

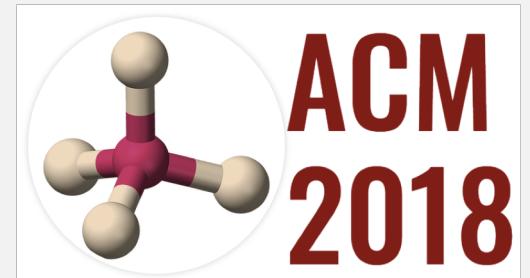
Observational Constraints on the Fate of the Hydroxy Nitrates produced in the Reaction of Isoprene Peroxy Radicals with NO

Krystal T. Vasquez¹ (kvasquez@caltech.edu),

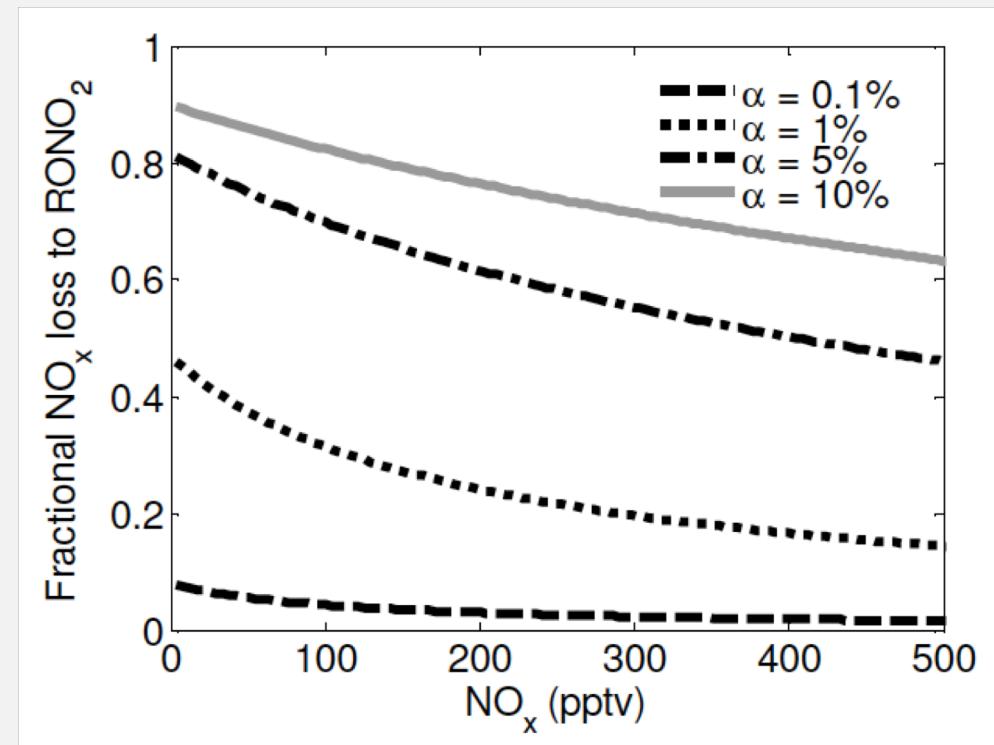
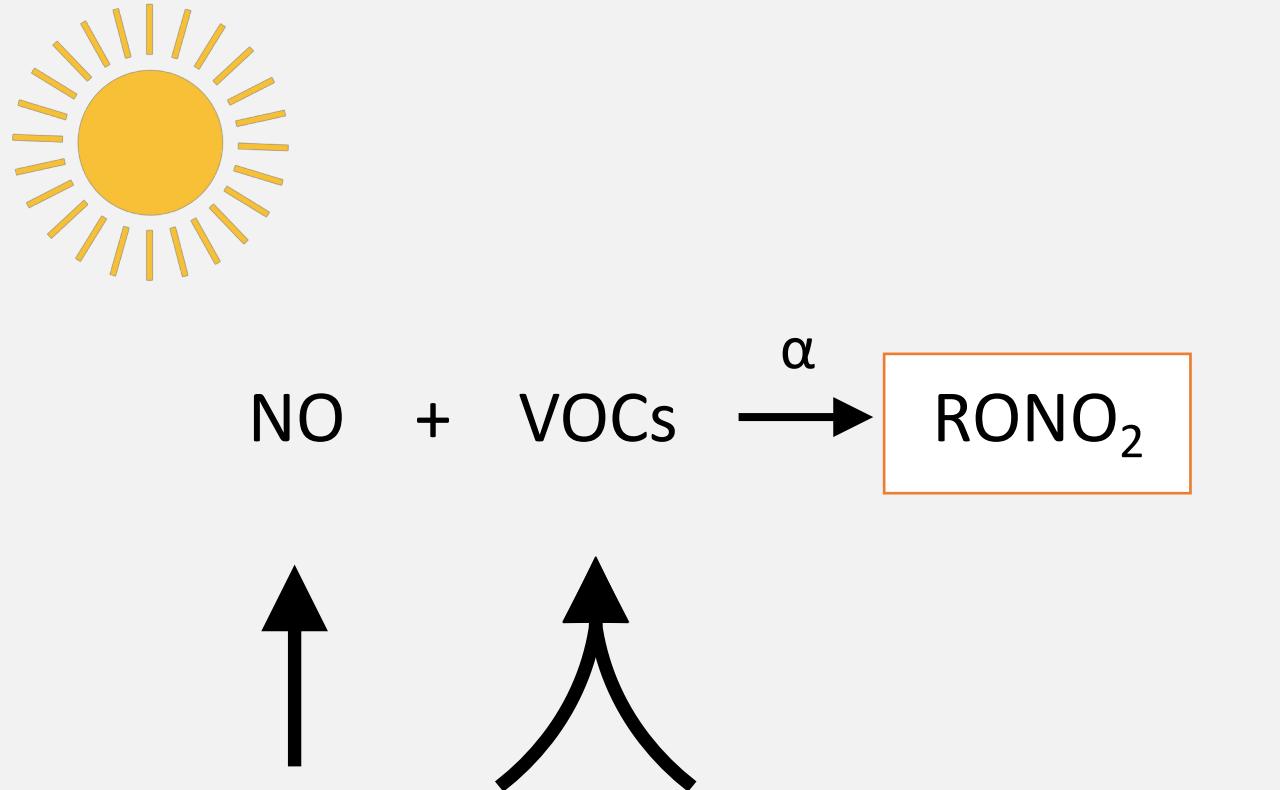
John D. Crounse², Lu Xu², Hannah M. Allen¹, Alexander P. Teng^{2,a}, Eric Praske¹,
Kelvin H. Bates³ and Paul O. Wennberg^{2,4}

Affiliations

1. Division of Chemistry, Caltech
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 3. Center for the Environment, Harvard University
 4. Division of Engineering and Applied Sciences, Caltech
- a. Now at Divergent 3D

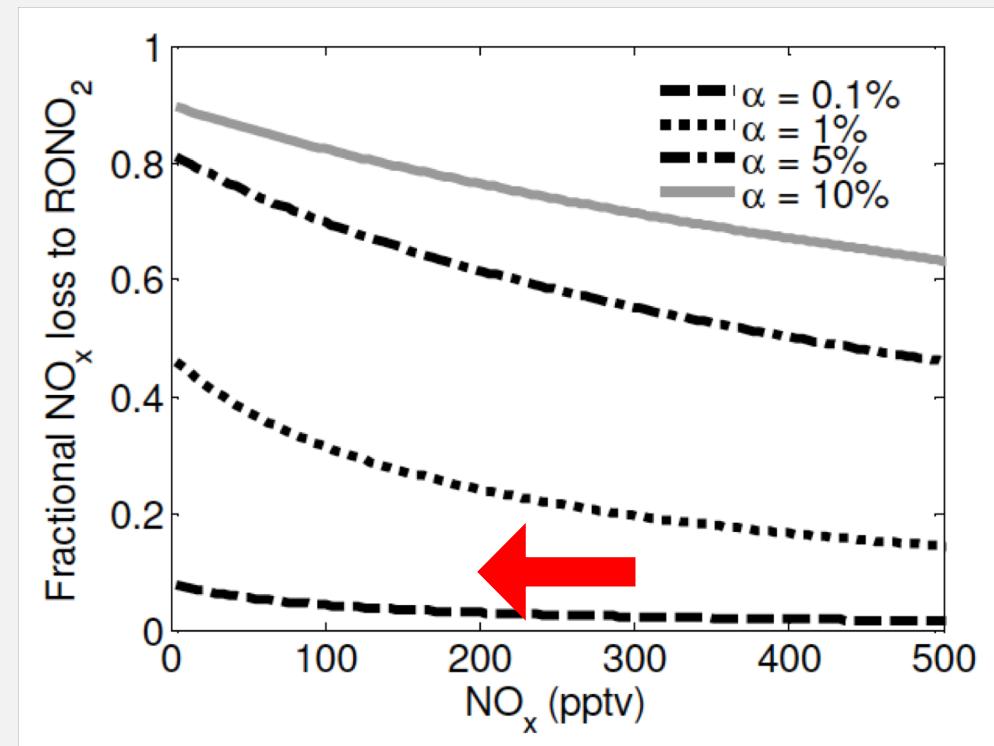
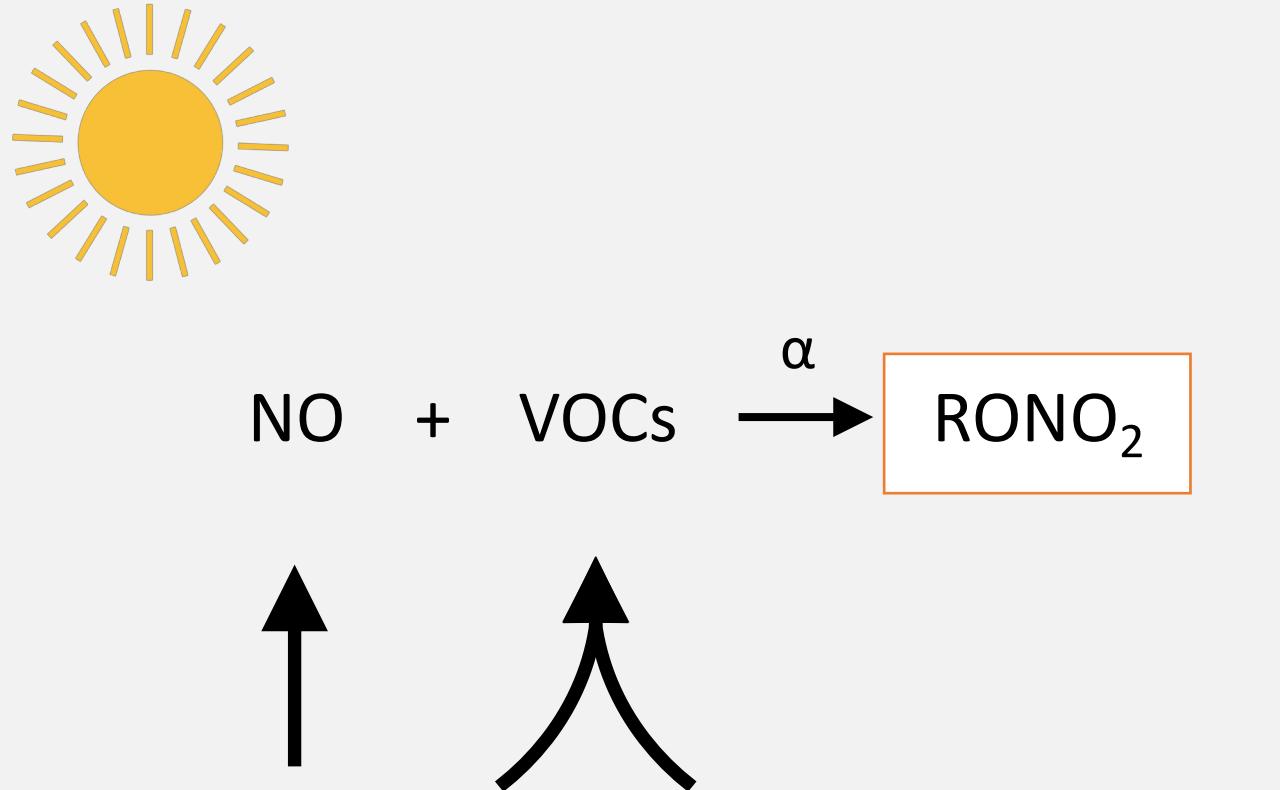


Organic Nitrates



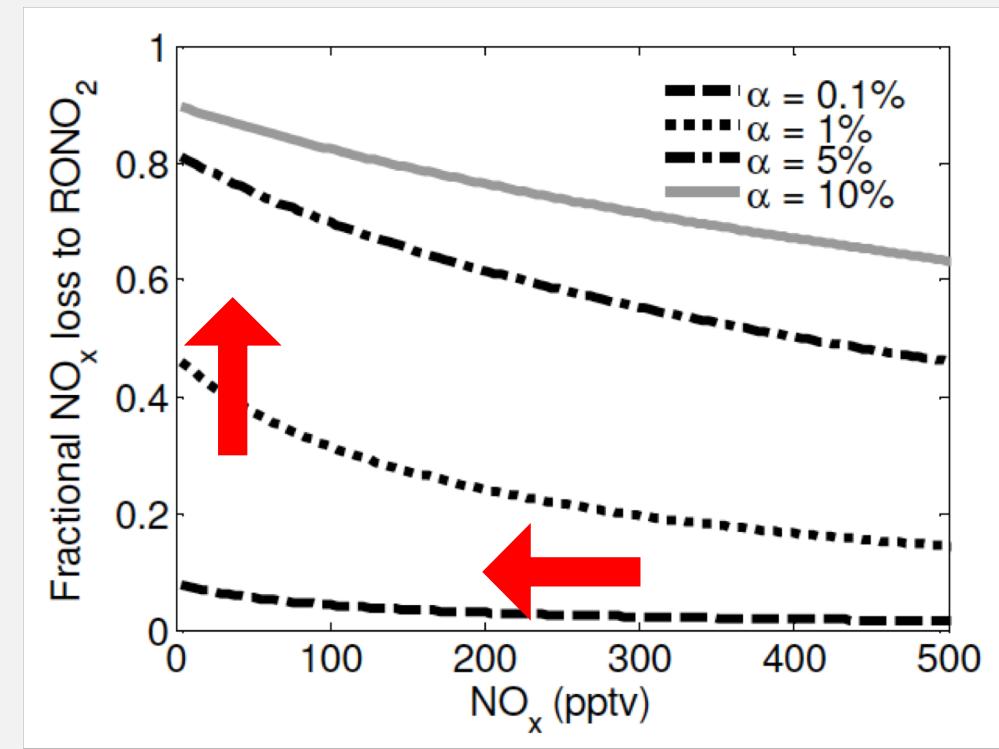
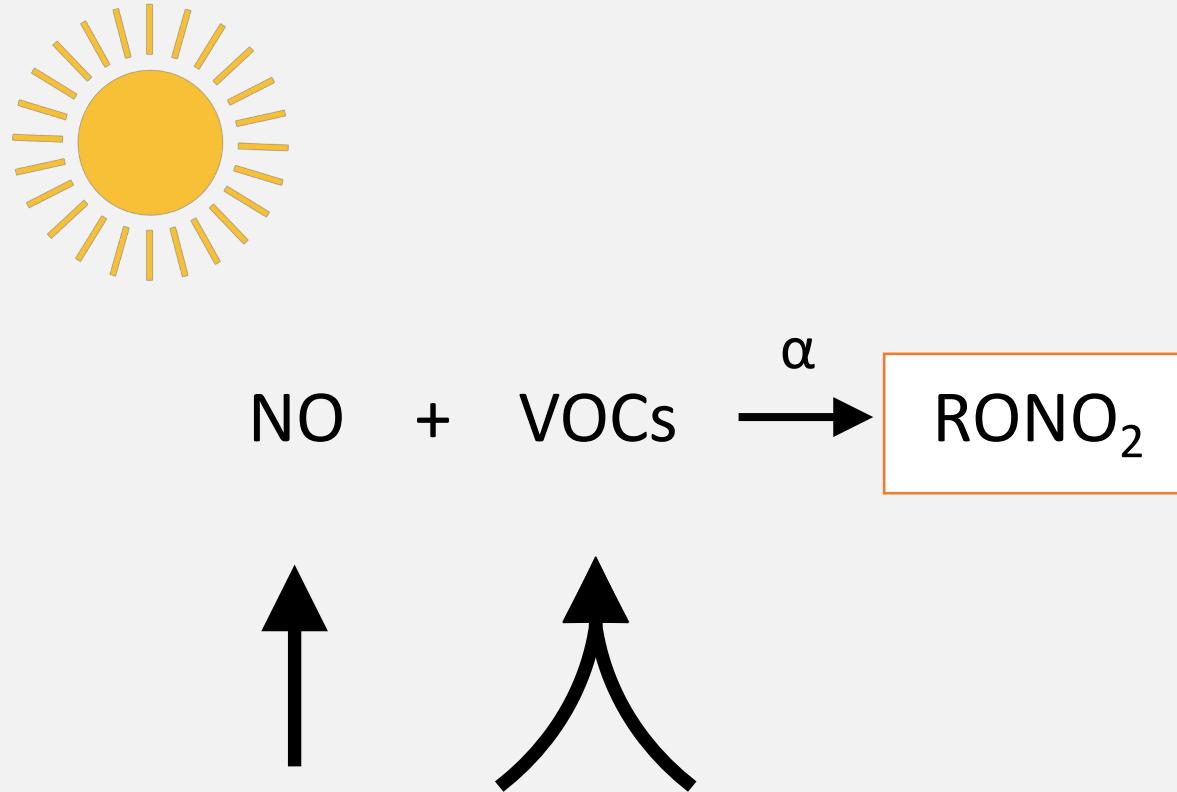
Browne and Cohen, ACP 2012

Organic Nitrates



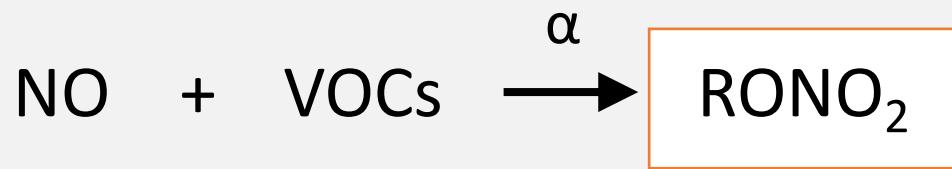
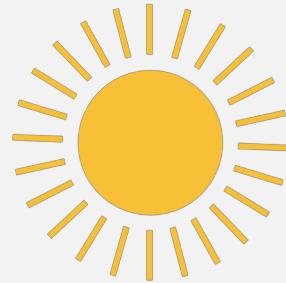
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Organic Nitrates



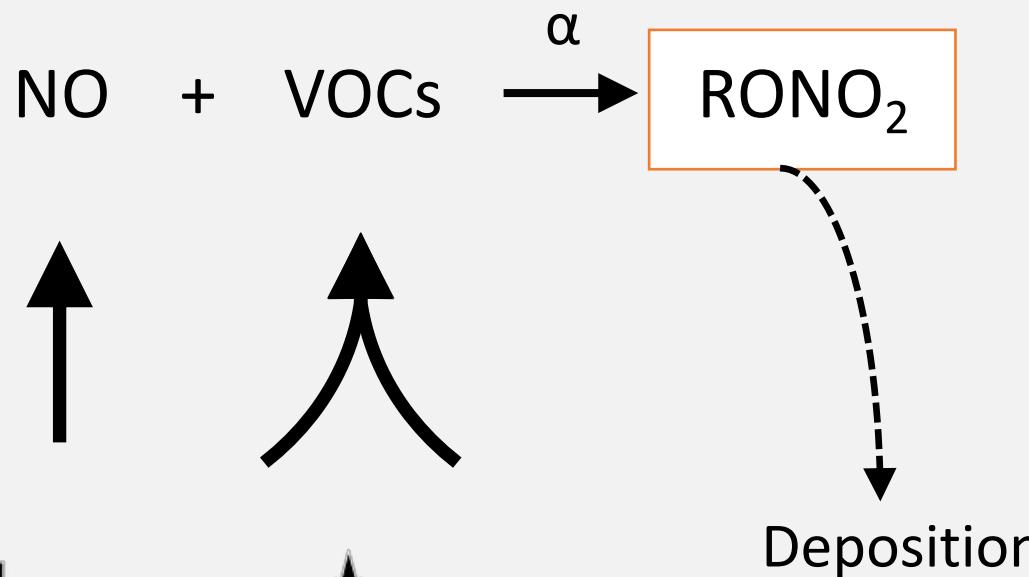
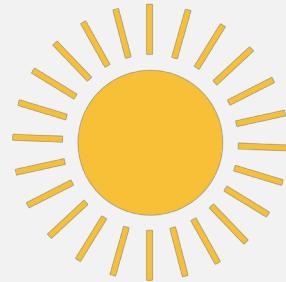
Browne and Cohen, ACP 2012

Organic Nitrates



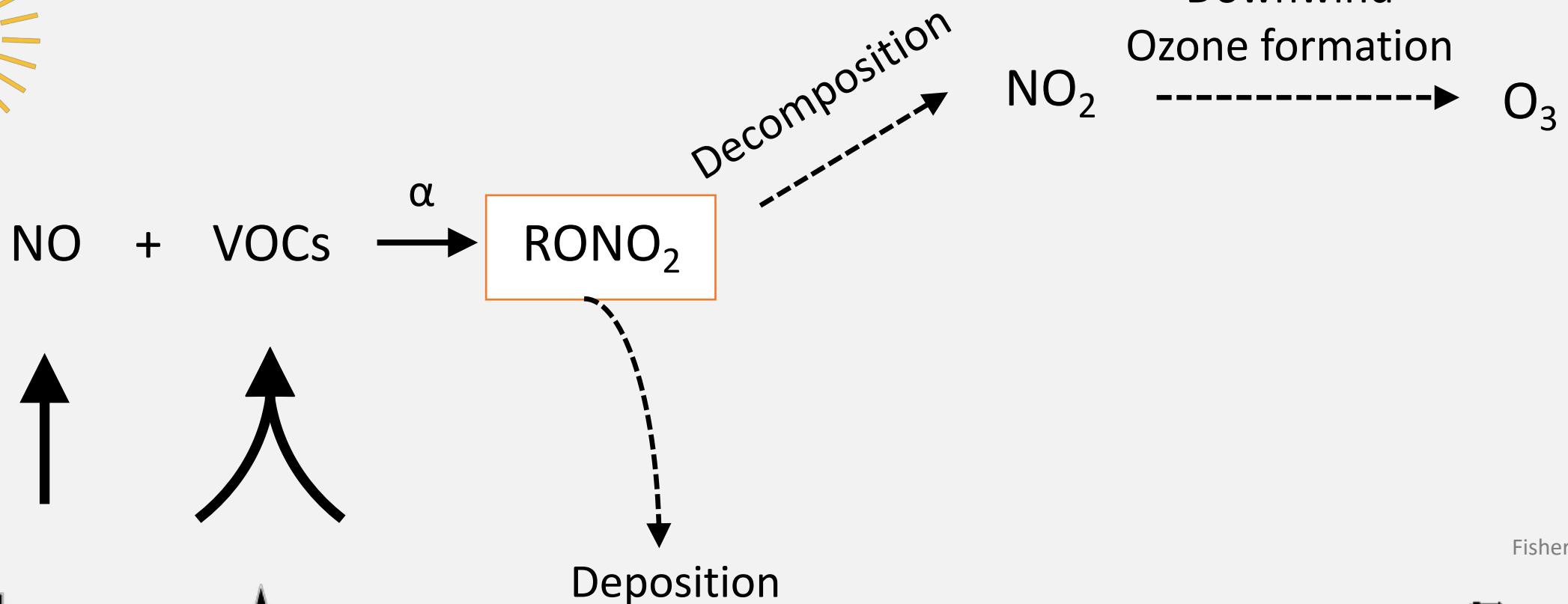
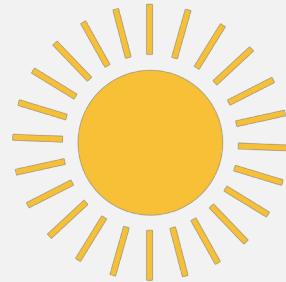
Fisher, et al. ACP 2016

Organic Nitrates



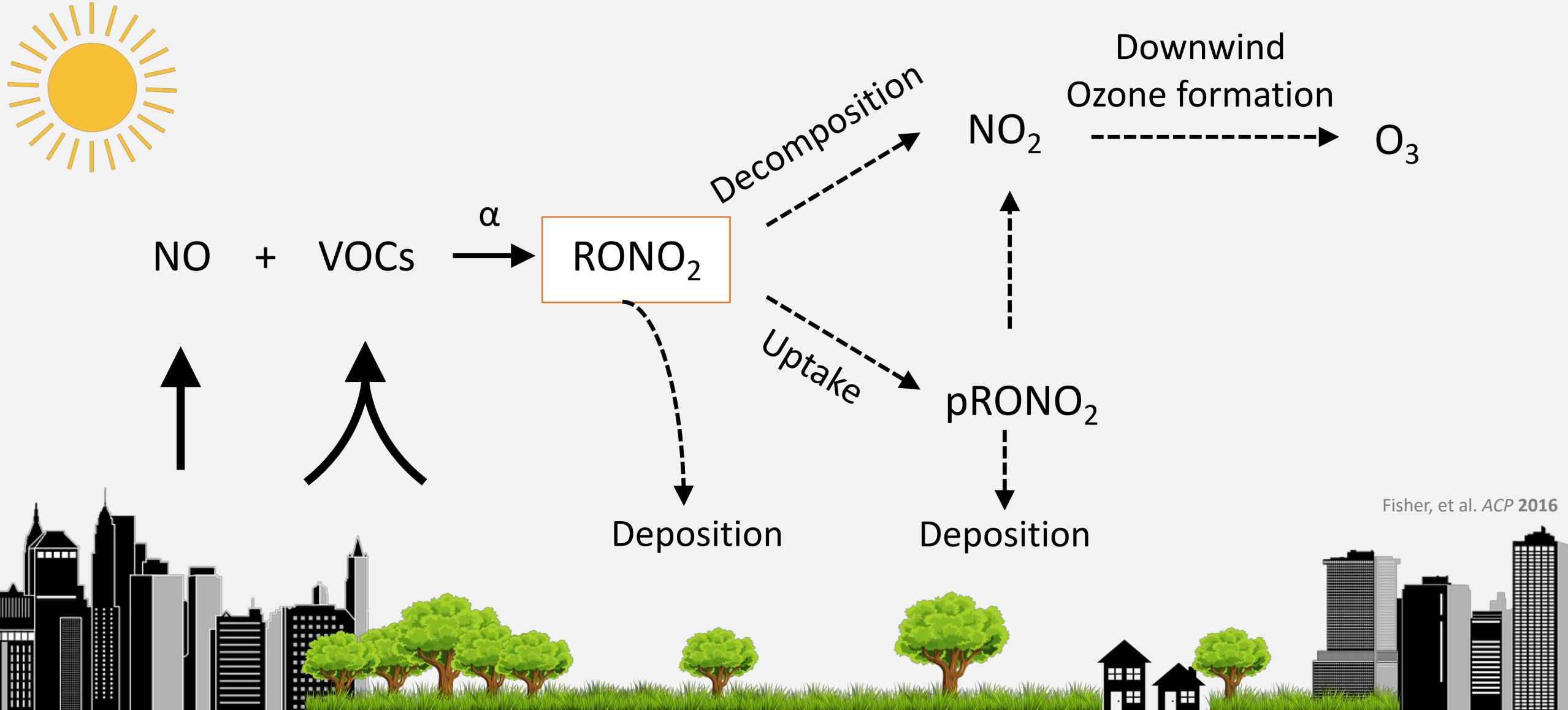
Fisher, et al. ACP 2016

Organic Nitrates

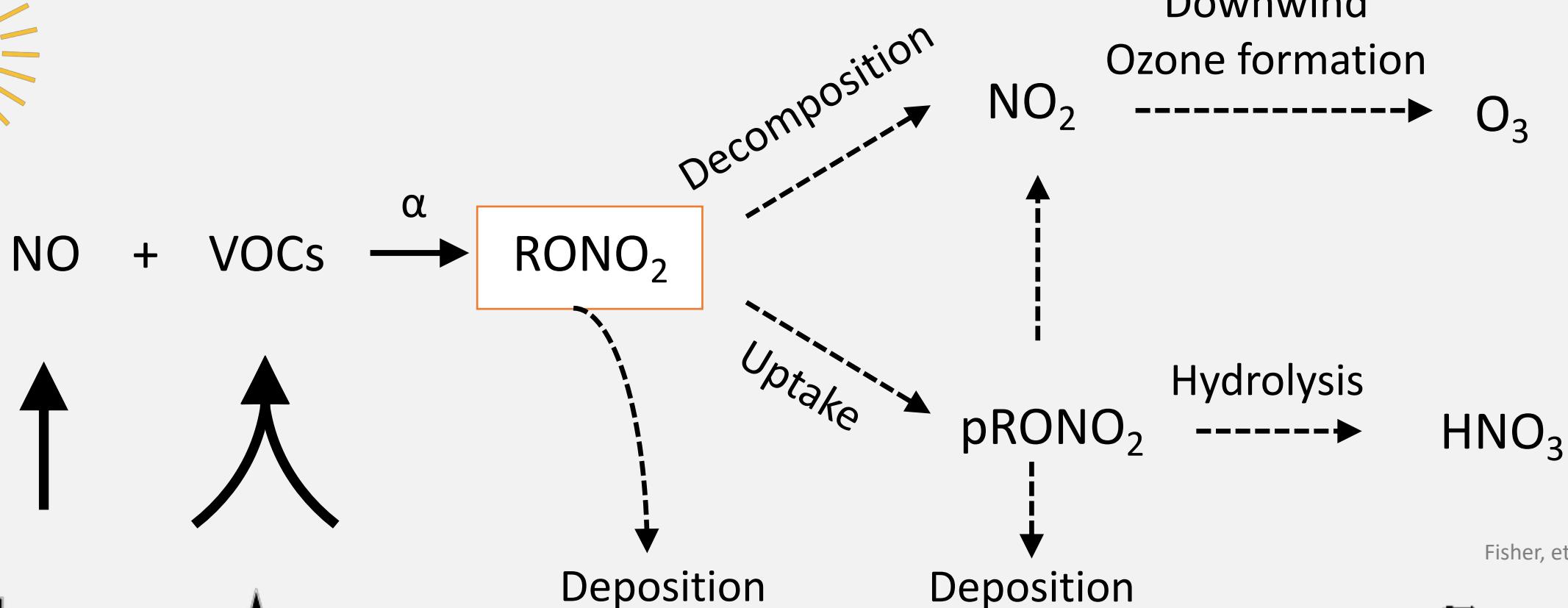
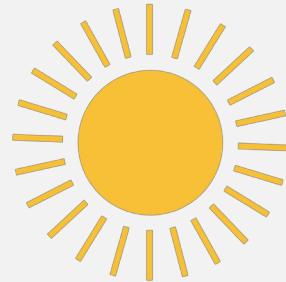


Fisher, et al. ACP 2016

Organic Nitrates

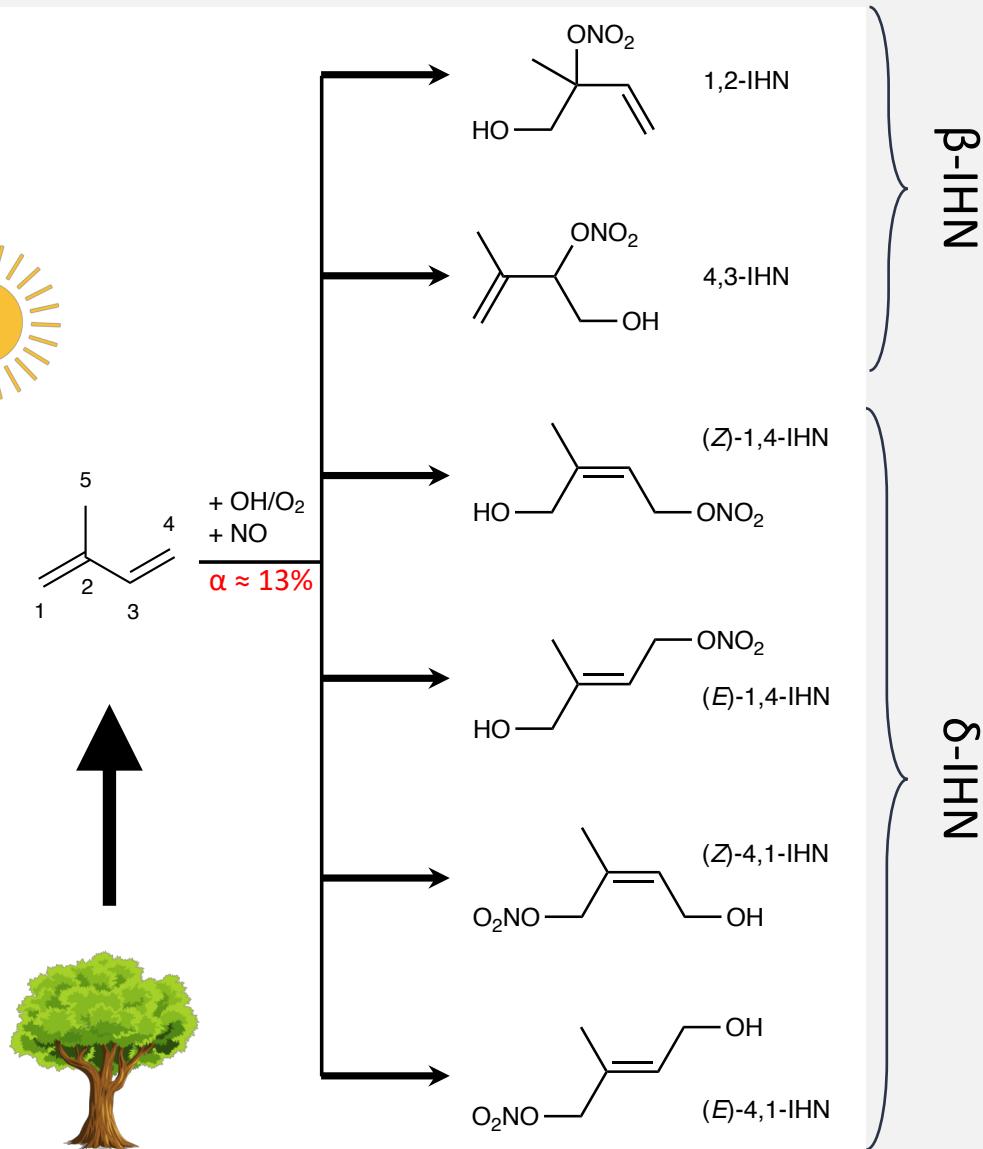


Organic Nitrates

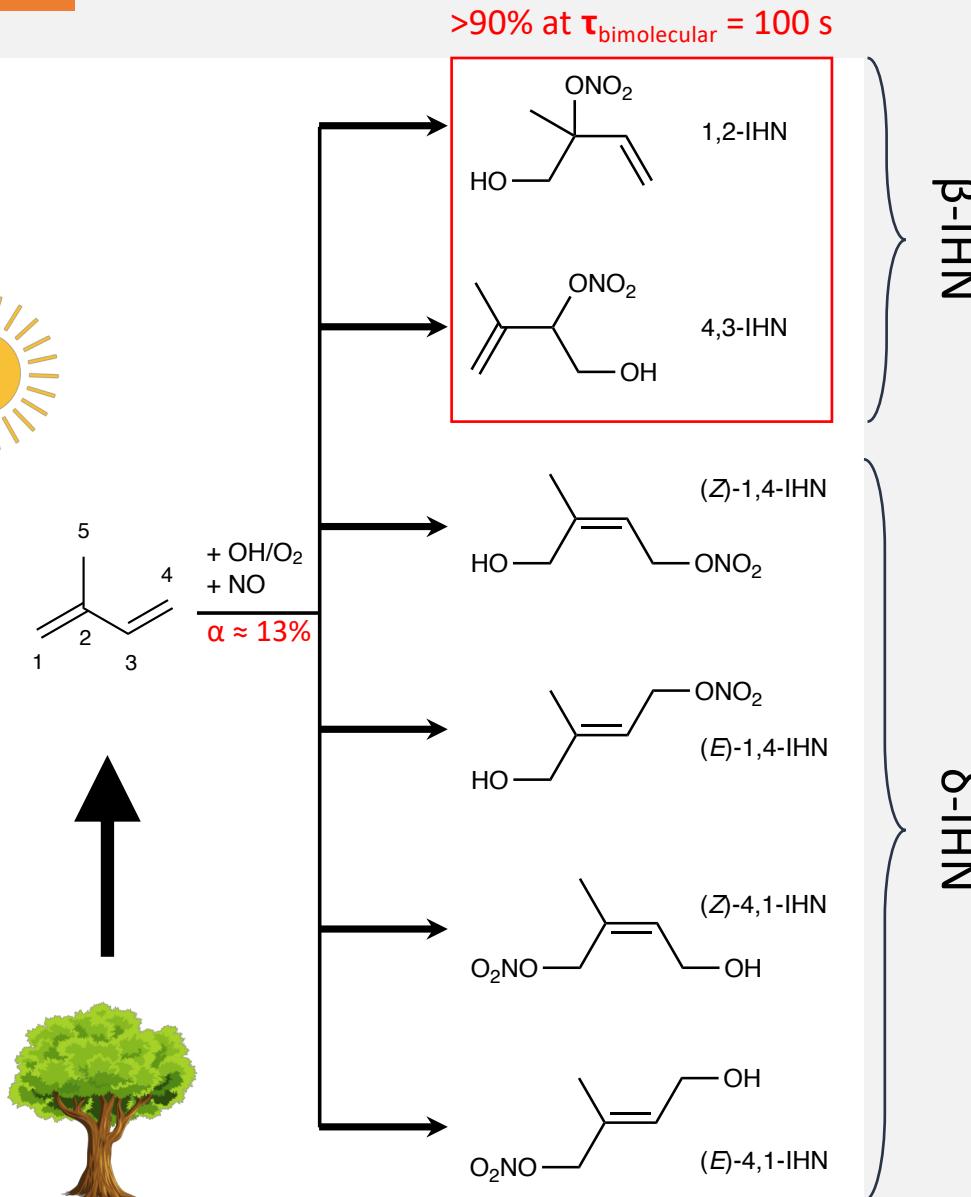


Fisher, et al. ACP 2016

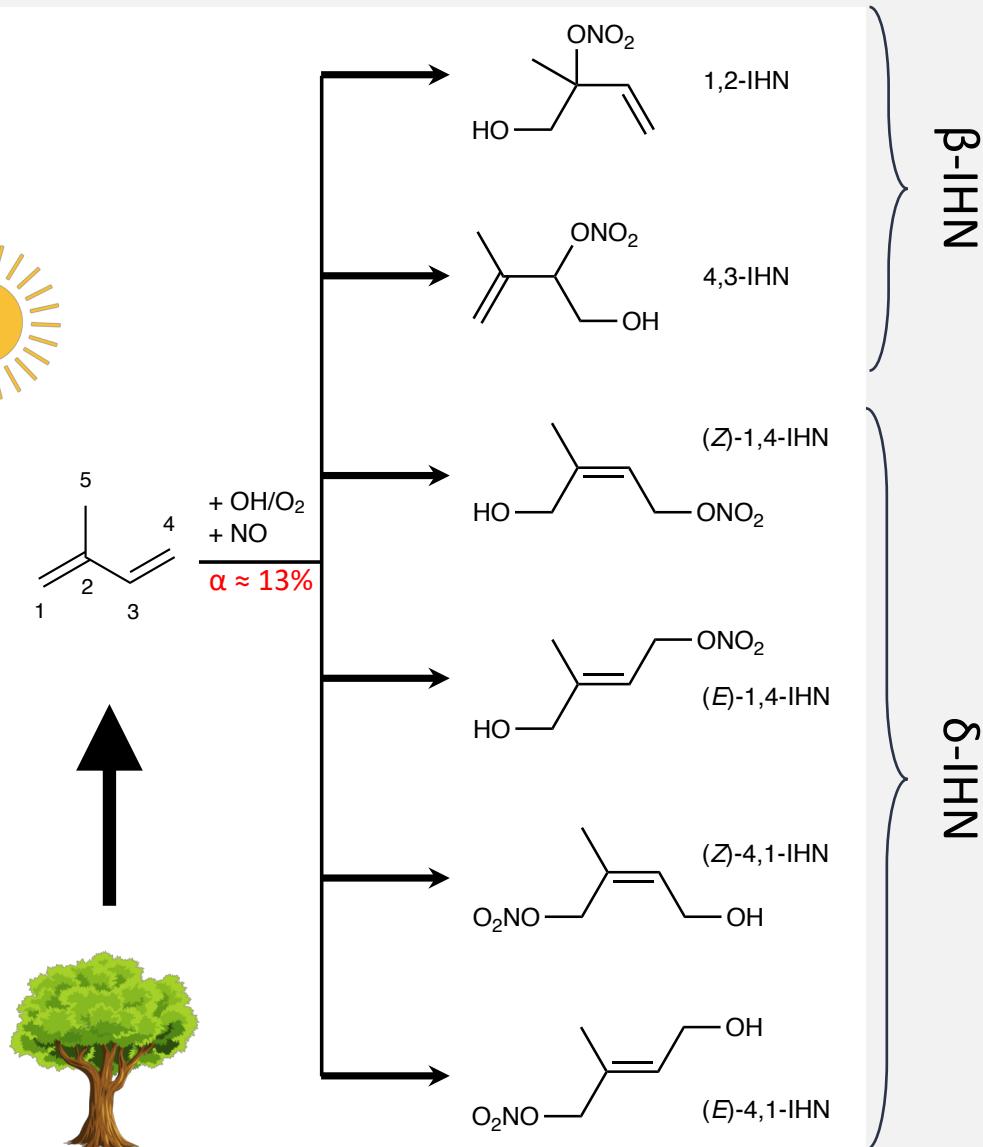
Isoprene Hydroxy Nitrates (IHN)



Isoprene Hydroxy Nitrates (IHN)



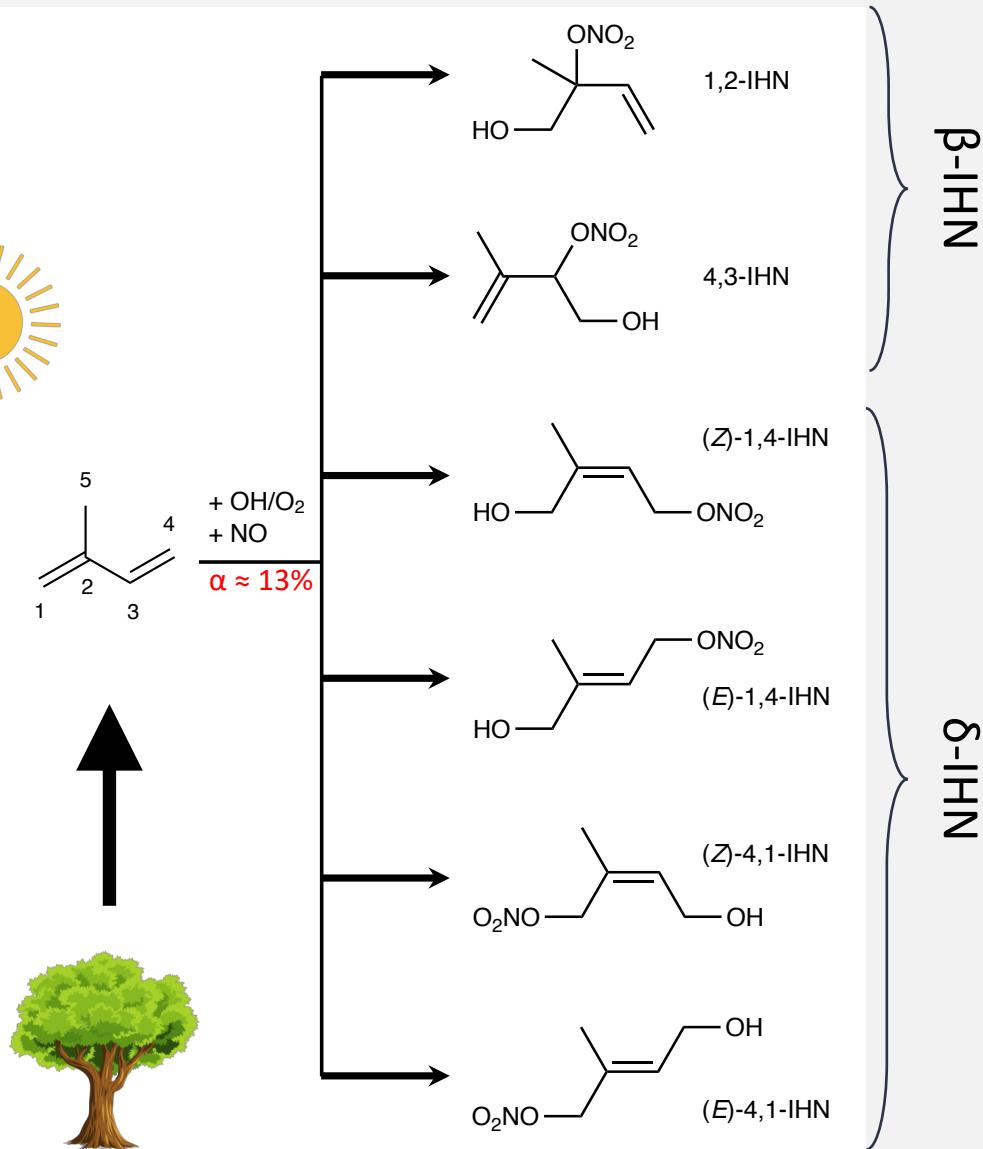
Isoprene Hydroxy Nitrates (IHN)



Relative abundance and isomer-specific fate determines the net effect of IHN

Loss Pathways	Lifetime (hours)		
	1,2-IHN	4,3-IHN	δ -IHN
OH Oxidation [OH] = 3×10^6 molec cm ⁻³	3	2	1
O ₃ Oxidation [O ₃] = 50 ppb	800	450	8
Deposition BLH = 1.5 km			24
Photolysis $j_{IHN} = 6.2 \times 10^{-6} s^{-1}$ (noon)			44

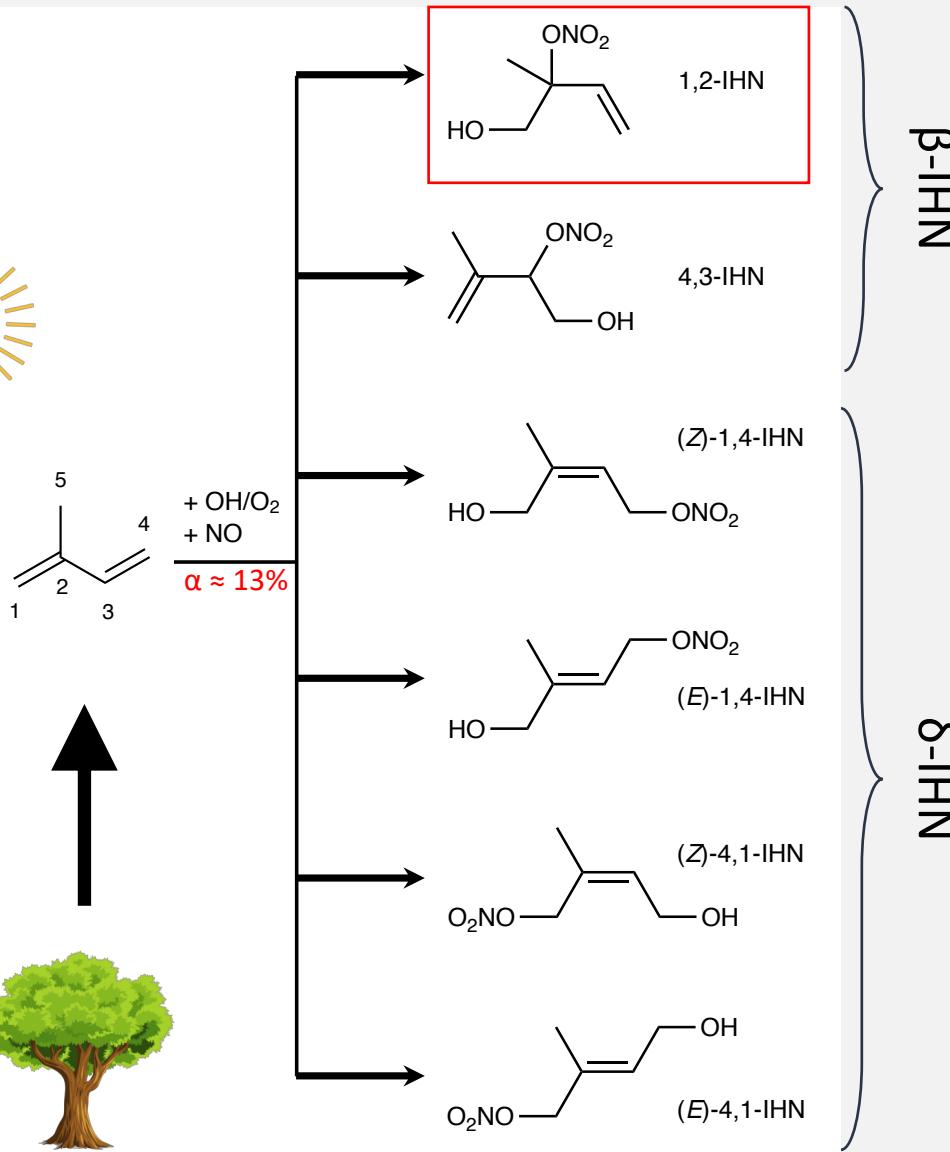
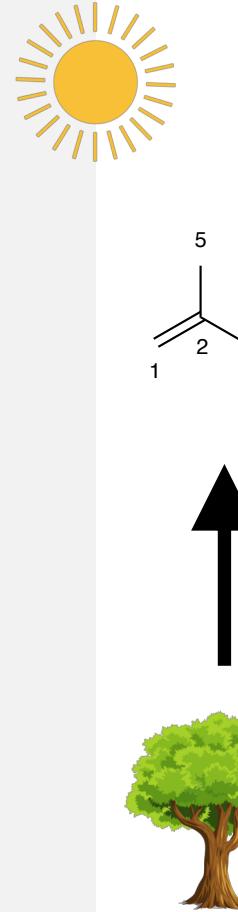
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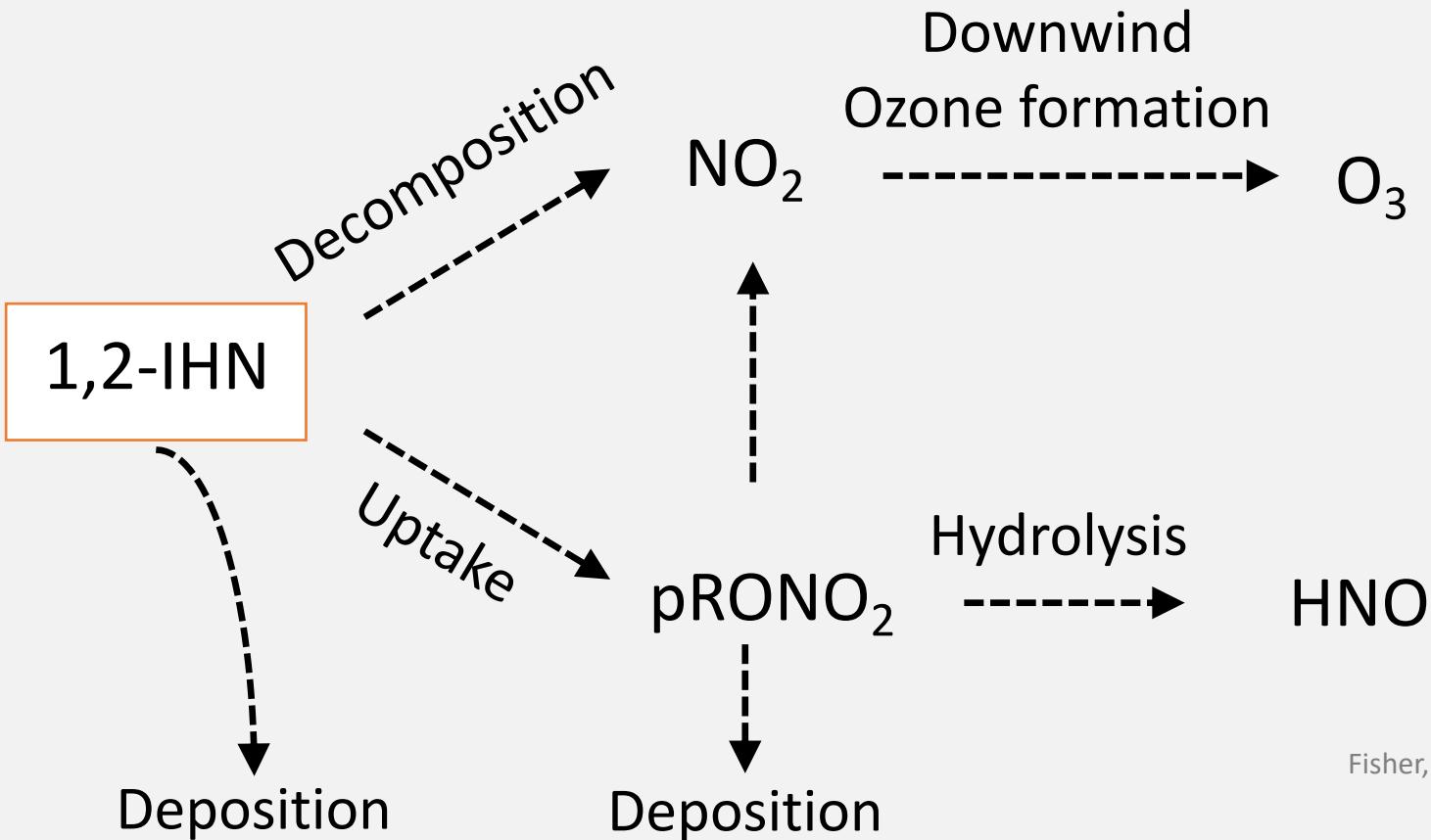
Isoprene Hydroxy Nitrates (IHN)



Relative abundance and isomer-specific fate
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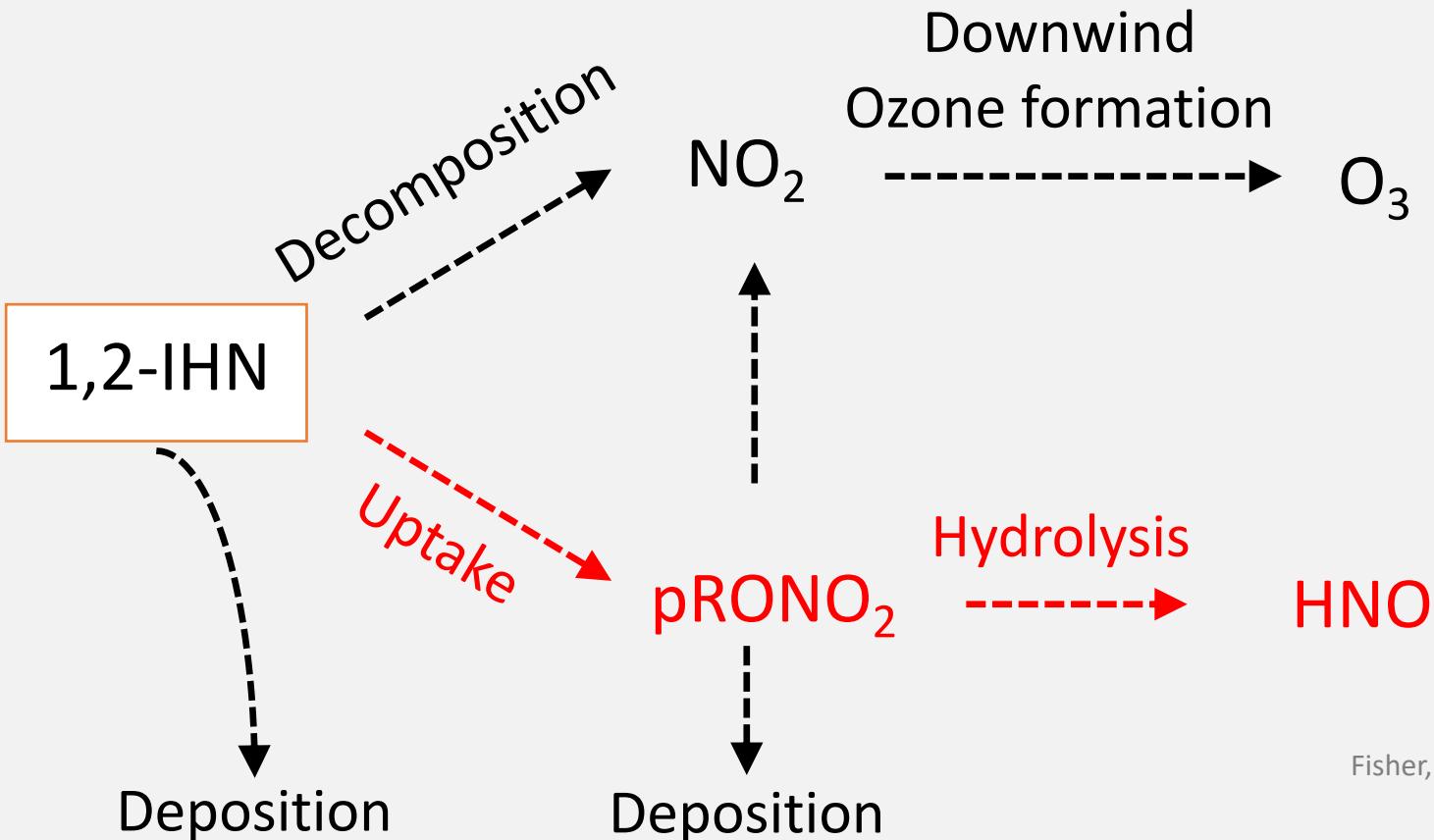
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Deposition BLH = 1.5 km			24
Photolysis $j_{\text{IHN}} = 6.2 \times 10^{-6} \text{ s}^{-1} (\text{noon})$			44
Hydrolysis	?		N/A

1,2-IHN



Fisher, et al. ACP 2016

1,2-IHN

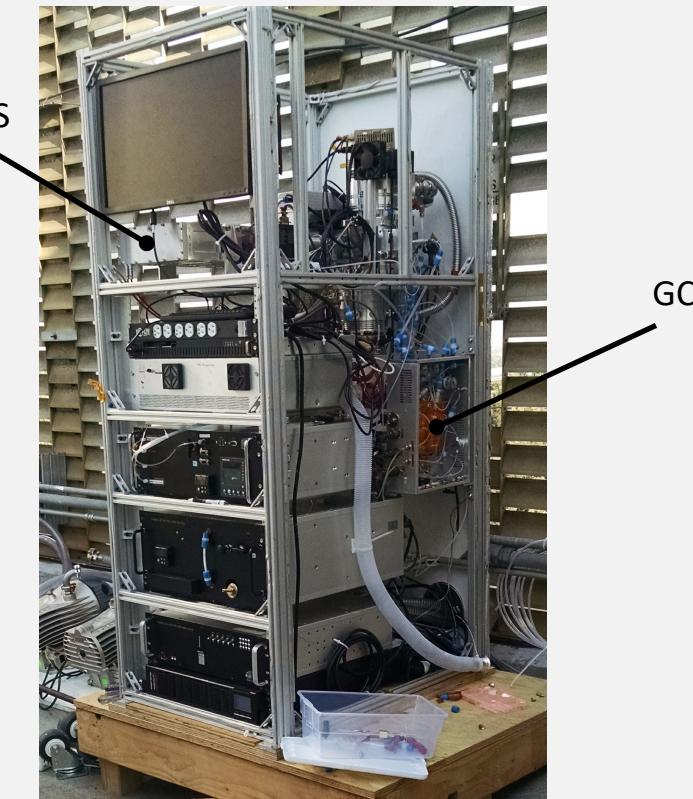
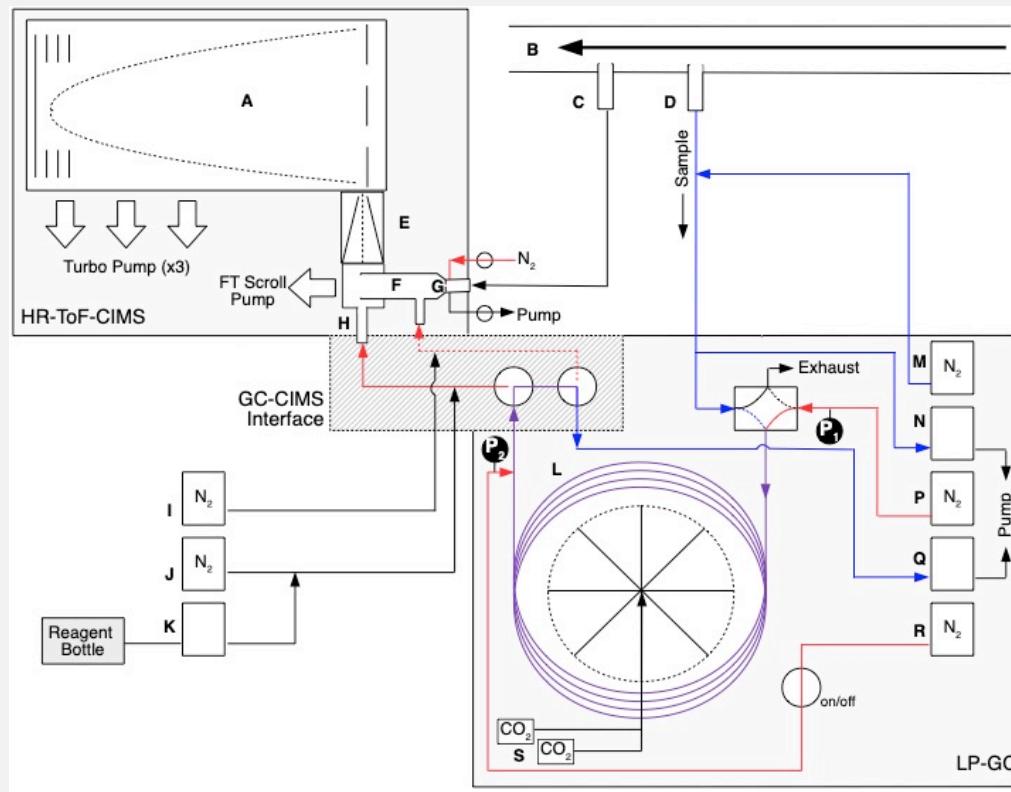


Fisher, et al. ACP 2016

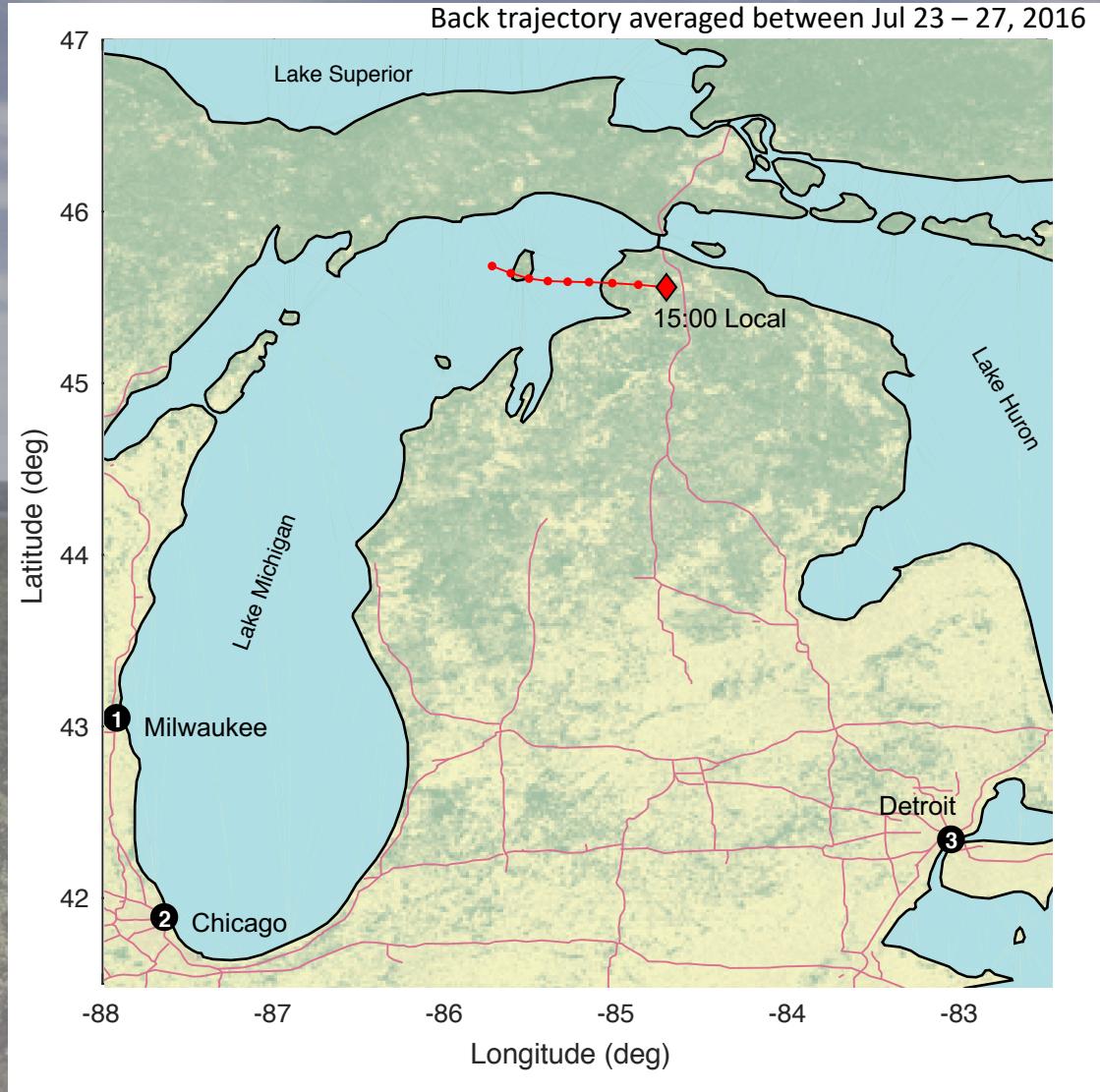
Do other losses (such as hydrolysis) affect the 1,2-IHN atmospheric lifetime?

Instrumentation

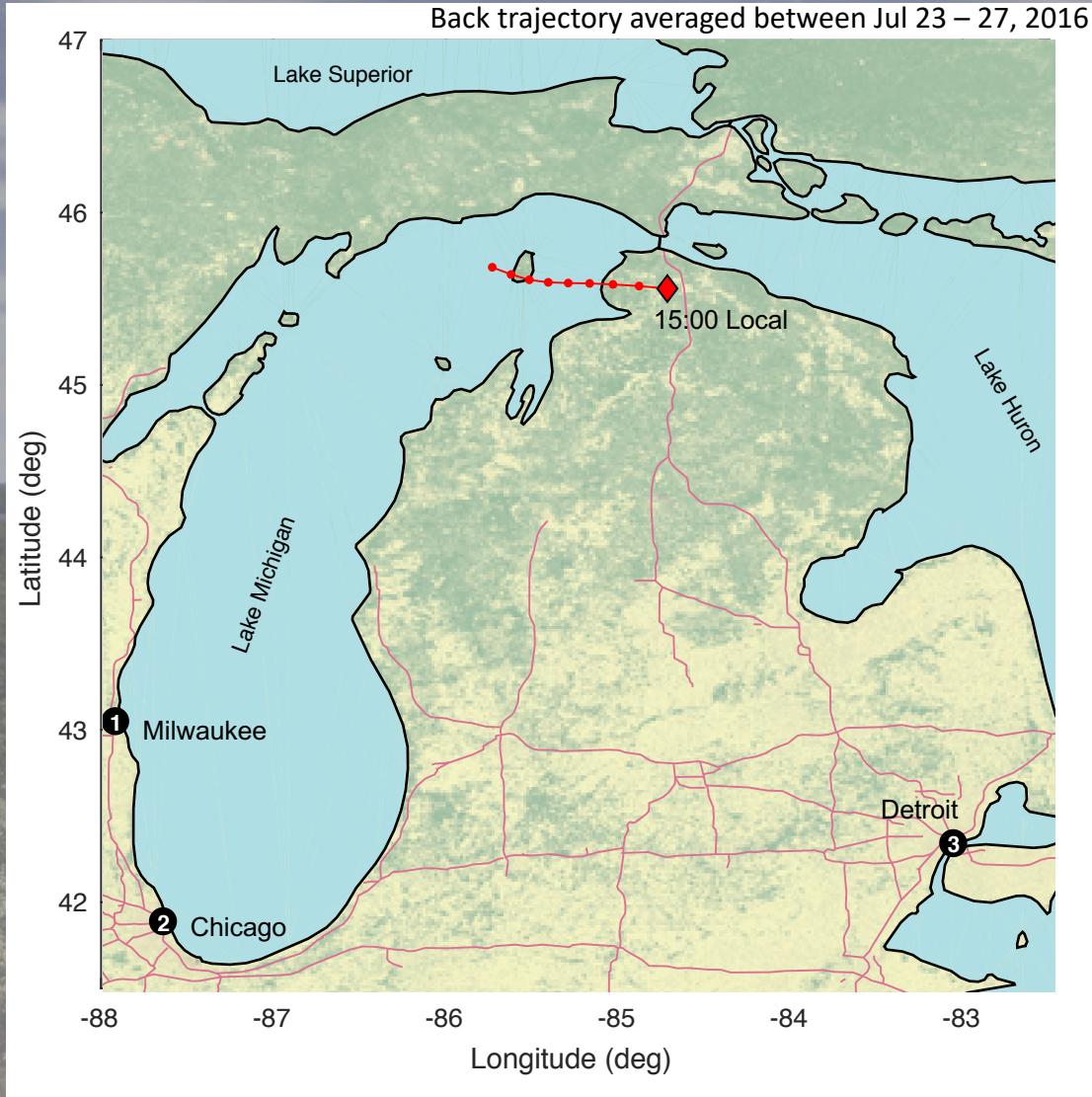
Low-pressure gas chromatography + chemical ionization mass spectrometry



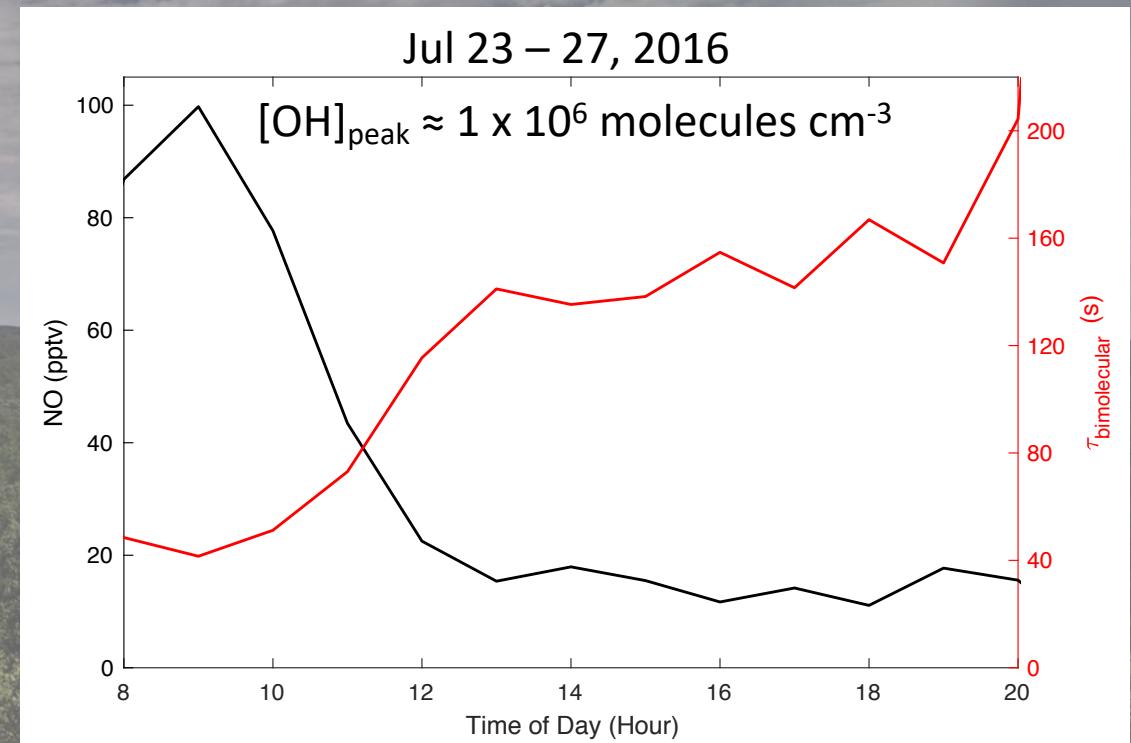
PROPHET 2016



PROPHET 2016

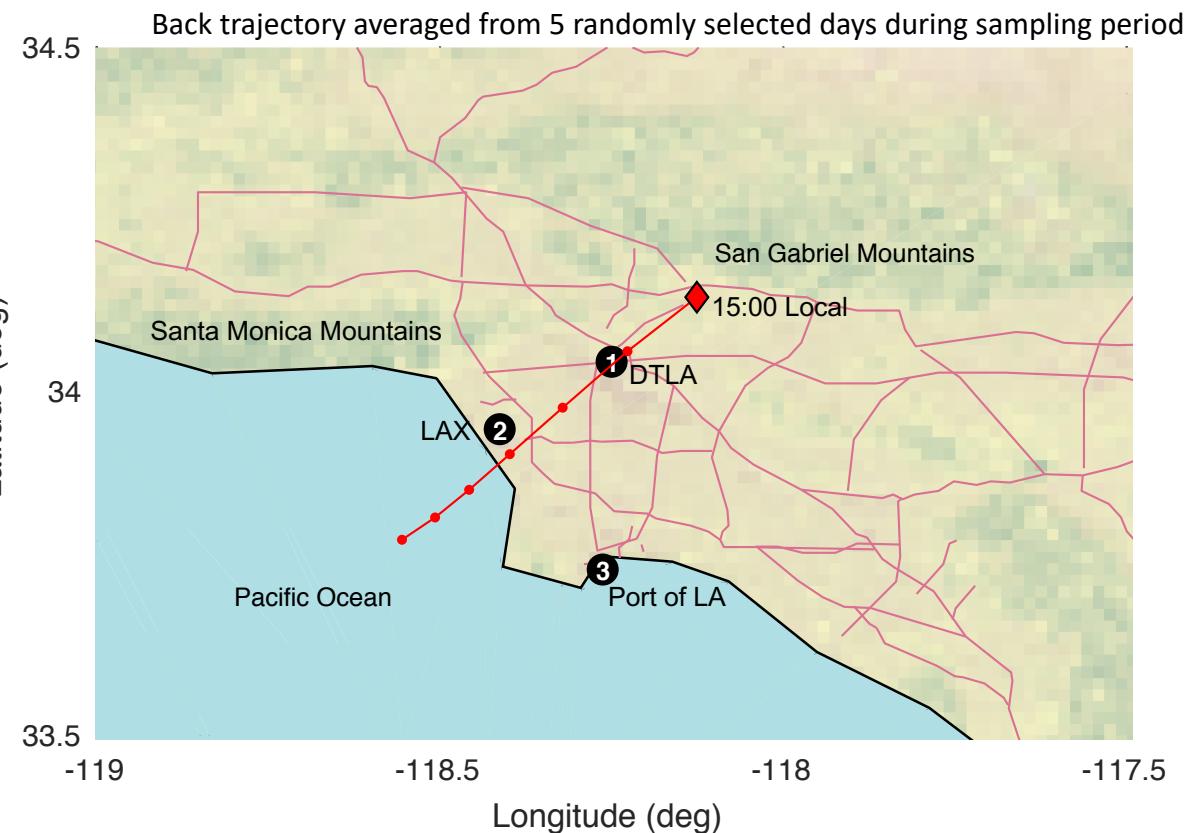


NOAA HYSPLIT: Stein, et al. BAMS 2015



OH Measurements by: Phil Stevens (Indiana University)
NO Measurements by: Andy Weinheimer, Geoff Tyndall, Denise Montzka (NCAR)

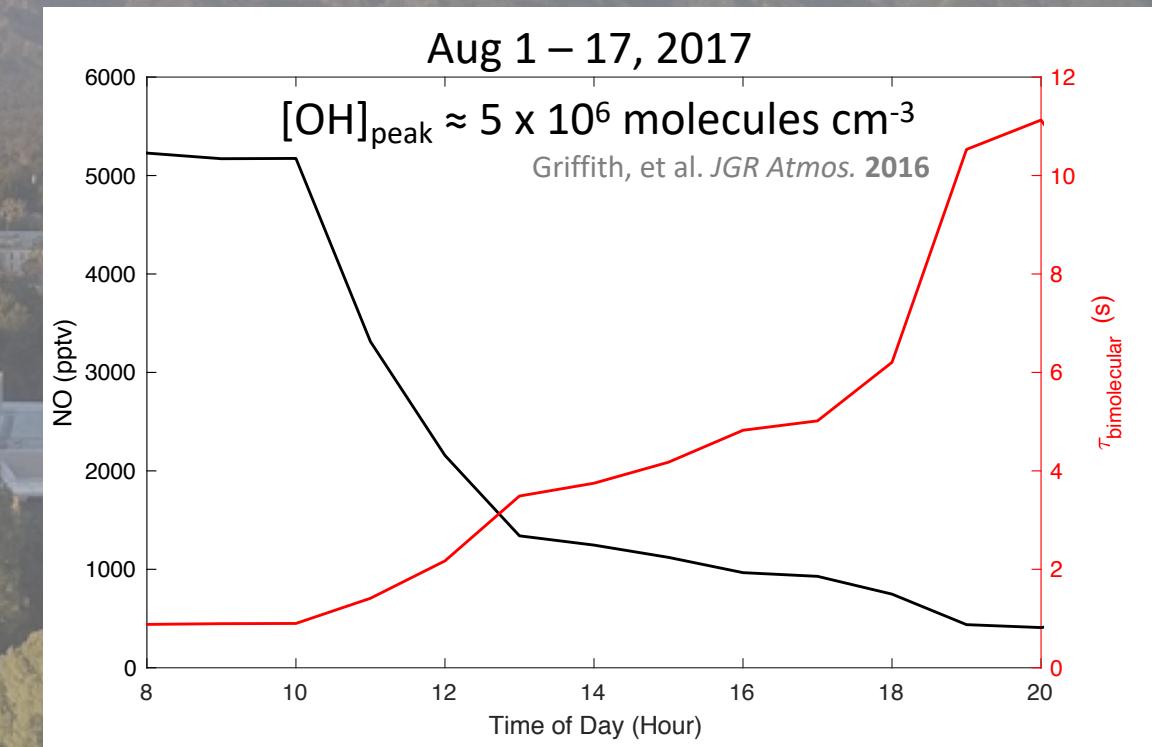
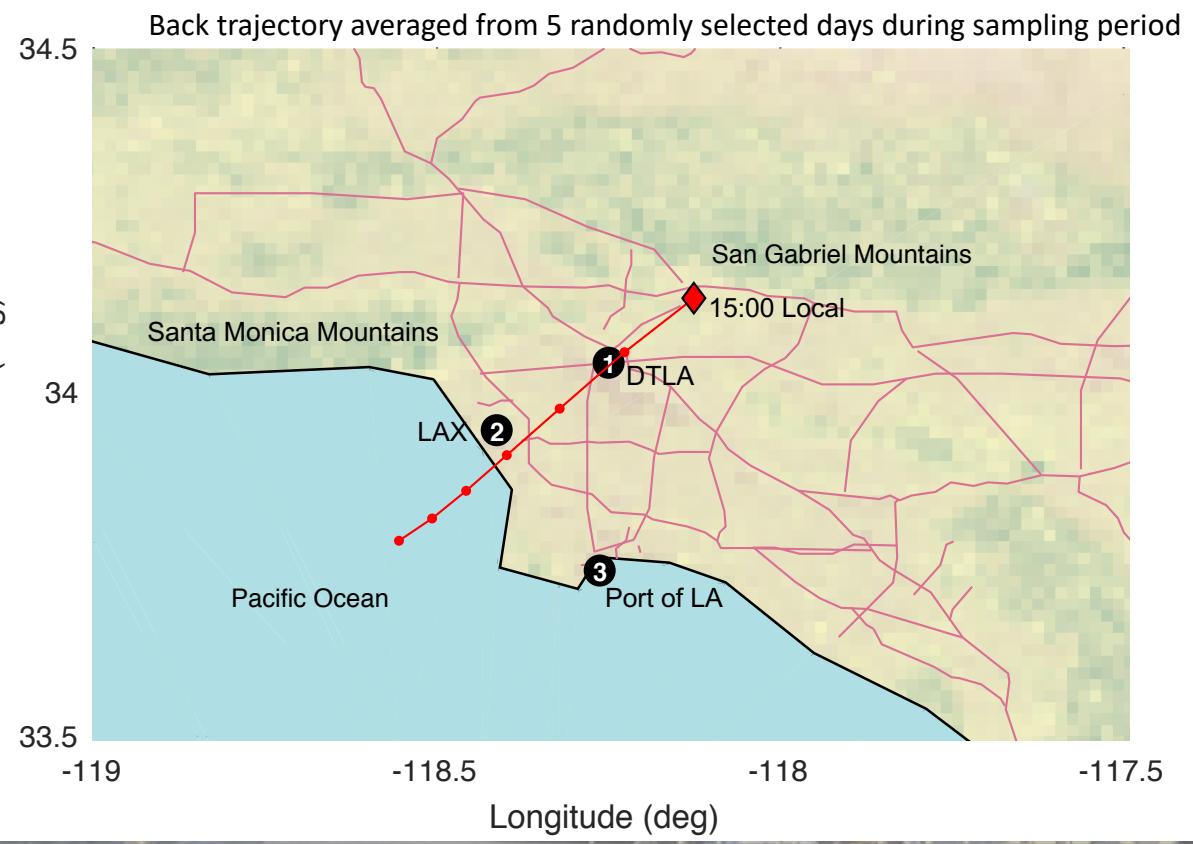
Caltech 2017



NOAA HYSPLIT: Stein, et al. *BAMS* 2015

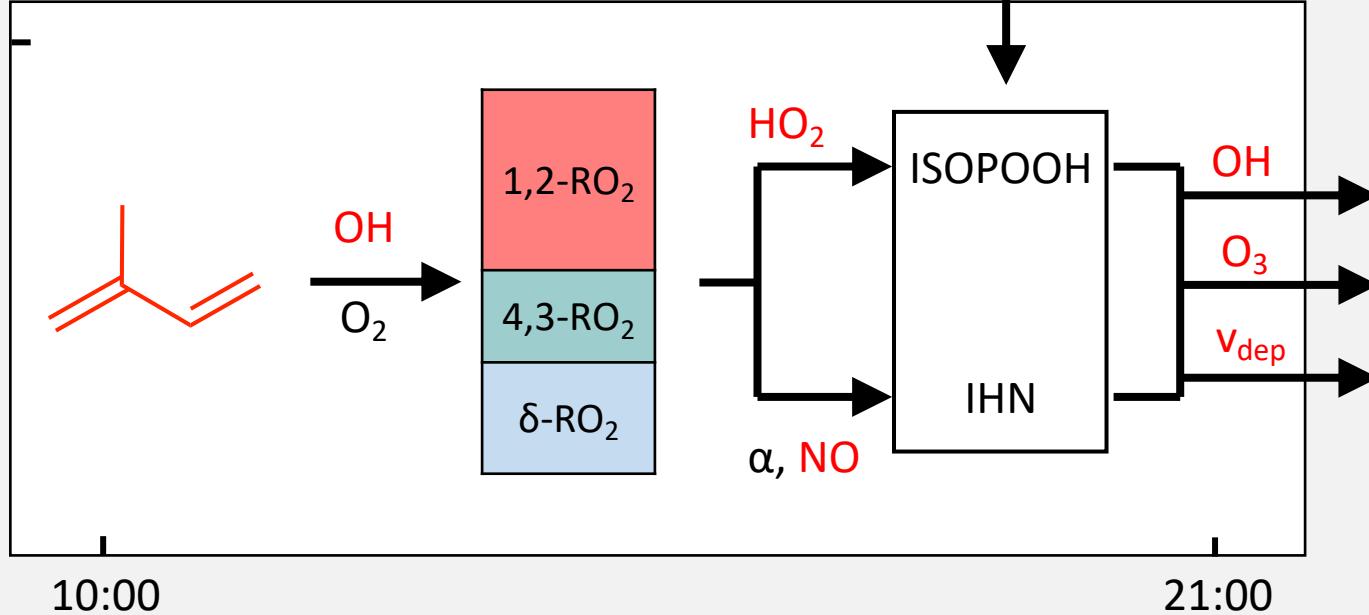


Caltech 2017



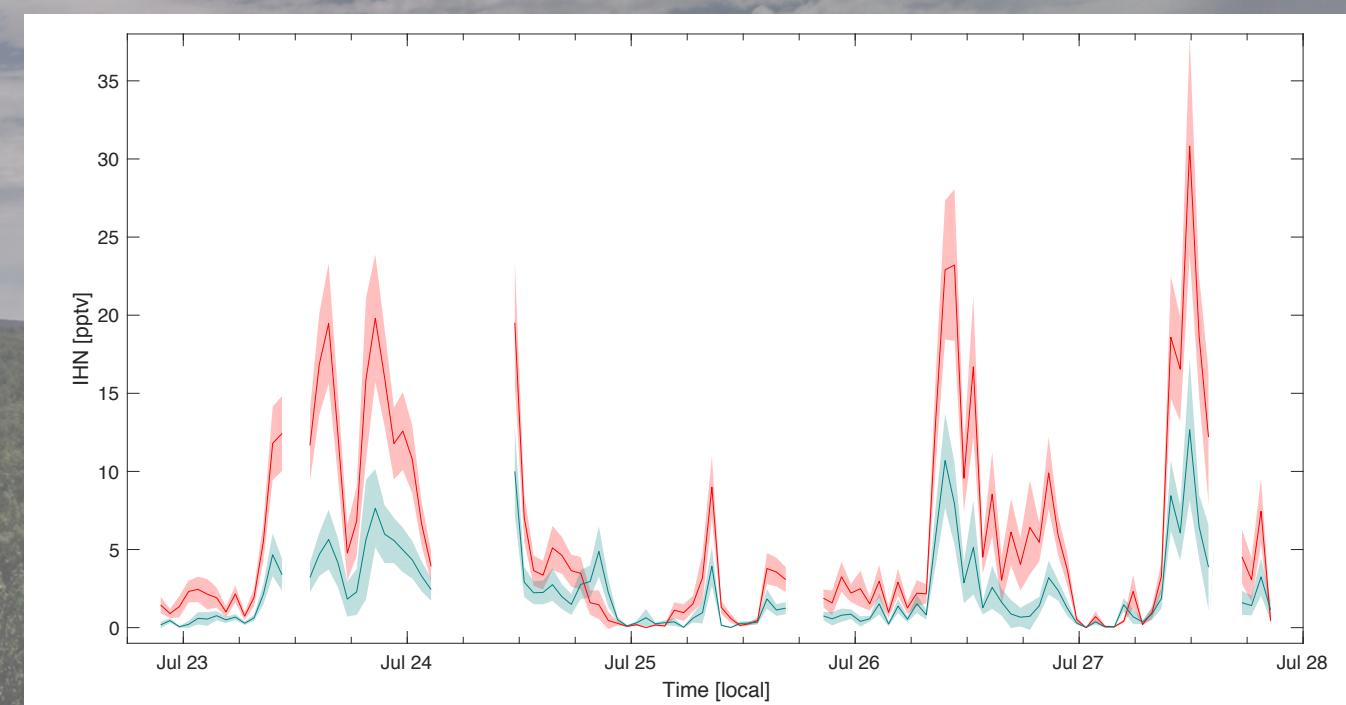
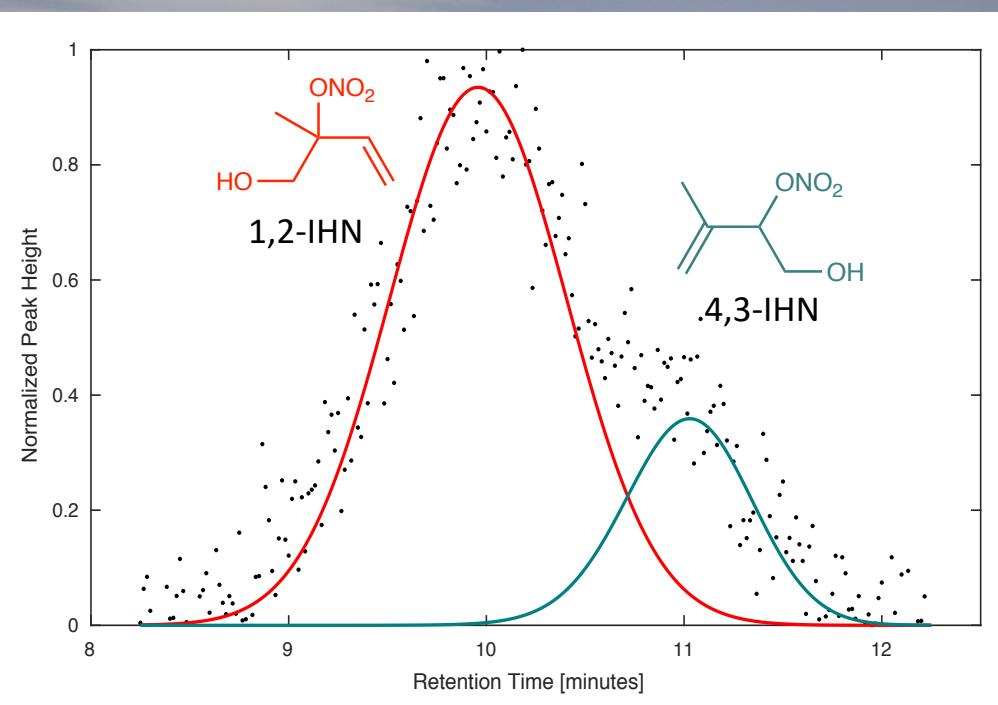
SS Box Modeling

BLH

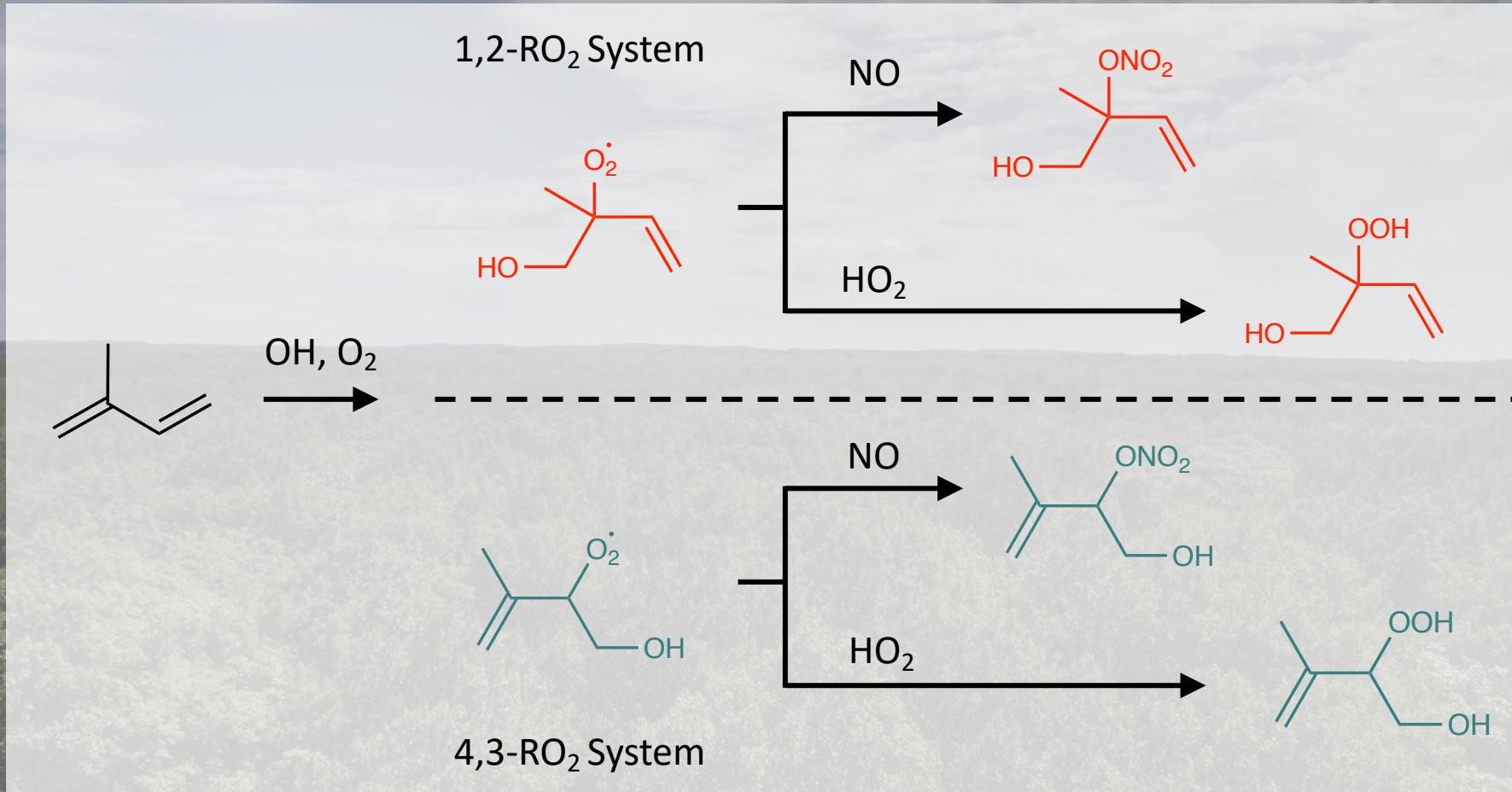


Parameters	PROPHET	Caltech
Isoprene	P. Millet	<i>CalNex 2010</i> (J. de Gouw)
OH	P. Stevens	<i>CalNex 2010</i> (P. Stevens)
HO ₂	P. Stevens	<i>CalNex 2010</i> (P. Stevens)
NO	NCAR	Measured at site
O ₃	J. Flynn	Measured at site
v _{dep}	<i>Nguyen et al., PNAS 2015</i>	
BLH	<i>From SOAS</i>	<i>CalNex 2010</i> (J. Stutz)
Rate Constants	<i>Wennberg et al., Chem. Rev. 2018</i>	

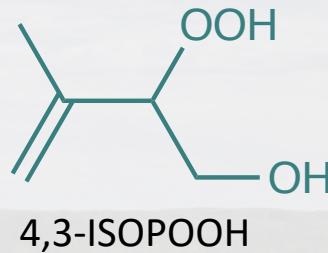
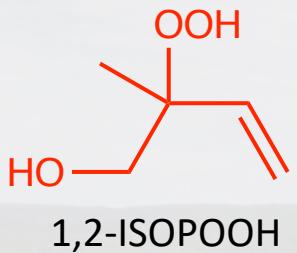
PROPHET 2016: Field Observations



Comparison to ISOPOOH



Comparison to ISOOPOH

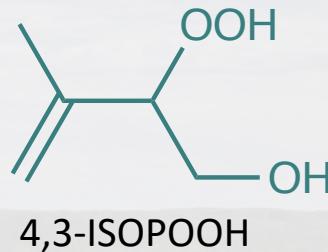
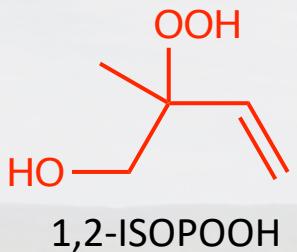


Comparison of IHN ratio to ISOOPOH

- Same precursor RO₂
- Similar gas-phase lifetime

1,2-to 4,3-isomer ratio	Compound	Base Model
	IHN	2.3
	ISOOPOH	2.6

Comparison to ISOOPOH

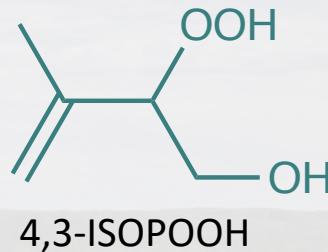
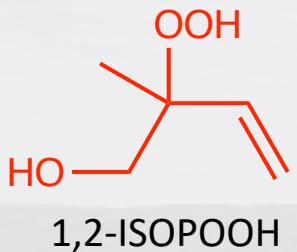


Comparison of IHN ratio to ISOOPOH

- Same precursor RO_2
- Similar gas-phase lifetime

1,2-to 4,3-isomer ratio	Compound	Base Model	PROPHET
	IHN	2.3	2.7
	ISOOPOH	2.6	7.9

Comparison to ISOOPOH

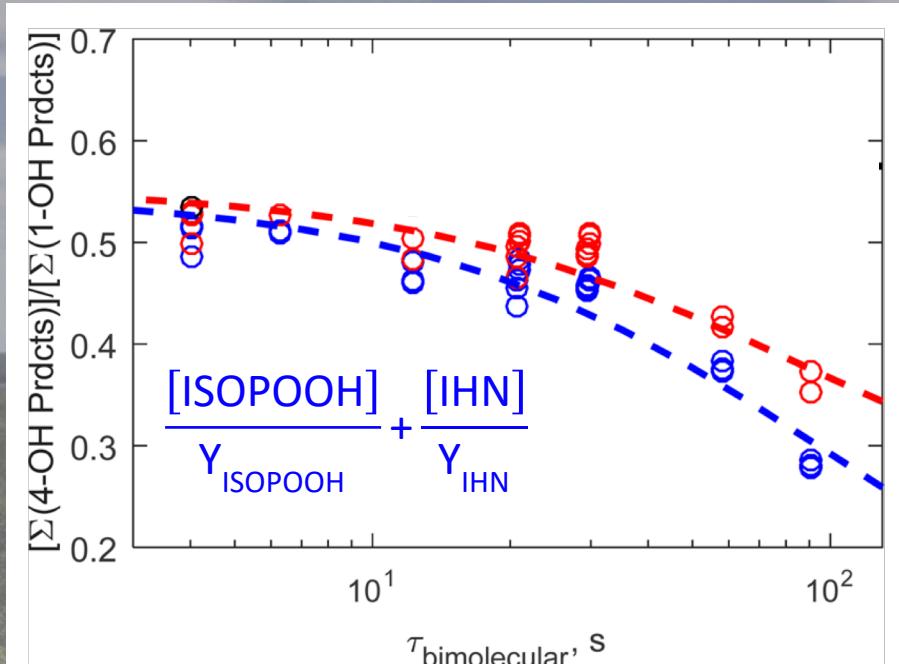


Comparison of IHN ratio to ISOOPOH

- Same precursor RO_2
- Similar gas-phase lifetime

1,2-to 4,3-isomer ratio	Compound	Base Model	PROPHET
	IHN	2.3	2.7
	ISOOPOH	2.6	7.9

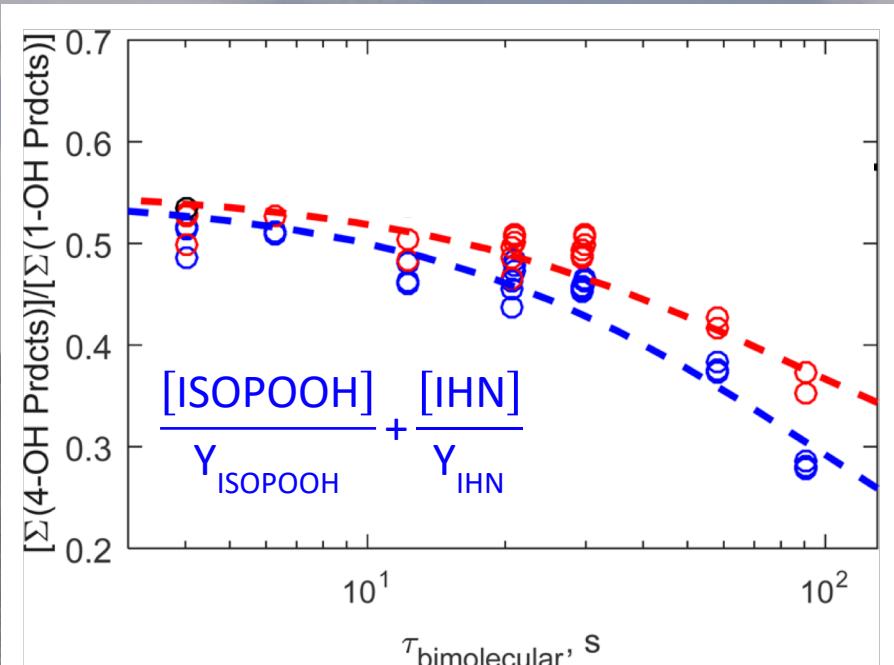
Comparison to Model



Adapted from Teng, et al. JACS 2017

1,2-to 4,3-isomer ratio	Compound	Base Model	PROPHET
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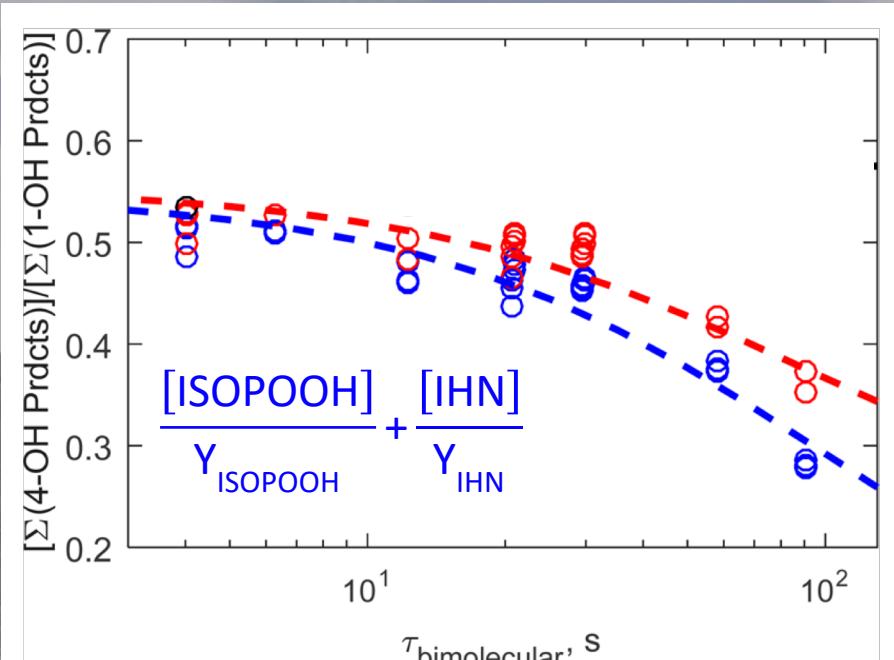
Comparison to Model



Adapted from Teng, et al. JACS 2017

1,2-to 4,3-isomer ratio	Compound	Base Model	PROPHET	Model + k_{isom}
	IHN	2.3	2.7	6
	ISOPOOH	2.6	7.9	7.6

Comparison to Model

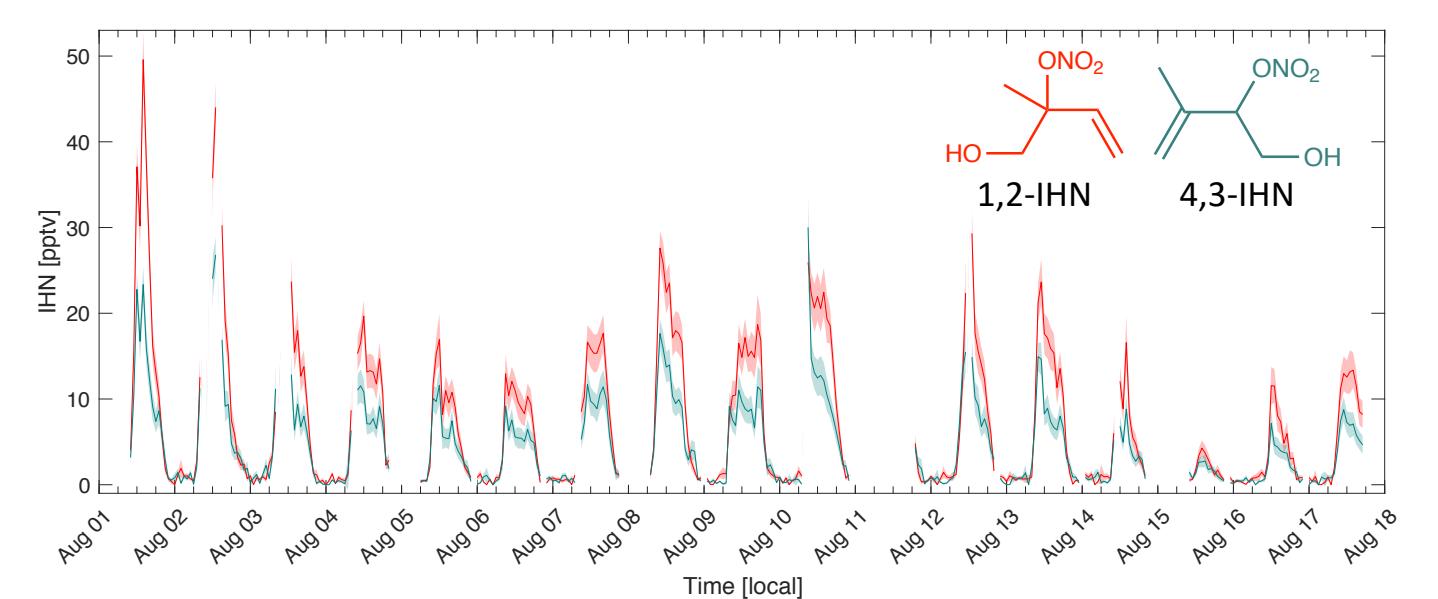


Adapted from Teng, et al. JACS 2017

1,2-to 4,3-isomer ratio	Compound	Base Model	PROPHET	Model + k _{isom}
	IHN	2.3	2.7	6
	ISOPOOH	2.6	7.9	7.6

Discrepancy to model and ISOPOOH suggests unexplained loss unique to IHN

Caltech 2017: Field Observations

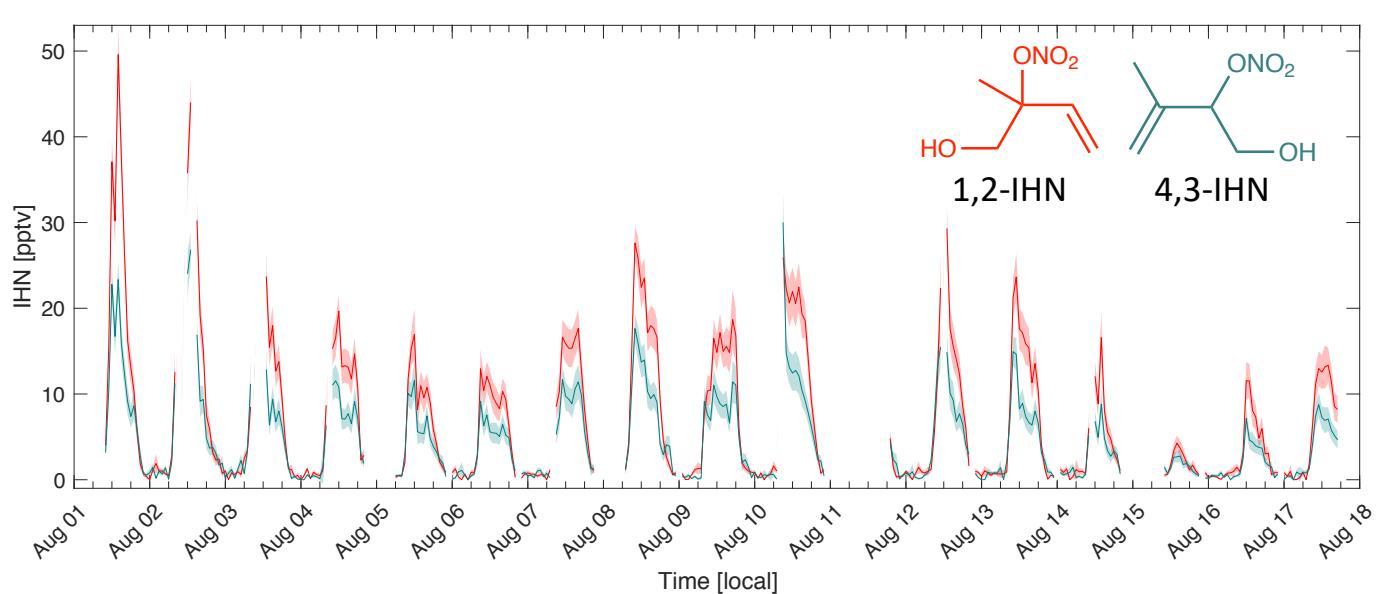


1,2-to 4,3-isomer ratio	Caltech	PROPHET
	1.6	2.3

Difference in ratio partially reflects differences in RO₂ chemistry

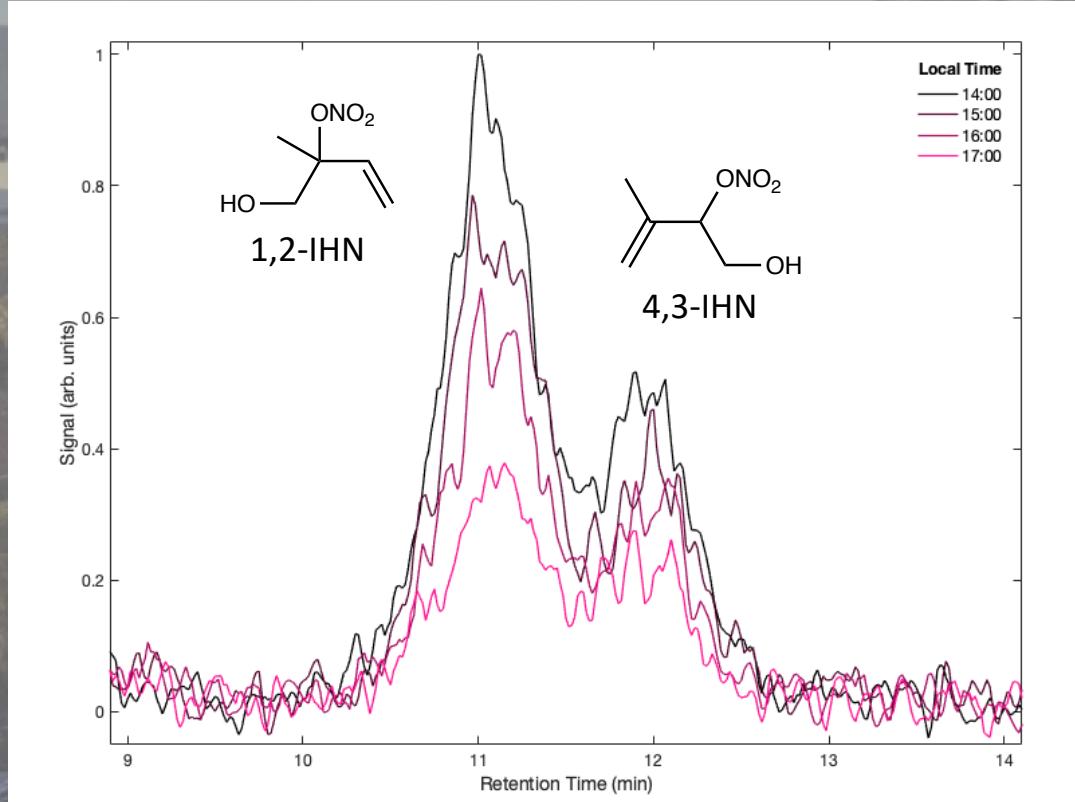
- 11% of 4,3-RO₂ underwent RO₂ isomerization at Caltech

Caltech 2017: Field Observations

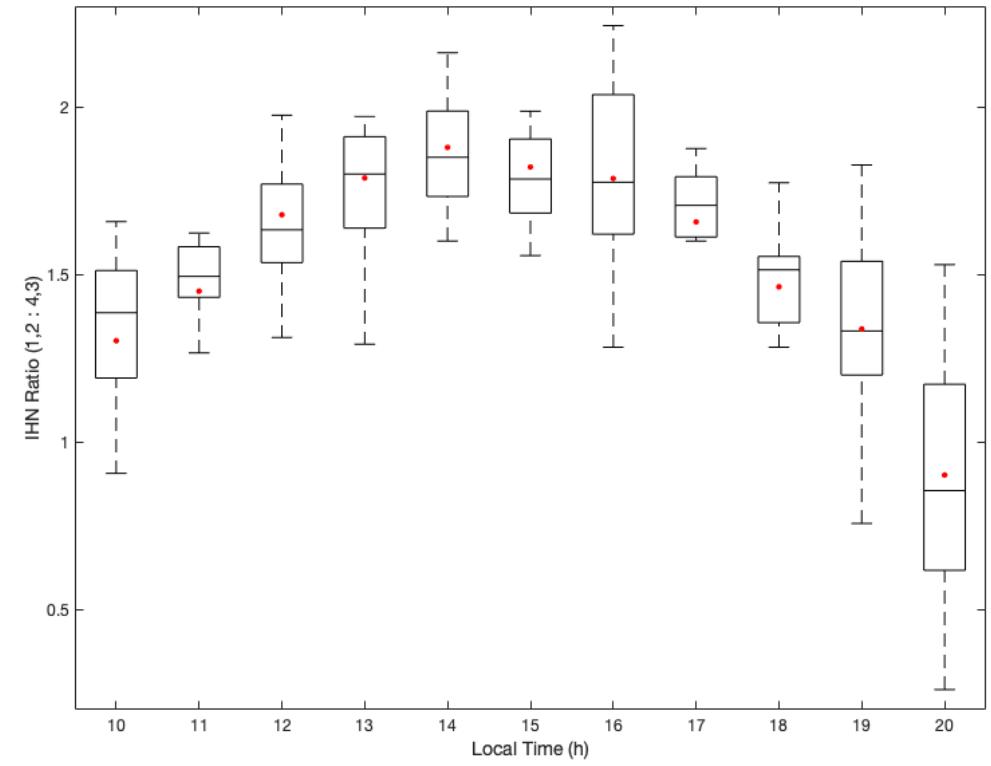
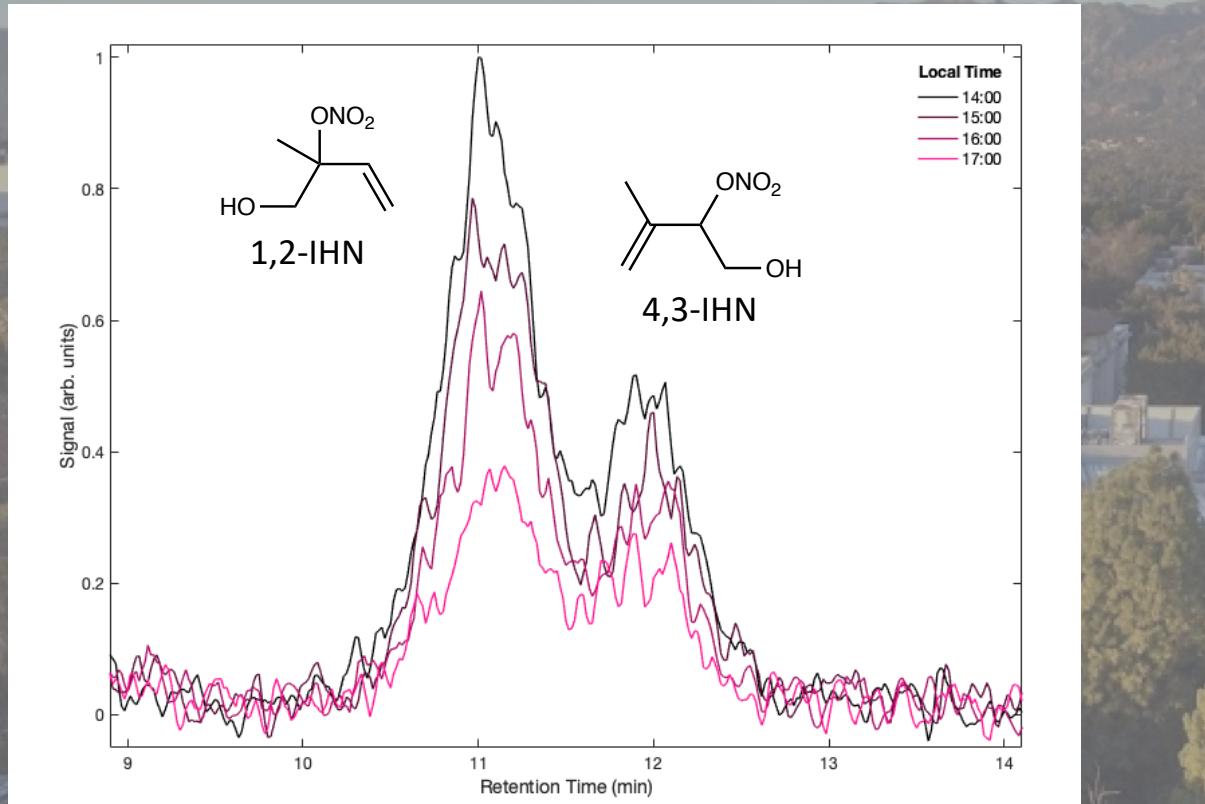


1,2-to 4,3-isomer ratio	Caltech	PROPHET	Base Model	Model + k_{isom}
	1.6	2.3	2.5	2.8

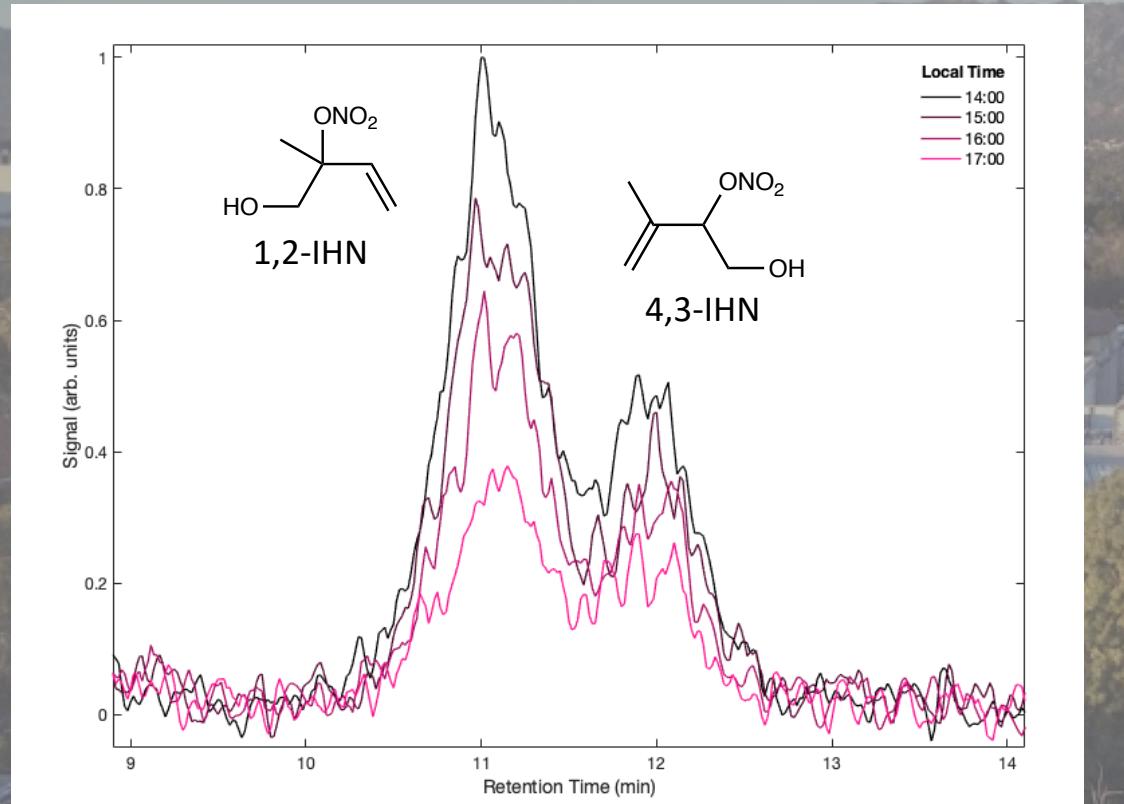
Rapid 1,2-IHN Loss



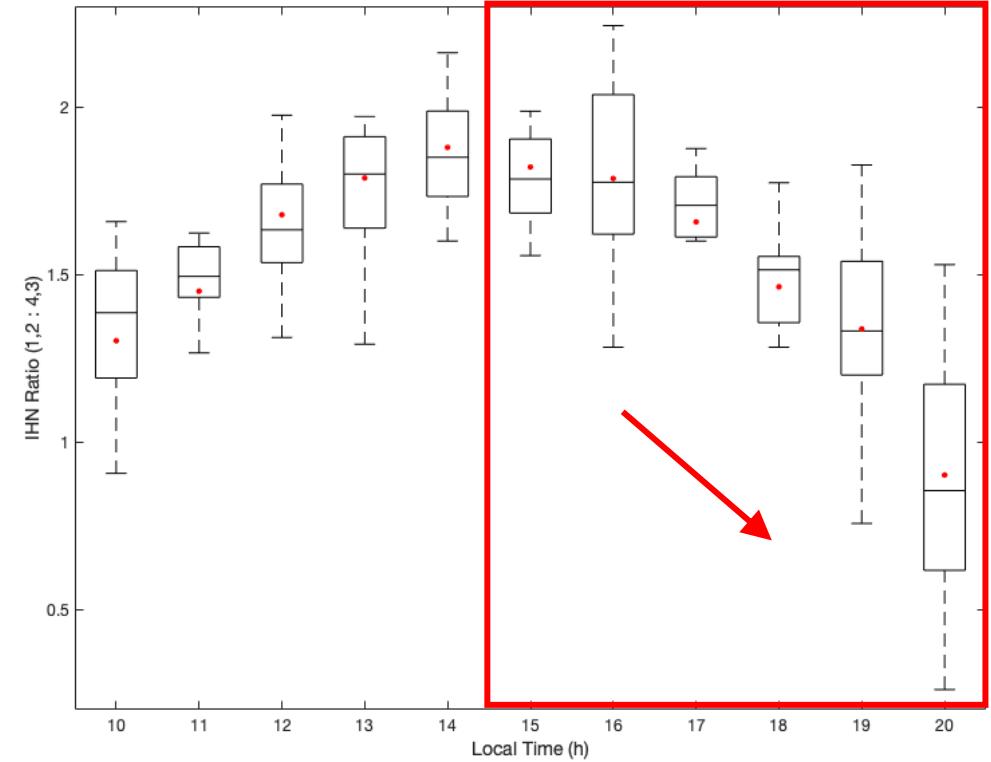
Rapid 1,2-IHN Loss



Rapid 1,2-IHN Loss

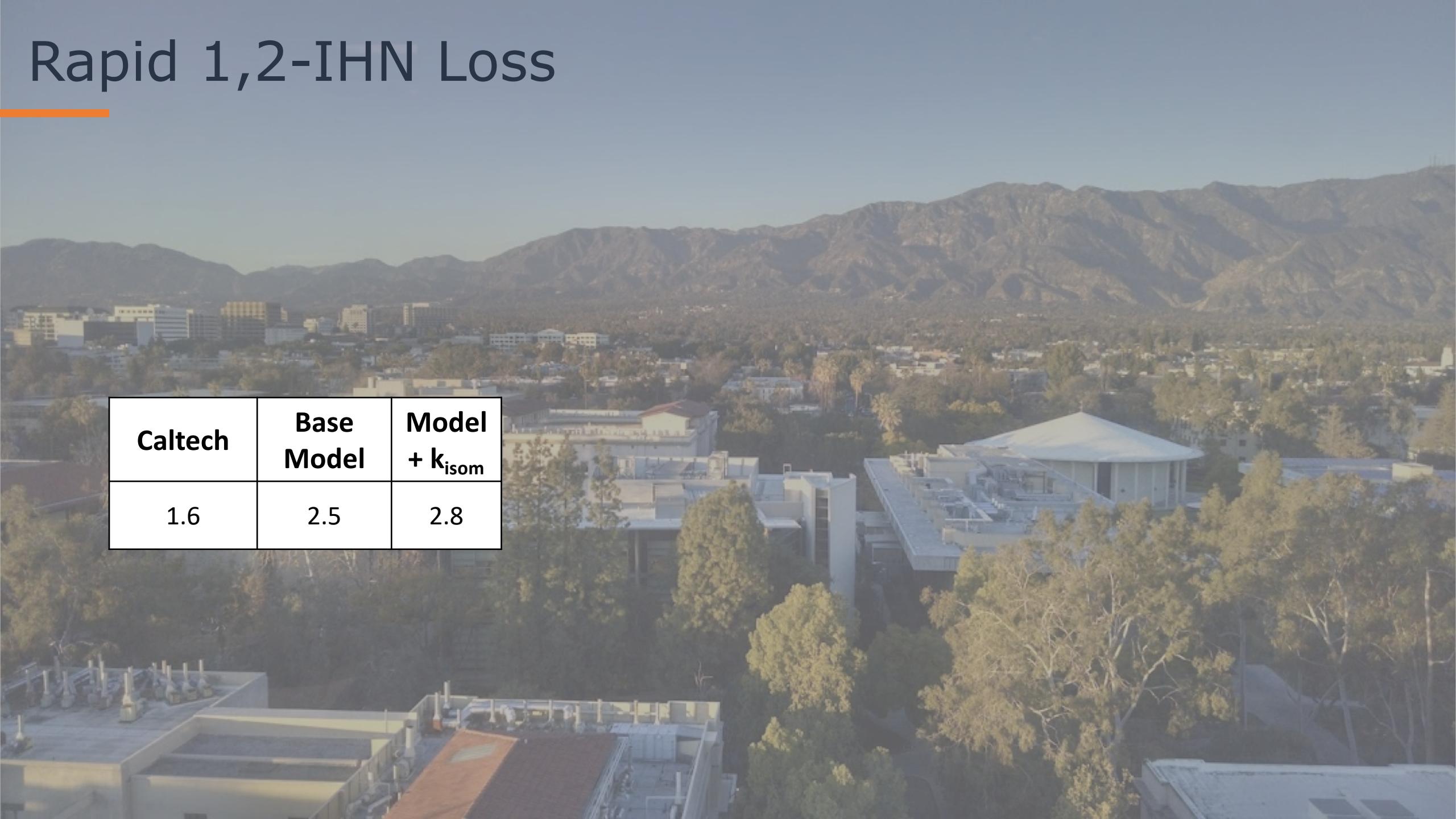


Loss(1,2-IHN) > Loss(4,3-IHN)



Rapid 1,2-IHN Loss

Caltech	Base Model	Model + k_{isom}
1.6	2.5	2.8

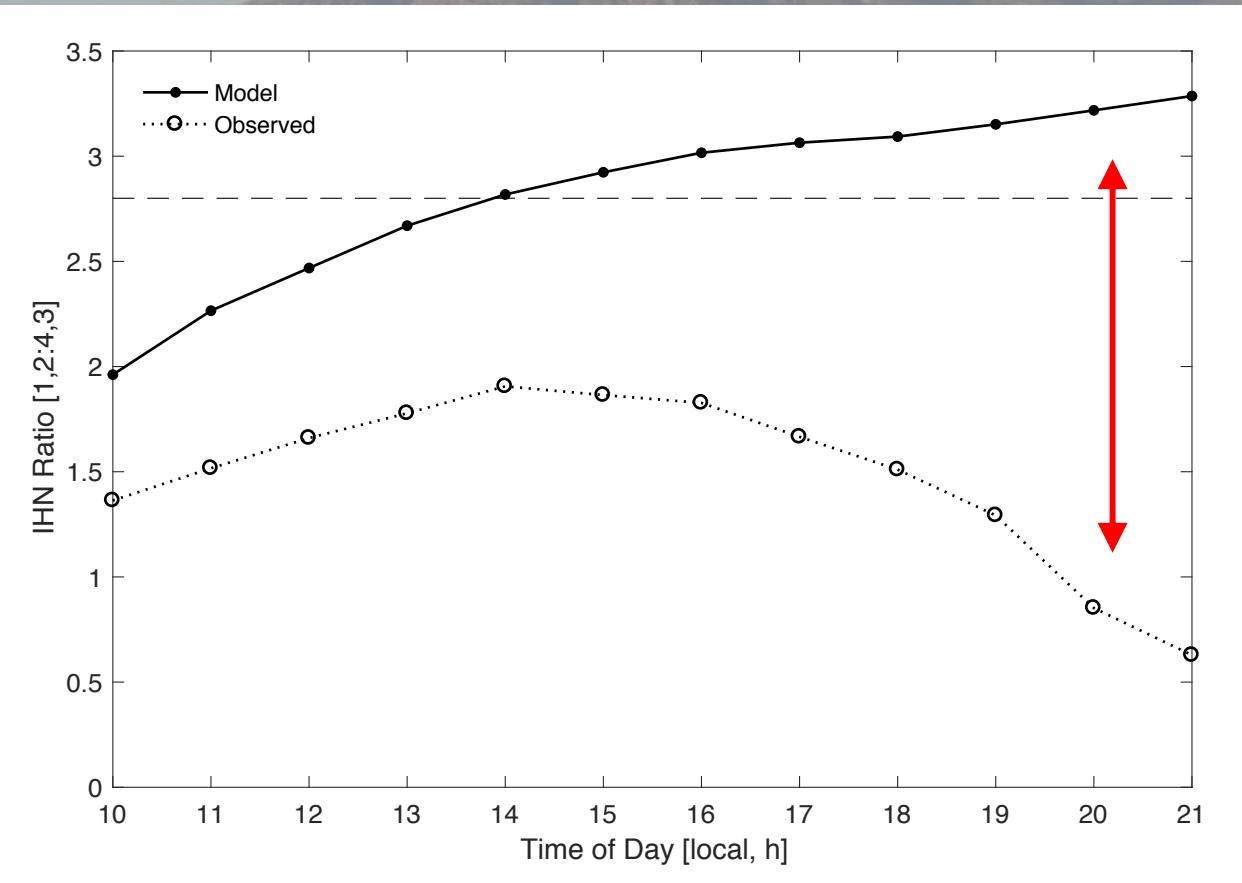


Rapid 1,2-IHN Loss

Caltech	Base Model	Model + k_{isom}
1.6	2.5	2.8

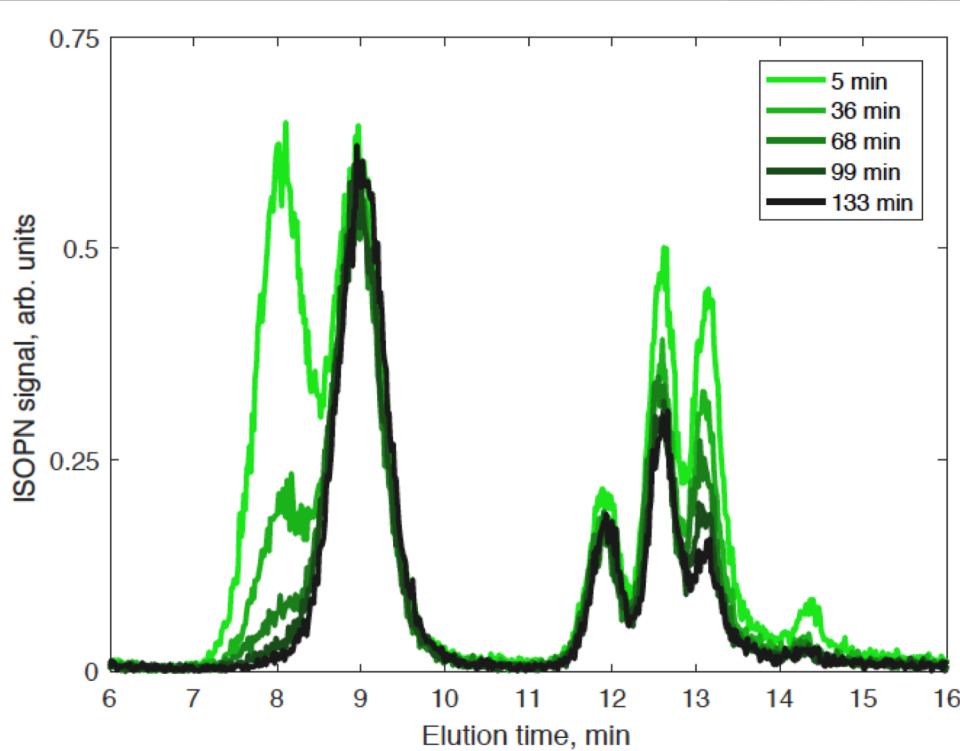
Rapid 1,2-IHN Loss

Caltech	Base Model	Model + k_{isom}
1.6	2.5	2.8



Rapid 1,2-IHN Loss

Humidified Chamber

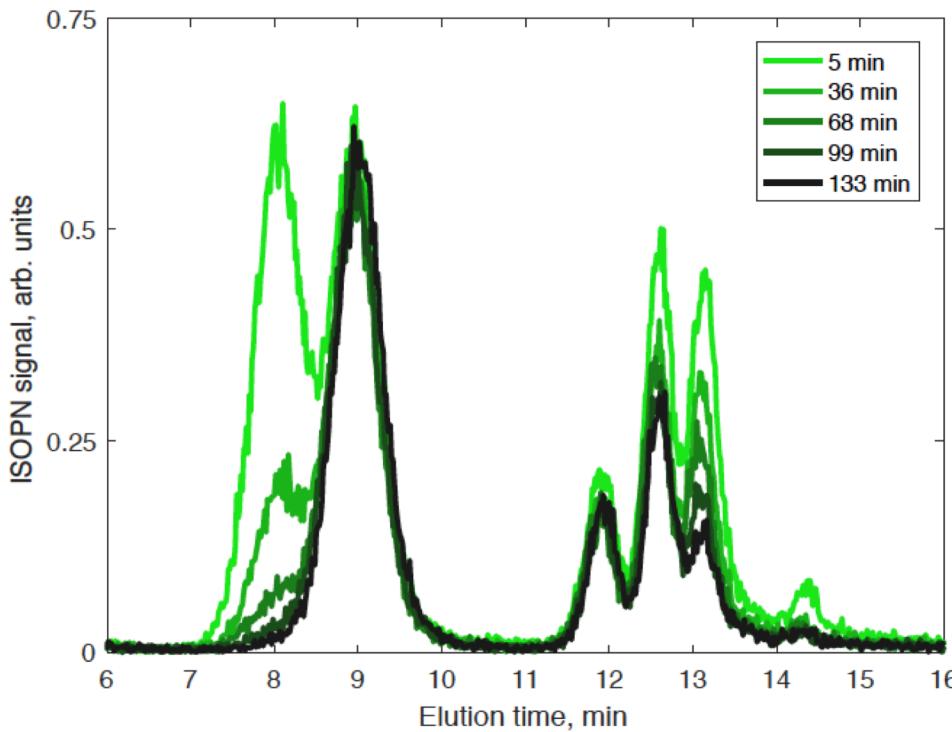


Strong dependence between RH and lifetime of 1,2-IHN

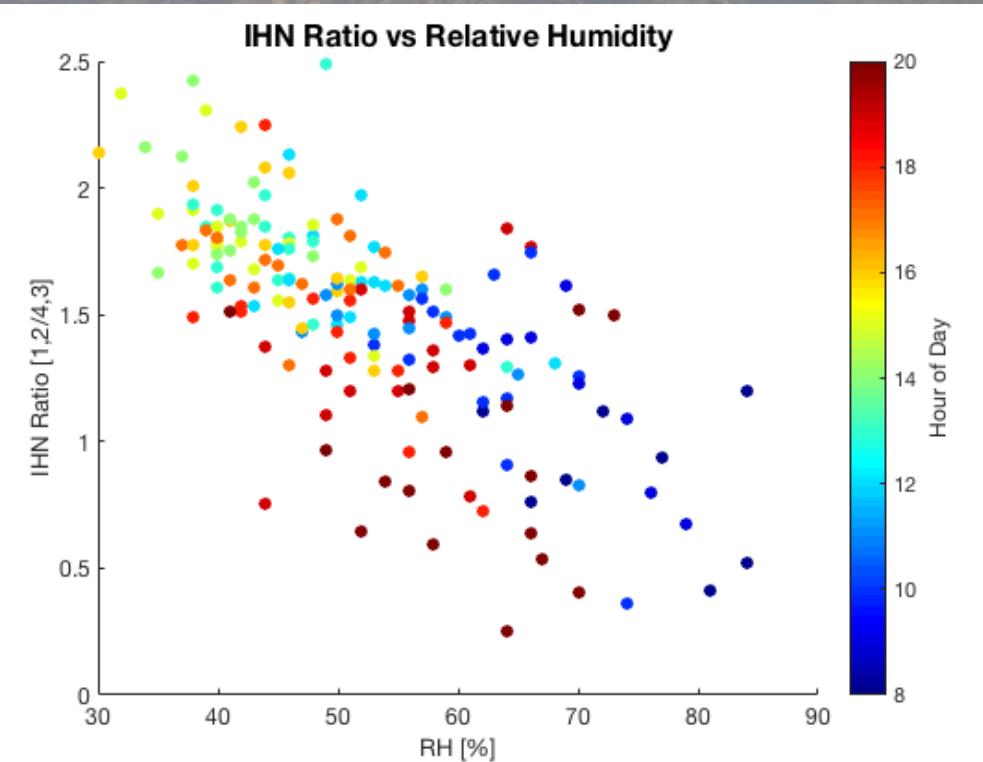
- Correlation not present in a clean chamber bag implying uptake onto wet surfaces
- NMR experiments provide an upper limit of < 10 s for hydrolysis lifetime

Rapid 1,2-IHN Loss

Humidified Chamber

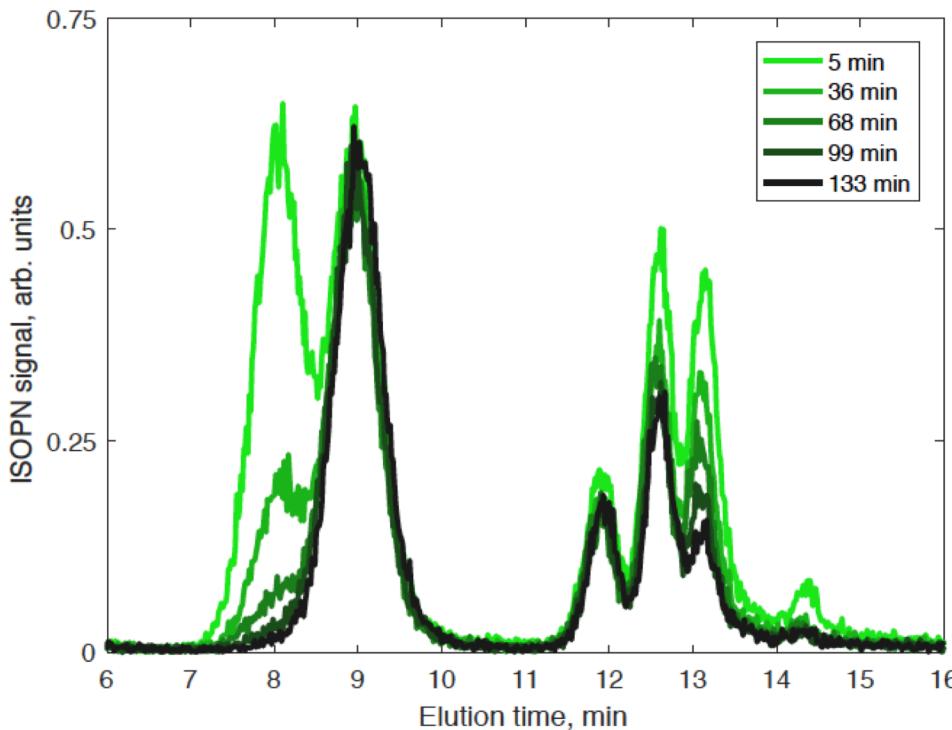


Ambient Data

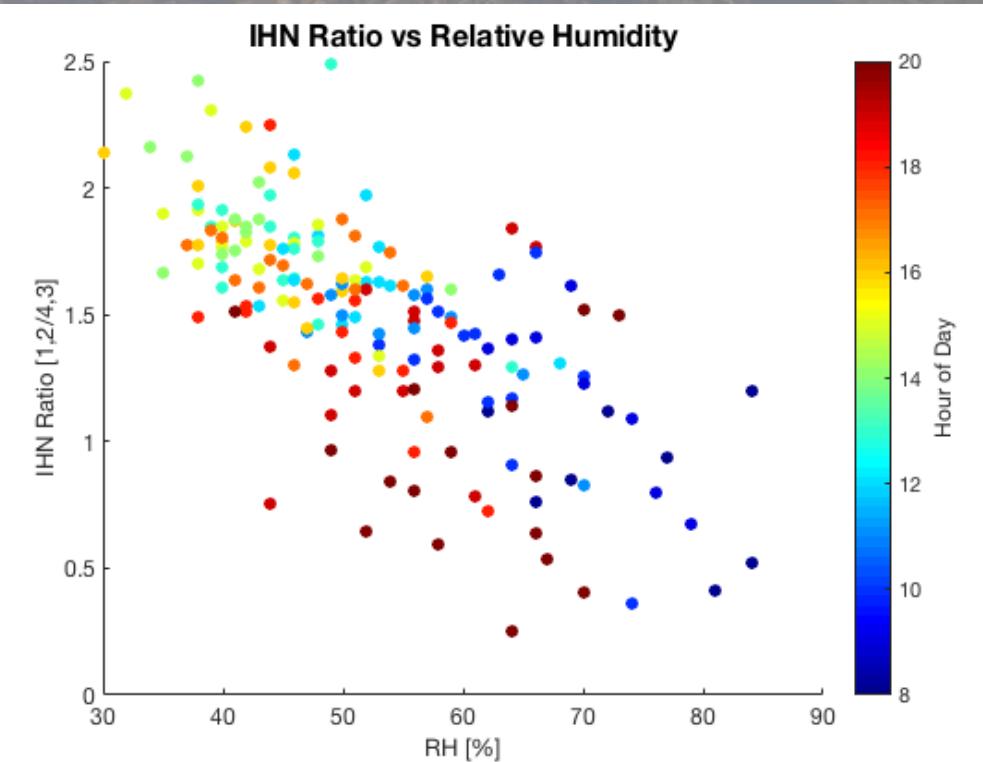


Rapid 1,2-IHN Loss

Humidified Chamber

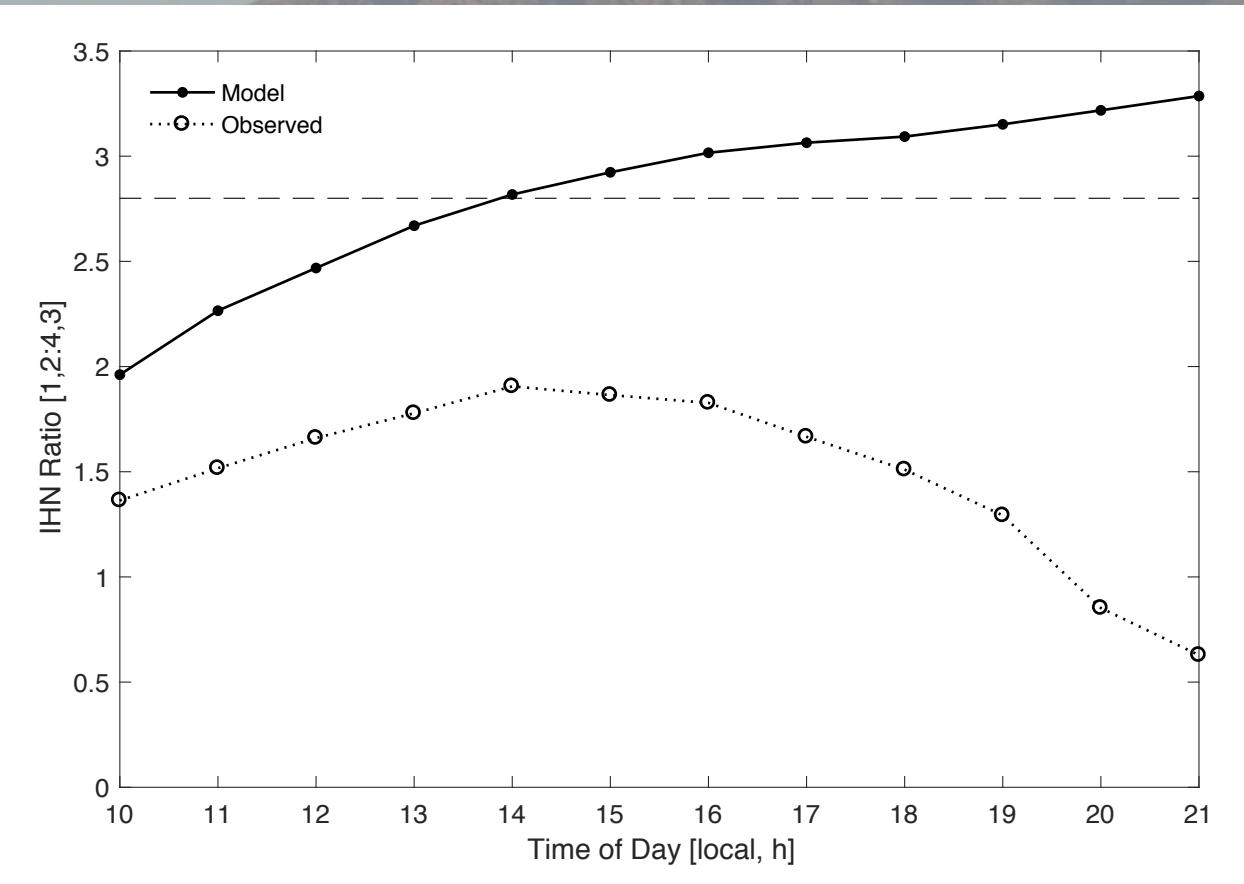
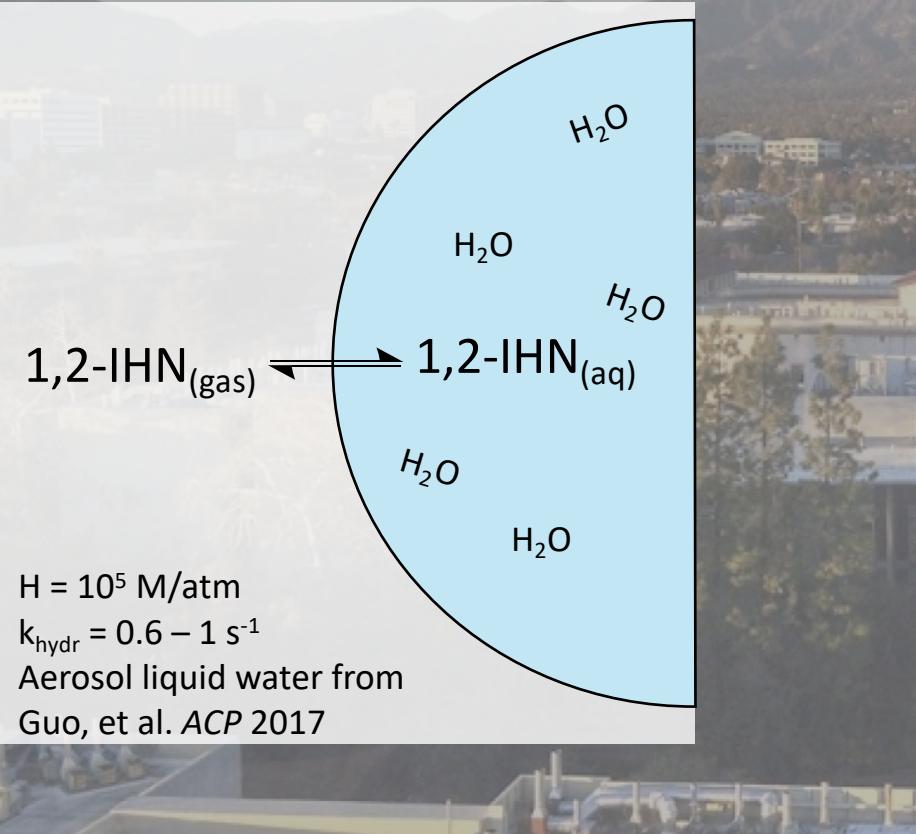


Ambient Data

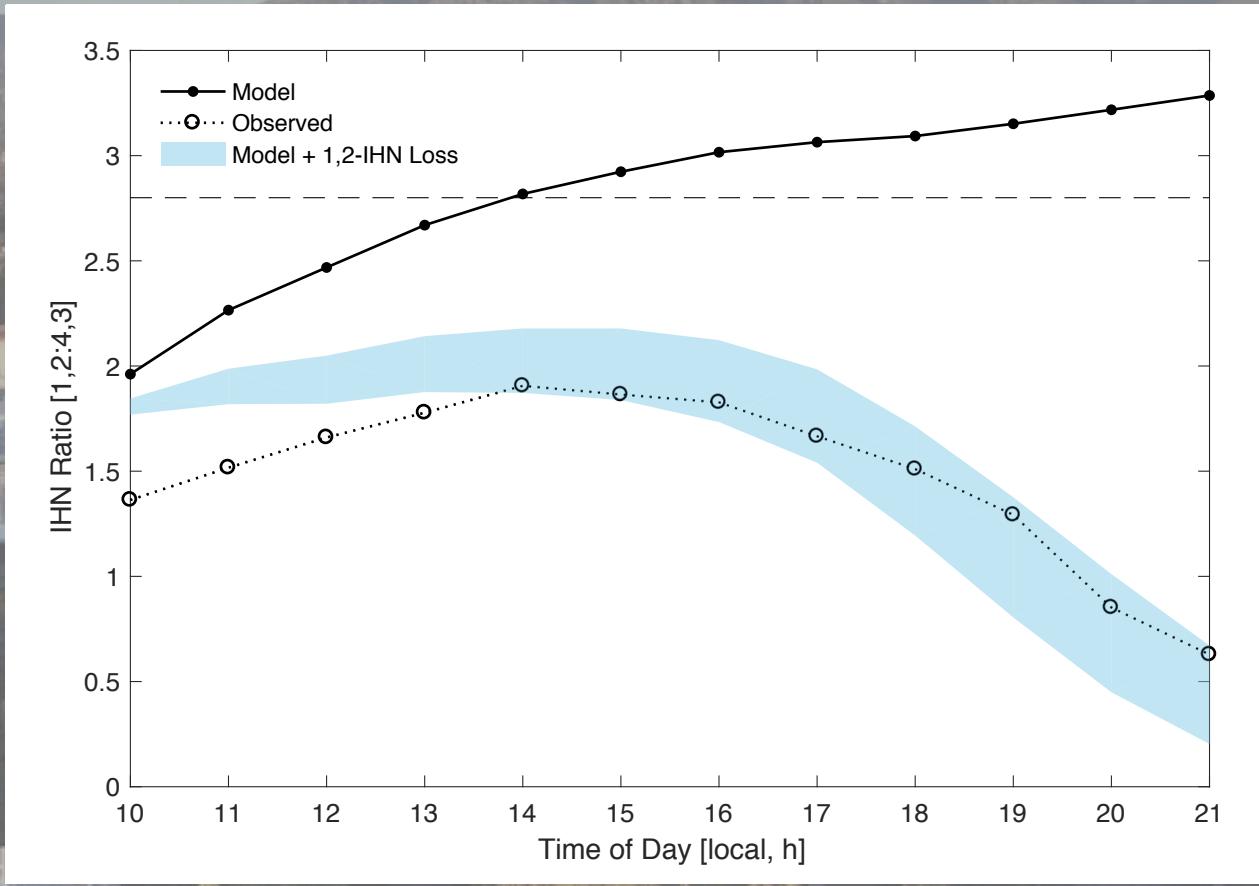
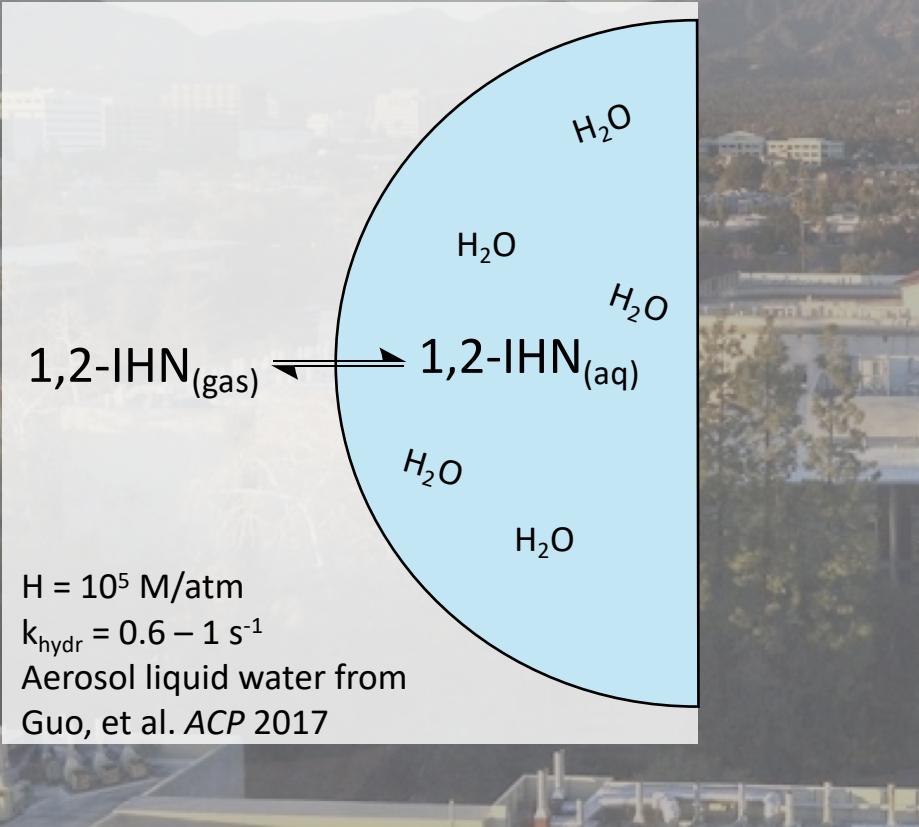


Hypothesis: Hydrolysis affects the 1,2-IHN atmospheric lifetime

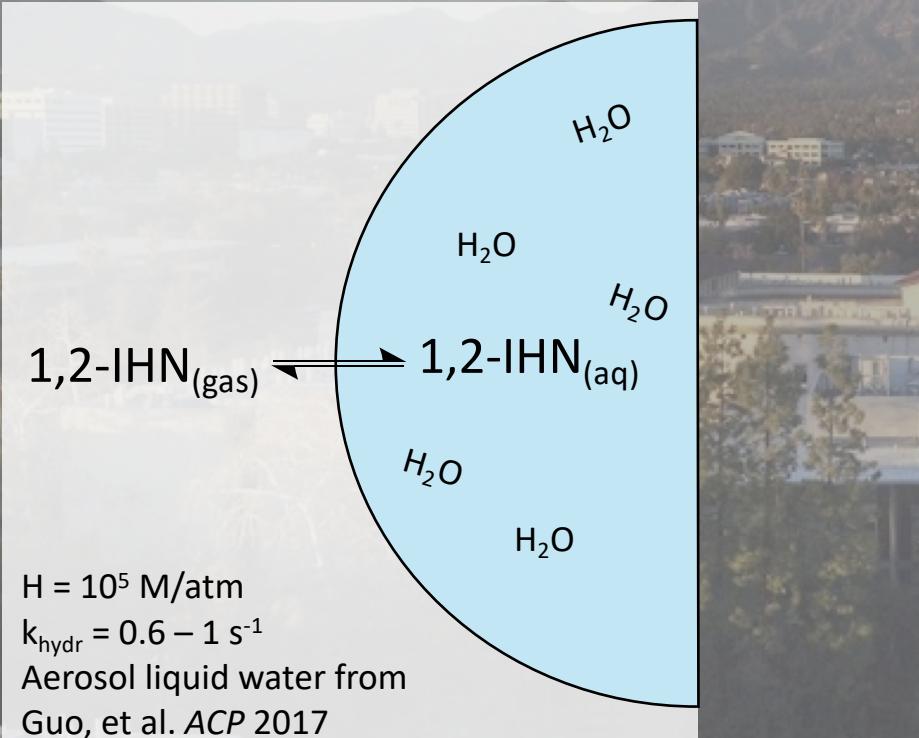
Rapid 1,2-IHN Loss



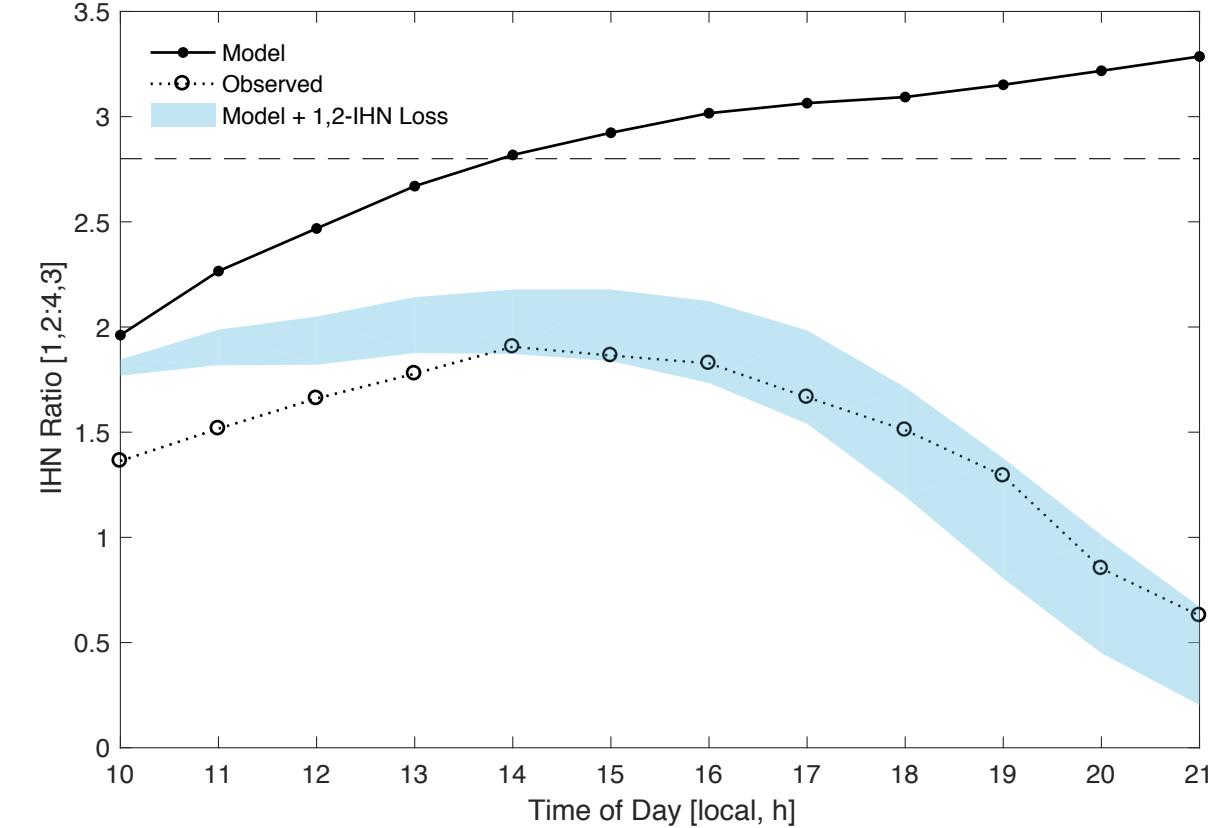
Rapid 1,2-IHN Loss



Rapid 1,2-IHN Loss



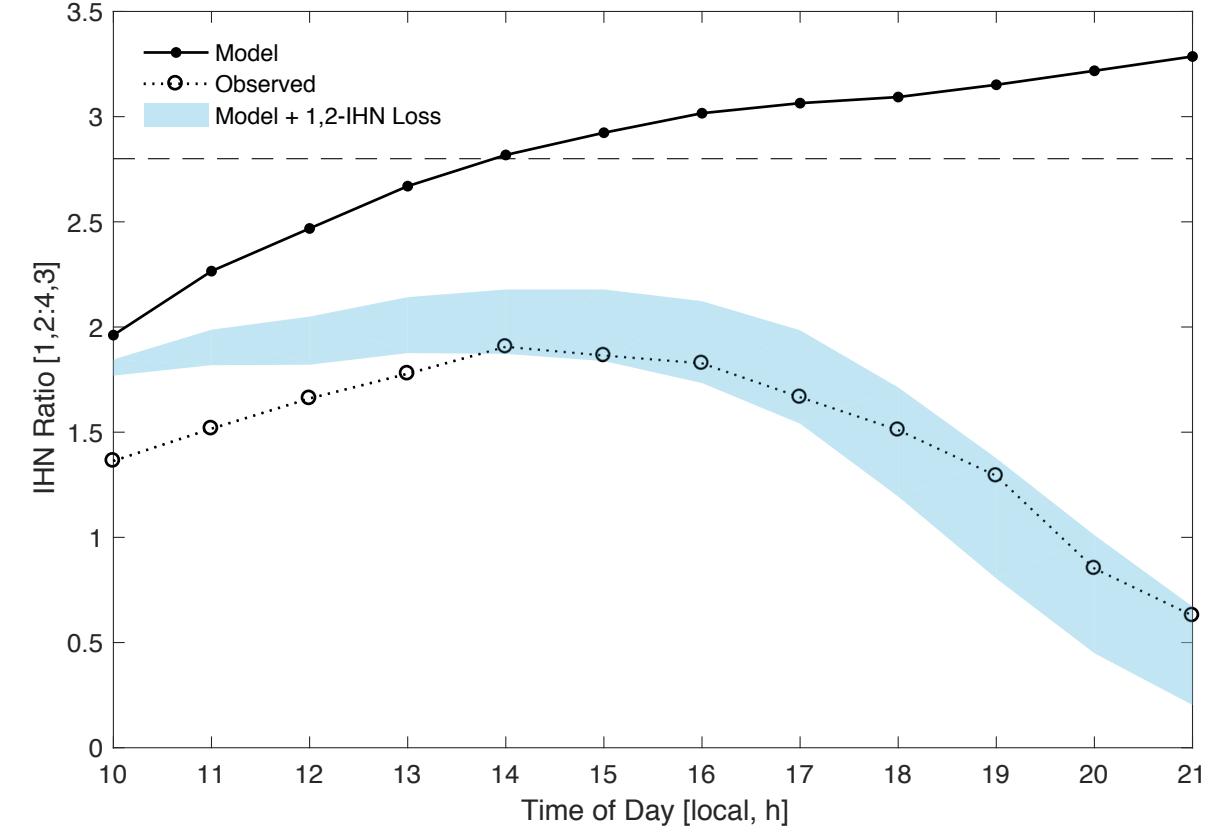
2 - 5 hour lifetime against hydrolysis



Rapid 1,2-IHN Loss

1,2-IHN Loss Pathways	Lifetime (hours)
OH Oxidation (Caltech) $[OH] = 3 \times 10^6 \text{ molec cm}^{-3}$	3
OH Oxidation (PROPHET) $[OH] = 1 \times 10^6 \text{ molec cm}^{-3}$	9
Deposition BLH = 1.5 km	24

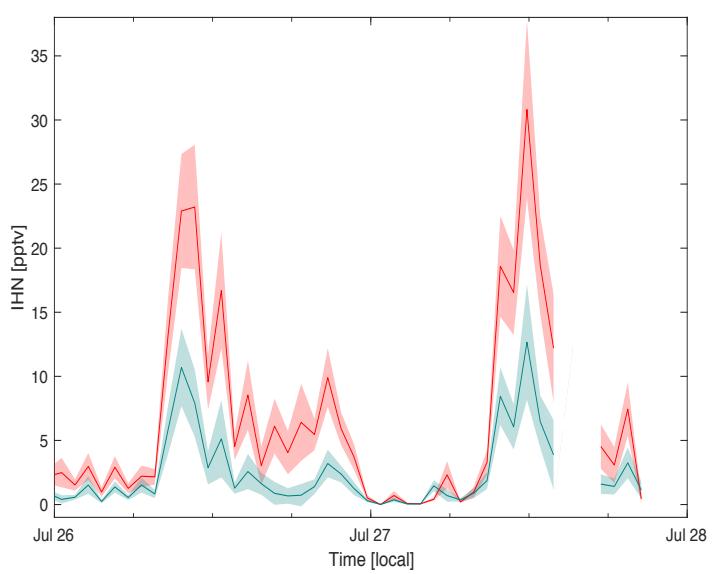
2 - 5 hour lifetime against hydrolysis



Conclusion

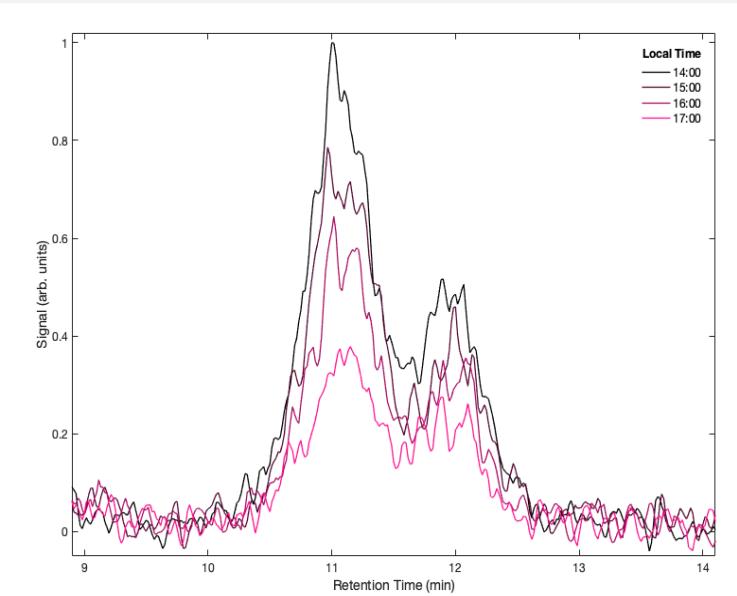
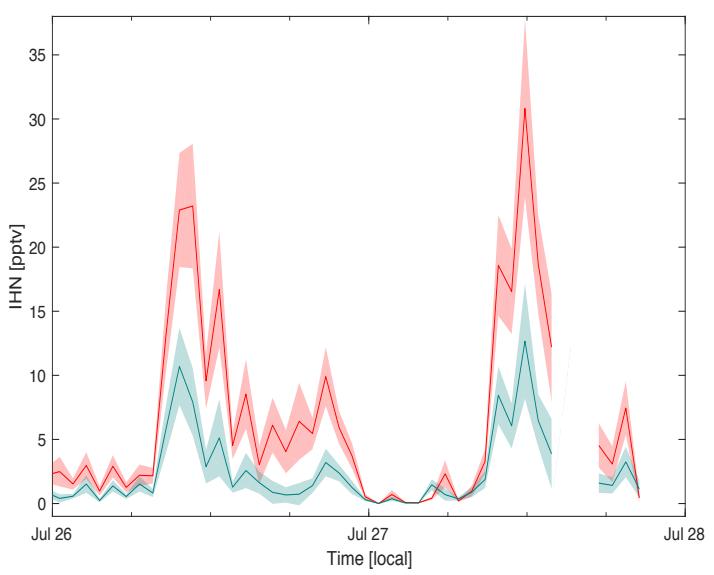
Conclusion

1. Obtained isomer specific measurements of IHN from two field sites with differing [OH] and [NO]



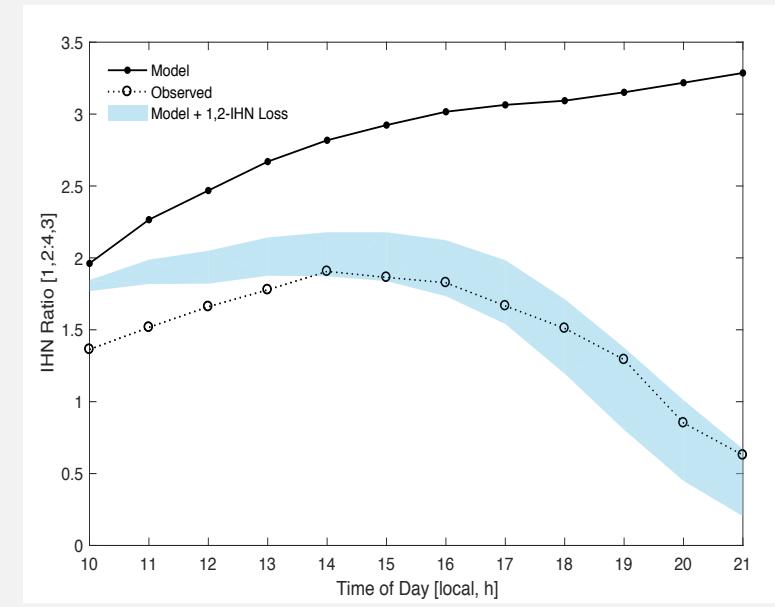
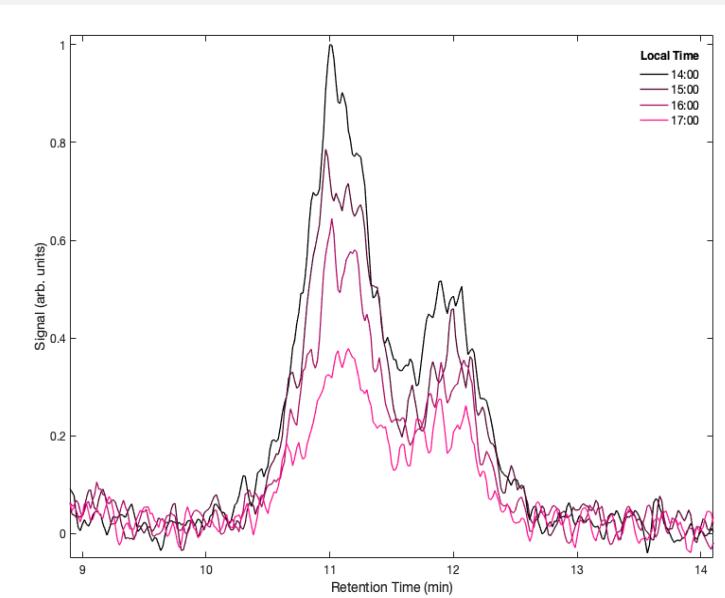
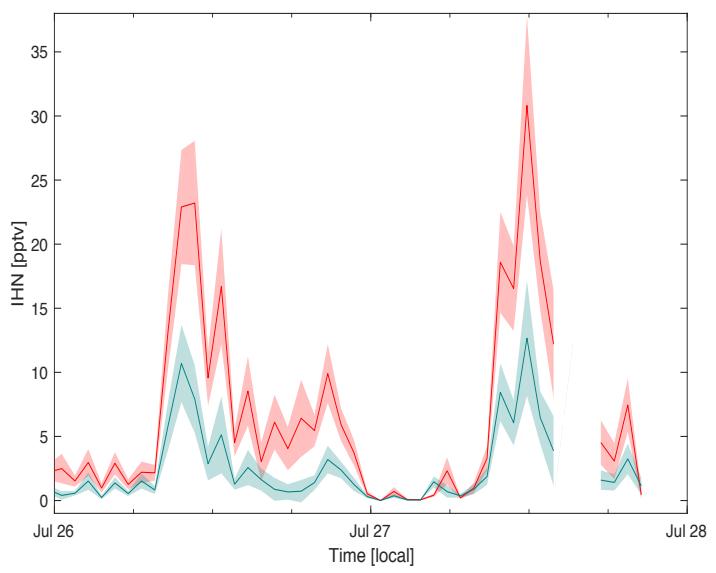
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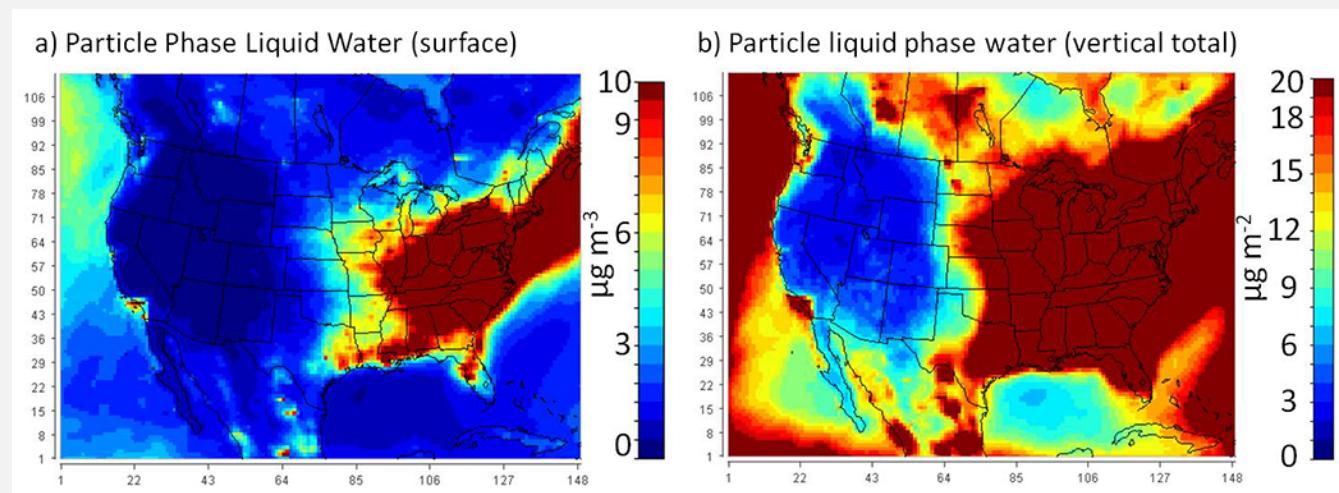
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Dependency on aerosol liquid water yet to be explored