

# Glyoxal Yields Of Selected Hydrocarbon Oxidations

## PANORAMA

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### 1) Air pollution...

...is the leading cause of environmental deaths worldwide, responsible for approximately **9 million deaths per year**. Glyoxal is thought to contribute to the formation of harmful secondary organic aerosols (SOAs).

### 2) Field Measurements...

...allow for the measurement of a wide range of volatile organic compounds (VOCs). However, for global monitoring this is expensive and human intensive.

### 3) Satellites...

...provide an alternative method of global VOC monitoring. However, very few emitted compounds can be detected.



### 4) Oxidation Products...

...such as glyoxal and formaldehyde can be detected by satellite. Most classes of VOC give produce specific formaldehyde:glyoxal ratios so if a satellite can detect these compounds, the emissions' source can be estimated.

### 5) The Marine Boundary Layer...

...is used as a pristine environment with minimal anthropogenic activity. There is currently a discrepancy in glyoxal concentration between field measurements and computer models (the latter predicting concentrations 2-4 times lower).

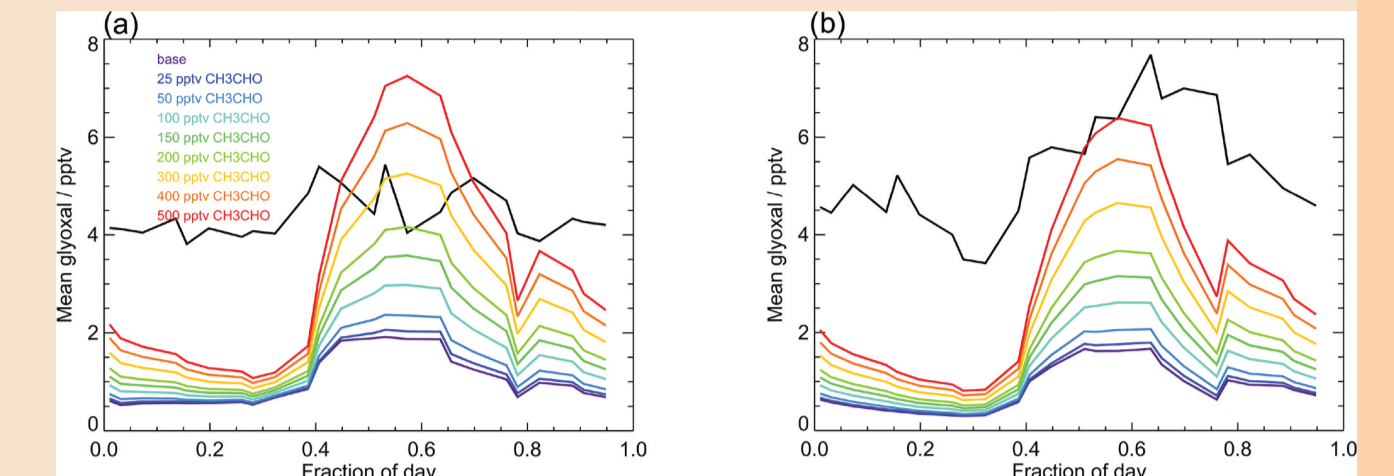
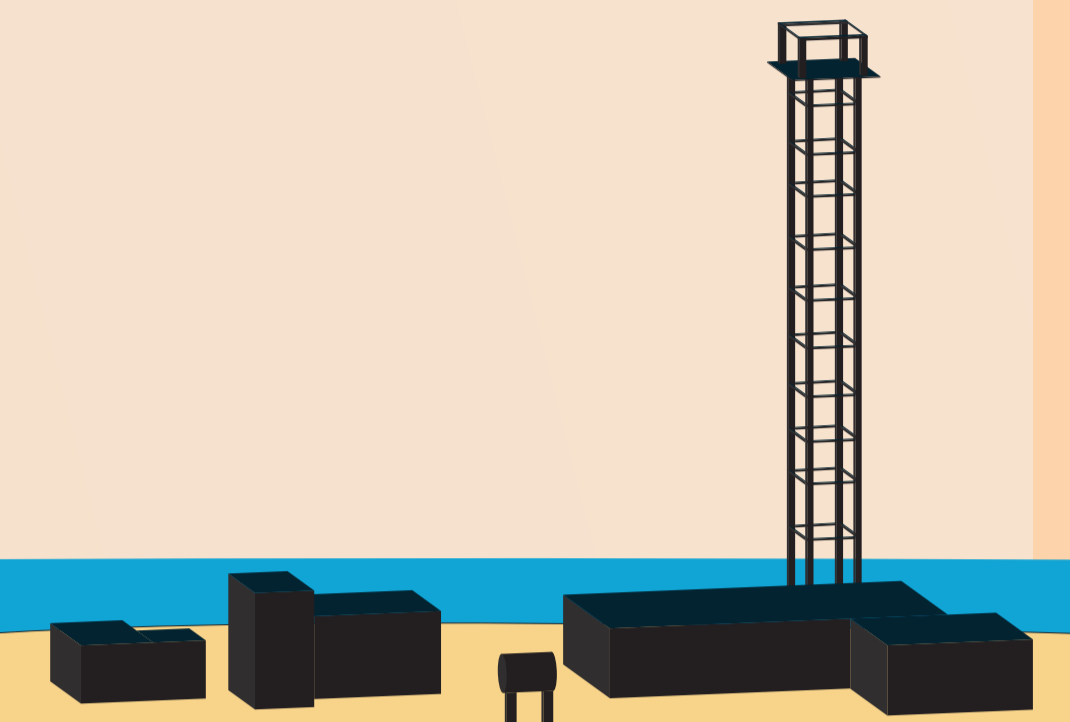


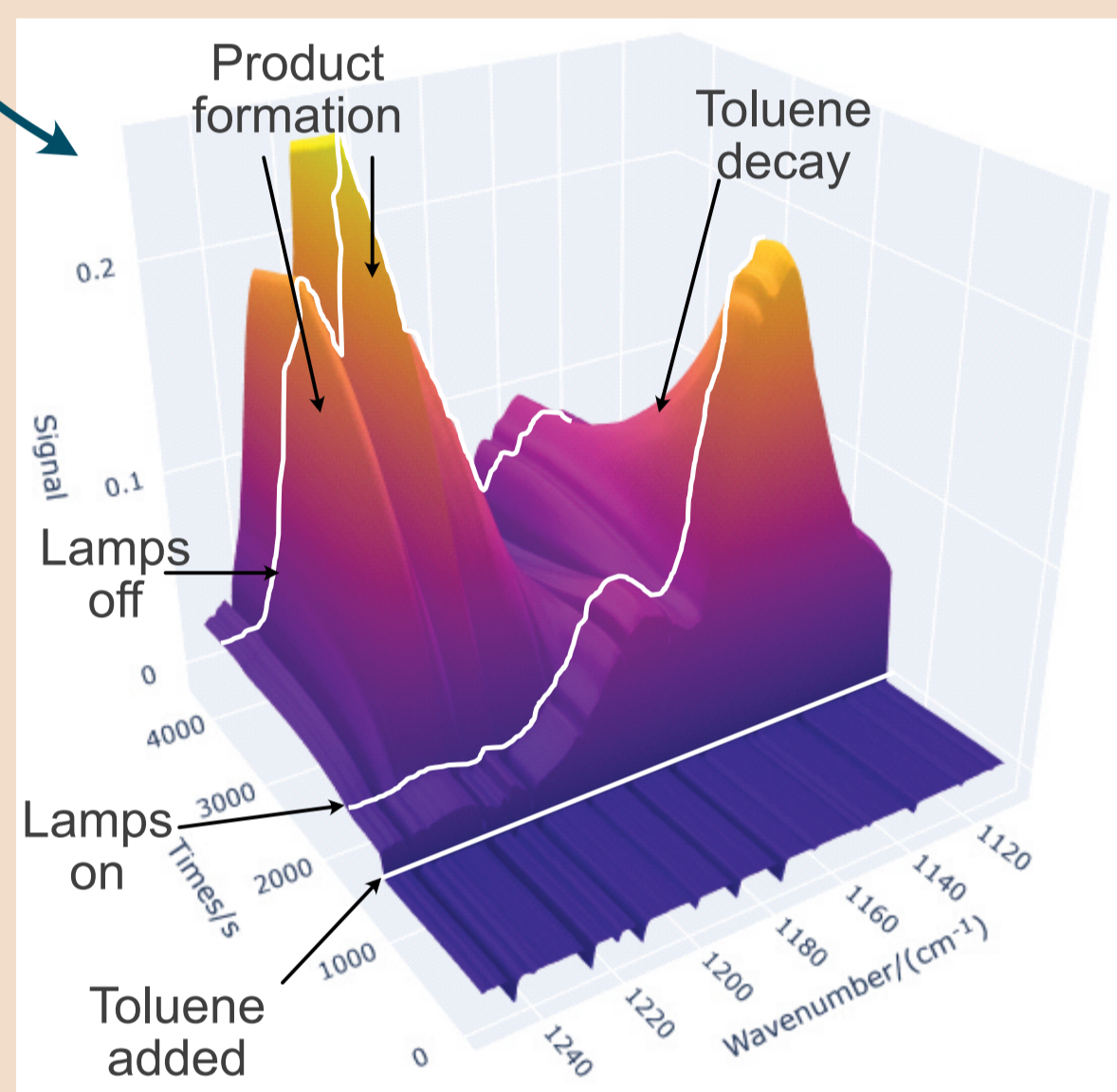
Figure shows measured (black) glyoxal concentrations vs computer model (purple). Increasing the acetaldehyde concentration can go some way to explain the discrepancy.

These measurements were taken at Cape Verde Atmospheric Observatory (depicted below).



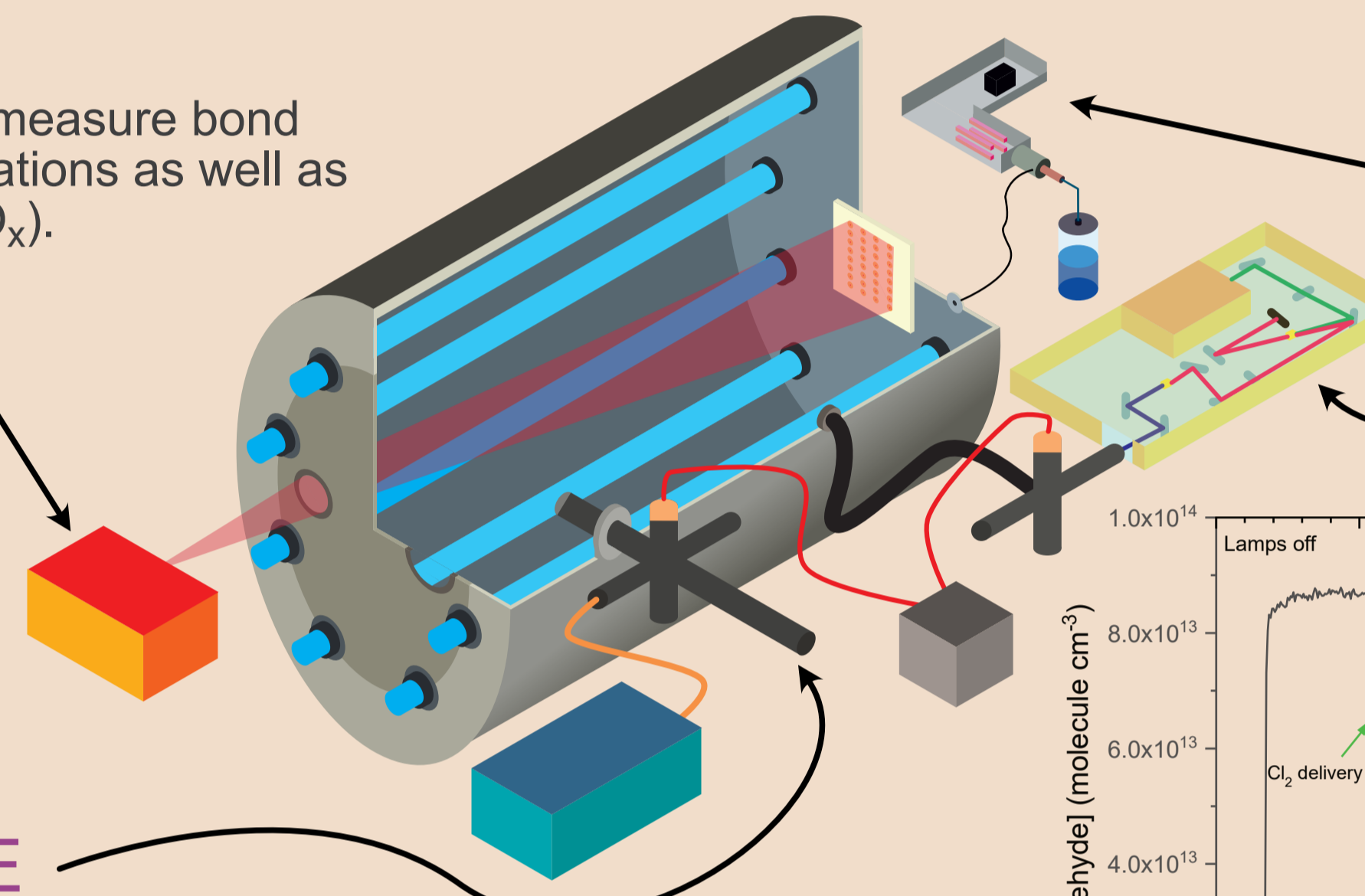
### FTIR

Fourier Transform Infra-Red Spectroscopy is used to measure bond vibrations. This is useful for monitoring VOC concentrations as well as some inorganic compounds (such as CO/CO<sub>2</sub> and NO<sub>x</sub>).



### FAGE

Fluorescence Assay by Gas Expansion is a method used to detect OH and HO<sub>2</sub> - important radical species in the atmosphere.



## The HIRAC Chamber

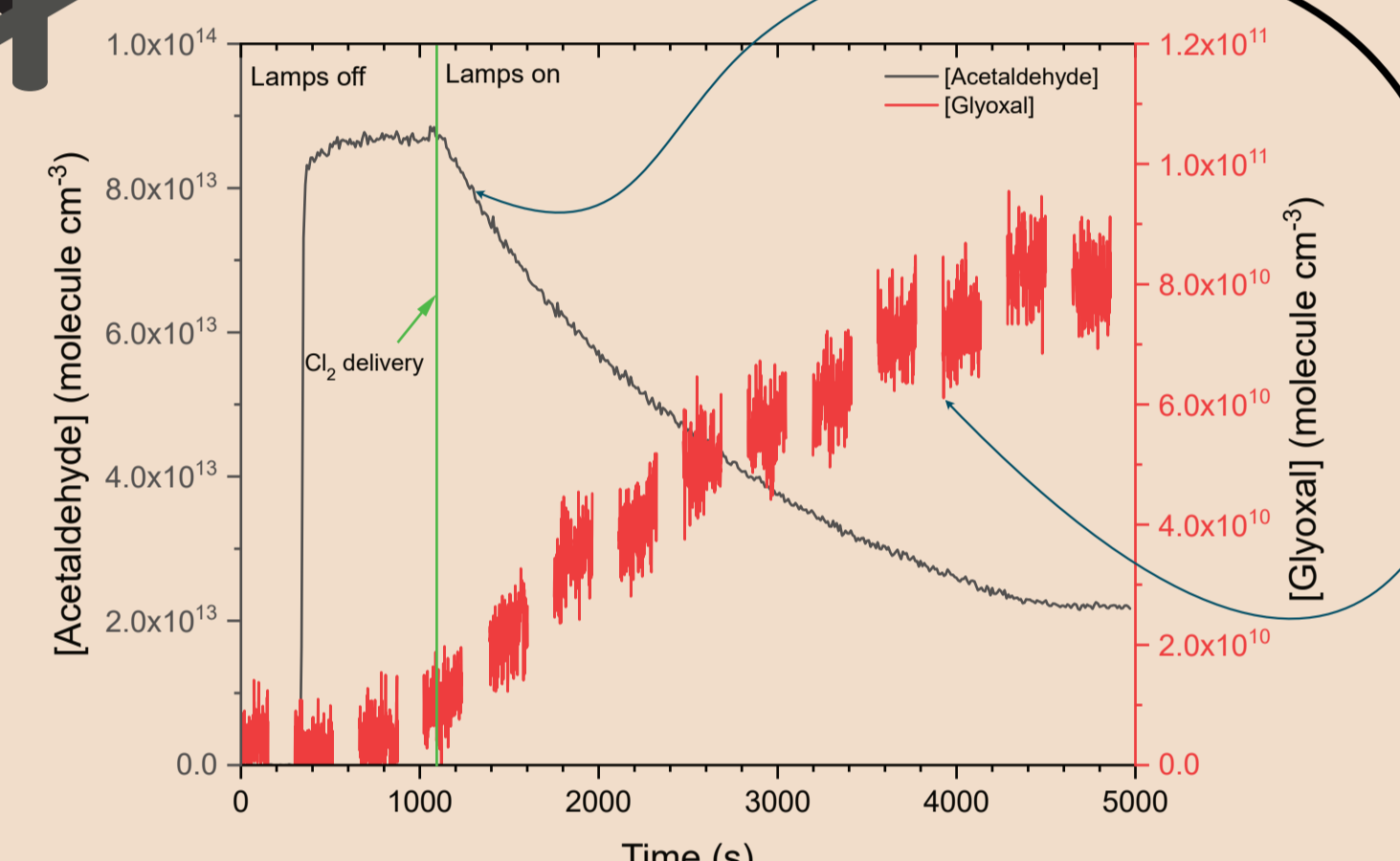
Lab based experiments at the University of Leeds were used to study glyoxal yields from VOC oxidations

### PTR-MS

Proton Transfer Reaction Mass Spectrometry is used to detect compounds with higher proton affinities than water. This accounts for most VOCs however, glyoxal cannot be measured this way.

### Glyoxal-LIP

Laser Induced Phosphorescence instruments have their lasers tuned to excite a particular transition in a molecule. This makes them highly selective. In the HIRAC chamber a laser is tuned to 440 nm to measure glyoxal phosphorescence.

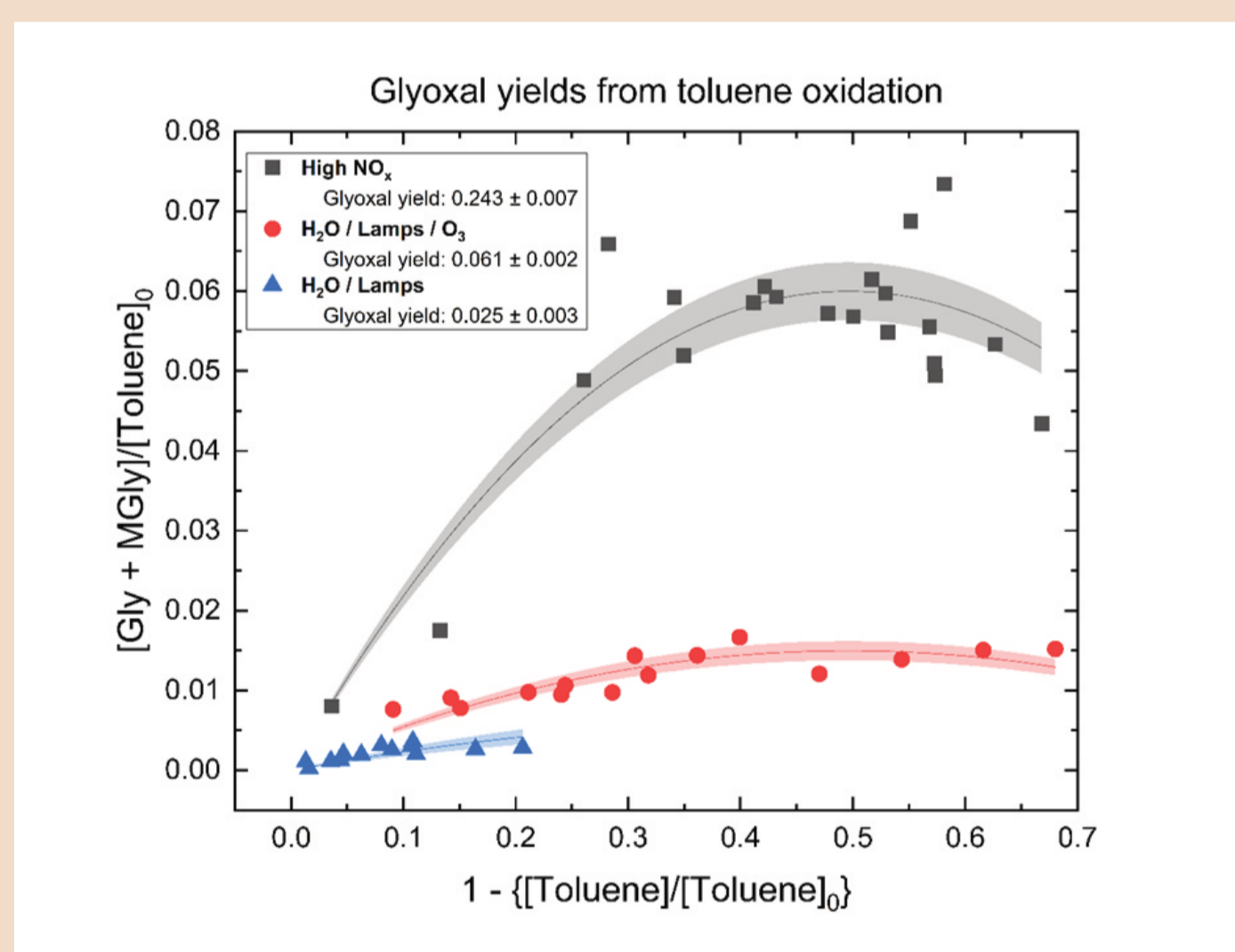


## Glyoxal Yield Calculations

These are calculated using the equation below.

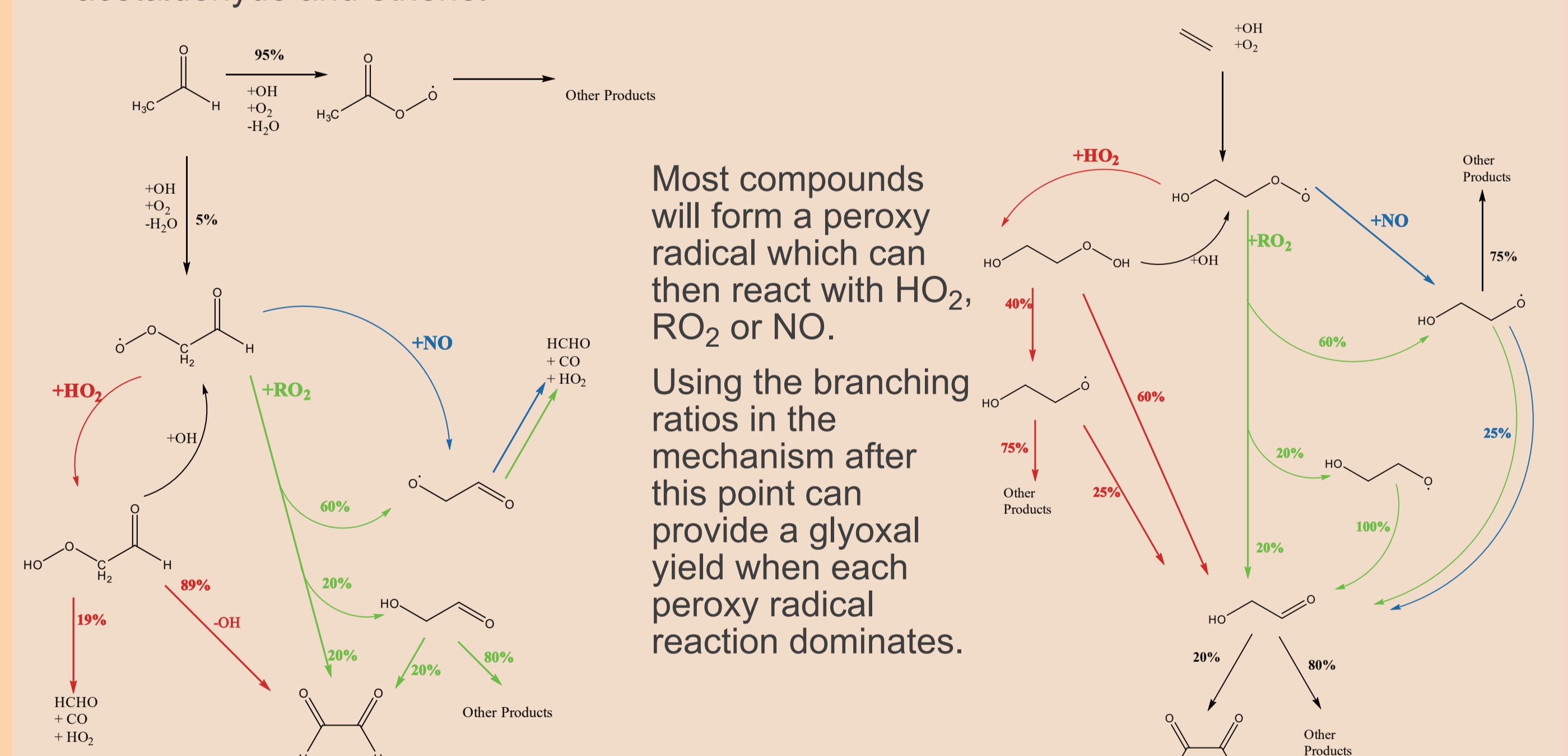
$$\text{Glyoxal Yield} = \frac{\text{Formation of Glyoxal}}{\text{Removal of Reactant}}$$

However, in reality a more complicated equation is required to take into account glyoxal loss. We can fit more complex equations to the data as shown.



## Computer Predictions

Computer models are based around the Master Chemical Mechanism. It compiles known reaction rates to construct a chemical mechanism. These are shown below for acetaldehyde and ethene.



Most compounds will form a peroxy radical which can then react with HO<sub>2</sub>, RO<sub>2</sub> or NO.

Using the branching ratios in the mechanism after this point can provide a glyoxal yield when each peroxy radical reaction dominates.

Environment	Dominant Reaction	Glyoxal Yield (%)
MBL	HO <sub>2</sub>	4.5
MBL	RO <sub>2</sub>	1
Urban	NO	0

Environment	Dominant Reaction	Glyoxal Yield (%)
MBL	HO <sub>2</sub>	14
MBL	RO <sub>2</sub>	11
Urban	NO	5

## Results

The table below presents the experimentally found glyoxal yields compared to literature values where possible. All experiments were OH initiated unless otherwise stated.

Experiment	Experimental Results		MCM Predictions		Literature Values (%)
	Low NO <sub>x</sub> (%)	High NO <sub>x</sub> (%)	Low NO <sub>x</sub> (%)	High NO <sub>x</sub> (%)	
Toluene	2.5 ± 0.3	24 ± 0.7	17	29	(High NO <sub>x</sub> ) 8 - 39
Acetaldehyde	0.28 ± 0.01	0.06 ± 0.07	1 - 4.5	0	
Acetaldehyde (Cl initiated)	0.13 ± 0.05		1-4.5	0	
Ethene	0.6 ± 0.1	Under investigation	11 - 14	5	(High NO <sub>x</sub> estimate) 2 (3)
Glycolaldehyde (Cl initiated)	25 ± 4		20	20	
Glycolaldehyde	Under investigation		20	20	(High NO <sub>x</sub> ) 22 ± 6

\*The MCM does not have data on Cl initiated oxidation so glyoxal yields of Cl and OH initiated reactions are assumed to be similar.

## Discussion & Conclusions

Comparison of glyoxal yields of high NO<sub>x</sub> toluene oxidation shows good agreement with the MCM and literature values.

These experiments show the first glyoxal yield results in a low NO<sub>x</sub> chamber for ethene, acetaldehyde and toluene oxidation.

Low glyoxal yields from acetaldehyde and ethene (known emitters in the MBL) do not explain the glyoxal concentration discrepancy between fields measurements and computer models. However there is new evidence of aromatic compounds in the MBL and this study shows that glyoxal yields from this class of compound may be significant (4).

There is also growing evidence that direct emissions of some compounds are not fully accounted for in field measurements and therefore cannot be represented in models properly (5).

## References

- 1) A. Piersanti, Atmos. 12(2), p 196 (2021)
- 2) H. Walker et al., Atmos. Chem. Phys., 22, 5535–5557 (2022)
- 3) J. J. Orlando et al., J. Phys. Chem. A, 102, 42, 8116–8123 (1998)
- 4) Wohl et al., Sci. Adv.9, eadd9031 (2023)
- 5) V Ferracci, Nat Commun., 22, 15(1):2571 (2024).