

# A new database for the kinetics of the gas-phase atmospheric reactions of organic compounds

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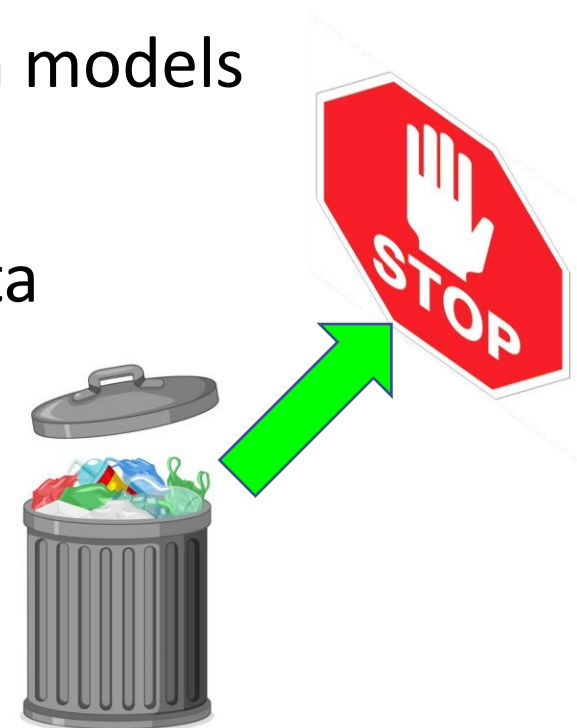
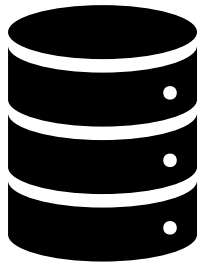
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# Why did we build this new database?

*And how does this relate to structure-activity relationships?*

- To test, improve and possibly develop structure-activity relationships
- SARs are an inexpensive method to estimate chemical reactivity
- Detailed atmospheric chemical mechanisms are **huge**
- $\therefore$  SARs are necessary to assign reactivity in such models
- SARs are empirical, they are data-hungry
- $\therefore$  both SARs and models need lots of kinetic data
- This data must be high-quality, otherwise, GIGO



# Which other databases exist?

Database	Expert evaluation	Searchable	Download	Freely available	High coverage	Update cycle
IUPAC	✓	~	~	✓	✗	variable
JPL	✓	✗	~	✓	✗	~5 years
Calvert et al.	✓	✗	✗	✗	~	discontinued
NIST	✗	✓	✗	✓	~	?
"Ideal DB"	✓	✓	✓	✓	✓	<1 year

**IUPAC:** Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr/>

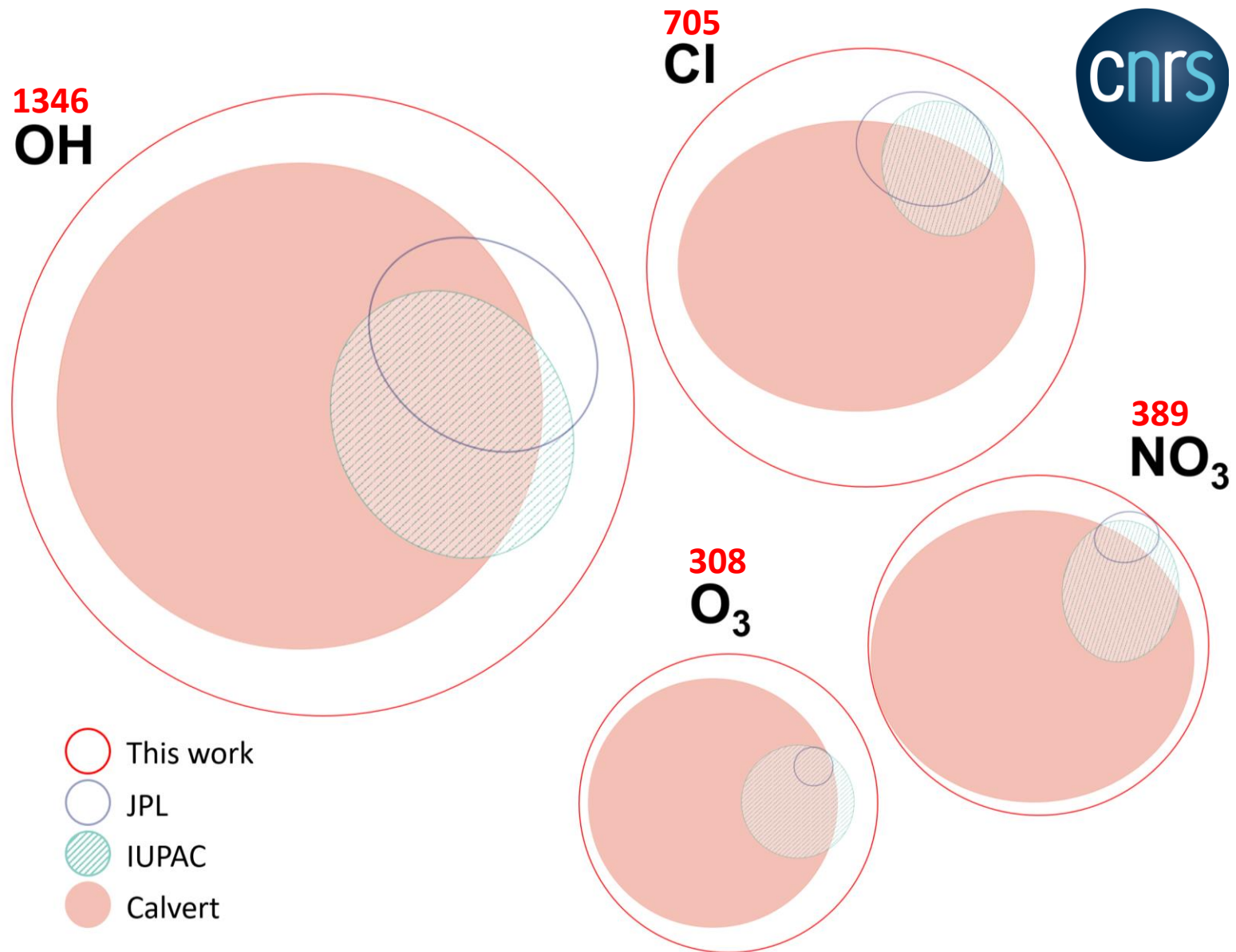
**JPL:** Chemical kinetics and photochemical data for use in atmospheric studies, no. 18, <http://jpldataeval.jpl.nasa.gov>

**Calvert et al.:** The Mechanism of Atmospheric Oxidation of Alkanes/ Alkenes/ Aromatics Hydrocarbons/ Oxygenates

**NIST:** Chemical Kinetics Database, <https://kinetics.nist.gov/kinetics/>

# Coverage

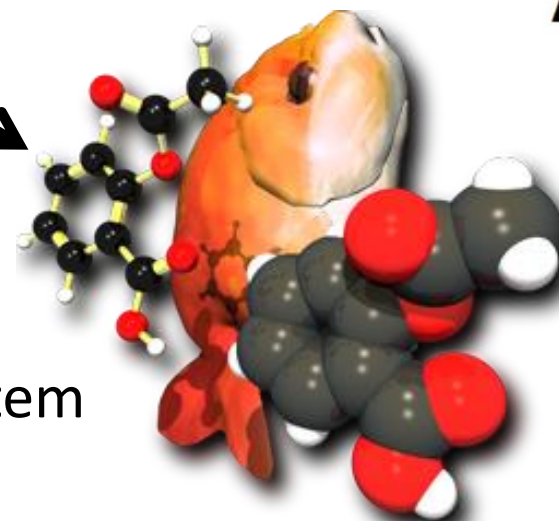
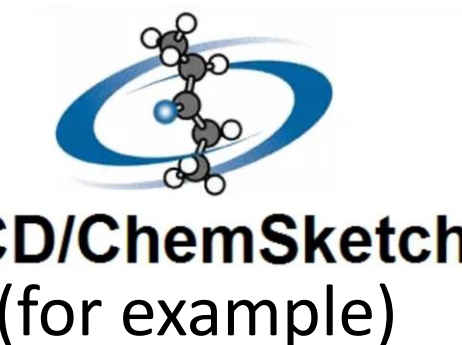
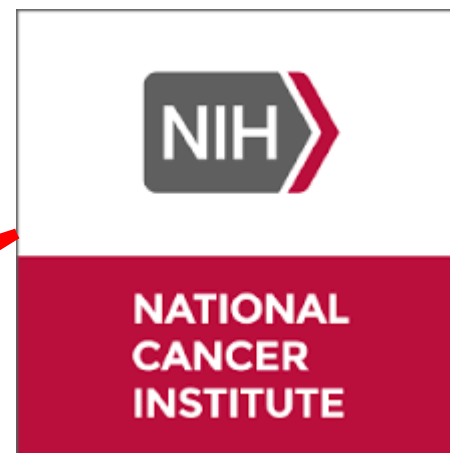
- Largest DB of its type
- Absorbs previous expert evaluations
- Current focus on OH, Cl, NO<sub>3</sub> and O<sub>3</sub>
- Regular updates are planned
- Further extensions are anticipated



McGillen et al. *Earth Sys. Sci. Data*, 12, 1203–1216, 2020

# Searchability

- Chemical name(s)
- Molecular formula
- SMILES (canonical, InChified)
- InChI
- Functionality



**Open Babel**

**SMILES** = Simplified Molecular-Input Line-Entry System  
**InChI** = International Chemical Identifier



# Searchability

VS



AutoSave - AtmVOC.m 1.3.xls - Compatibility Mode

Find compounds on database using various lookup methods		Part of Name or Alias -> butanol	
Clear All	Atom Nos (e.g., C2H5Cl) ->		
	Compound type (from table C to right) ->		<- Give type code no. (See Table C)
	Structure type (fill in table S to right)	(Fill in Table S)	
23	<-Number of Compounds listed		
Clear List	List k's ->	All OH NO3 O3 CI	Info on compound in selected row
			List k's" results in "Compound List Info" sheet
			Selected compound info in "Selected Compound Info" sheet

No.	Name	Smiles	
11	293	2-methylpropan-2-ol	CC(O)(C)C
12	294	2-methylpropan-1-ol	OCC(C)C
13	295	2-butanol	CCC(O)C
14	296	1-butanol	CCCCO
15	363	1-nitrooxy-2-butanol-3-ene	[O-][N+](=O)OCC
16	364	4-nitrooxy-1-butanol-2-ene	[O-][N+](=O)OCC
17	368	3-nitrooxy-1-butanol	[O-][N+](=O)OCC
18	369	4-nitrooxy-2-butanol	[O-][N+](=O)OCC
19	370	2-nitrooxy-1-butanol	CCC(O[N+](=O)O)C
20	371	1-nitrooxy-2-butanol	[O-][N+](=O)OCC
21	372	4-nitrooxy-1-butanol	OCCCCO[N+](=O)O
22	397	2,2,3,4,4,4-hexafluoro-1-butanol	OCC(C(C(F)(F)F)(F)F)C
23	408	2,2,3,3,4,4,4-heptafluoro-1-butanol	OCC(C(C(F)(F)F)(F)F)C
24	474	3-methyl-2-butanol	CC(C(C)C)CO

AutoSave - AtmVOC.m 1.3.xls - Compatibility Mode

2-butanol										CmpdNo
1										295
2	Smiles	CCC(O)C								
4	Atoms	CAH10O								
5	Type	Alcohol or Glycol							Ask for Cmpd No.	
6										
7	Rxn									
8	with	k298	Unc.	A	B	n	Low T	High T	Ref	Rate constants in cm3 molec-1 s-1
9	OH	8.94E-12	15%	5.01E-13	-863	2.1	223	1178		Recommended rate parameters fitted manually. See below.
10	OH	8.70E-12	41%						1	Not the recommendation.
11	OH	8.14E-12	15%	2.70E-12	-329				2	Not the recommendation.
12										
13	NO3	2.00E-15	100%						1	Recommended.
14	NO3	2.10E-15							3	Not the recommendation.
15	NO3	2.60E-15	31%						2	Code="<=" ?
16										
17	CI	1.10E-10	15%	6.10E-11	-179		267	384	2	Recommended.
18										
19	T	k(T)	Unc	k(fit)	%Err				Ref	Manually fitted data for reaction with OH
20	263	9.98E-12	20%	1.01E-11	1				4	kt098
21	268	9.77E-12	20%	9.90E-12	1				4	kt098
22	273	9.34E-12	20%	9.70E-12	4				4	kt098
23	278	8.40E-12	20%	9.52E-12	13				4	kt098
24	283	8.07E-12	20%	9.35E-12	16				4	kt098
25	288	7.90E-12	20%	9.20E-12	17				4	kt098
26	298	8.77E-12	20%	8.94E-12	2				4	kt098
27	303	8.51E-12	20%	8.83E-12	4				4	kt098
28	321	8.32E-12	20%	8.49E-12	2				4	kt098
29	327	7.93E-12	20%	8.41E-12	6				4	kt098
30	338	6.99E-12	20%	8.27E-12	18				4	kt098
31	354	6.64E-12	20%	8.12E-12	22				4	kt098
32	223.05	1.29E-11	10%	1.29E-11	0				5	kt093
33	225.65	1.28E-11	10%	1.28E-11	0				5	kt093
34	227.45	1.23E-11	10%	1.24E-11	1				5	kt093
35	233.45	1.27E-11	10%	1.19E-11	-6				5	kt093
36	234.45	1.24E-11	10%	1.18E-11	-4				5	kt093
37	237.05	1.17E-11	10%	1.16E-11	0				5	kt093

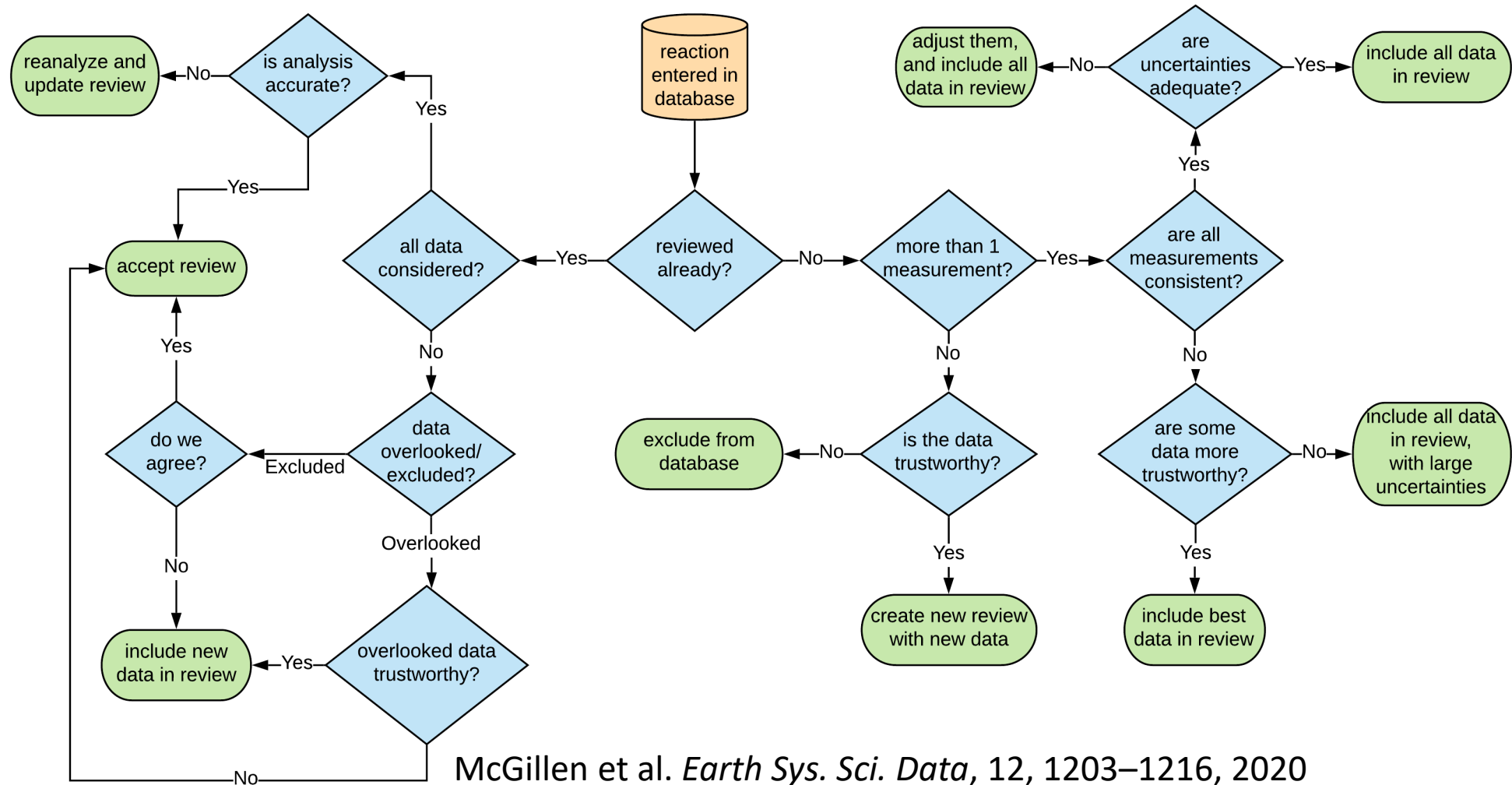
# Availability

EUROCHAMP  
2020



- Database is free to download as an Excel spreadsheet from the EUROCHAMP data centre:
- <https://data.eurochamp.org/data-access/kin/>
- The accompanying paper is available in the open access journal *Earth System Science Data*:
- McGillen, M.R., Carter, W.P.L., Mellouki, A., Orlando, J.J., Picquet-Varrault, B., Wallington, T.J. *Earth System Science Data*, 12, 1203–1216, 2020

# Data evaluation







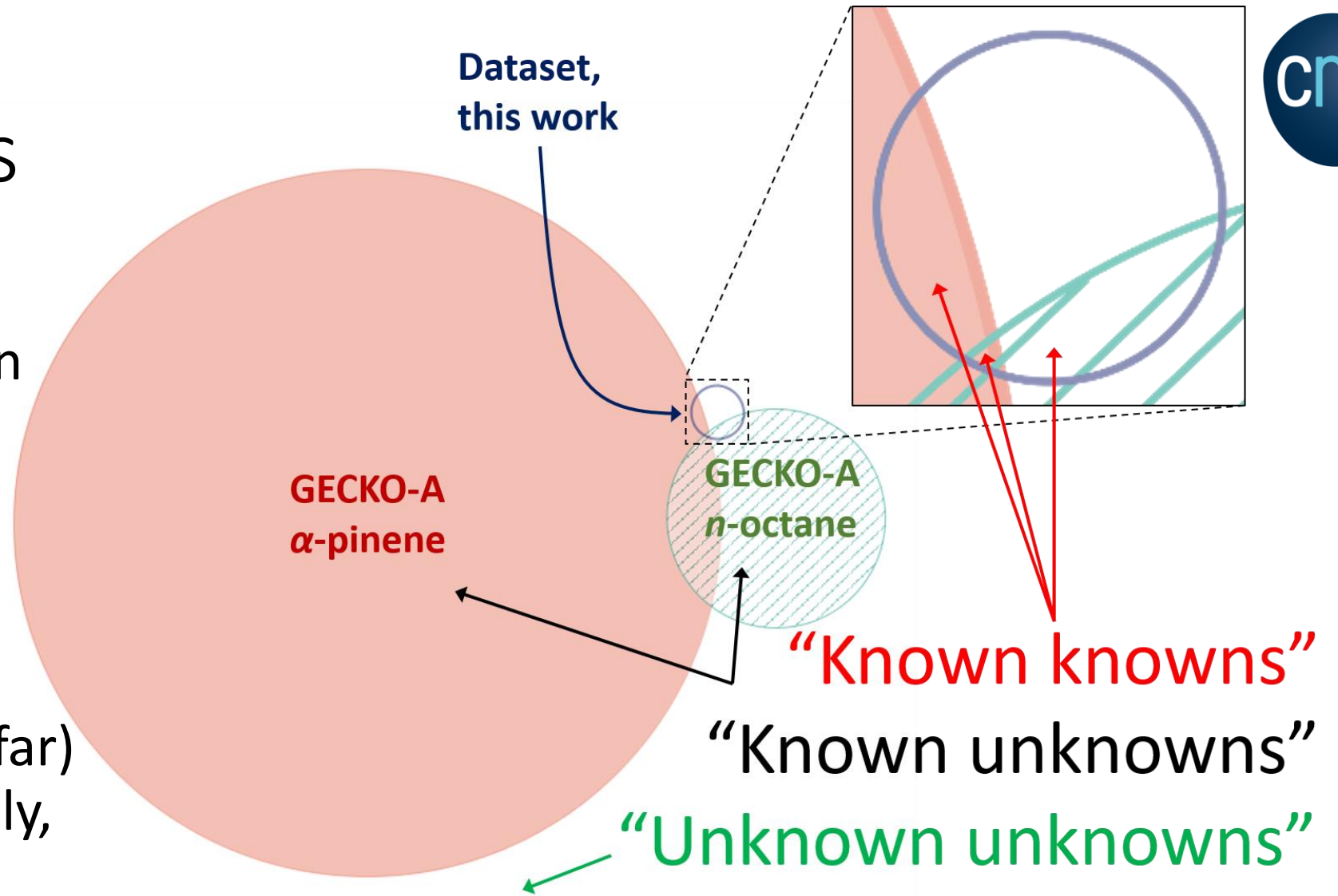
# Database update cycle

- Current version 1.3
- Additional data (mostly from 2019–2020) has been compiled and is awaiting evaluation
- 63 new experimental kinetic studies, concerning 124 species
- 23 of which are totally new to the database
- (So far) we are on track for an update cycle of <1 year
- But this project is young, this can change

# Perspectives

## Coverage

- Far fewer species than explicit models
- Overlap is tiny
- This is only 2 species
- What about the  $10^{4-5}$  species observed (so far) (Goldstein and Galbally, 2007)



McGillen et al. *Earth Sys. Sci. Data*, 12, 1203–1216, 2020

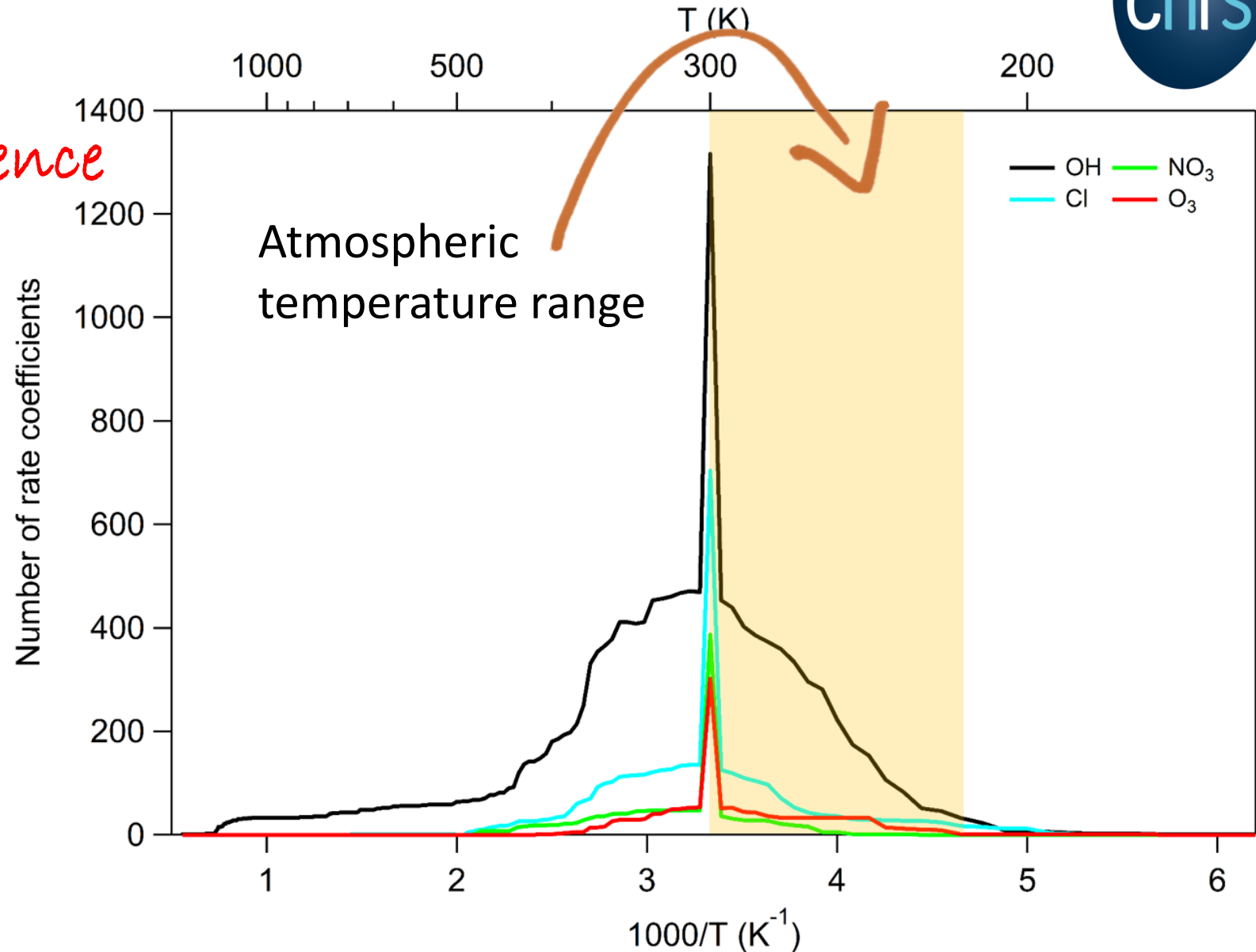
Valorso et al. *Atmos. Chem. Phys.*, 11, 6895–6910, 2011

Goldstein and Galbally, *Environ. Sci. Technol.*, 41, 1514–1521, 2007

# Perspectives

## Temperature dependence

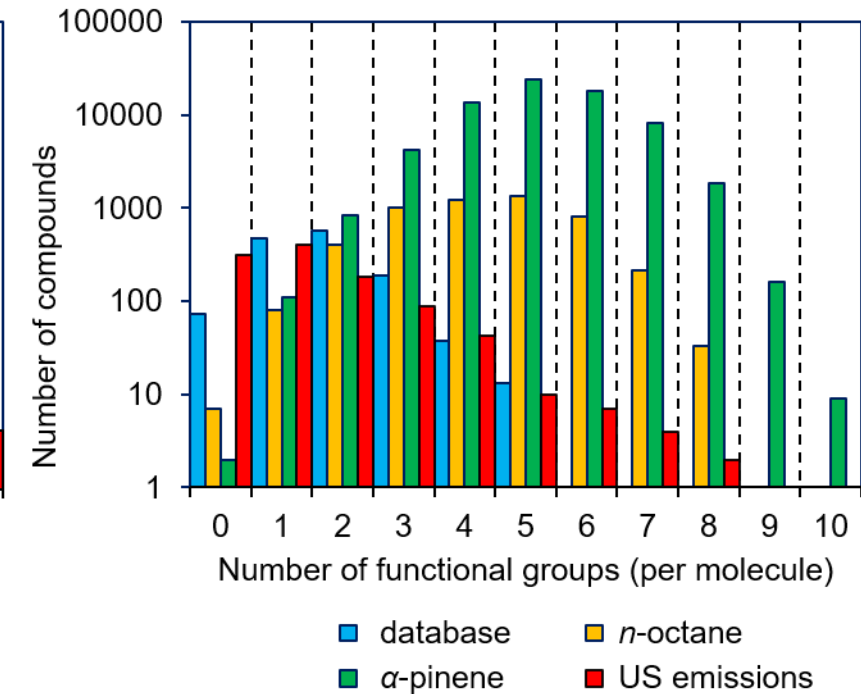
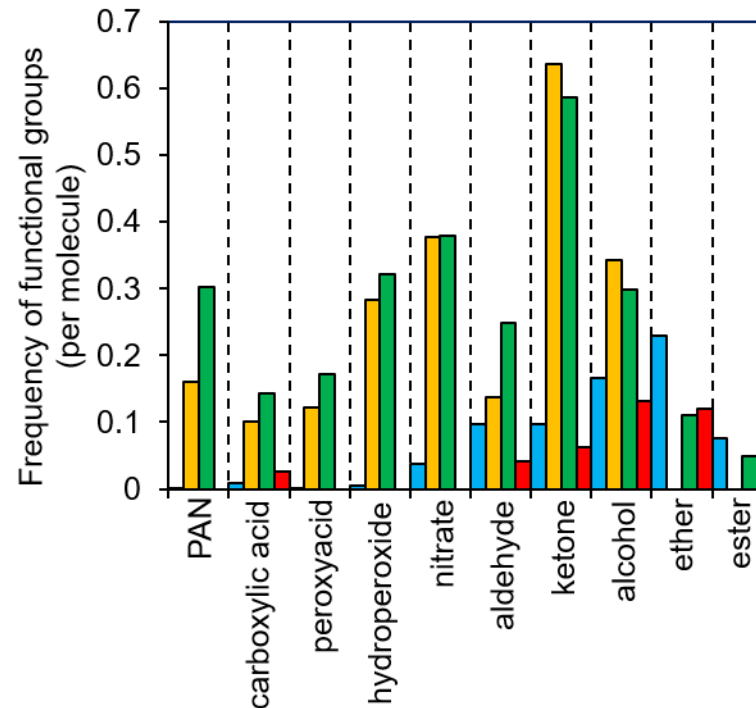
- Vast majority of measurements are room-temperature
- Very few species measured over full atmospheric T-range
- Partly a consequence of conventional chamber design



# Perspectives

## Functionalization

- “atmospheric” functional groups are poorly represented
- # functional groups are also poorly represented
- Probably relates to the O:C ratio and volatility...



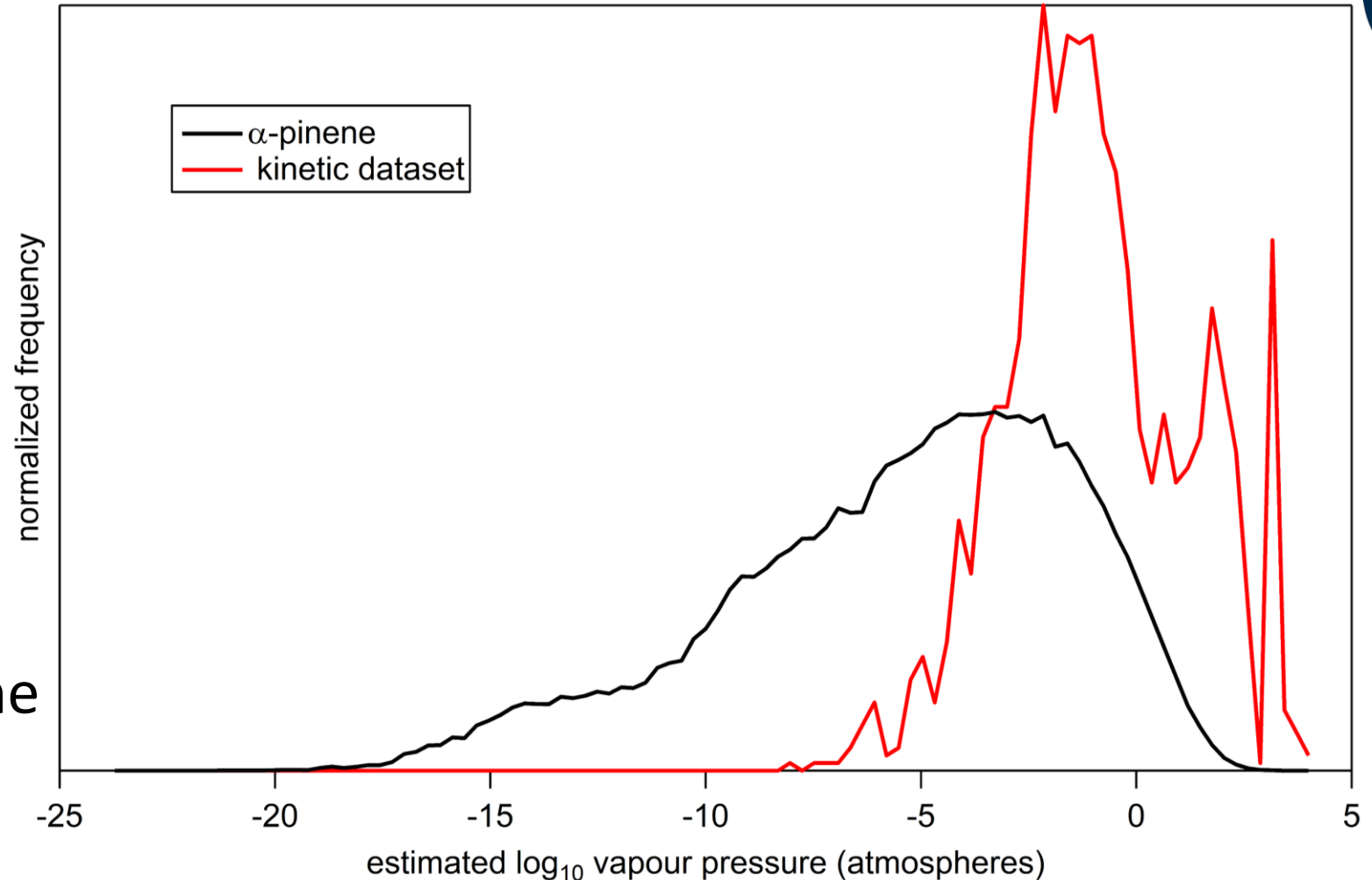
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Valorso et al. *Atmos. Chem. Phys.*, 11, 6895–6910, 2011

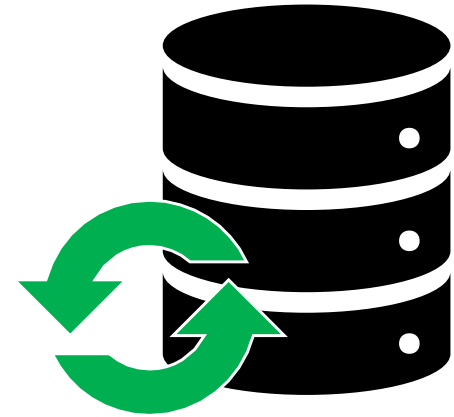
# Perspectives

*volatility*

- Very different distribution
- Comes from experimental difficulties
- How can we overcome this problem?



Estimates: UManSysProp, <http://umansysprop.seaes.manchester.ac.uk/>  
Topping et al. *Geosci. Model Dev*, 9, 899–914, 2016



# Future directions

- Branching ratios
- Further oxidants:  $O(^3P)$ ,  $O(^1D)$ , Cls, H, Br?
- Metadata: techniques, references compounds, reactor details
- Improved treatment of uncertainties
- Aqueous phase?