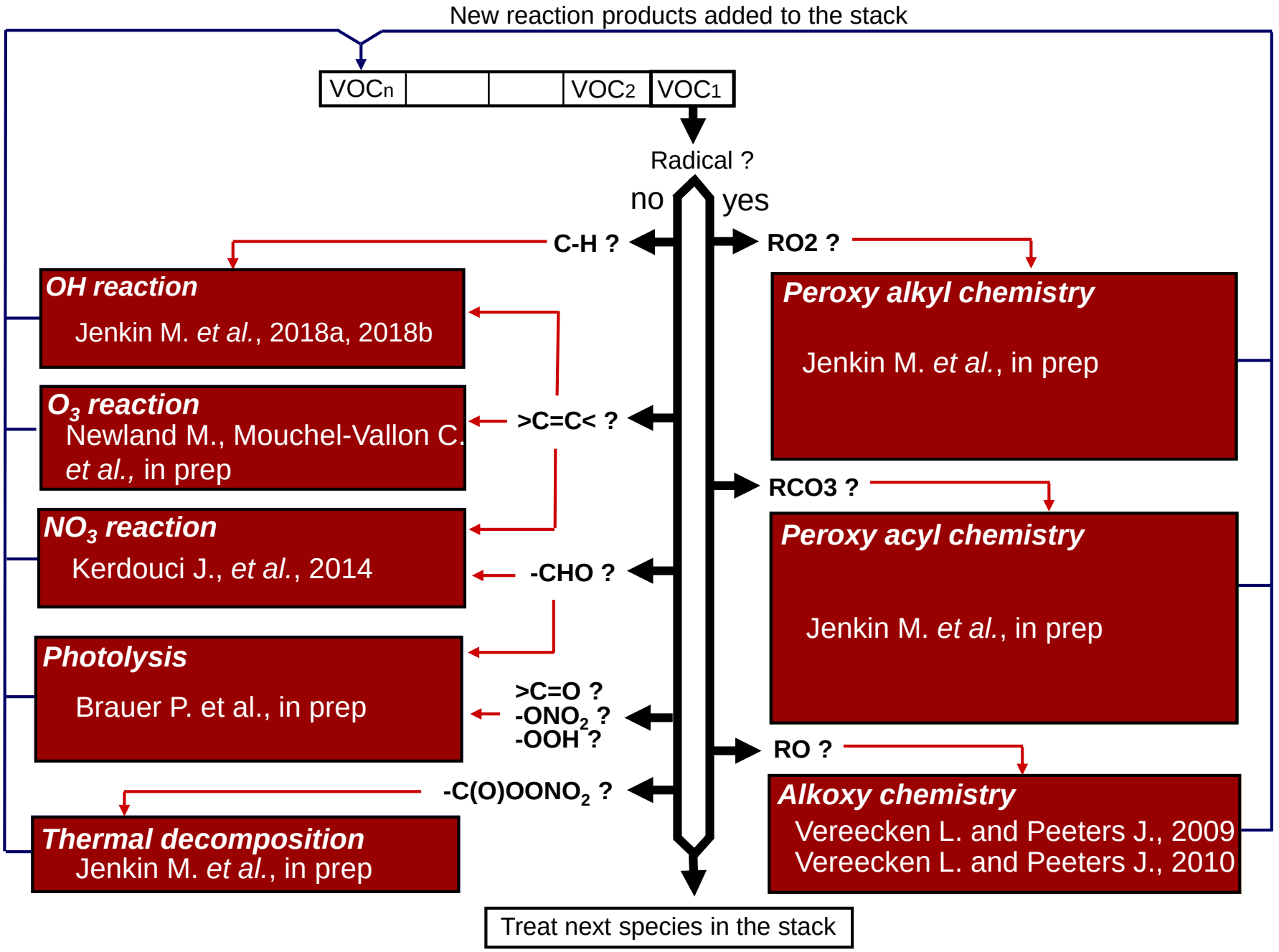
NERC
SCIENCE OF THE ENVIRONMENT

grant NE/M013448/1

The Magnify project



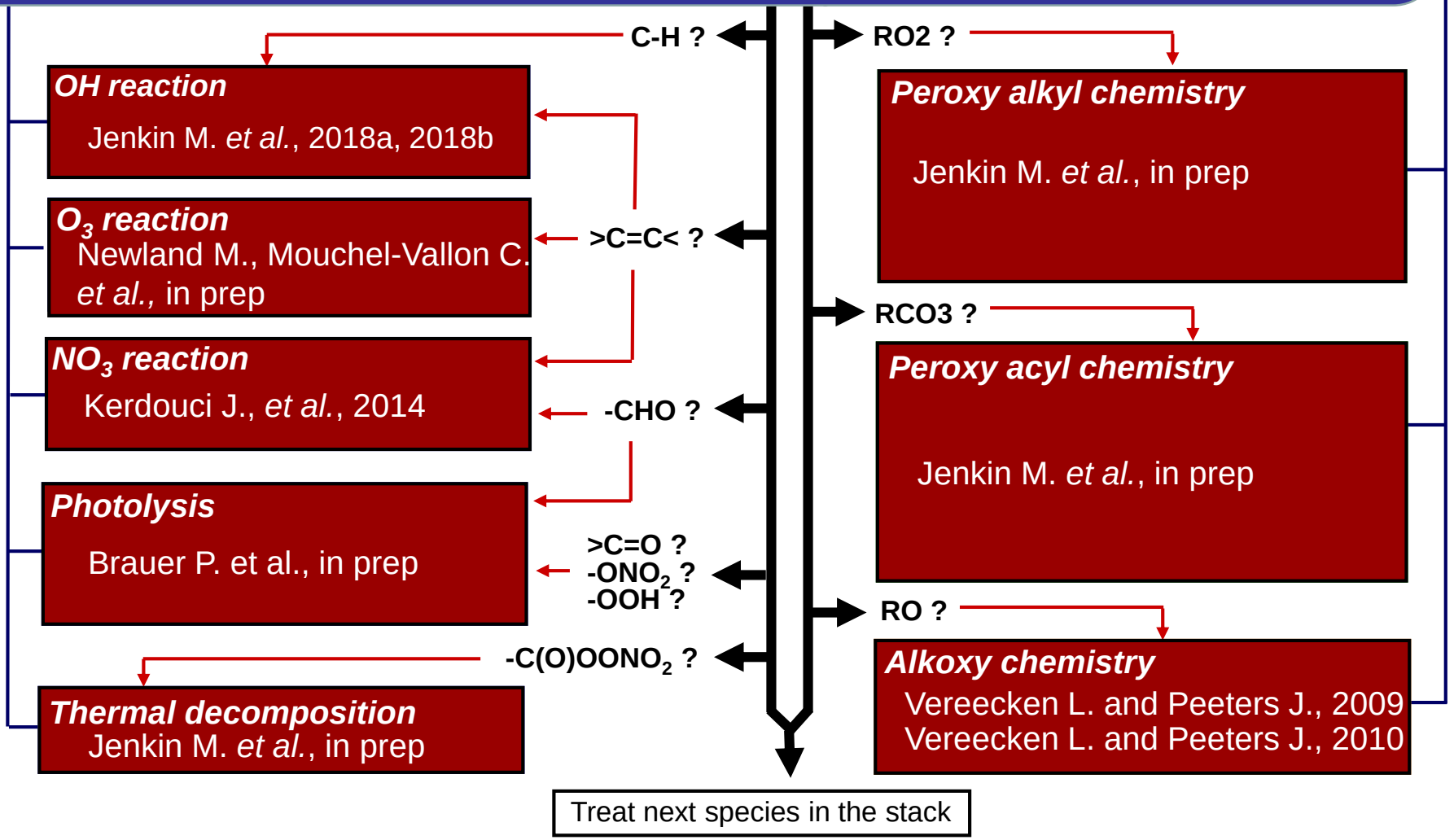
SAR in the MCM/GECKOA chemical protocol



SAR in the MCM/GECKOA chemical protocol

The current version GECKOA generates mechanism for alkane, alkene and (mono-cyclic) aromatic compounds and their oxidation products (alcohol, ketone, ester, ether, nitrate, nitro, hydroperoxide, …) .

See poster 4 by Andrew Rickard et al. for additional information about the Magnify project and chemical protocol in MCM/GECKOA

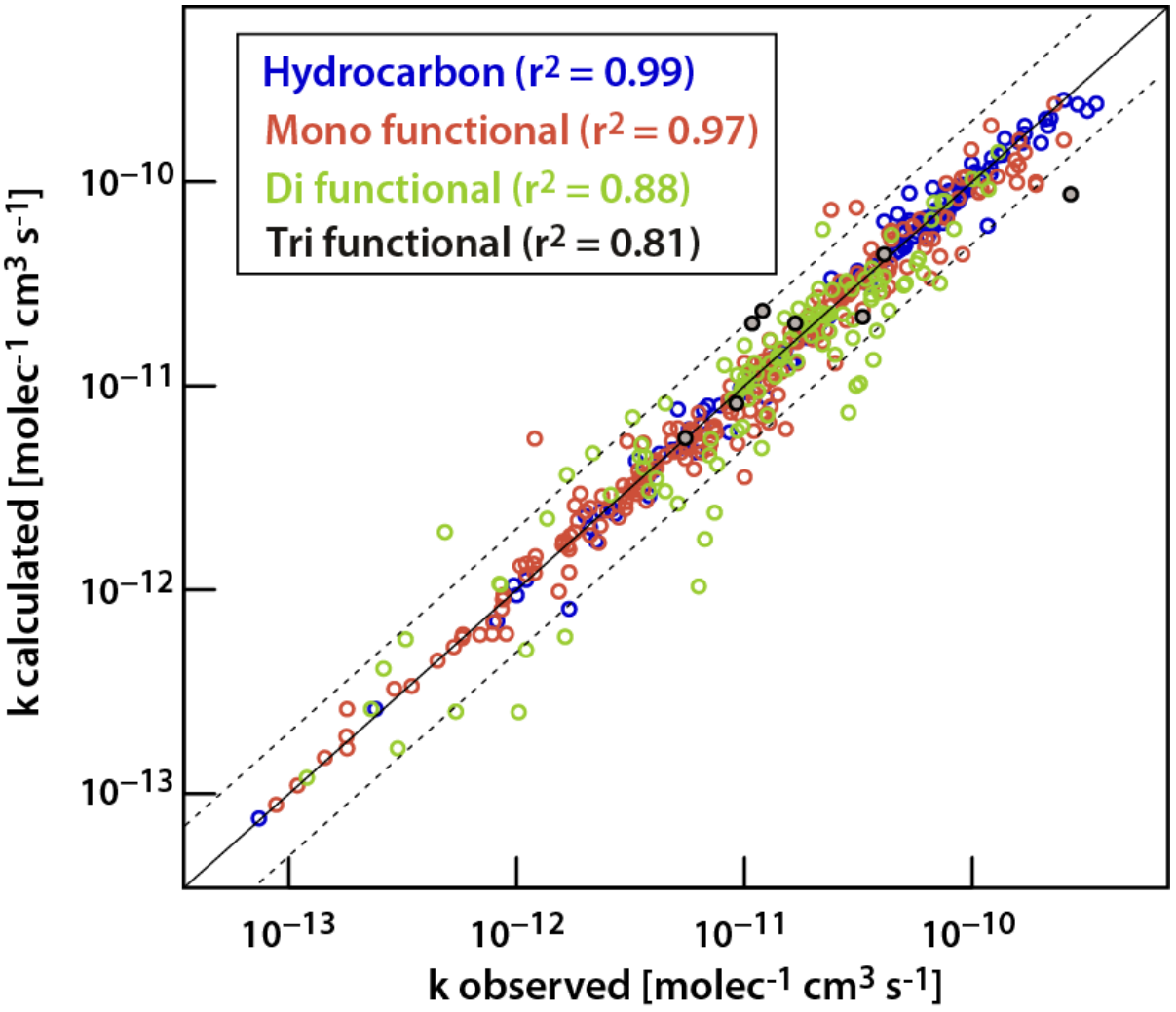


Some SAR assessment used in the MCM/GECKO protocols …

VOC+OH – Estimation of rate constants based on SAR

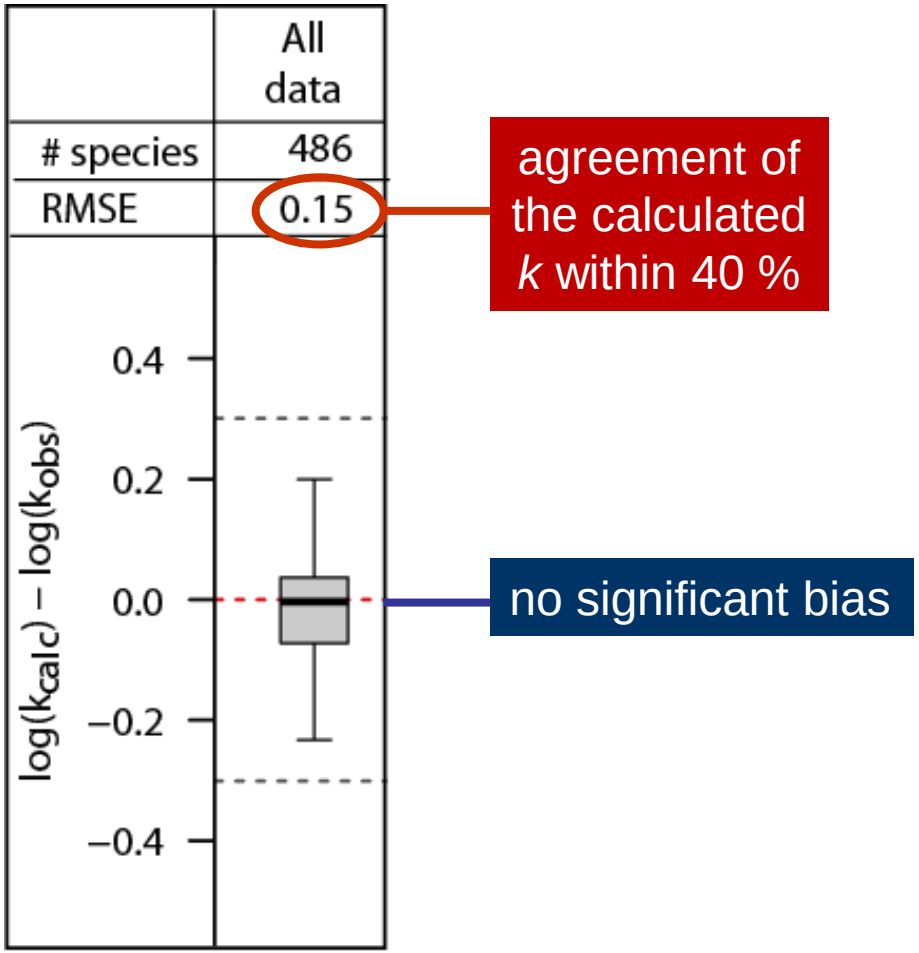
The experimental database for aliphatic species:

- 147 hydrocarbons
- 213 monofunctional species (alcohol, aldehyde, ketone, nitrate, ether, ester, nitro, carboxylic acid, hydroperoxide)
- 115 di-functional species
- **8** tri-functional species



[Jenkin et al., ACP, 2018]

VOC+OH – Estimation of rate constants based on SAR



agreement of the calculated *k* within 40 %

no significant bias

[Jenkin et al., ACP, 2018]

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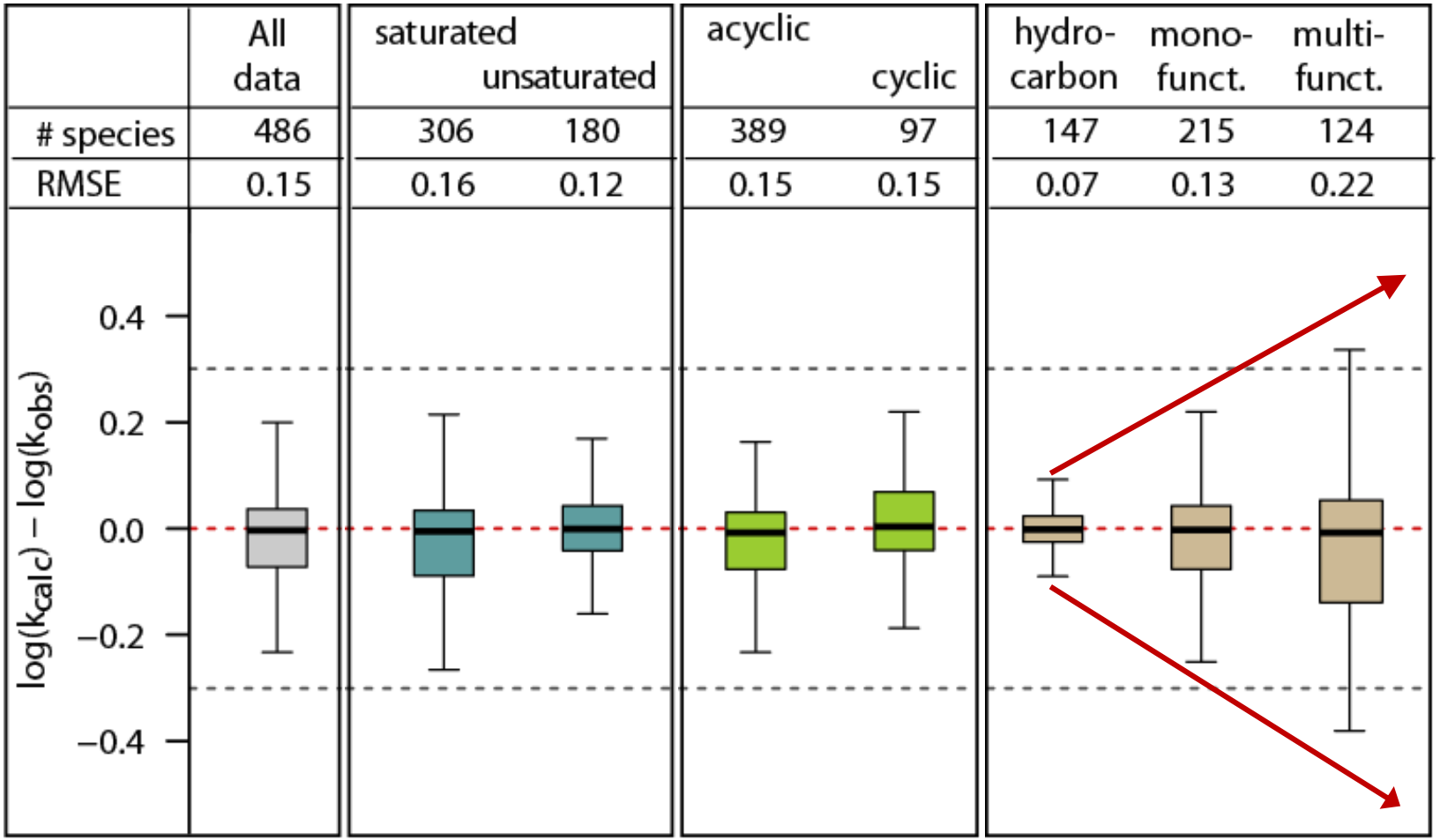
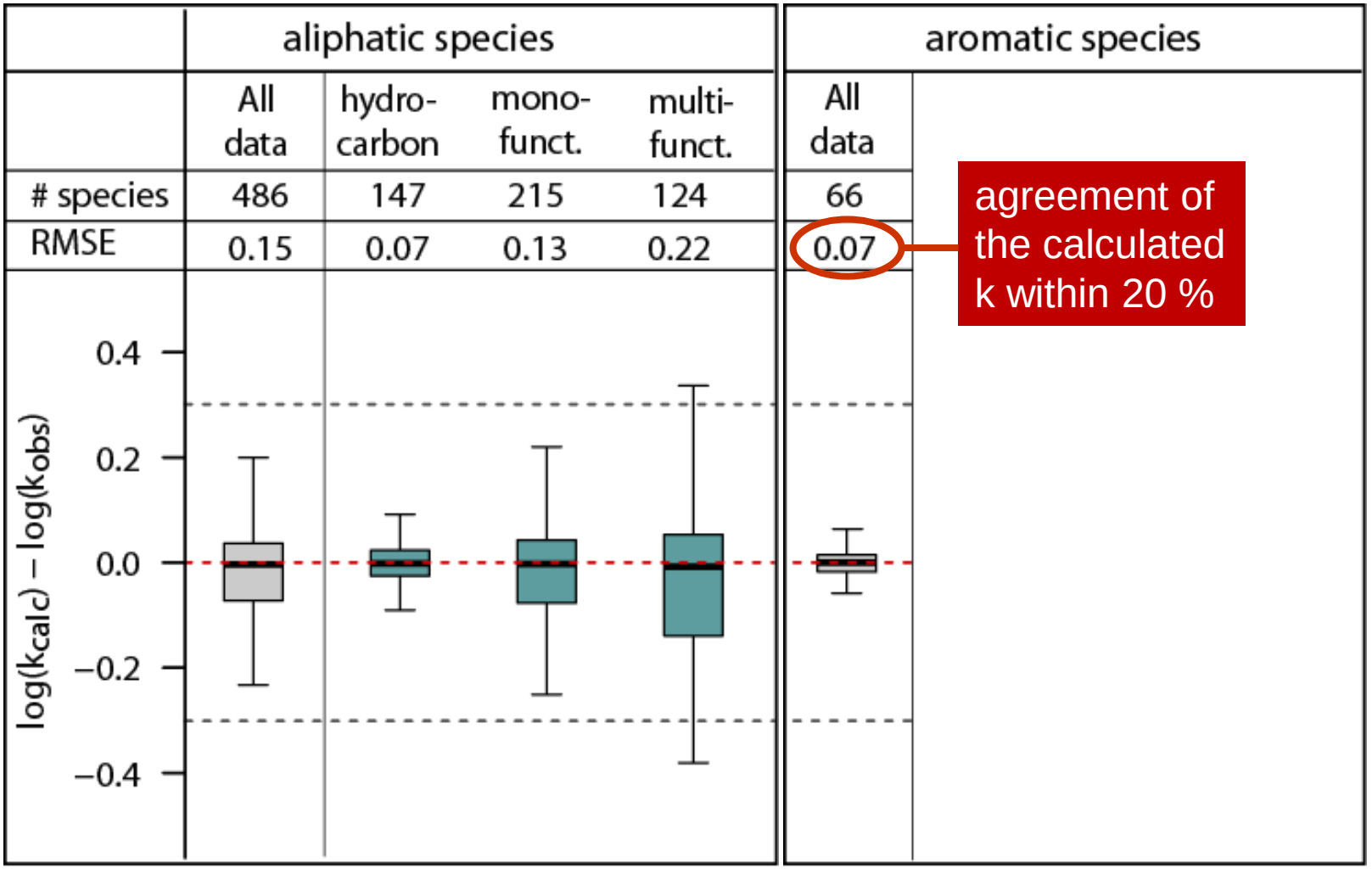


the reliability of the SARs decreases with the number of functional groups on the carbon skeleton

[Jenkin et al., ACP, 2018]

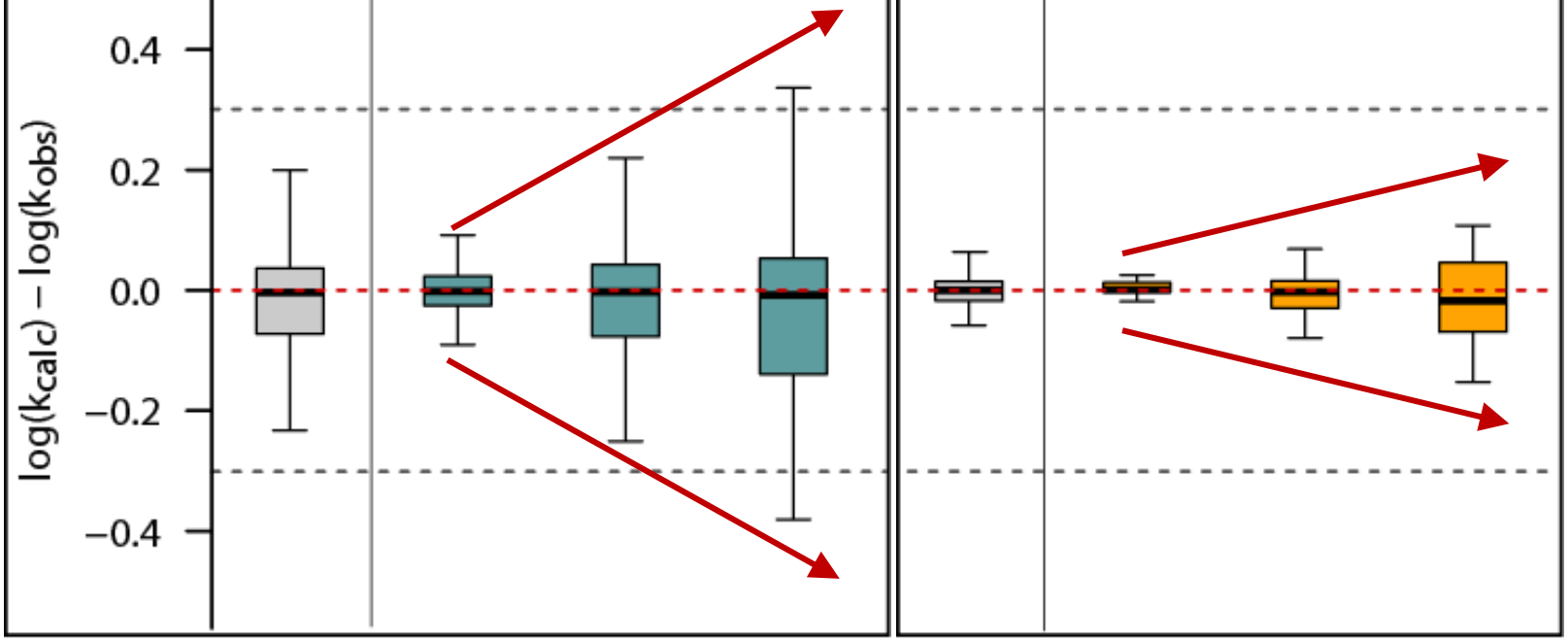
VOC+OH – Estimation of rate constants based on SAR



[Jenkin et al., ACP, 2018]

VOC+OH – Estimation of rate constants based on SAR

	aliphatic species				aromatic species			
	All data	hydro-carbon	mono-funct.	multi-funct.	All data	hydro-carbon	mono-funct.	di-funct.
# species	486	147	215	124	66	25	30	11
RMSE	0.15	0.07	0.13	0.22	0.07	0.06	0.07	0.08

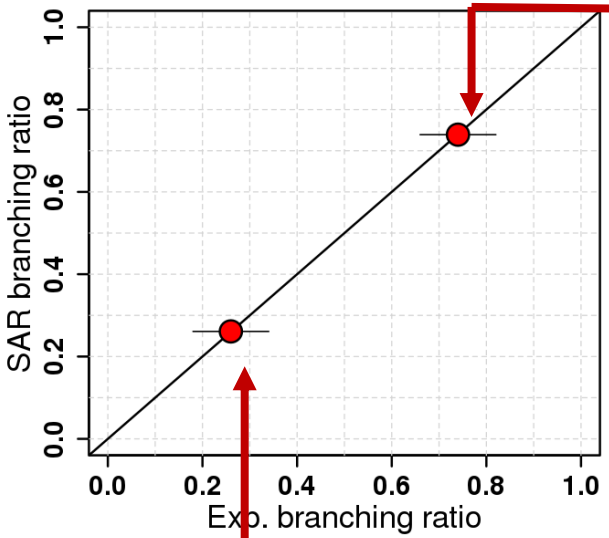


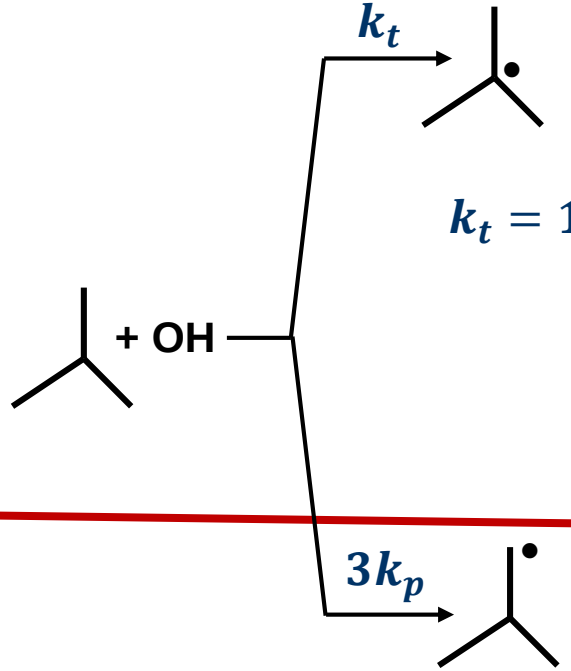
the reliability of the SARs decreases with the number of functional groups on the carbon skeleton

[Jenkin et al., ACP, 2018]

Assessment of branching ratio estimation based on SAR (VOC+OH reaction)

Example: isobutane branching ratio (@298K):





SAR: $\alpha_t = \frac{k_t}{k_{SAR}} = 0.739$

Exp: $\alpha_p = 0.74 \pm 0.08$

$k_t = 1.53 \times 10^{-12}\ cm^3\ s^{-1}$

SAR: $\alpha_p = \frac{3k_p}{k_{SAR}} = 0.261$

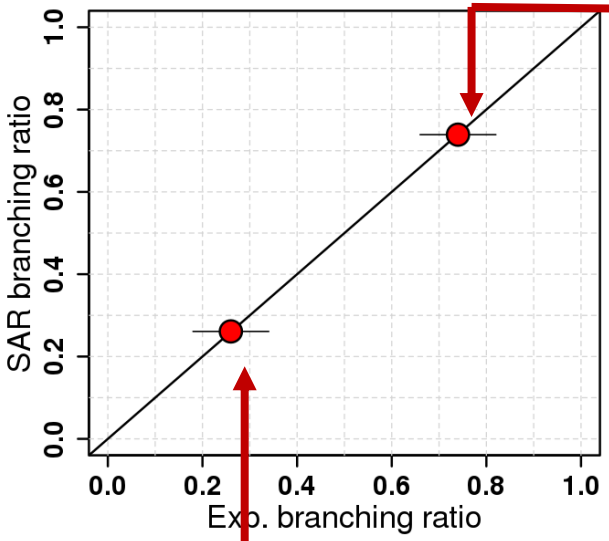
Exp: $\alpha_p = 0.26 \pm 0.08$

$3k_p = 5.41 \times 10^{-13}\ cm^3\ s^{-1}$

$k_{SAR} = 3k_p + k_t = 2.07 \times 10^{-12}\ cm^3\ s^{-1}$

$k_{Exp.} = (2.10 \pm 0.42) \times 10^{-12}\ cm^3\ s^{-1}$

Assessment of branching ratio estimation based on SAR (VOC+OH reaction)



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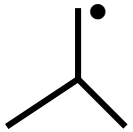
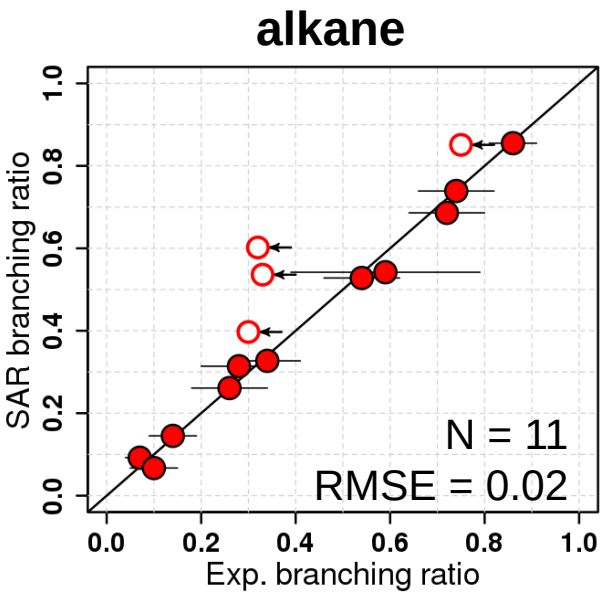


SAR: $\alpha_p = \frac{3k_p}{k_{SAR}} = 0.261$

Exp: $\alpha_p = 0.26 \pm 0.08$

Database for branching ratios (Acknowledgment: John Orlando, NCAR)

- 135 branching ratios for 79 species (C≥2 without halogen)
- Alkane, mono-functional species (alcohol, ether, ester, carbonyls, acid) and multifunctional species
- Values inferred (mostly) from product distributions provided in Calvert *et al.* books



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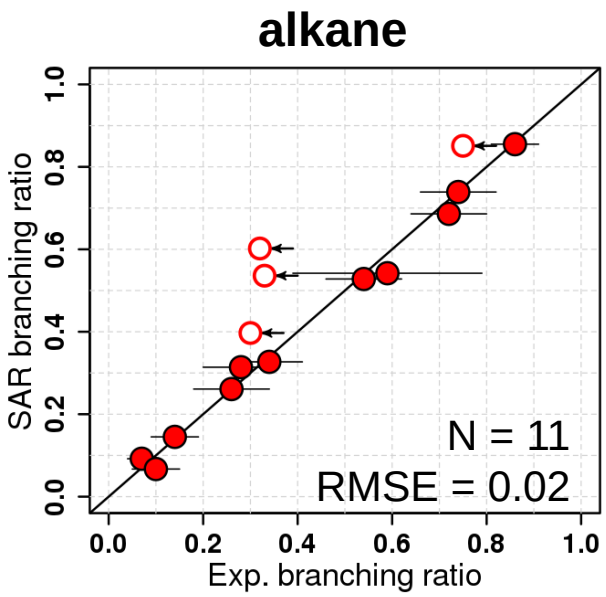
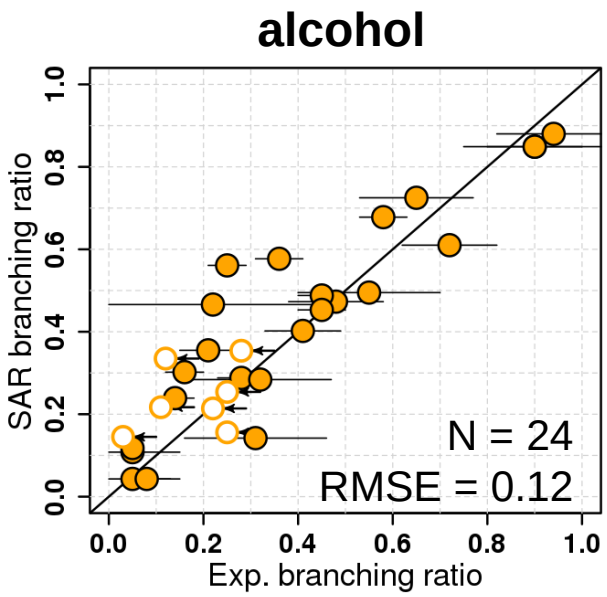
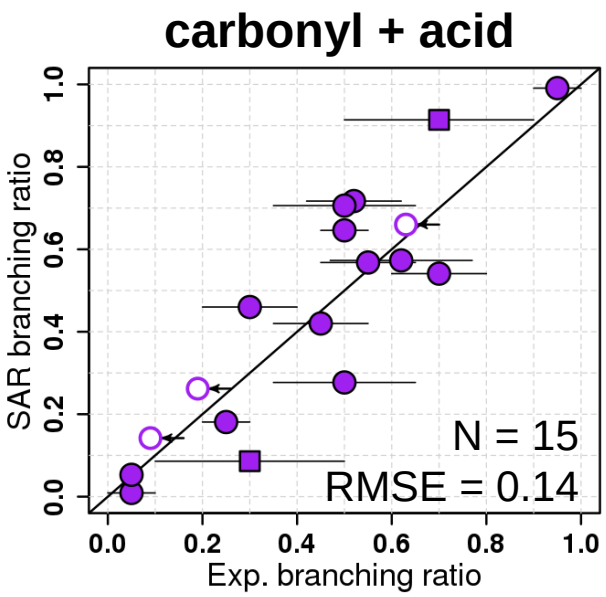
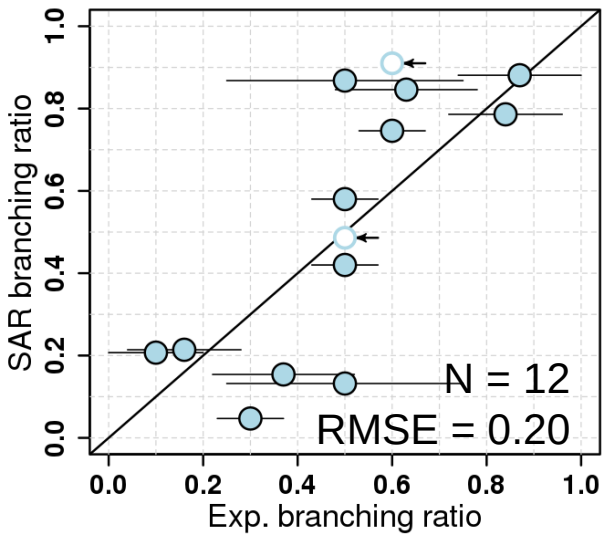
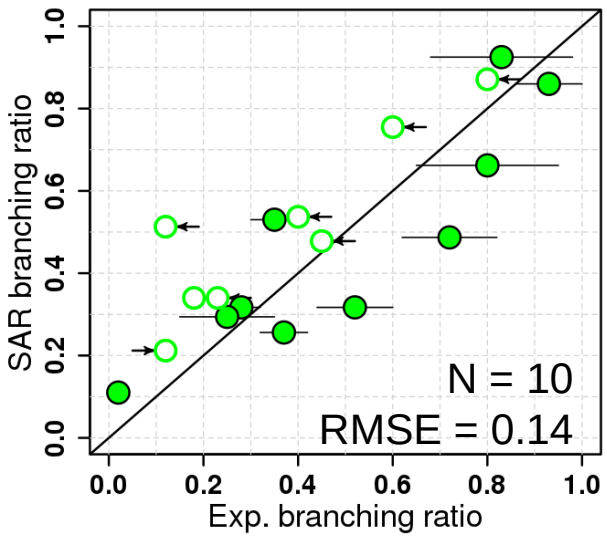
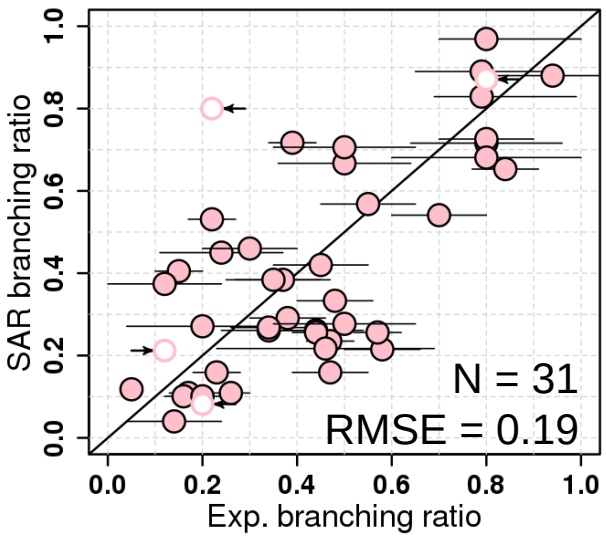




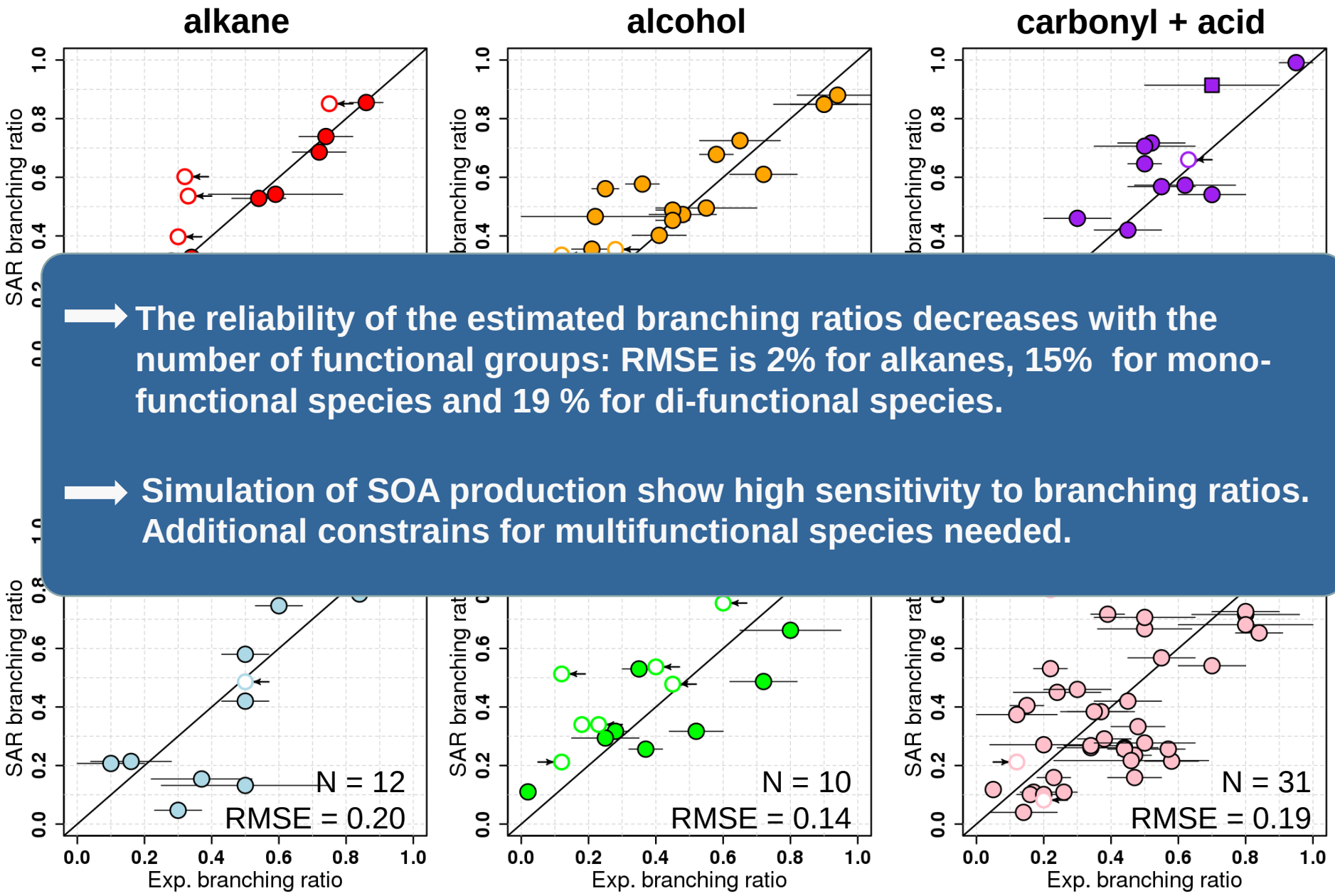








Assessment of branching ratio estimation based on SAR (VOC+OH reaction)



- The reliability of the estimated branching ratios decreases with the number of functional groups: RMSE is 2% for alkanes, 15% for mono-functional species and 19 % for di-functional species.
- Simulation of SOA production show high sensitivity to branching ratios. Additional constrains for multifunctional species needed.

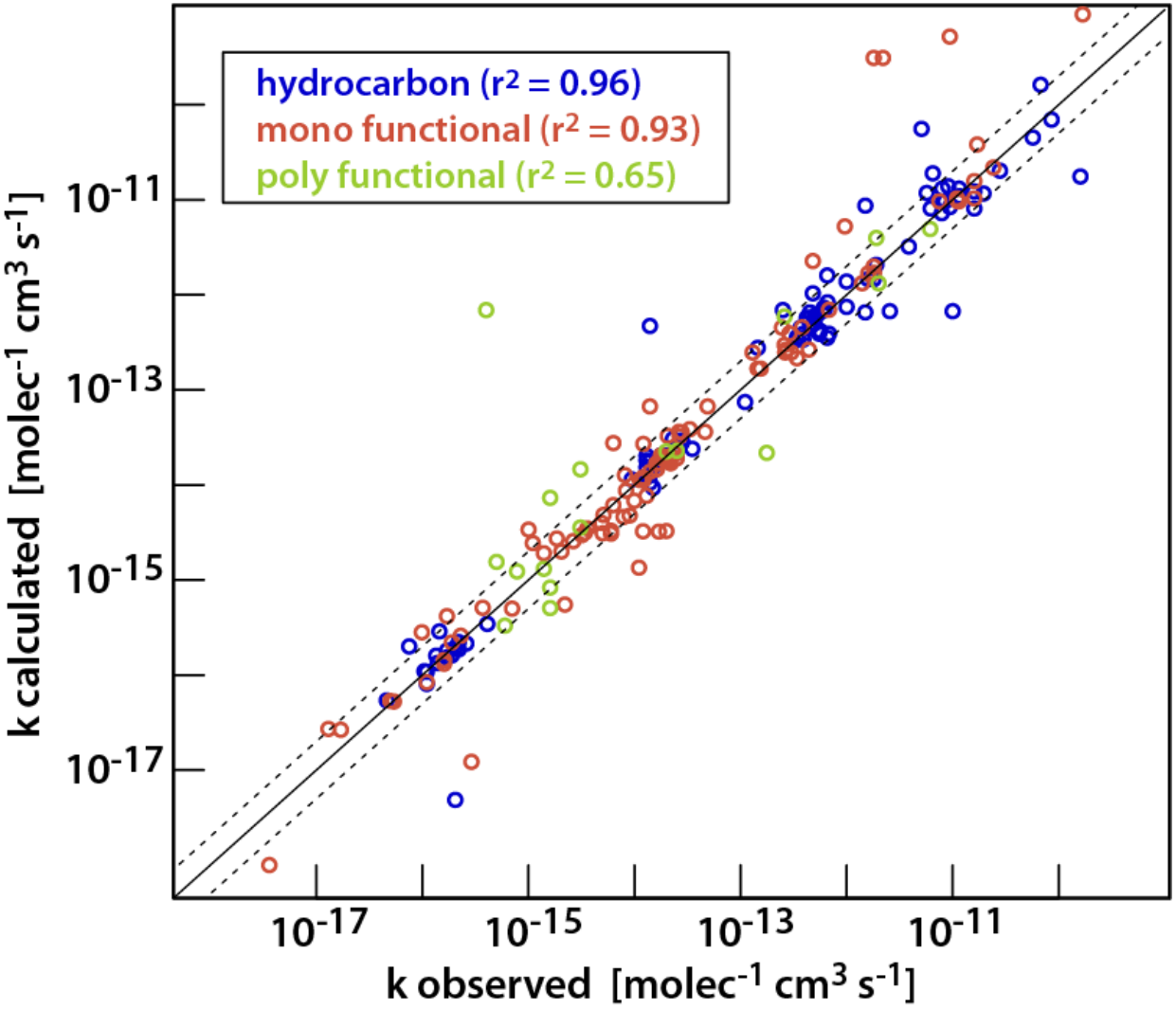
VOC+NO3 – Estimation of rate constants based on SAR

Selected SAR for the MCM/GECKO protocol:
group contribution method by Kerdouci et al., Atmos. Env., 2014

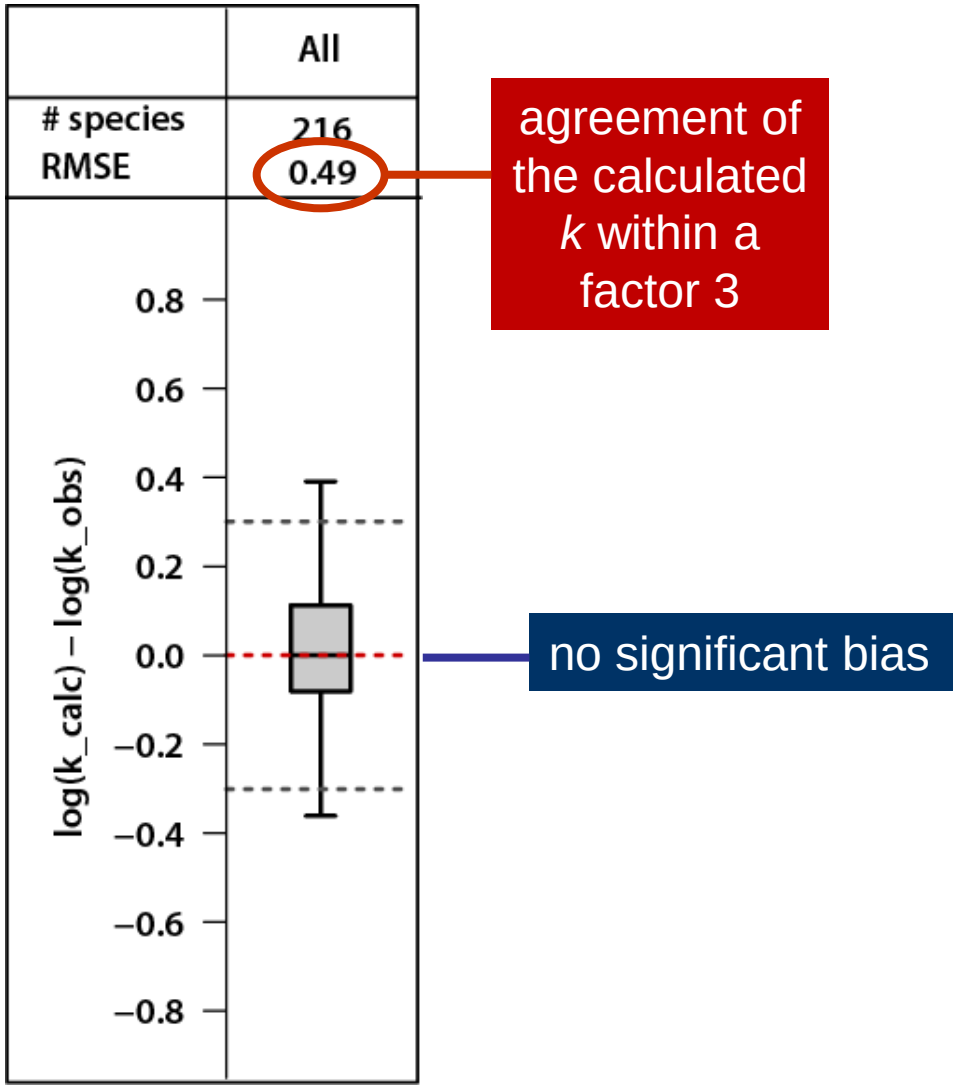
The experimental database for aliphatic species:

- **100** hydrocarbons
- **99** monofunctional species (alcohol, aldehyde, ketone, ether, ester)
- **17** multifunctional species

Acknowledgments:
Carter *et al.*, CRC project, 2017



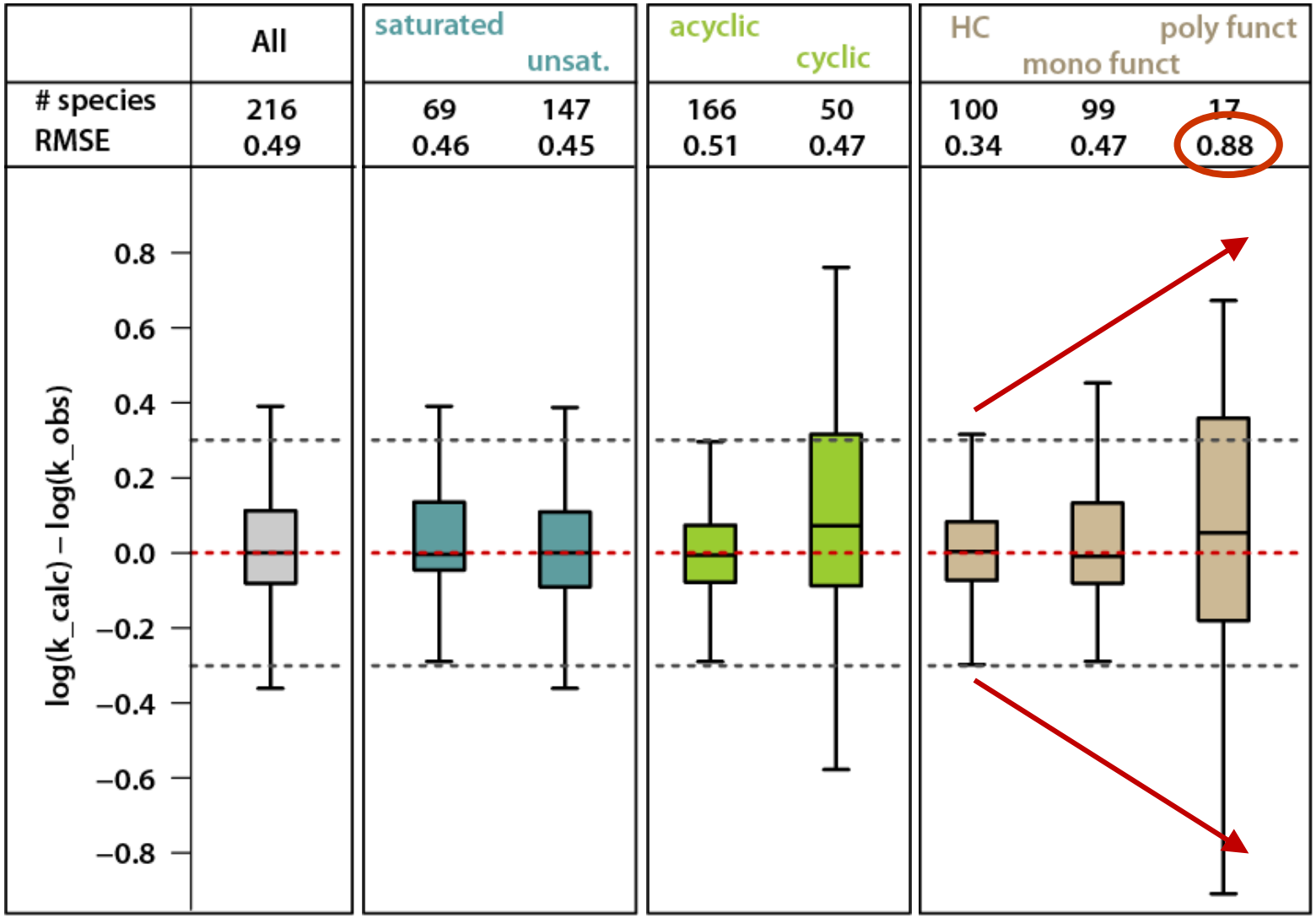
VOC+NO3 – Estimation of rate constants based on SAR



agreement of the calculated *k* within a factor 3

no significant bias

VOC+NO3 – Estimation of rate constants based on SAR



the reliability of the SARs decreases with the number of functional groups on the carbon skeleton

MCM 3.2
vs.
GECKOA/MCM

Development of scenarios to compare mechanisms

Objectives & Constrains

- Should represent a set of conditions, from remote to urban environments

- Oxidation mechanism of each VOC must be tested under identical conditions:
  - Same chemistry for inorganic species
  - The tested mechanism should not interfere with the chemical scenario
  - Chemical conditions must be “buffered”

  ➡ Initial conditions with only tiny amount of the tested VOC

Development of scenarios to compare mechanisms

Constrained concentrations:

	Remote	Remote continental	Continental	Polluted continental	Urban
NOx (ppb)	0.010	0.025	0.5	2	20
O_3 (ppb)	40	40	40	40	40
CH_4 (ppb)	1750	1750	1750	1750	1750
CO (ppb)	120	120	150	200	300
NMHC k_{OH} (s^{-1})	0	1	6	9	13
Add. HCHO (ppb)	0	0	2	5	10
Org. Aero. (µg m^{-3})	10	10	10	10	10

Simulation conditions:

- Solar zenith angle: 45° (fixed)
- Temperature: 298 K
- Relative humidity: 70 %
- Deposition (avoid accumulation) : HNO_3, H_2O_2, CH_3OOH

Butane oxidation

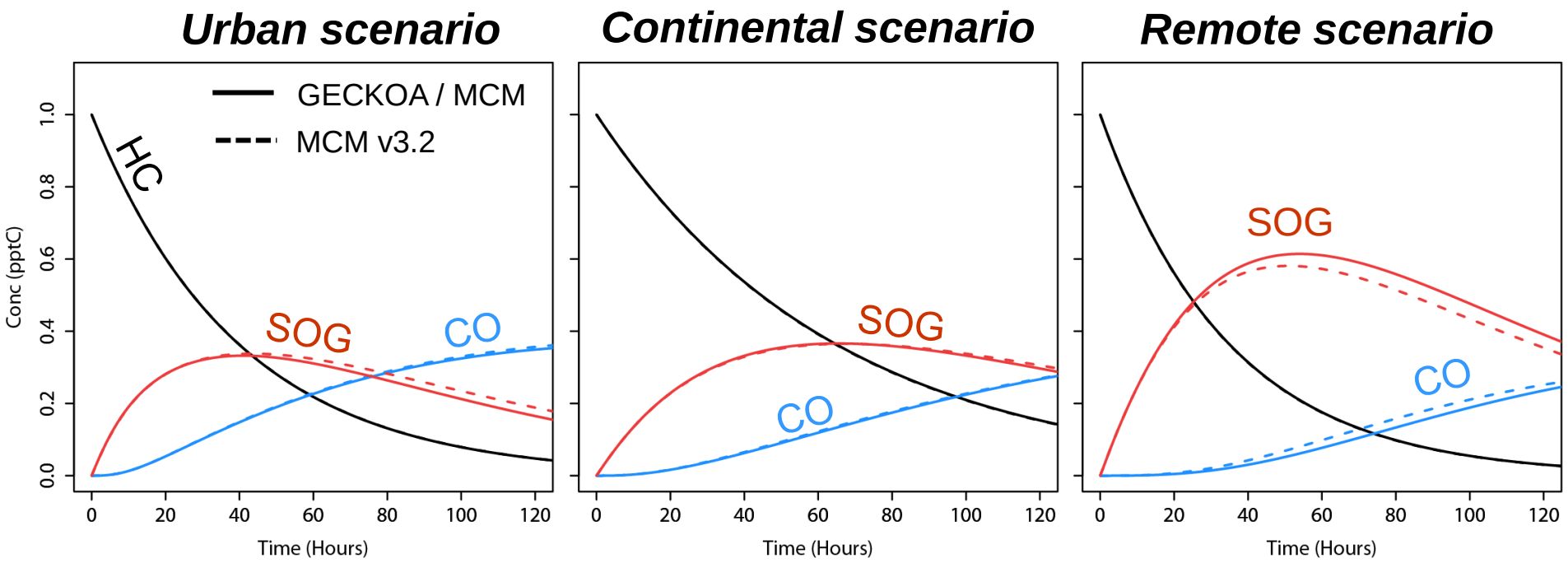
GECKOA/MCM scheme generation:

- Chemistry ignored if $P^{vap} < 10^{-13}$ atm
- Functional isomers lumped if yield < 5%
- Up to 8 generations accounted
  - → ≈ 2 230 species
  - → ≈ 18 000 reactions

MCM scheme:

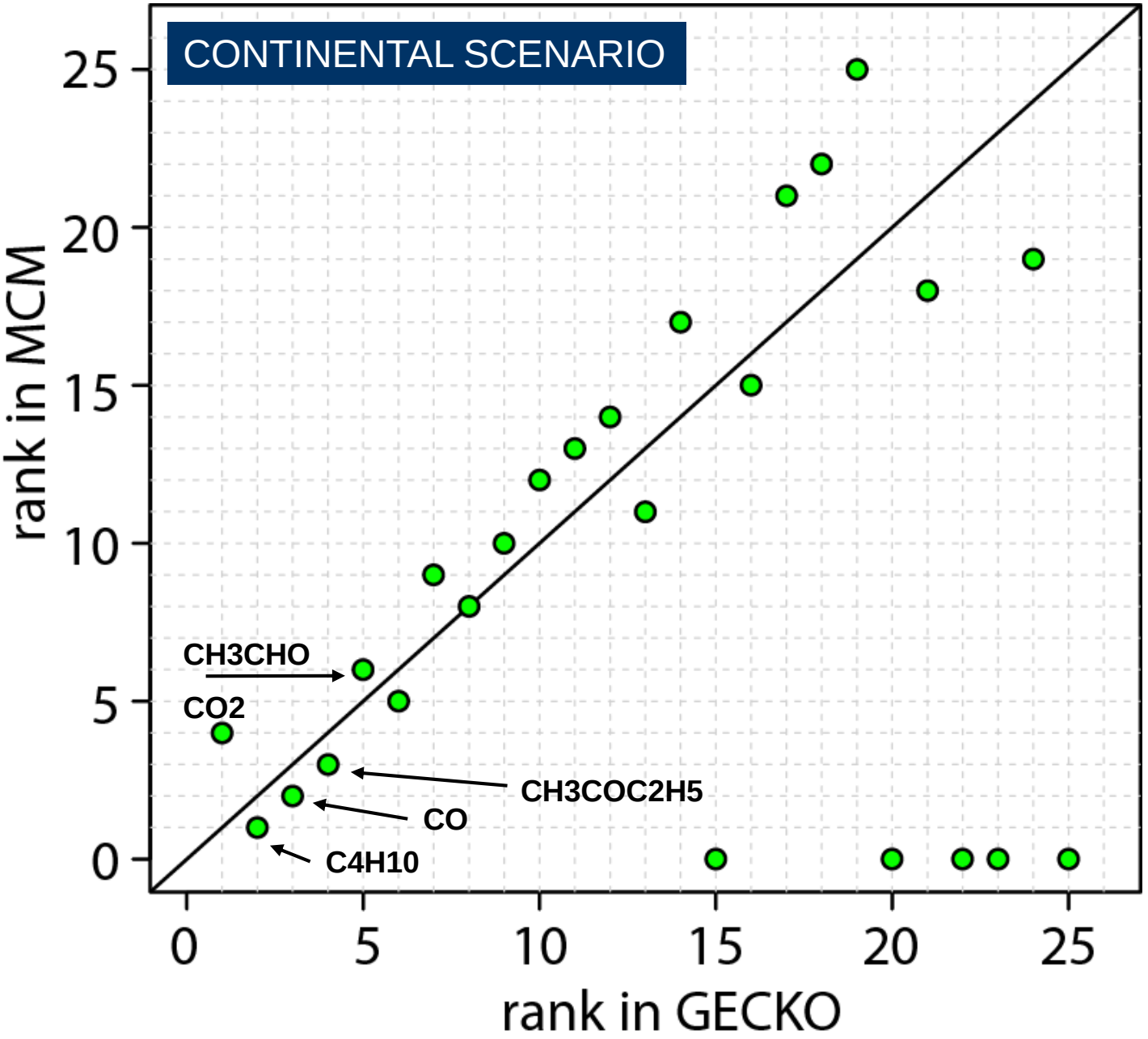
→ 171 species

→ 552 reactions

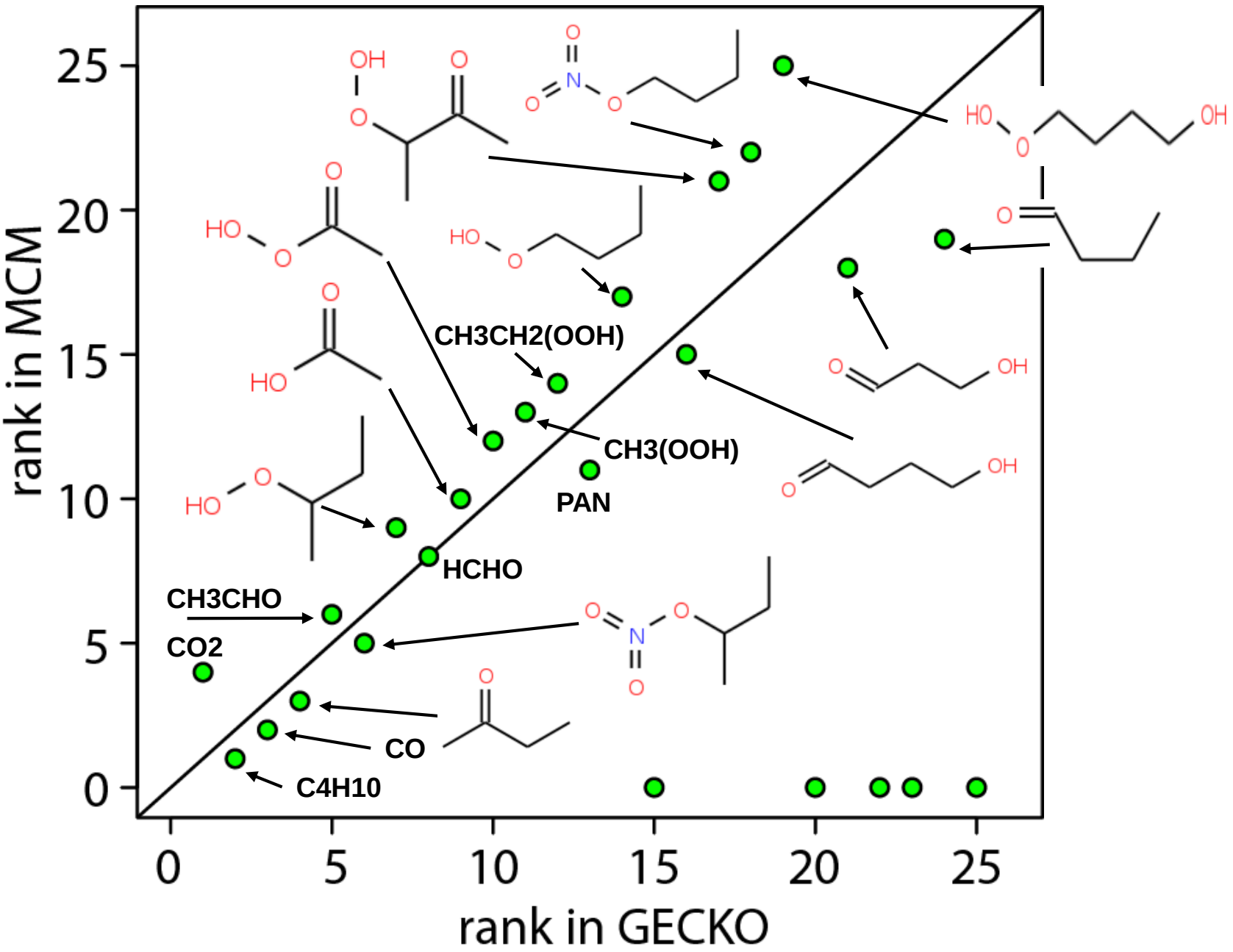


HC SOG CO

Butane oxidation – top contributors to the C budget



Butane oxidation – top contributors to the C budget



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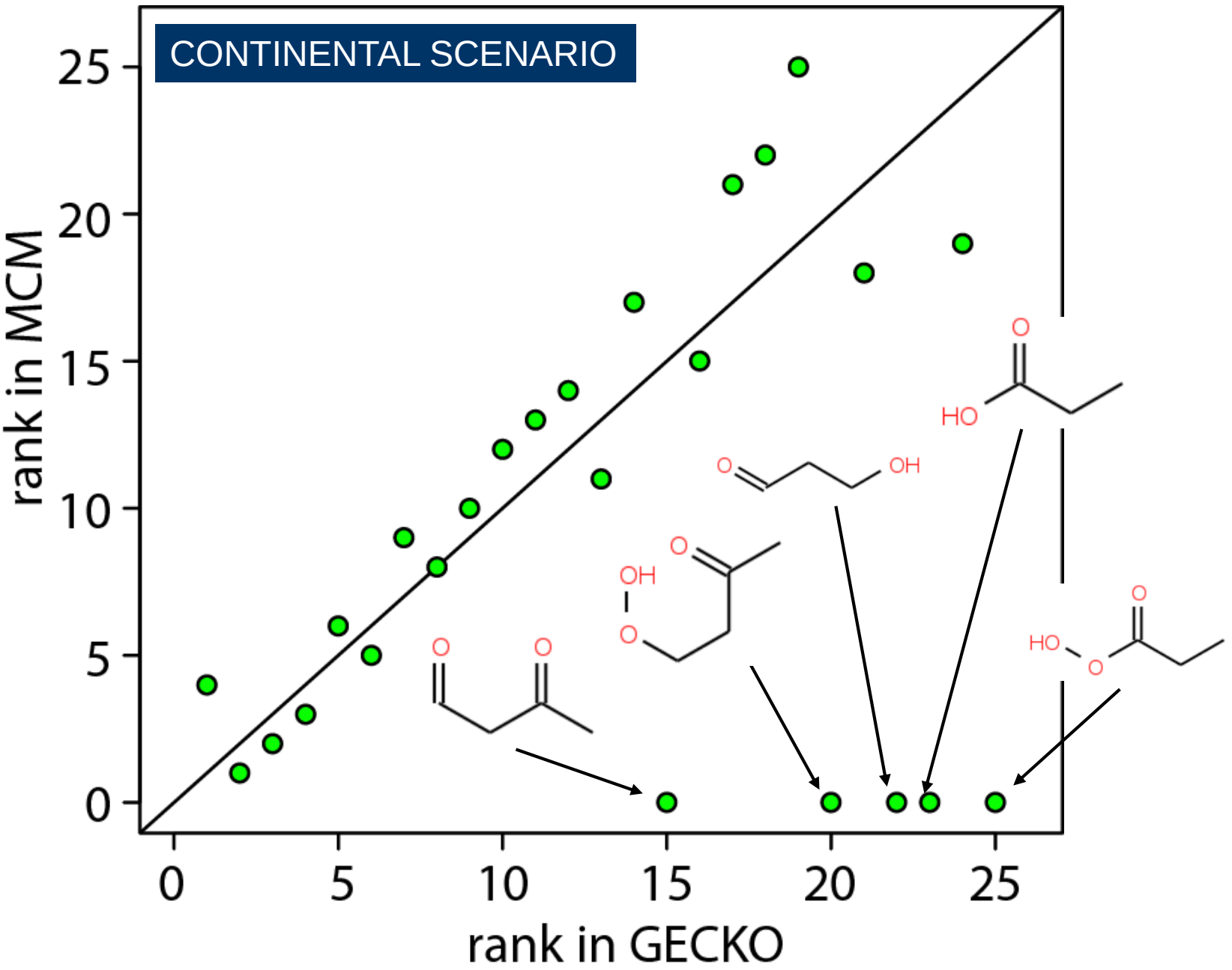

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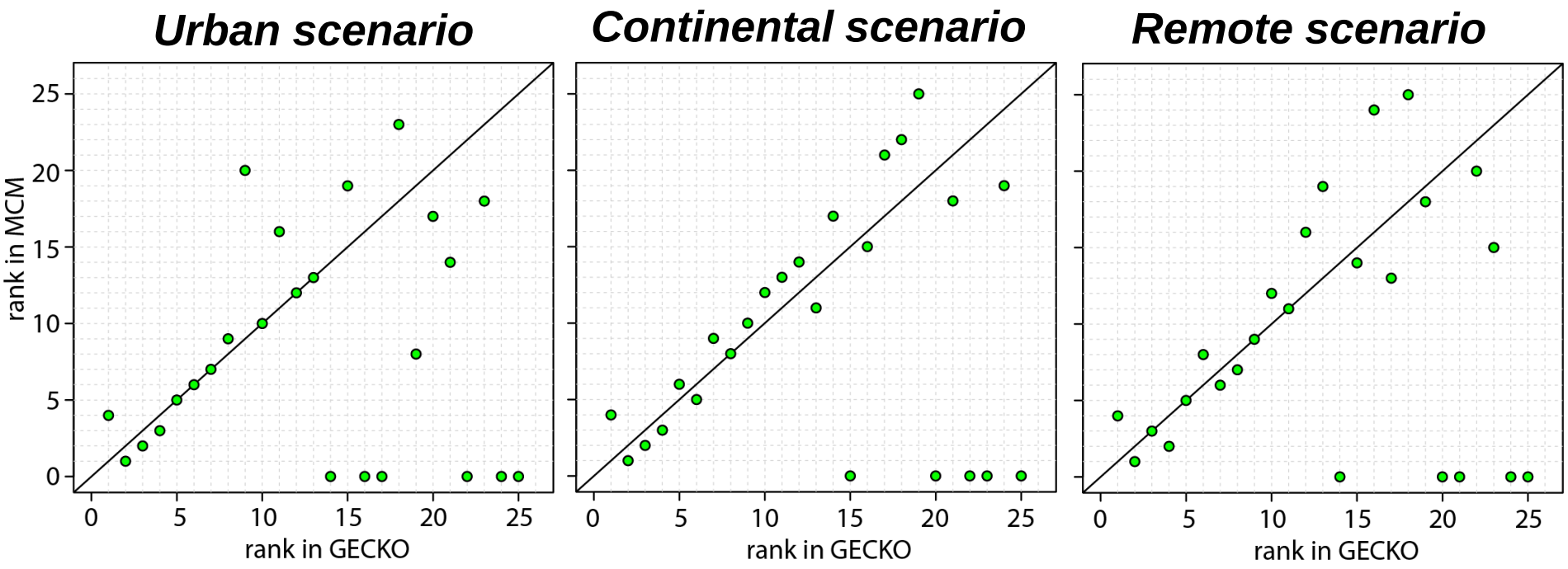


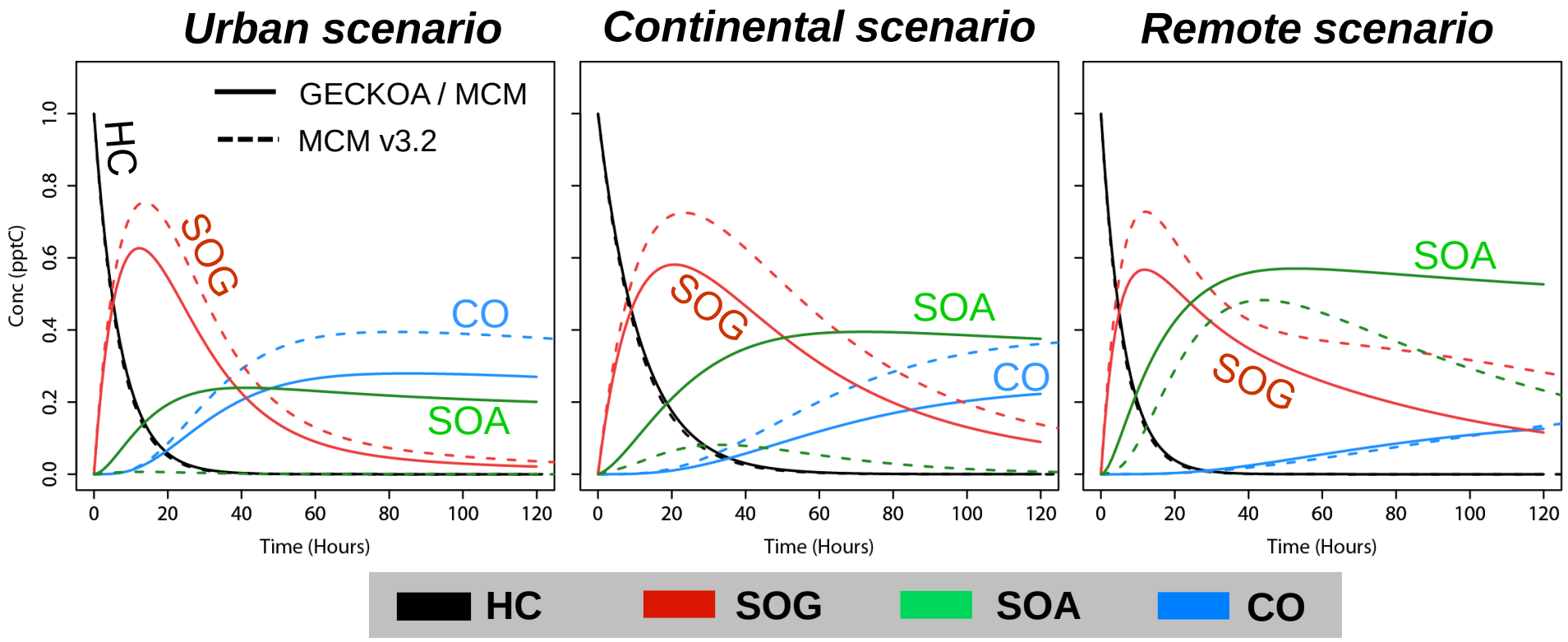
Dodecane oxidation

GECKOA/MCM scheme generation:

- Chemistry ignored if $P^{vap} < 10^{-13}$ atm
- Functional isomers lumped if yield < 5%
- Up to 8 generations accounted
  - → ≈ 1×10^5 species
  - → ≈ 7×10^5 reactions

MCM scheme:

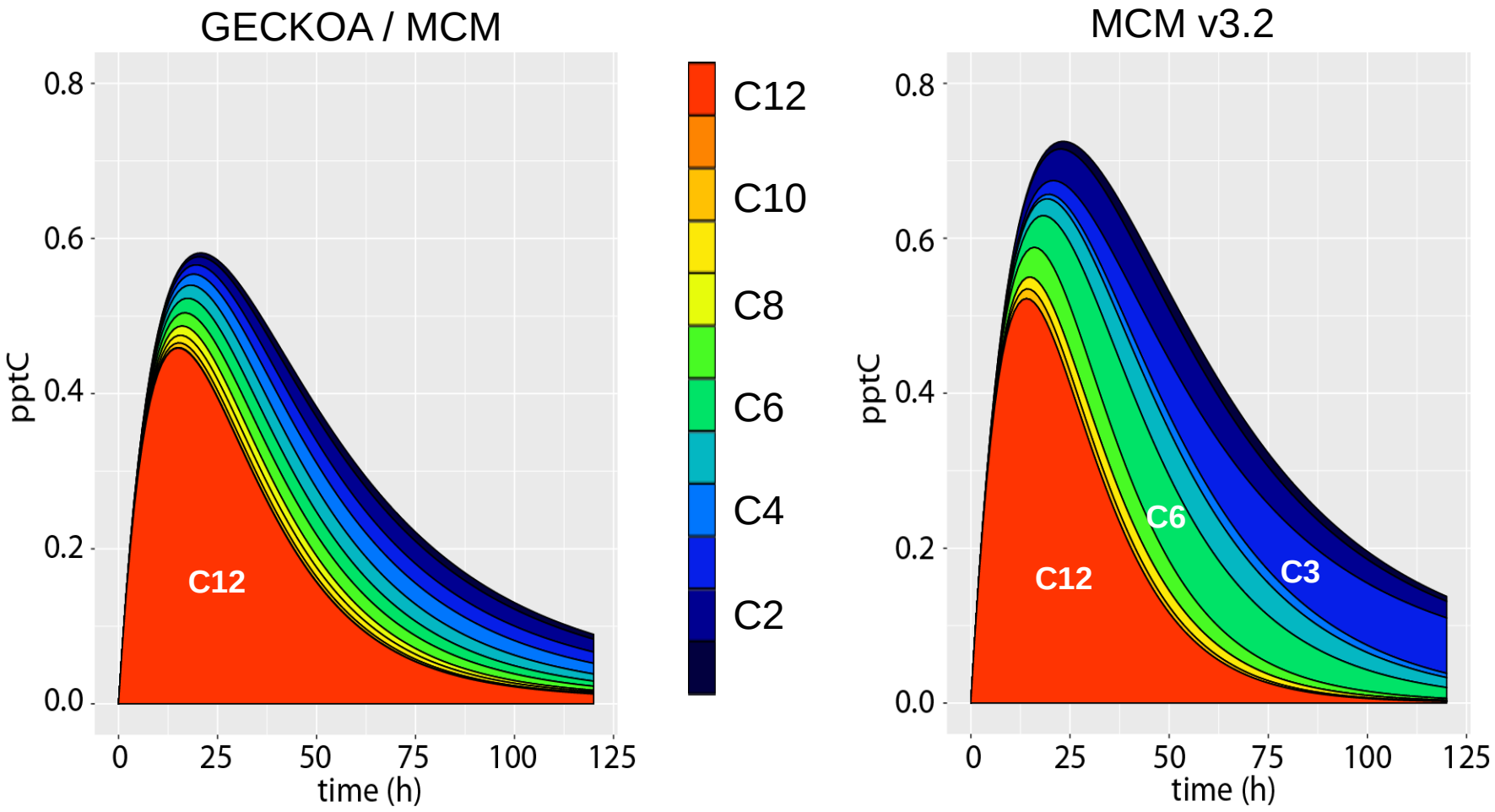
- → 400 species
- → 1 200 reactions



Dodecane oxidation – organic carbon budget

CONTINENTAL SCENARIO

Carbon chain length – gas phase only



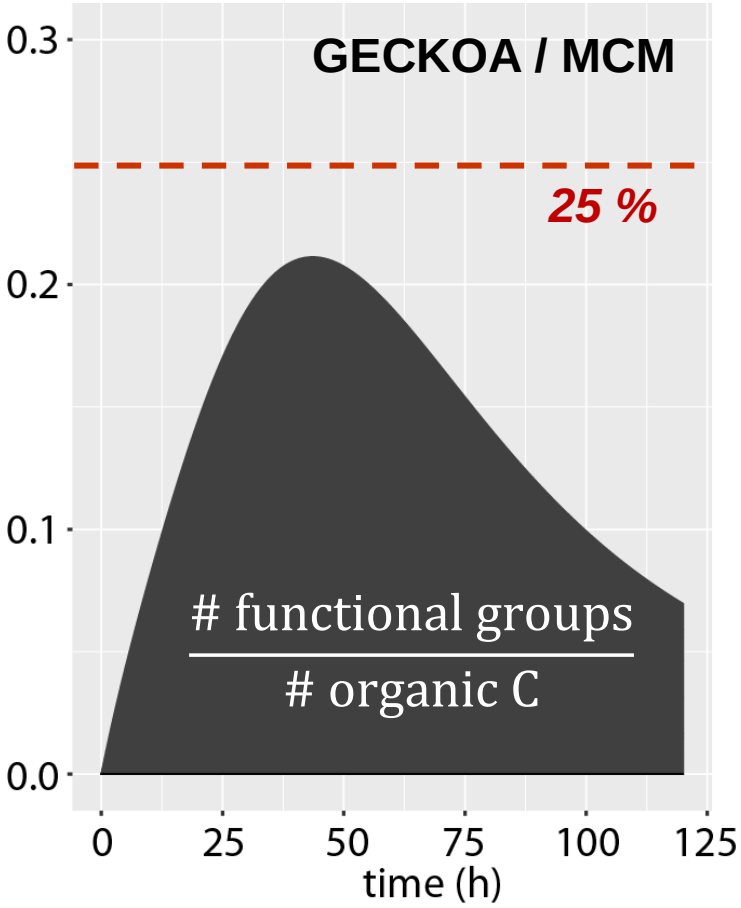
MCM favors fragmentation routes compared to MCM/GECKOA

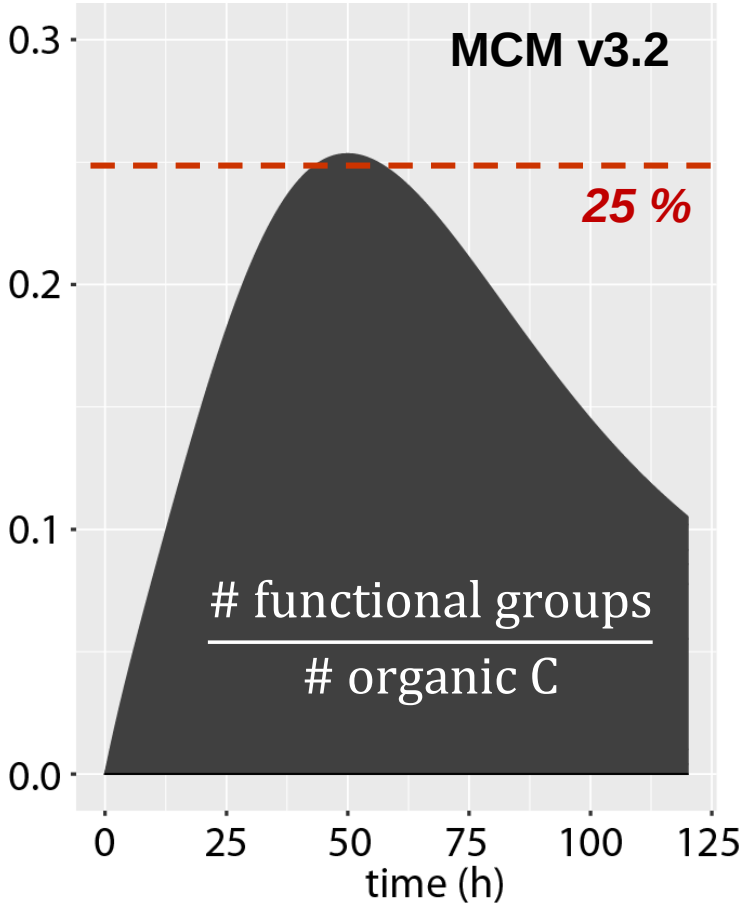
Dodecane oxidation – org. functional group distribution

CONTINENTAL SCENARIO

Functional group per carbon ratio – gas phase only

$$R_{i/C} = \frac{\text{Number of carbons bearing function i}}{\text{Total number of organic carbons}}$$





Dodecane oxidation – org. functional group distribution

CONTINENTAL SCENARIO

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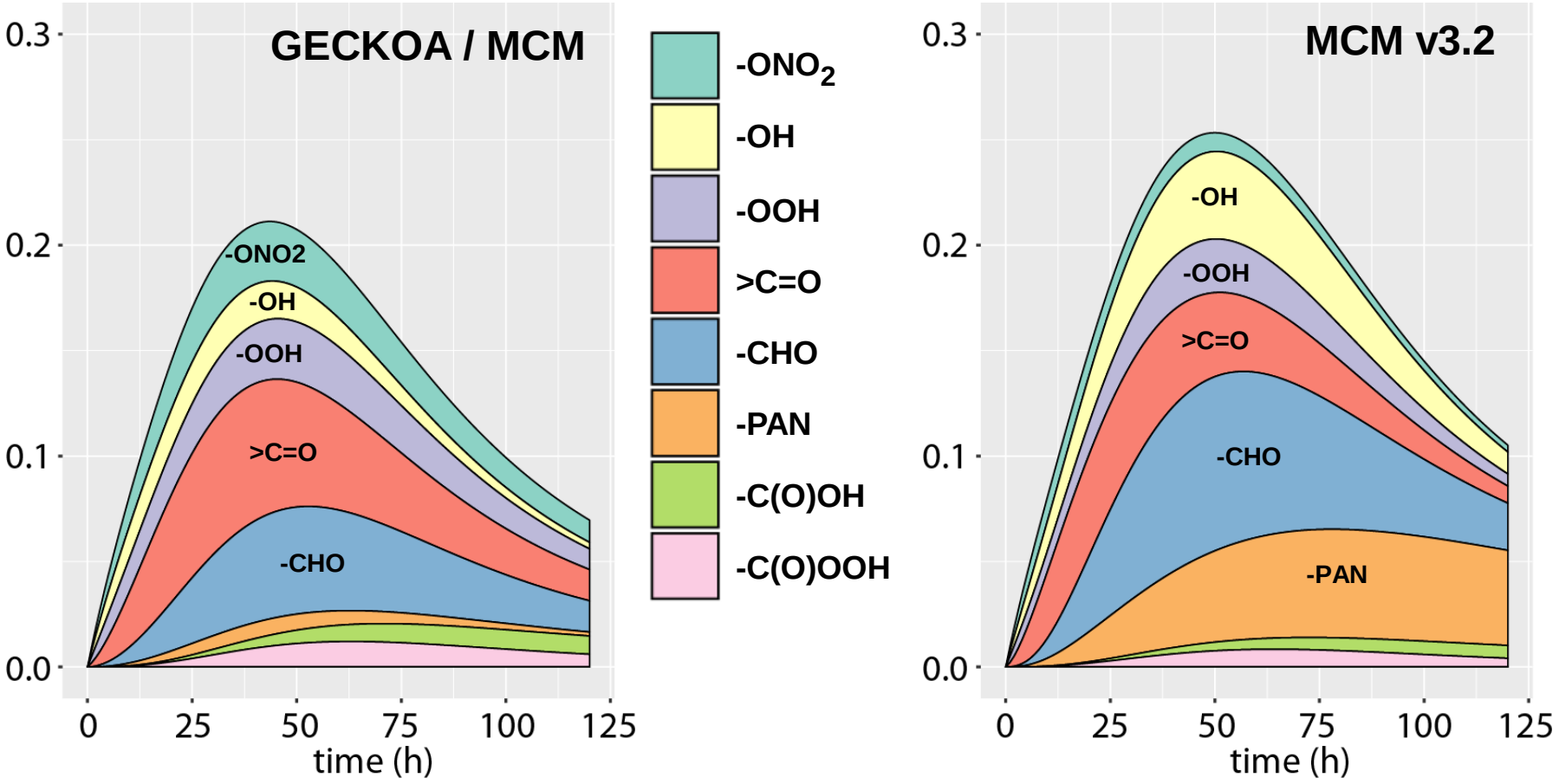
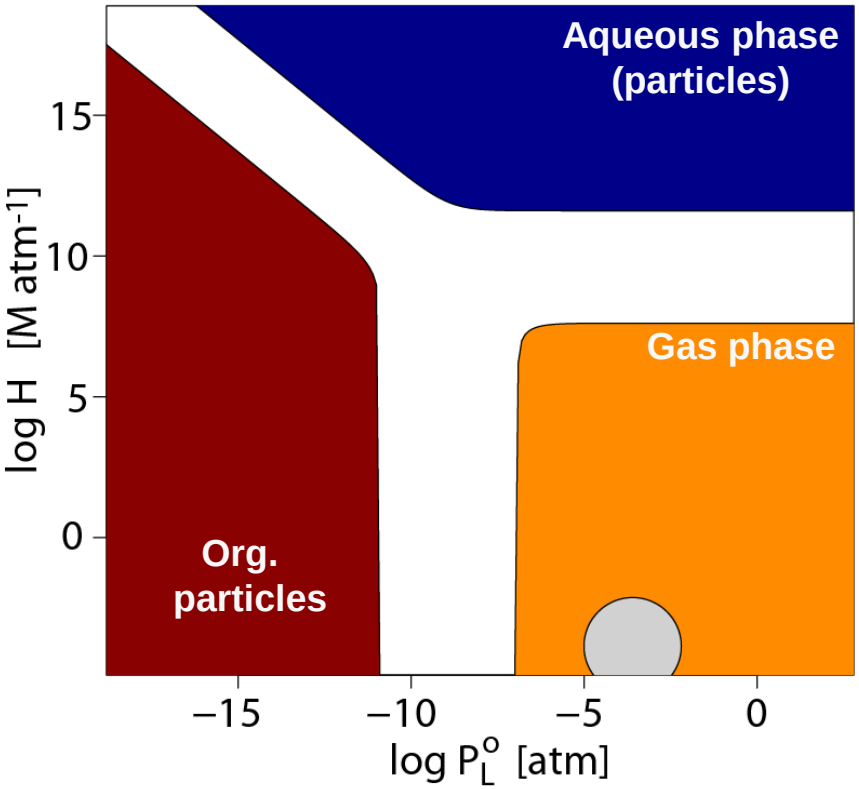


Dodecane oxidation – oxidation trajectories

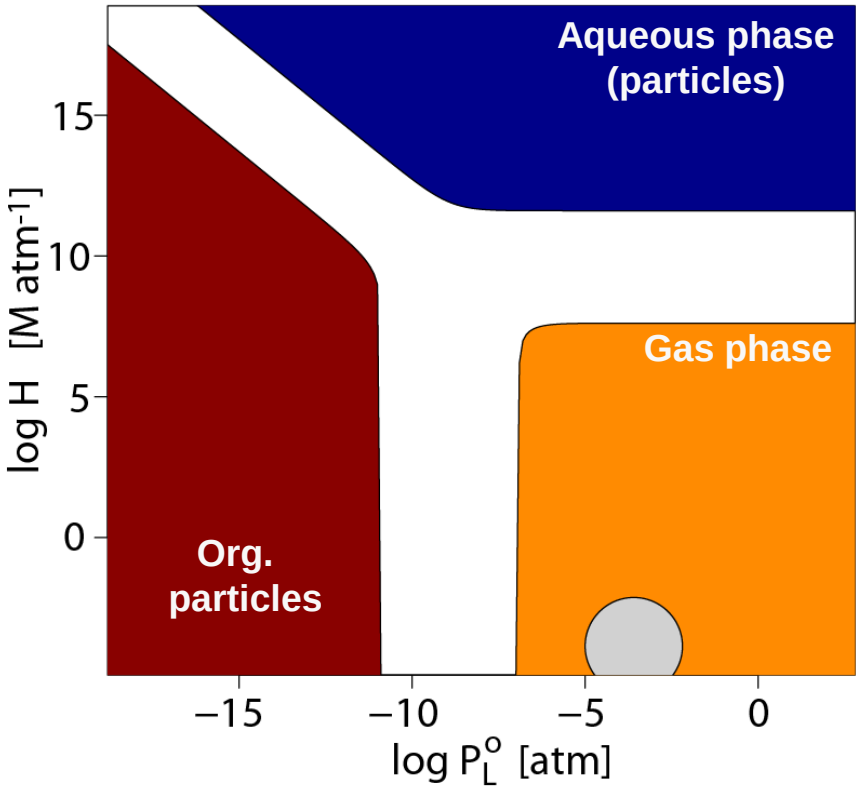
CONTINENTAL SCENARIO

time = 0

GECKOA / MCM



MCM v3.2



Phase partitioning (> 99 %) assuming:

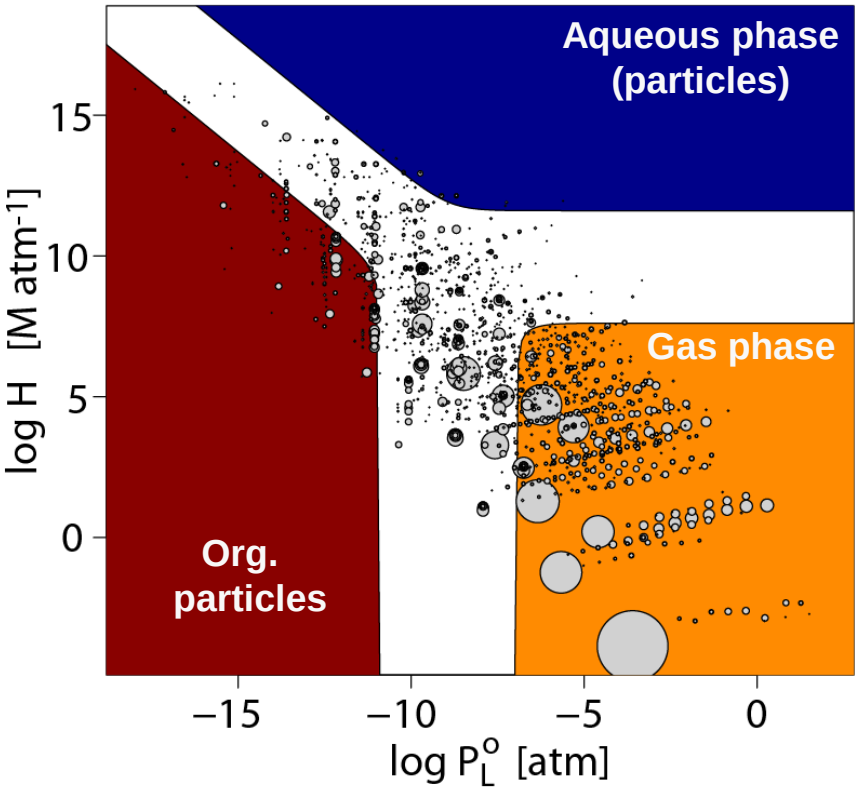
- C_{OA} = 10 µg m^{-3} , $MW_{aerosol}$ = 200 g mol^{-1}
- LWC = 10 µg m^{-3} (deliquescent particle)

Dodecane oxidation – oxidation trajectories

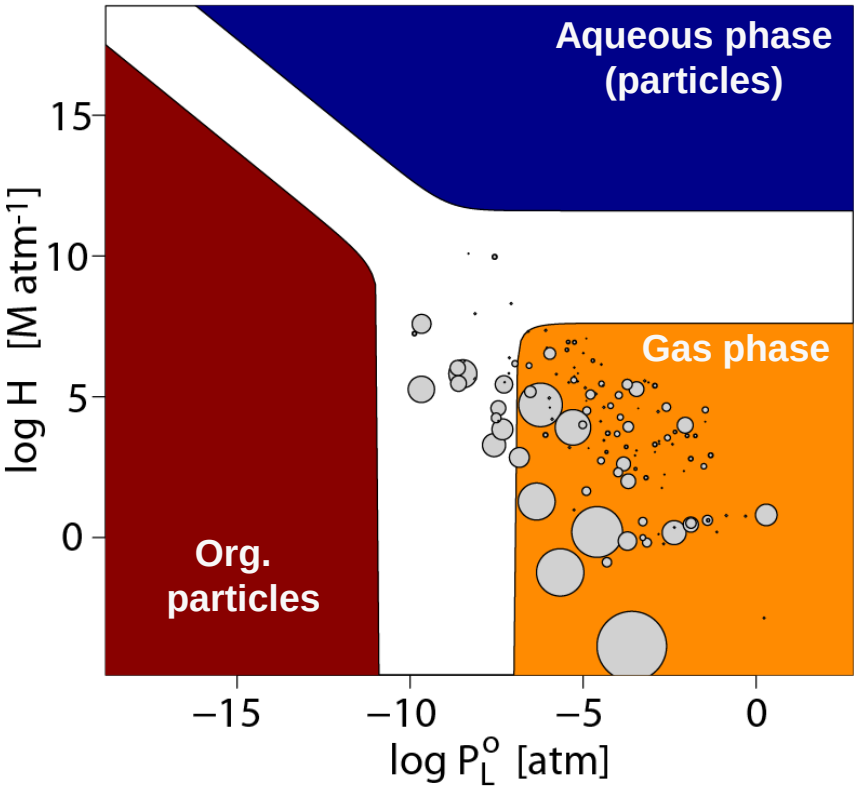
CONTINENTAL SCENARIO

time = 1×τ_{parent}

GECKOA / MCM



MCM v3.2



Phase partitioning (> 99 %) assuming:

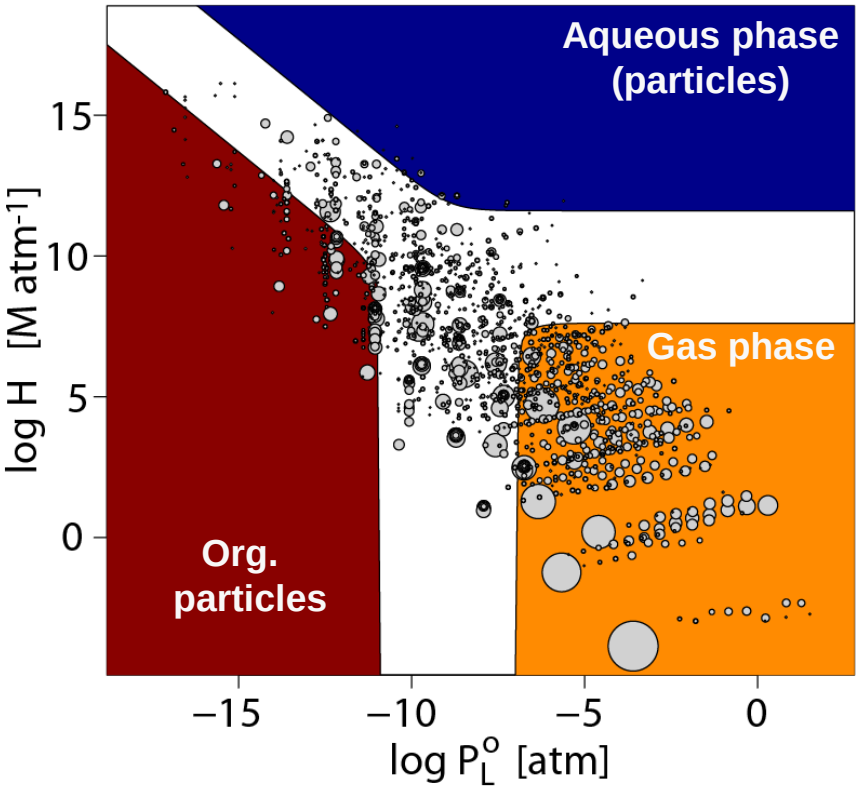
- C_{OA} = 10 µg m^{-3} , $MW_{aerosol}$ = 200 g mol^{-1}
- LWC = 10 µg m^{-3} (deliquescent particle)

Dodecane oxidation – oxidation trajectories

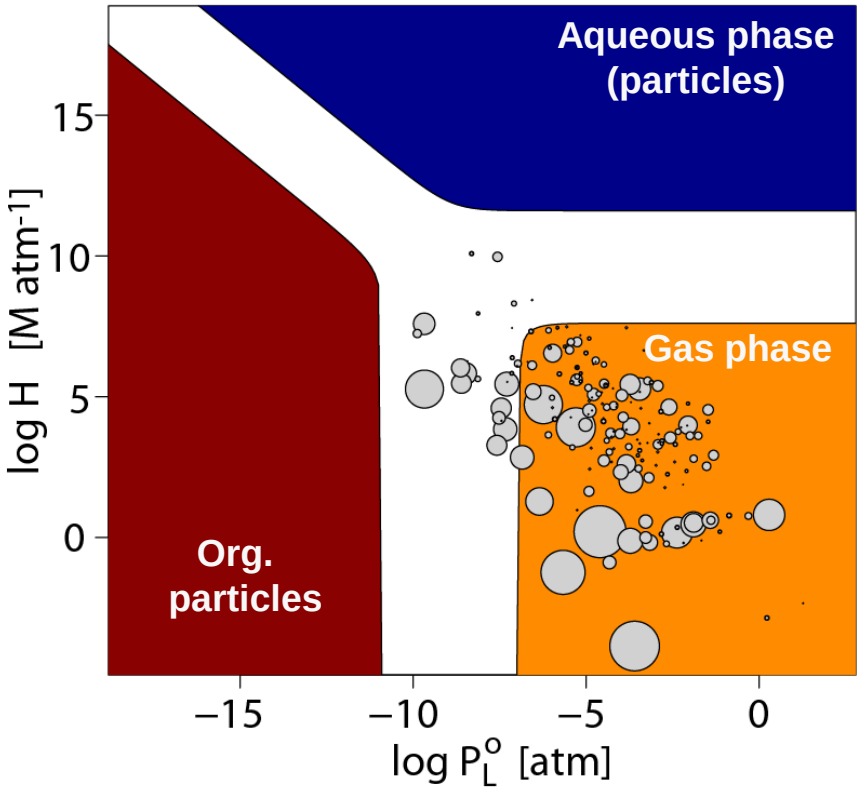
CONTINENTAL SCENARIO

time = 2×τ_{parent}

GECKOA / MCM



MCM v3.2



Phase partitioning (> 99 %) assuming:

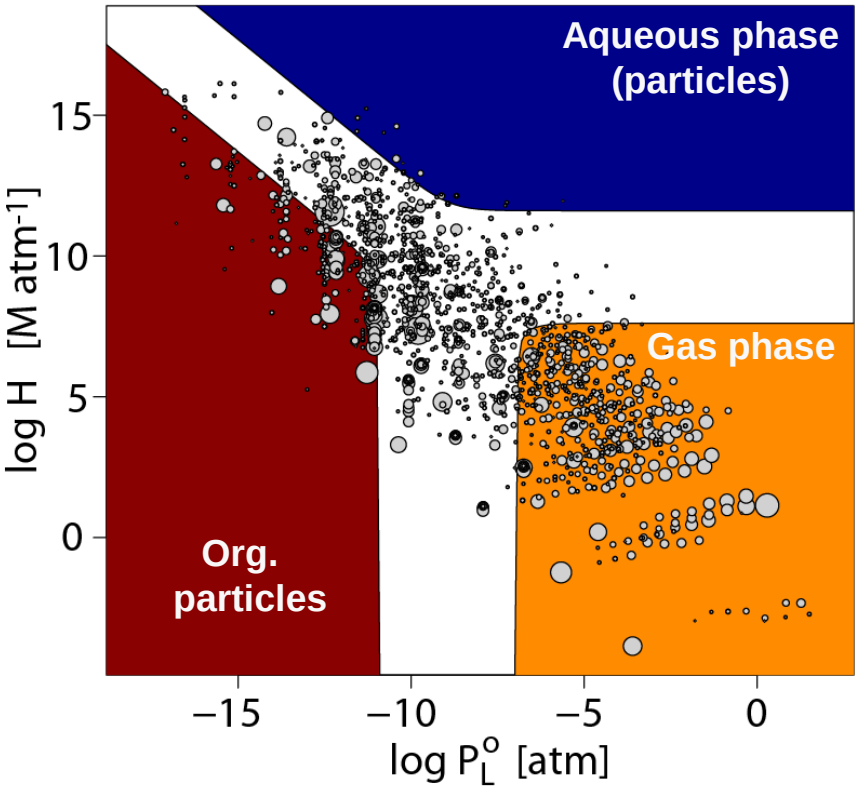
- C_{OA} = 10 µg m^{-3} , $MW_{aerosol}$ = 200 g mol^{-1}
- LWC = 10 µg m^{-3} (deliquescent particle)

Dodecane oxidation – oxidation trajectories

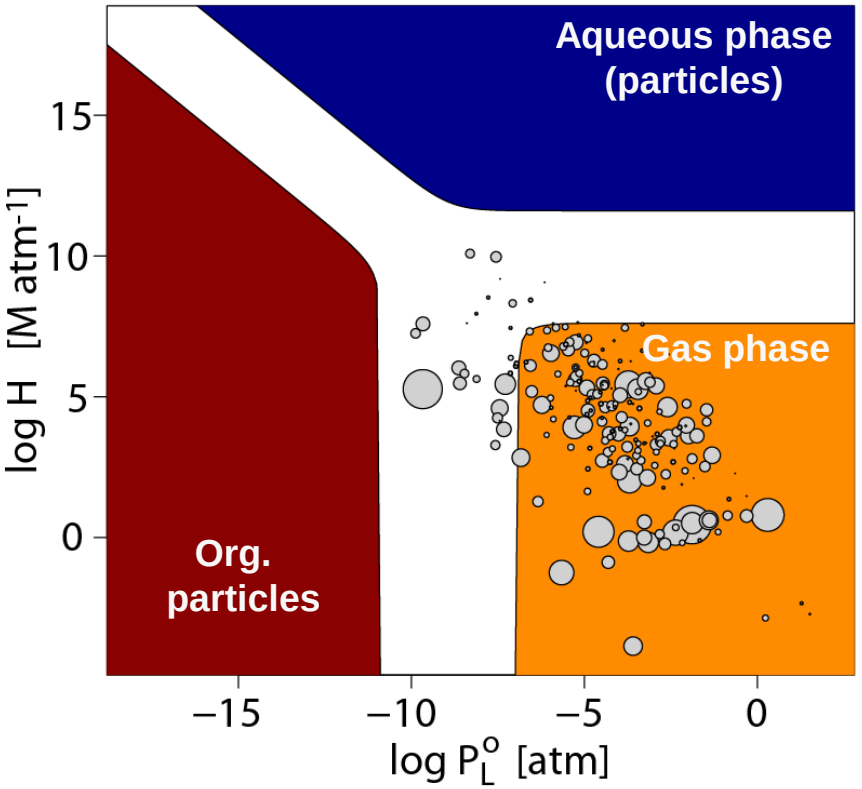
CONTINENTAL SCENARIO

time = 5×τ_{parent}

GECKOA / MCM



MCM v3.2



Phase partitioning (> 99 %) assuming:

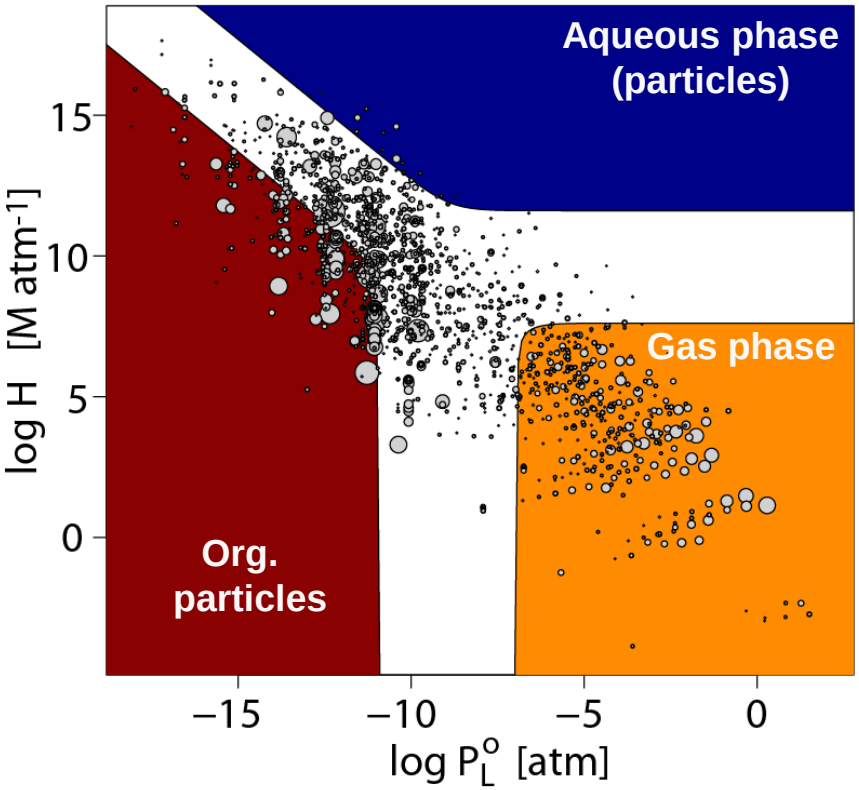
- C_{OA} = 10 µg m^{-3} , $MW_{aerosol}$ = 200 g mol^{-1}
- LWC = 10 µg m^{-3} (deliquescent particle)

Dodecane oxidation – oxidation trajectories

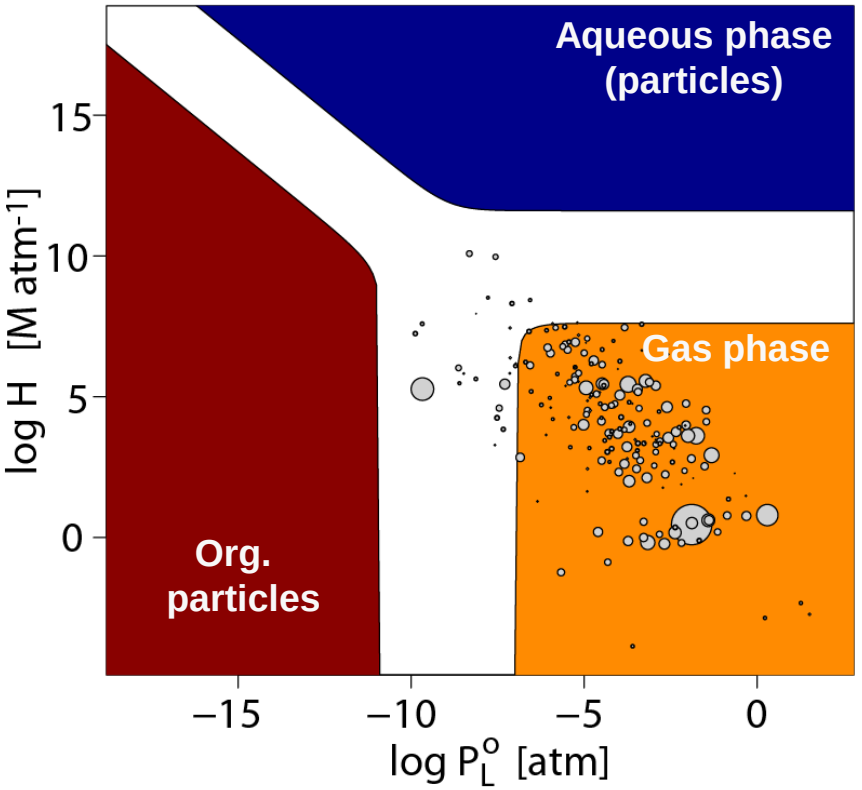
CONTINENTAL SCENARIO

time = 10×τ_{parent}

GECKOA / MCM



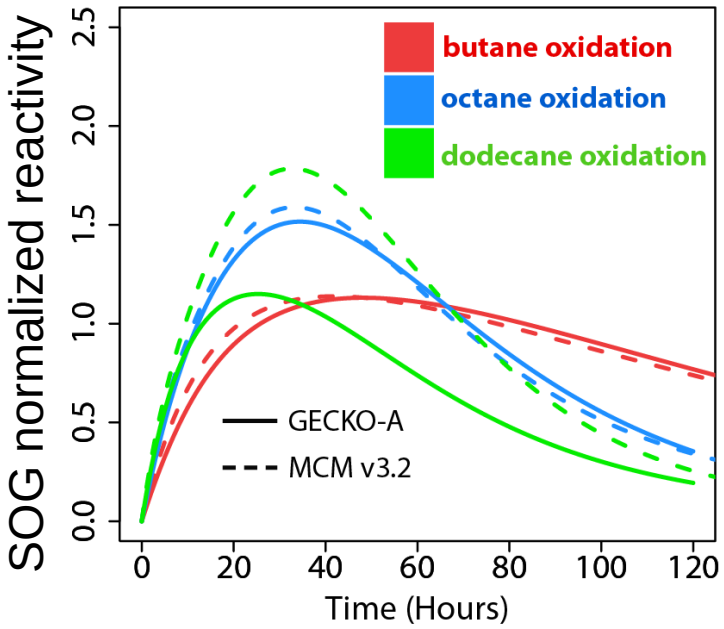
MCM v3.2

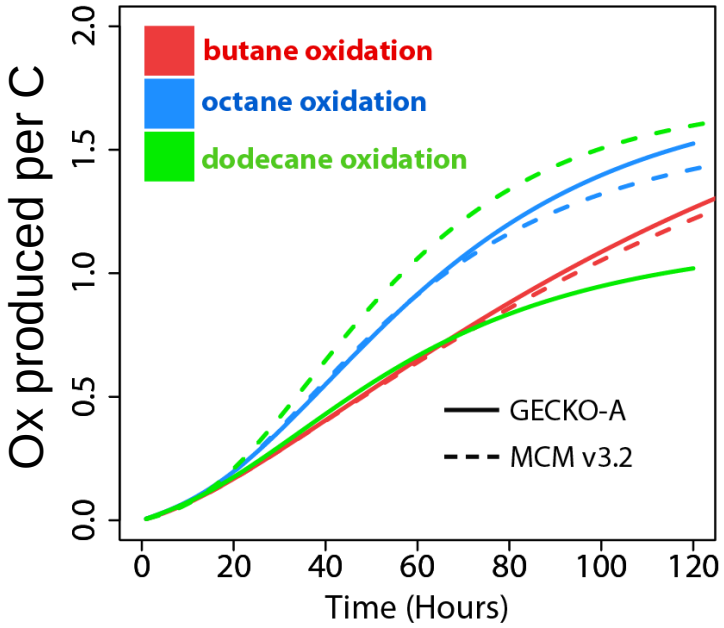


Phase partitioning (> 99 %) assuming:

- C_{OA} = 10 µg m^{-3} , $MW_{aerosol}$ = 200 g mol^{-1}
- LWC = 10 µg m^{-3} (deliquescent particle)

Alkane series – comparison of “integrative” variables





CONTINENTAL SCENARIO

$$SOG\ normalized\ reactivity = \frac{\sum k_i^{OH} \times [SOG_i]_t}{k_{parent}^{OH} \times [parent]_0}$$

Consistent results provided by MCM/GECKOA and MCM3.2 for short carbon skeletons. Discrepancies in oxidative trajectories increase with chain length.

$$Ox\ produced\ per\ C = \frac{[Ox\ produced]_t}{[C\ in\ parent]_0}$$

Summary & Conclusion

SAR for mechanism generation:

- Available SARs are sound for simple hydrocarbons and mono-functional VOC but less reliable for multifunctional species (rate constants and branching ratios).

➡ Critical need of additional experimental and/or theoretical data for multifunctional species to better constrain SAR

GECKOA/MCM versus MCM comparison:

- Consistent results provided by GECKOA and MCM3.2 for hydrocarbons having small carbon skeleton:

➡ The reduction protocol applied in MCM seems appropriate to describe the Ox/NOx/HOx chemistry

- Discrepancies highlighted between GECKOA and MCM3.2 in simulated oxidative trajectories for hydrocarbons having large carbon skeleton:
  - MCM favors fragmentation routes
  - GECKOA favors functionalization routes

➡ New protocols are required to reduce the size of the generated mechanism down to typical MCM size (10^4 species). A real challenge …