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The Master Chemical Mechanism

Development, Applications and Strategic Future (for Detailed Chemical Mechanisms…)

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Thanks also to: Mike Jenkin, Bernard Aumont, Richard Valorso, Mat Evans, Mike Pilling, Mike Newland, John Orlando, Dan Ellis…

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www.york.ac.uk/chemistry/research/wacl/

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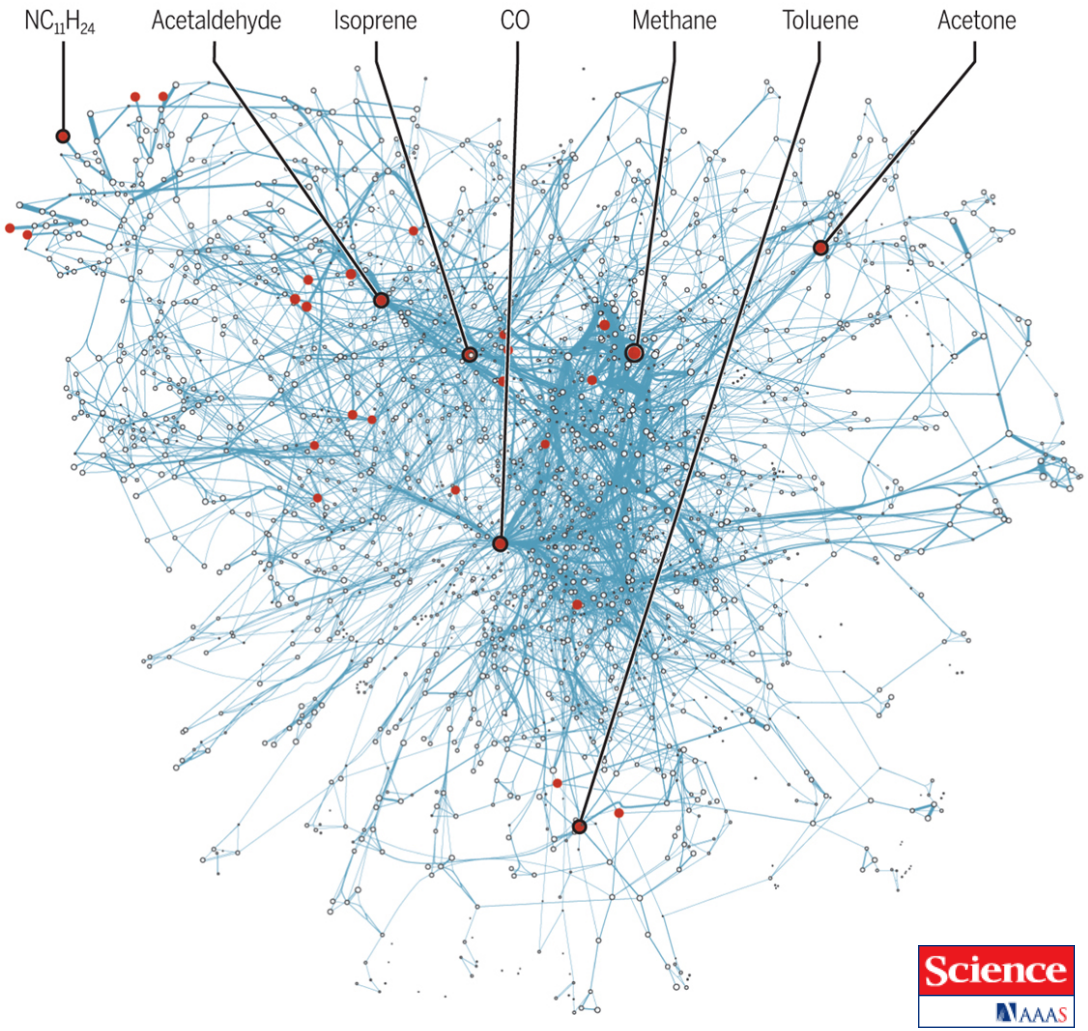
Numerical Models

- Different models use different levels of chemical complexity in deriving their chemical mechanisms, depending on their individual foci.
- However, there is an overarching need for a ‘gold standard’ or benchmark mechanism, which contains as full a representation of our fundamental ‘state of science’ understanding of atmospheric chemistry as is possible.
- For over a decade now this benchmark mechanism both in the UK and internationally has been the **Master Chemical Mechanism**.

A complex network of VOC reactions

A small number of initial emitted VOCs (red dots) react in the atmosphere to form a vast number of secondary compounds (white dots). In this graph representation, blue lines denote the reactions between compounds. See (*8*) for details.



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MCM – What is it?

- The **Master Chemical Mechanism (MCM)** is a near-explicit chemical mechanism describing the detailed gas-phase tropospheric degradation of a series of primary emitted volatile organic compounds (VOCs)
- Originally funded through the Department of the Environment (subsequently DEFRA) in order to model multi-day ozone formation over Europe (different to the general conditions experienced in the US at the time…)
- Extensively employed by the atmospheric science community in a wide variety of science and policy applications where chemical detail is required to assess issues related to air quality and climate

MCM – What is it?

- Used either directly, or as a benchmark "gold standard' against which to develop, optimise and test the fidelity of chemical schemes used in chemical transport models (e.g. GEOS-Chem, UKCA and CMAQ)
- Allows easy synthesis of our fundamental chemical understanding
- Provides a **direct** link from the laboratory though to the models
- Available to all, along with a series of interactive tools to facilitate its usage at:

http://mcm.leeds.ac.uk/MCM

mcm.york.ac.uk

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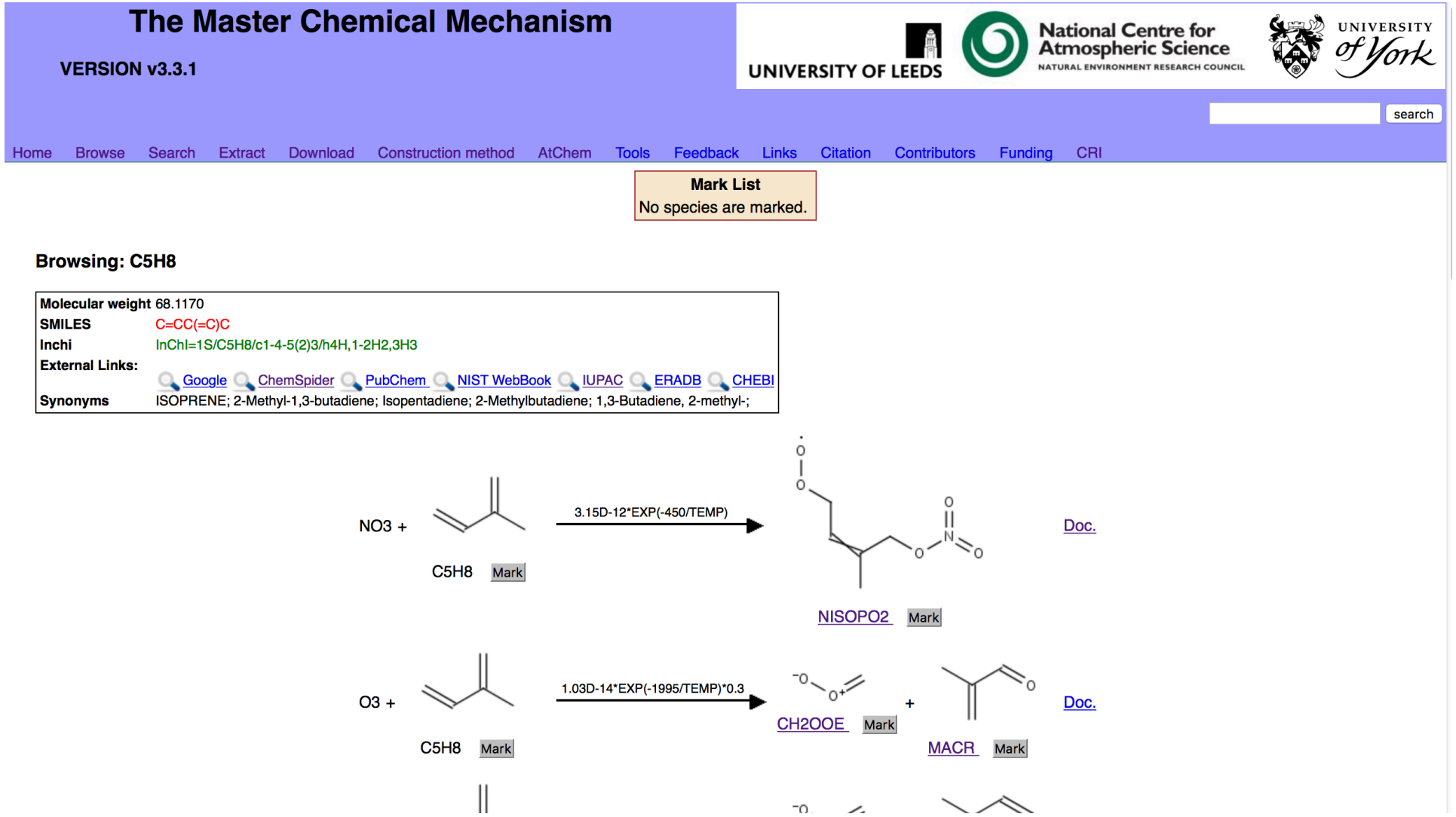
MCM – What is it?

mcm.york.ac.uk



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MCM – Historical Timeline

MCM version	Year	Emitted VOC	species	Reactions	comment
v1	1996	102 (+18)	2,400	7,100	(a)
v2	1999	124	3,800	11,400	(b)
v3	2002	126	4,400	12,700	(c)
v3.1	2004	136	5,900	13,500	(d)
v3.2	2011	143	6,700	17,000	(e)
v3.3.1	2014	143	6,900	17,500	(f)

(a) Jenkin et al. (Atmos. Env. 31, 81, 1997): non-aromatic species

(c) Saunders et al. (ACP, 3, 161, 2003): non-aromatic species

(c) Jenkin et al. (ACP, 3, 181, 2003): aromatic species

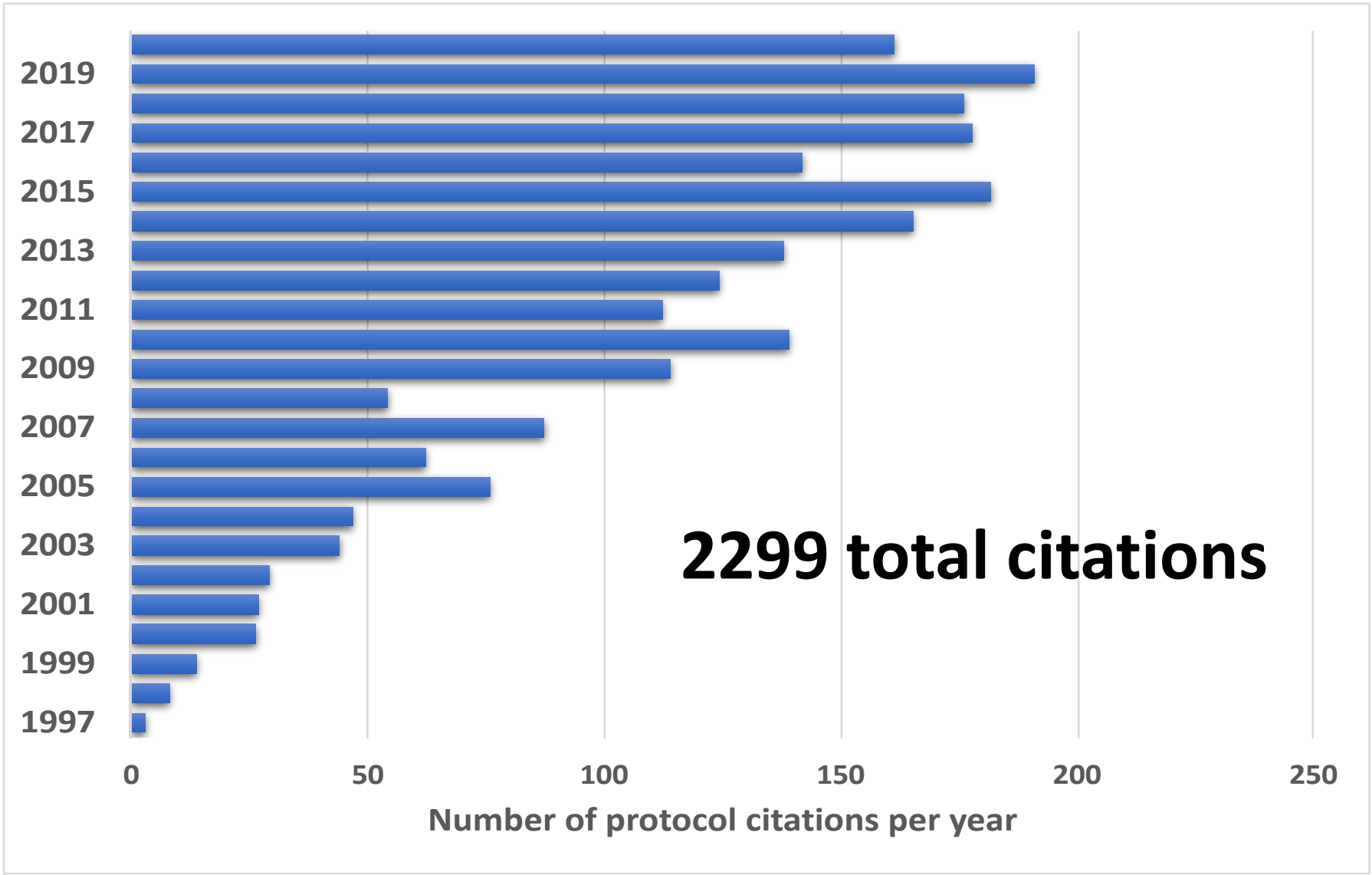
(d) Bloss et al. (ACP, 5, 641, 2005): aromatic species

(e) Jenkin et al., (ACP, 12, 2012): β-caryophyllene/monoterpenes

(f) Jenkin et al., (ACP, 15, 2015): isoprene

Manual updates; necessarily highly focused and specific

MCM – Citations (October 2020)



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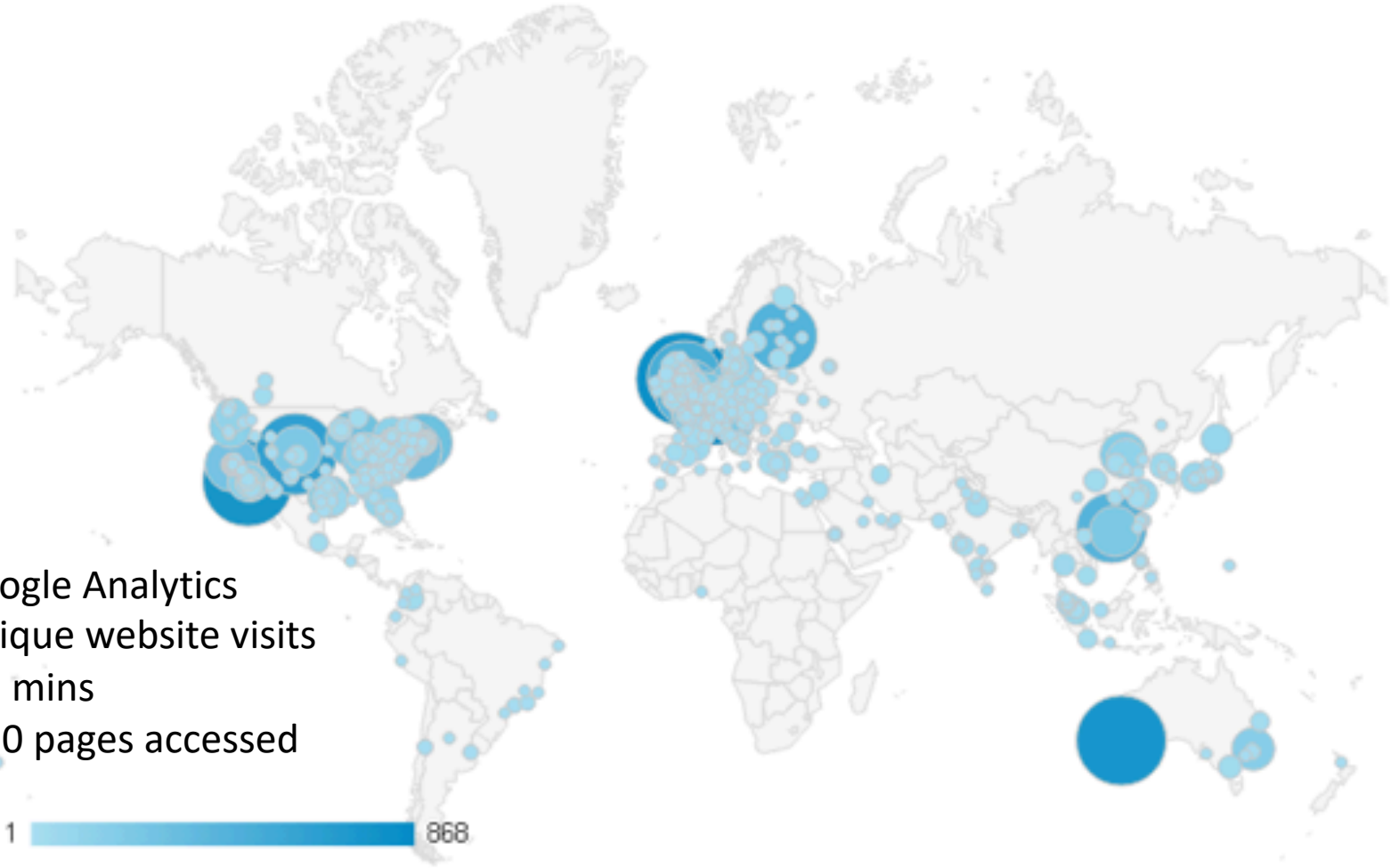
MCM – Geographical Outreach



- Google Analytics
- Unique website visits
- > 5 mins
- > 10 pages accessed

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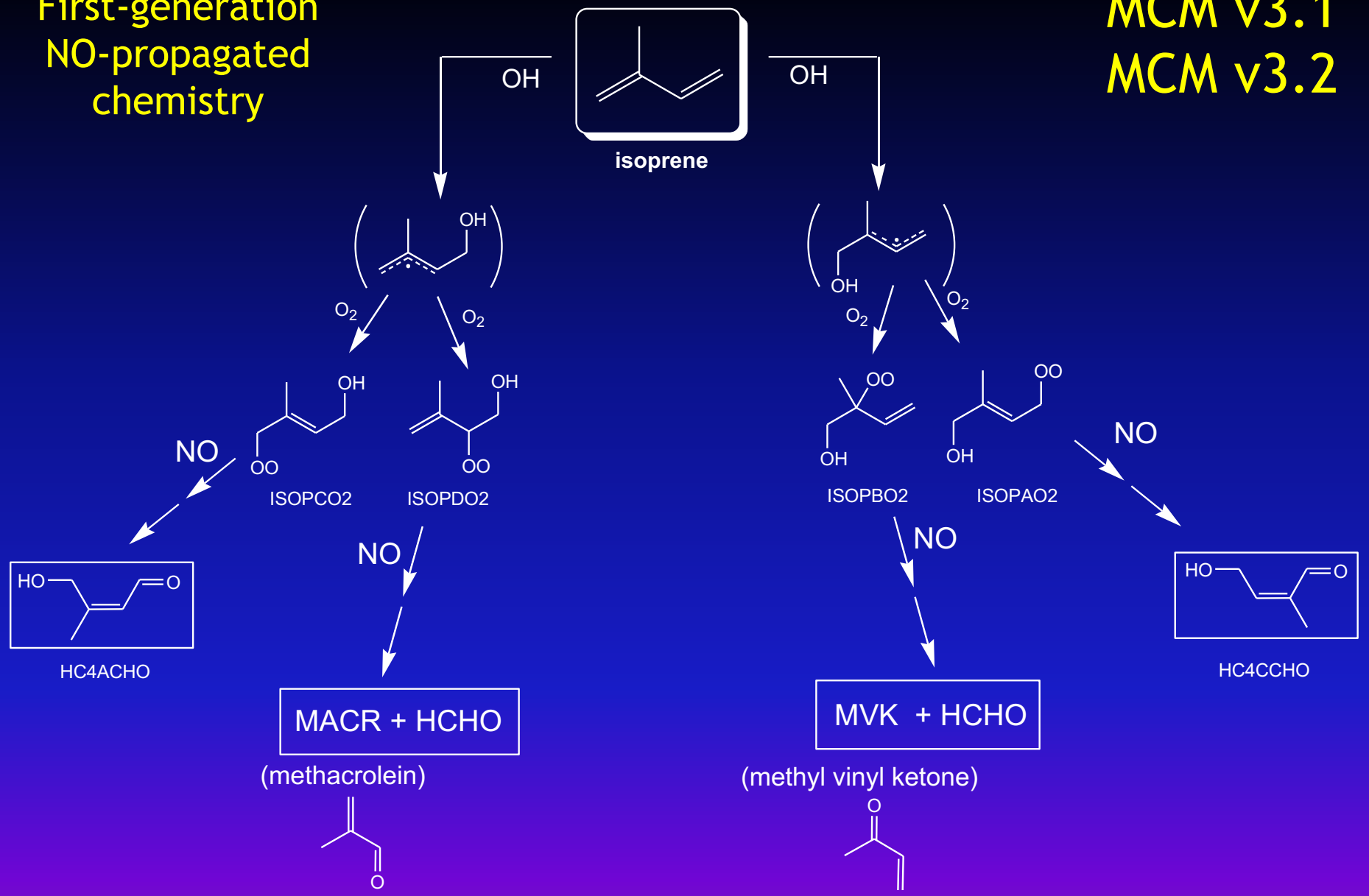
MCMv3.3.1 – isoprene update

Mechanism	Species	Reactions	Description	Year of release
MCMv3.1	201	605	Previous version of MCM. Available at: http://mcm.leeds.ac.uk/MCMv3.1/	2003
CRIv2.1	28	95	Reduced mechanism with performance traceable to MCM v3.1. Available at: http://mcm.leeds.ac.uk/CRI/	2011
MCMv3.2	447	1428	Previous version of MCM. Available at: http://mcm.leeds.ac.uk/MCMv3.2/	2011
MCMv3.3.1	602	1926	Current version of the MCM. Available at: http://mcm.york.ac.uk	2015
CRIv2.2	56	186	Reduced mechanism with performance traceable to MCM v3.3.1. Available at: http://cri.york.ac.uk	2019

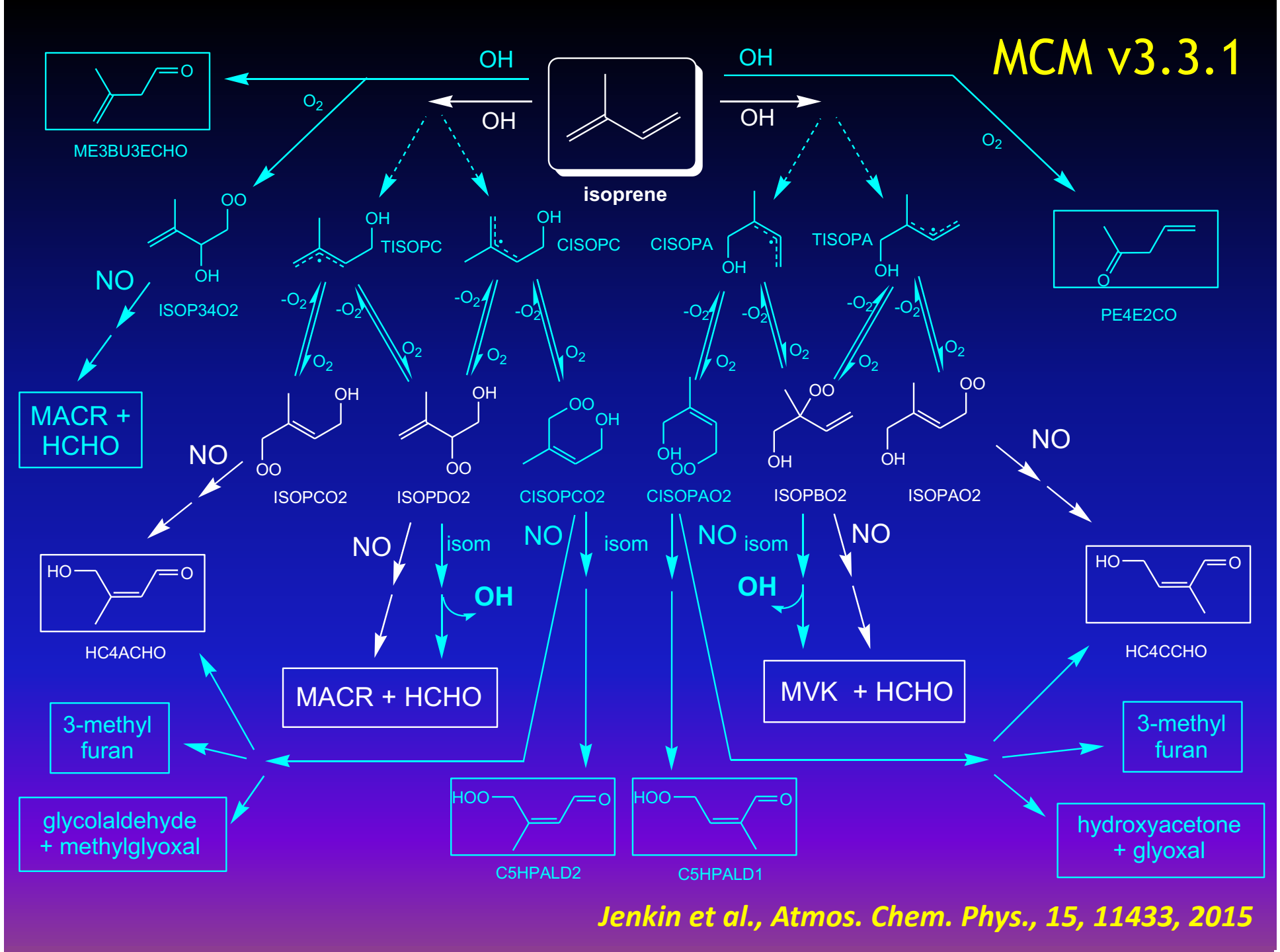
- Improved representation of isoprene radical recycling (based on optimised theory)
- Full representation of “minor” first generation pathways/products (SOA formation)

First-generation NO-propagated chemistry

MCM v3.1
MCM v3.2



Jenkin et al., Atmos. Chem. Phys., 15, 11433, 2015


MCM v3.3.1
isoprene
OH
OH
OH
OH
O2
ME3BU3ECHO
PE4E2CO
TISOPC
CISOPC
CISOPA
TISOPA
ISOP34O2
NO
MACR + HCHO
-O2
O2
ISOPCO2
ISOPDO2
CISOPCO2
CISOPAO2
ISOPBO2
ISOPAO2
NO
isom
OH
HC4ACHO
HC4CCHO
MACR + HCHO
MVK + HCHO
3-methyl furan
glycolaldehyde + methylglyoxal
hydroxyacetone + glyoxal
C5HPALD2
C5HPALD1
Jenkin et al., Atmos. Chem. Phys., 15, 11433, 2015

MCM – Applications

"Benchmark mechanism for atmospheric chemistry"

- Modelling radical chemistry in support of field campaigns
- Modelling oxidant formation and the production and loss of oxidised intermediates
- Modelling secondary aerosol formation (SOA)
- Policy support to Defra, especially in relation to ozone (POCP index)
- Development and validation of reduced mechanisms (for regional AQ and global modelling)
- Modelling simulation chamber processes

EUROCHAMP 2020

MCM – Strategic Development (next steps…)

- Recent updates (2003-2015) strategic and timely
- Sustainable development requires a fundamental revision in the methods applied to its maintenance into the future
- **MAGNIFY**: NERC/ANR project partnership between York, Paris and Atmospheric Chemistry Services.
- Activities fall broadly into three key strategic categories:

i. Development and maintenance of an updated mechanism development protocol; launch of a web-based protocol facility.

ii. Development of an automatic generator (**MCM-GECKO-A**), based on the protocol rules, to allow automated generation of future versions of the MCM (and other mechanisms).

iii. Development (encourage development of) of automatic mechanism reduction methods, using the MCM as a benchmark mechanism.

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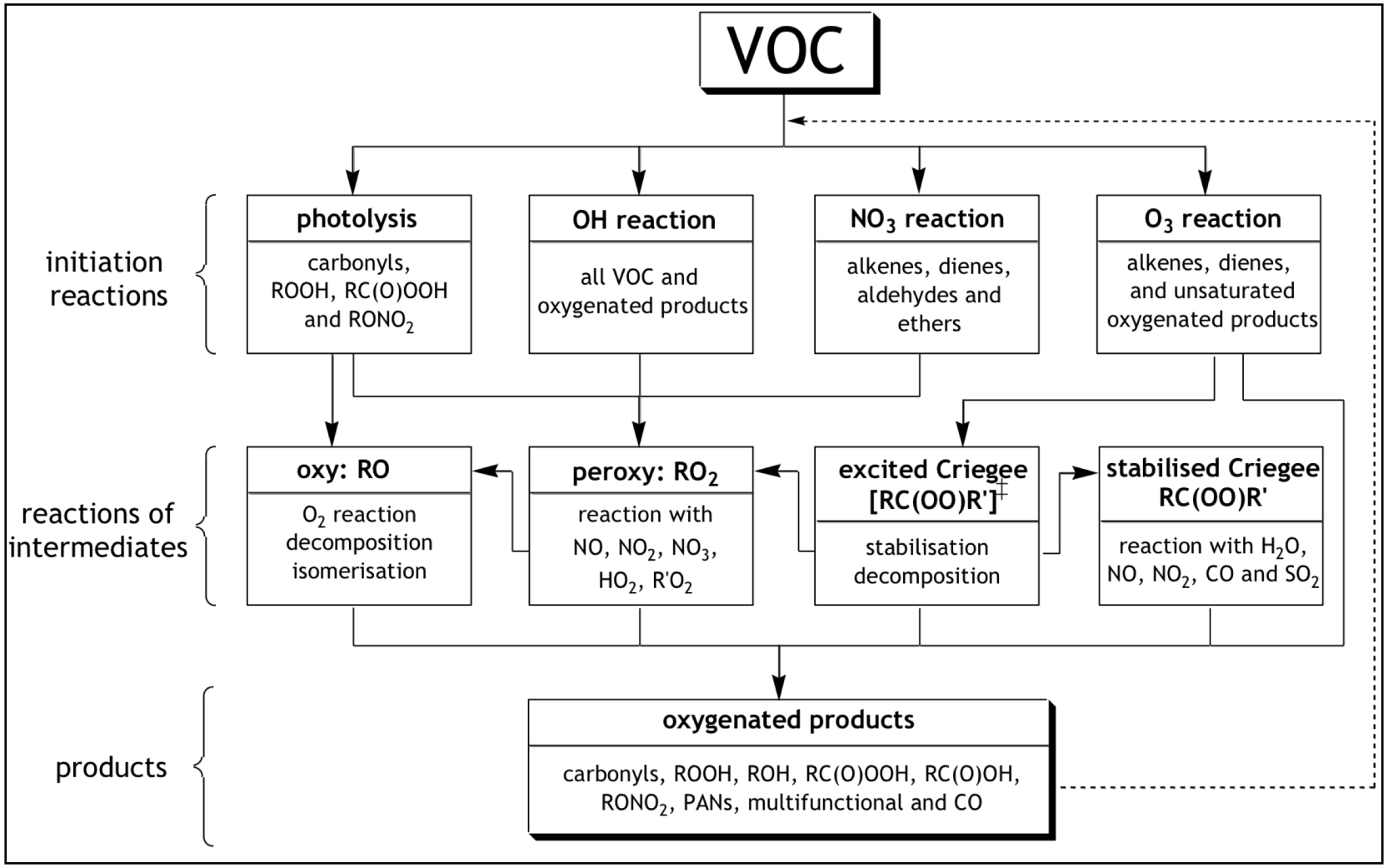
(i) Development and maintenance of an updated mechanism development protocol

- MCM philosophy…
- The protocol defines a set of rules which guide the development of the degradation mechanisms, in principle allowing two or more people to write consistent and compatible mechanisms
- Designed with automatic mechanism generation in mind (GECKO-A)
- Makes use of published experimental data for elementary reactions where possible, adopting parameters evaluated by expert groups (i.e. IUPAC and CRC group gas kinetics database), where available
- The method also relies heavily on the use of structure-activity-relationships (SARs), either taken from the literature or defined within the protocol

(i) Development and maintenance of an updated mechanism development protocol



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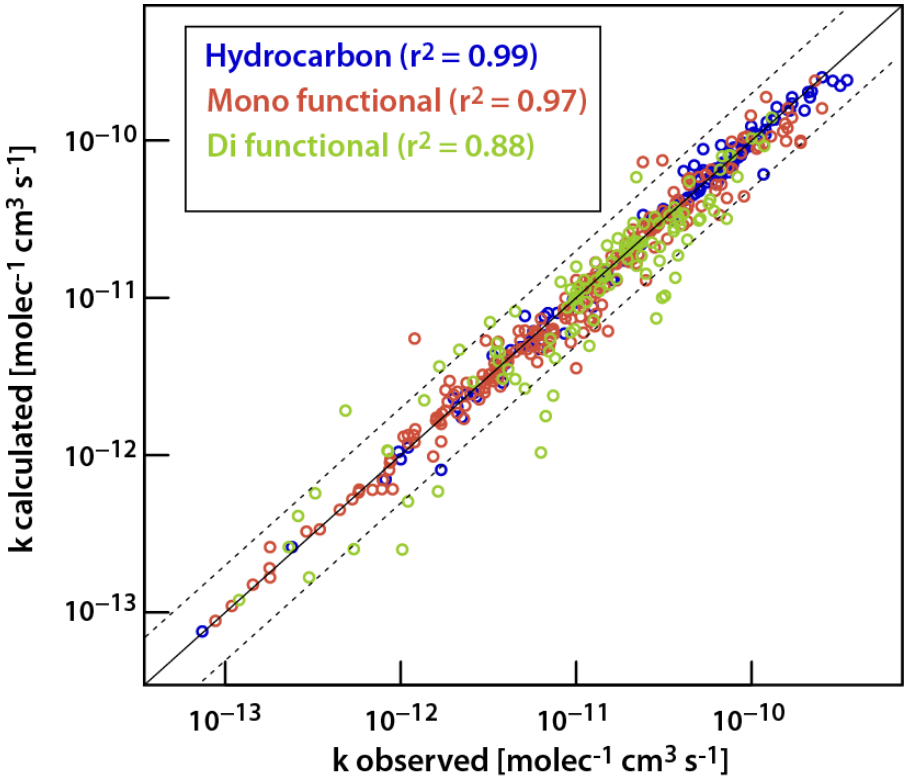
OH abstract SARs (aliphatics)

[Jenkin et al., ACP, 2018a]

- Group contribution methods were optimized using an updated experimental kinetic database for aliphatic species
- **489** total aliphatic species

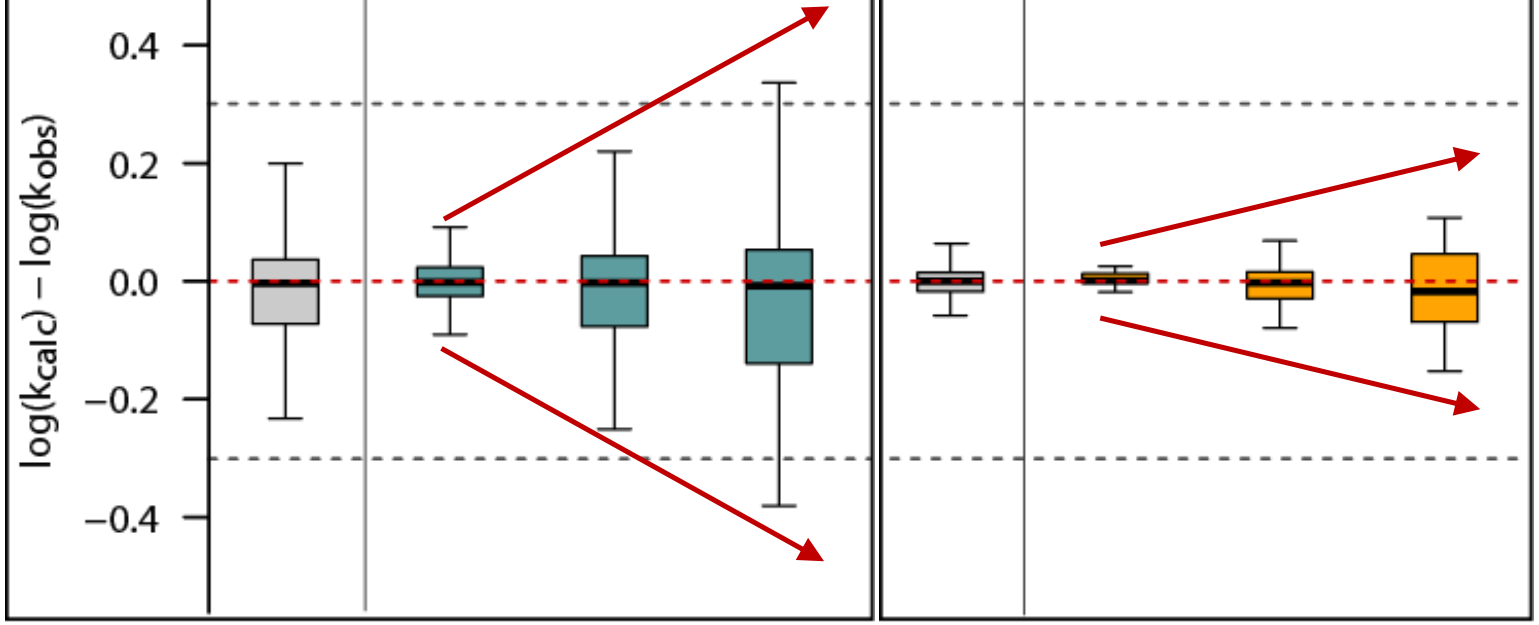
- **147 hydrocarbons**
- **213 monofunctional species (alcohol, aldehyde, ketone, nitrate, ether, ester, nitro, carboxylic acid, hydroperoxide)**
- **115 di-functional species**
- **8 tri-functional species**



OH abstract SARs (aliphatic/aromatic)

[Jenkin et al., ACP, 2018a]
[Jenkin et al., ACP, 2018b]

	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

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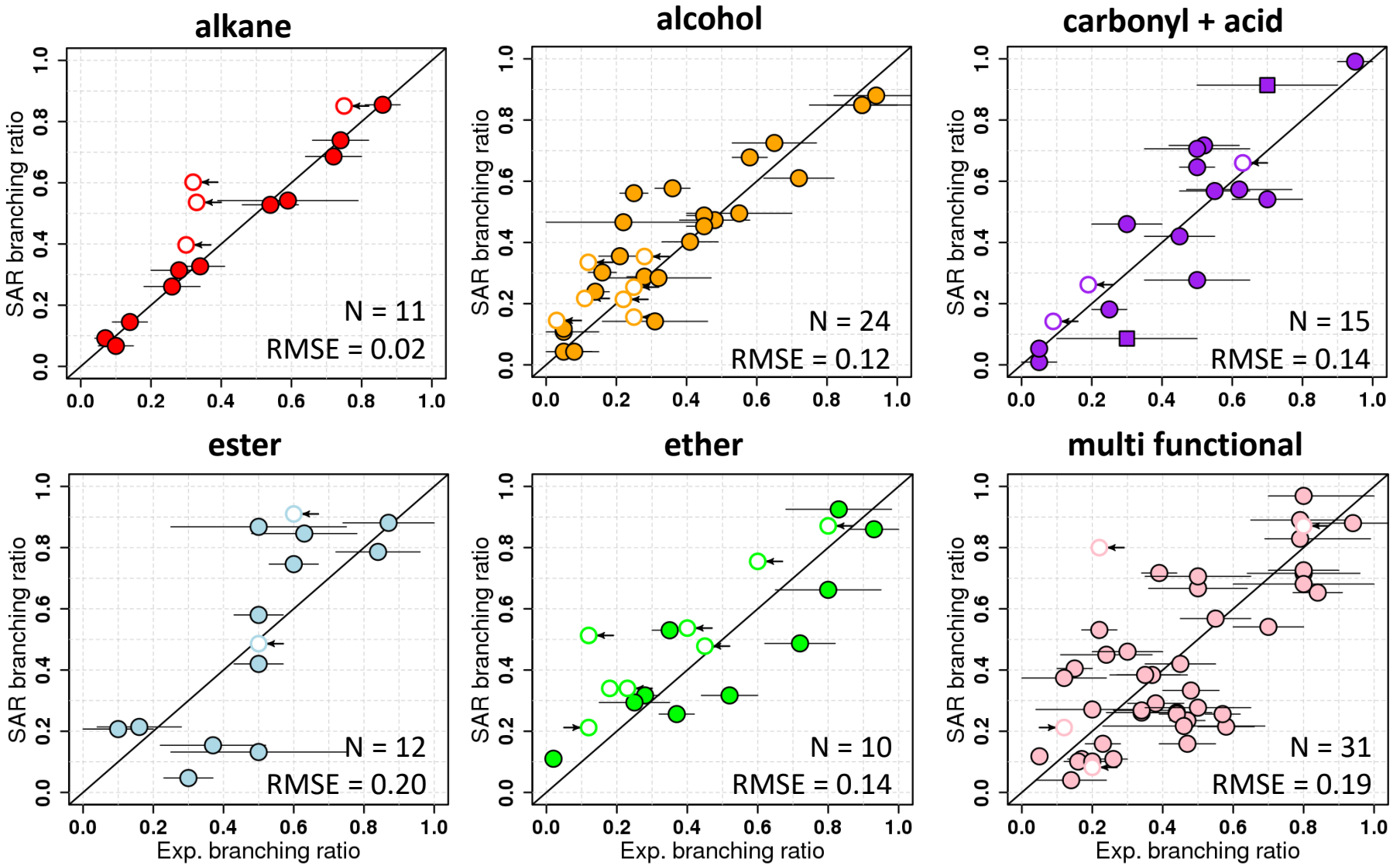
Protocol Evaluation (Aumont and Orlando)



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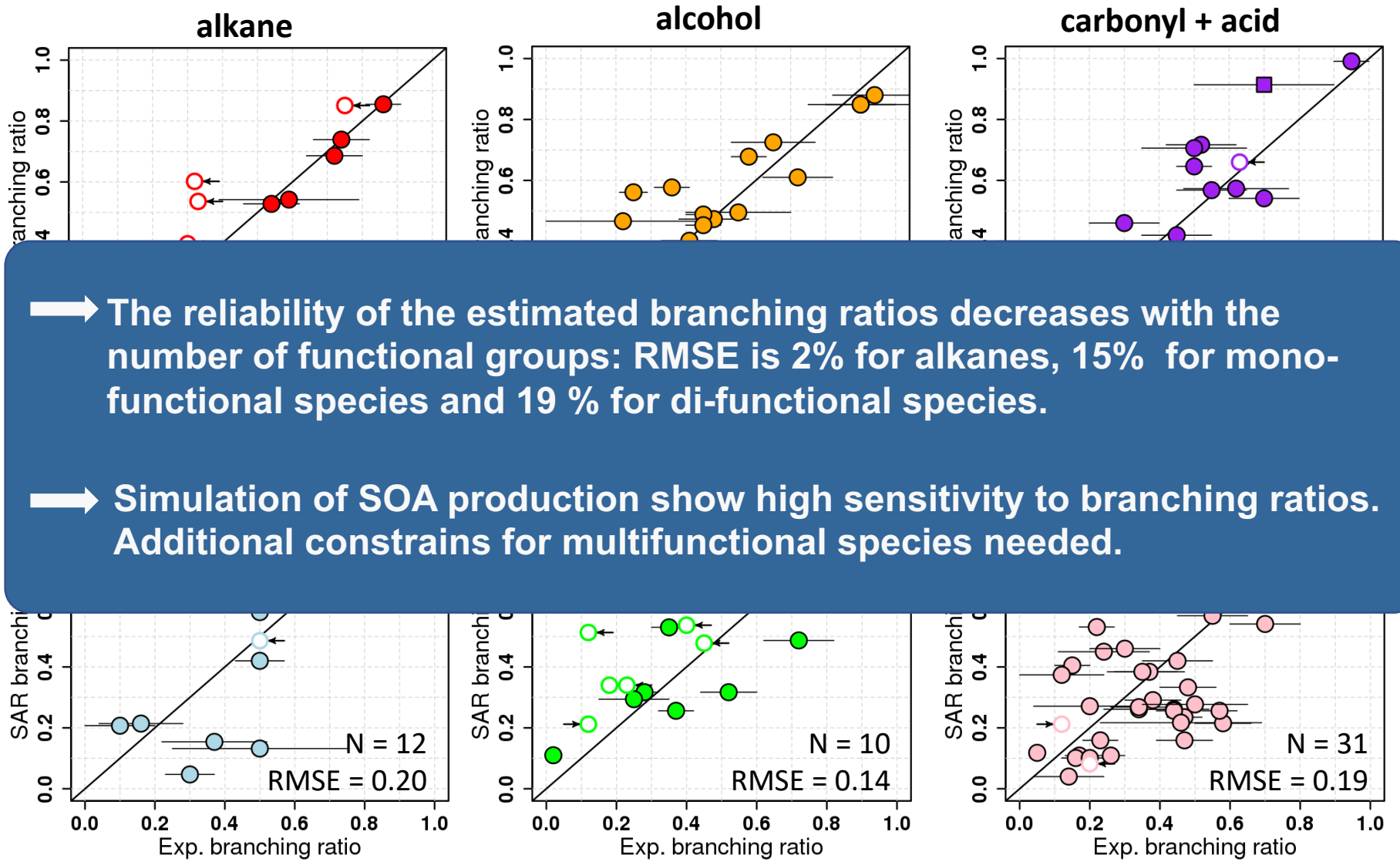

- The reliability of the estimated branching ratios decreases with the number of functional groups: RMSE is 2% for alkanes, 15% for mono-functional species and 19 % for di-functional species.
- Simulation of SOA production show high sensitivity to branching ratios. Additional constrains for multifunctional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

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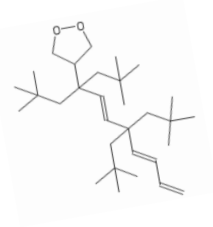
(ii) Development of an automatic generator, based on the protocol rules, to allow automated generation of future MCM versions



- The iterative process by which mechanisms are constructed can be easily represented mathematically:
  - ***Structure*** – unique mathematical representation of molecules
  - ***Generation***
  - ***Rules***
  - ***Reduction***

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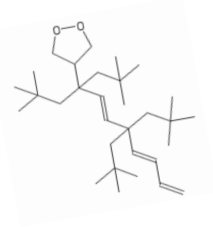

- The iterative process by which mechanisms are constructed can be easily represented mathematically:
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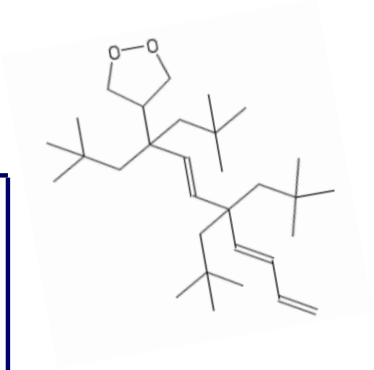
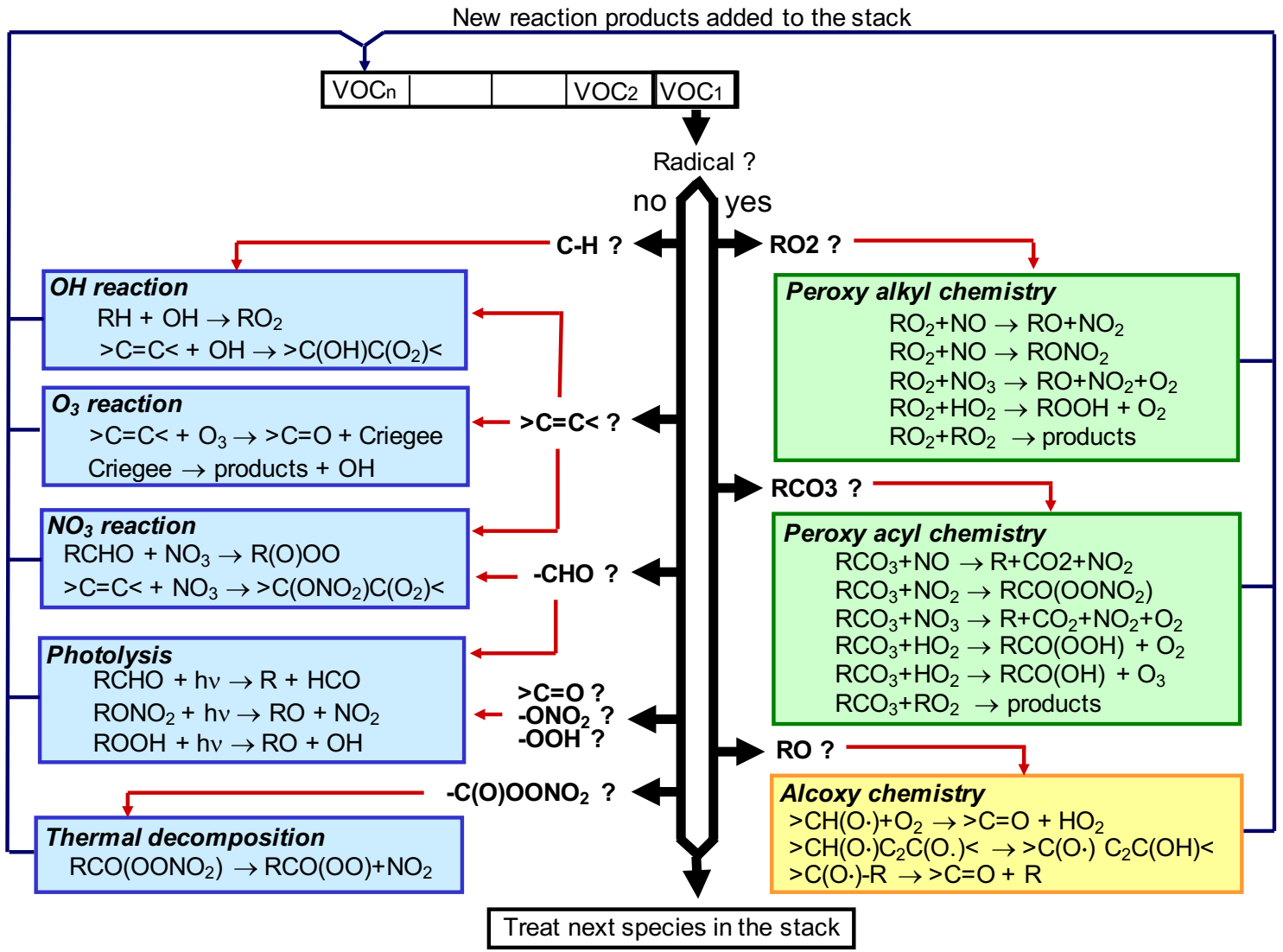
GECKO-A – Automatic Generator





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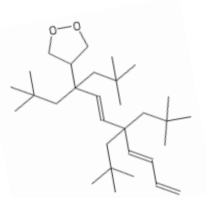

- The iterative process by which mechanisms are constructed can be easily represented mathematically:
  - ***Structure*** – unique mathematical representation of molecules
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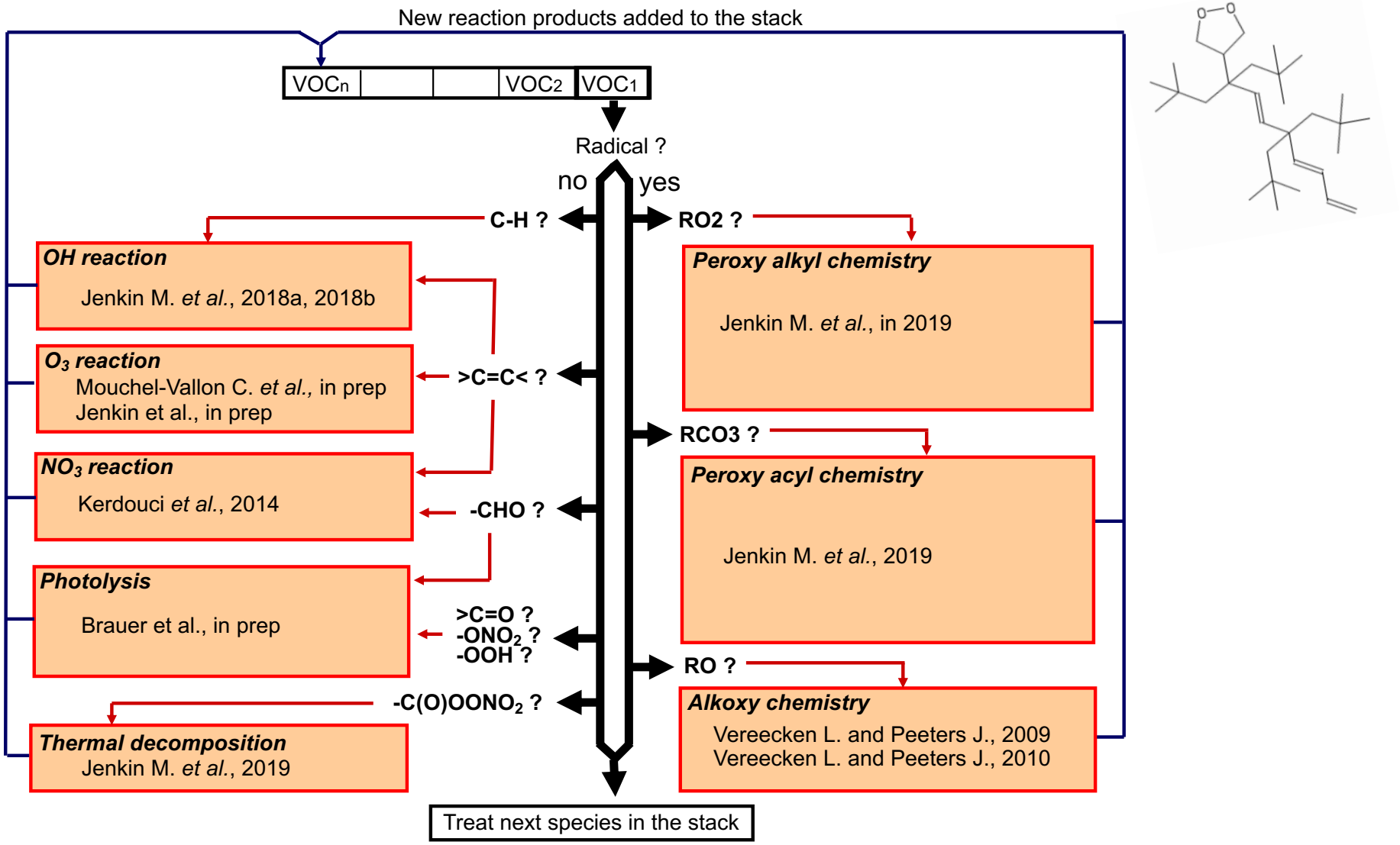
  - ***Rules*** – application of protocol rules as a set of algorithms that describe generically how a molecule can be chemically transformed into another molecule
  - based on a database of laboratory measurements or an estimation of the rate constant and reaction products is made based on the defined rules
  - ***Reduction***

MCM/GECKO-A – Automatic Generator



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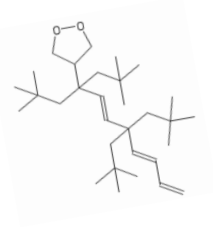

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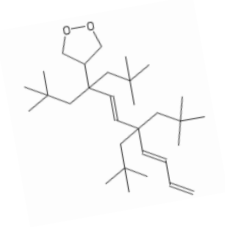
  - ***Reduction*** – application of mechanism reduction rules

(ii) Development of an automatic generator, based on the protocol rules, to allow automated generation of future MCM versions



Automatic generation of the MCM will allow:

(i) the mechanism to respond much more rapidly to advances in kinetic and mechanistic understanding;

(ii) allow schemes for new VOCs of interest to be generated in a responsive mode on a reduced timescale and at a reduced cost;

(iii) allow the sensitivity of the performance of the SARs and the mechanisms to be tested against observations (chamber/field)

(iv) facilitate robust application of reduction techniques

(iii) Development of automatic mechanism reduction methods

Objective of this activity:

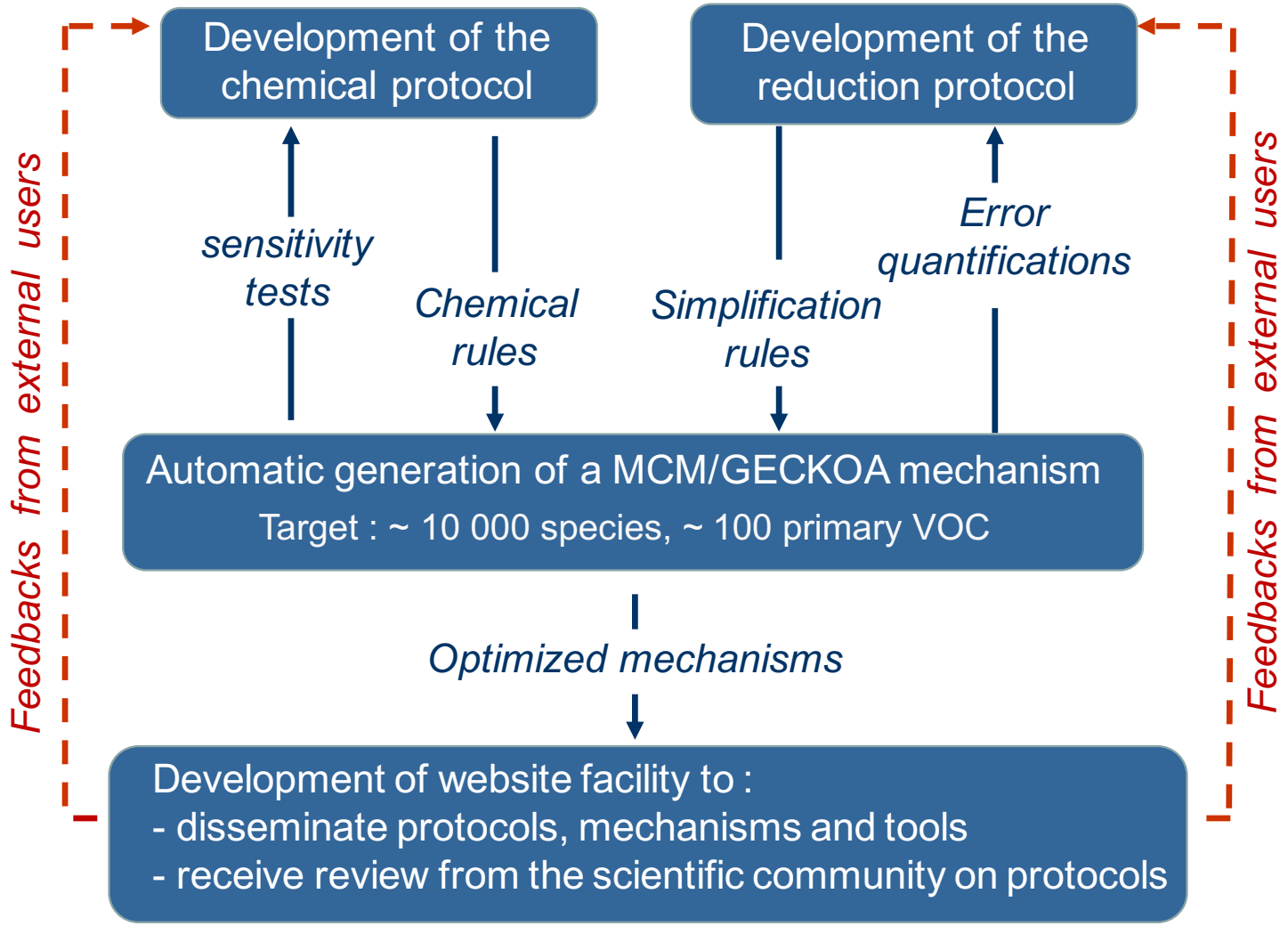
"To develop automatic mechanism reduction methods. These would aim to automate existing mechanism reduction methods, and would also seek to develop new approaches."

Automatic generation and lumping processes need to be integrated in some way

(iii) Development of automatic mechanism reduction methods

- Overarching aim is to establish a framework to encourage chemical mechanisms used in AQMs/CTMs/ESMs to be **demonstrably traceable to fundamental understanding**
- Final step in the knowledge transfer is the development of methods to reduce the size and complexity of the mechanisms, whilst adequately reproducing the performance needed
- It is anticipated that the above activities would stimulate the development of a new generation of reduced mechanisms, traceable to the MCM - *hierarchy of traceable mechanisms*
- Need input from other communities (combustion, maths, engineering…) – multidisciplinary science

MCM/GECKO-A – A Framework for Mechanism Development



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- Majority of the MCMs 7,500 species are **multifunctional**

[Vereecken et al., IJCK, 2018]

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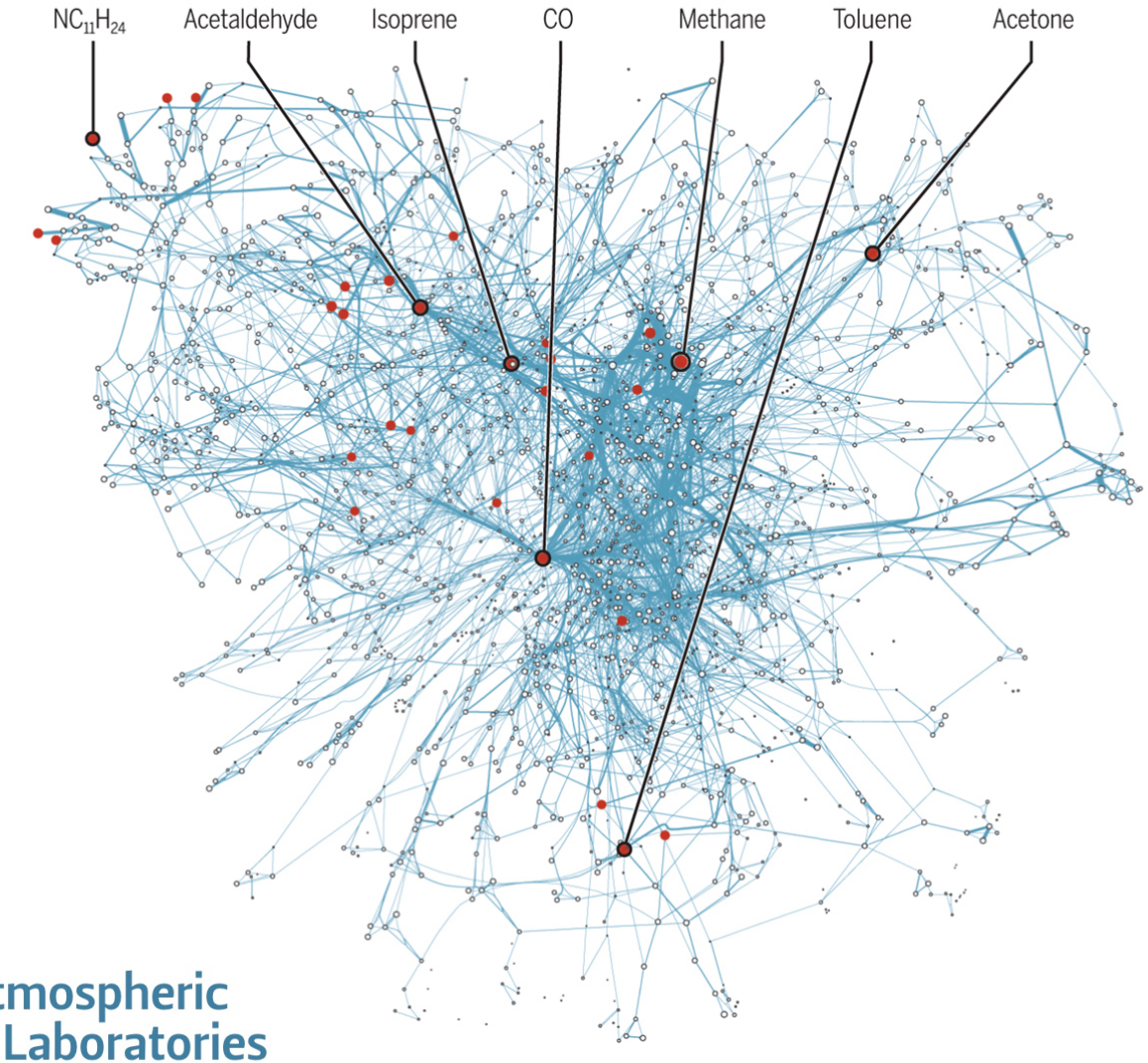
A complex network of VOC reactions

A small number of initial emitted VOCs (red dots) react in the atmosphere to form a vast number of secondary compounds (white dots). In this graph representation, blue lines denote the reactions between compounds. See (*8*) for details.



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Alastair C. Lewis Science 2018;359:744-745

Published by AAAS

Structure Activity Relationships (SARs)

- Many hundreds reactions have been measured in the laboratory for the OH initiated degradation
- However, many 1000s more are emitted or are formed in atmospheric photochemical oxidation for which no measurements exist.
- A structure-activity relationship (SAR) allows parameters such as rate coefficients to be related to structural properties of chemical species, thereby providing a method of parameter estimation.
- SARs are developed from datasets of experimentally-determined parameters.

- Not only do SARs allow us to estimate the rate of reaction, they can also provides useful information on the ***partial rate coefficients*** at each specific attack site in the molecule.
- This provides information on reaction products (branching ratios)
- Crucial to the **MCM** construction methodology

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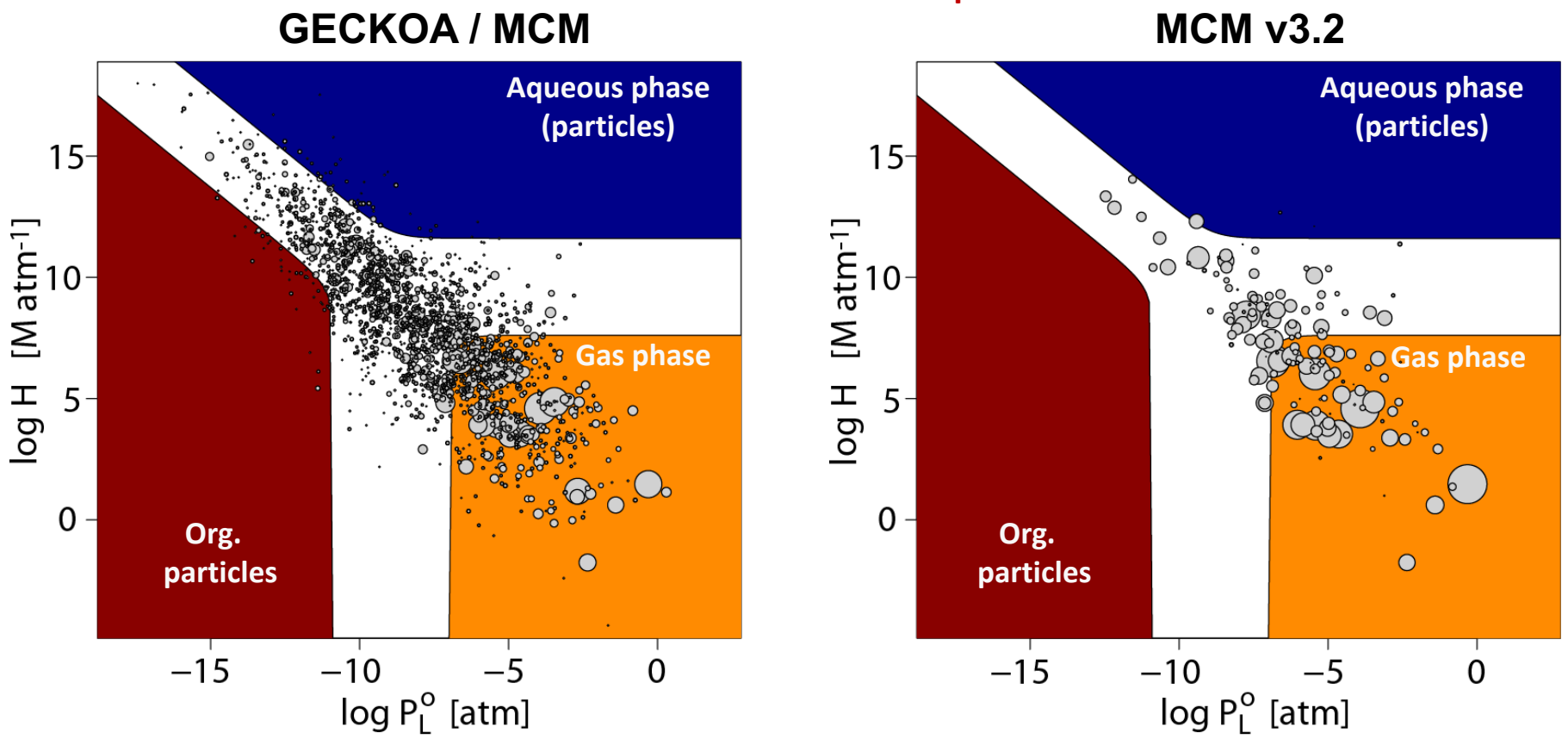
α-pinene oxidation – Oxidation trajectories

CONTINENTAL SCENARIO

***time* = 5×τ_{parent}**



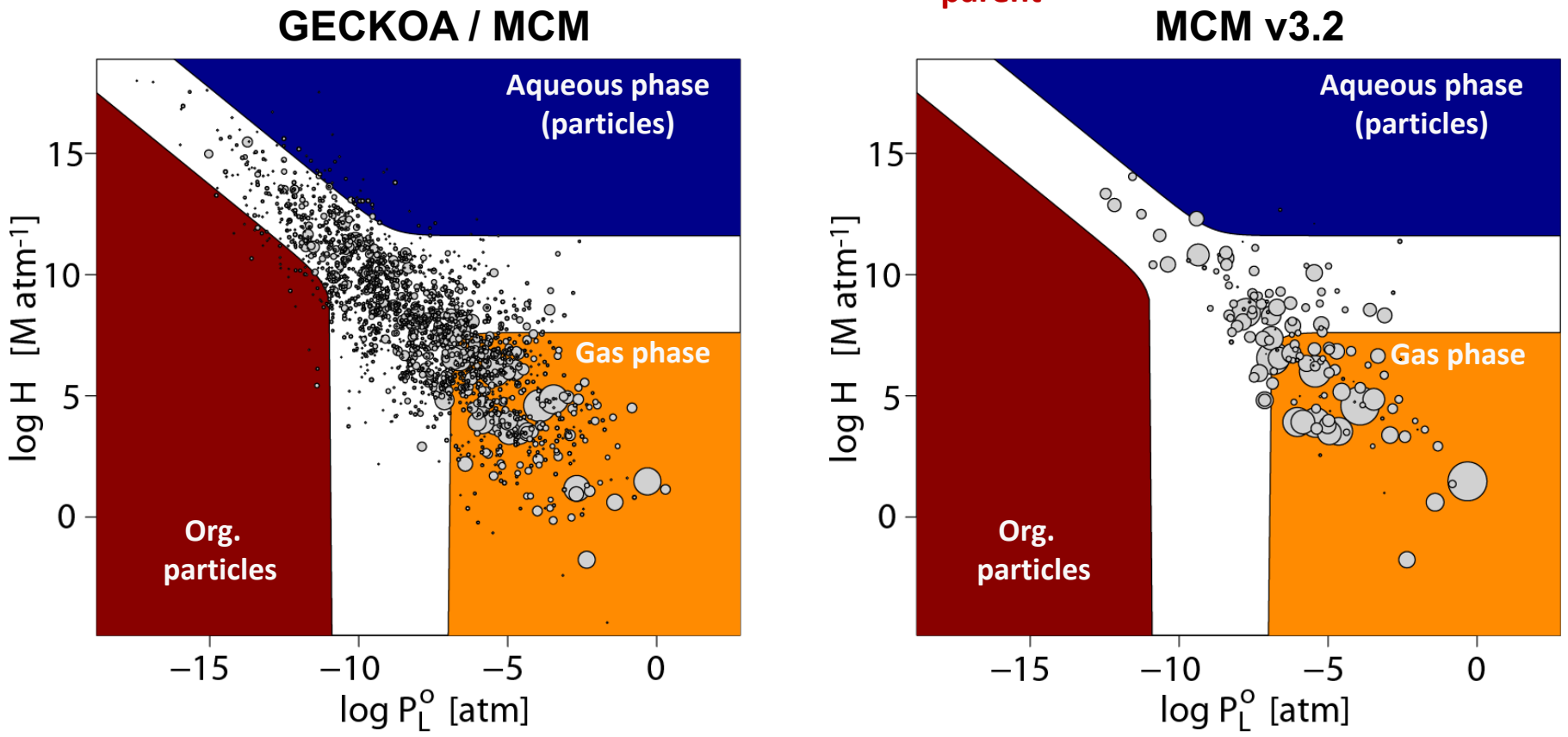
Phase partitioning (> 99 %) assuming:

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

α-pinene oxidation – Oxidation trajectories

CONTINENTAL SCENARIO

***time* = 5×τ_{parent}**



Discrepancies highlighted between GECKOA and MCM3.2 in simulated oxidative trajectories for hydrocarbons having large carbon skeleton

- **MCMv3.2** favours fragmentation routes - **MCM/GECKO-A** favours functionalization routes