

Chamber Studies of Volatile Chemical Product Oxidation: The CSU-NOAA SCENTS Study



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1: CIRES 2: NOAA 3: CSU

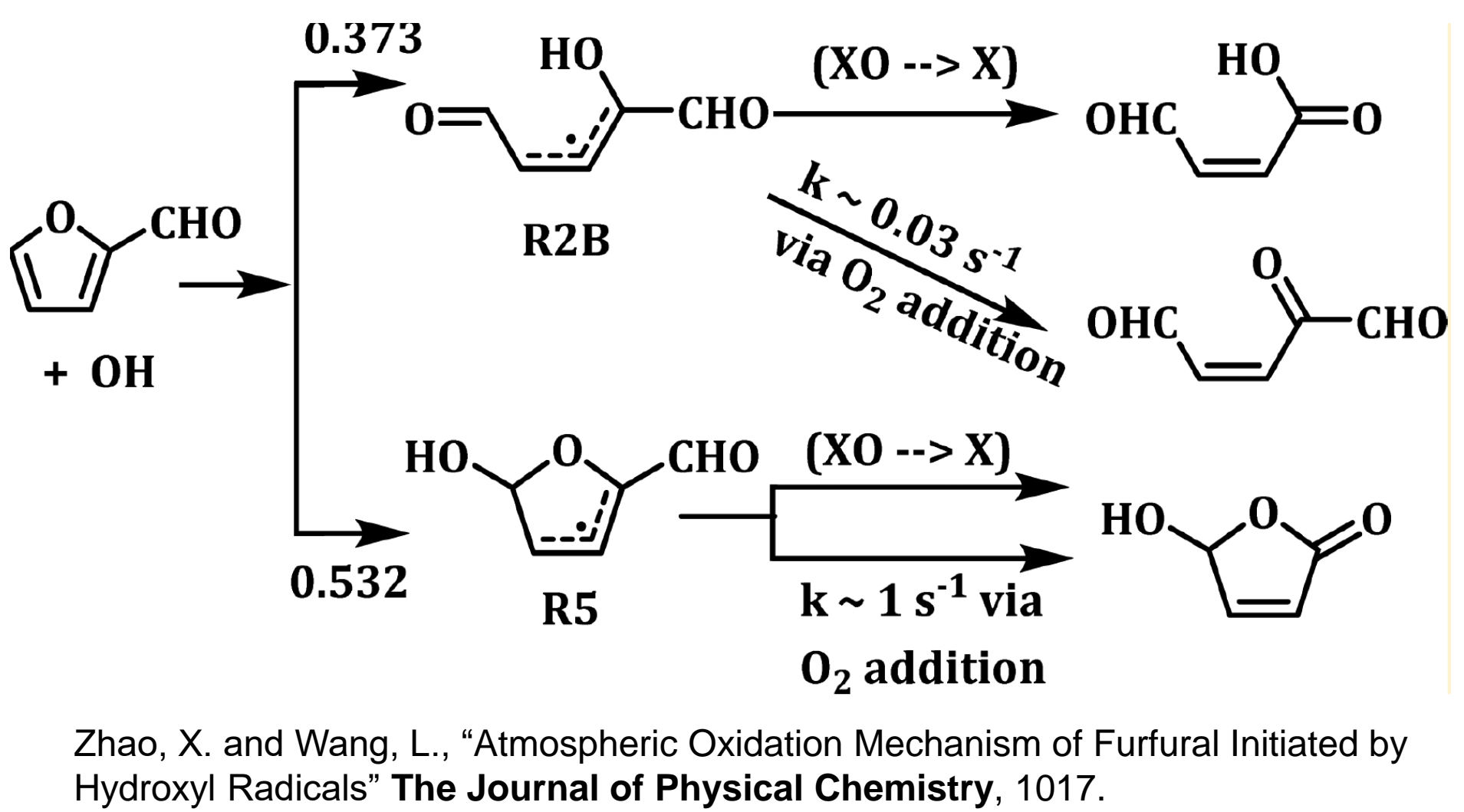
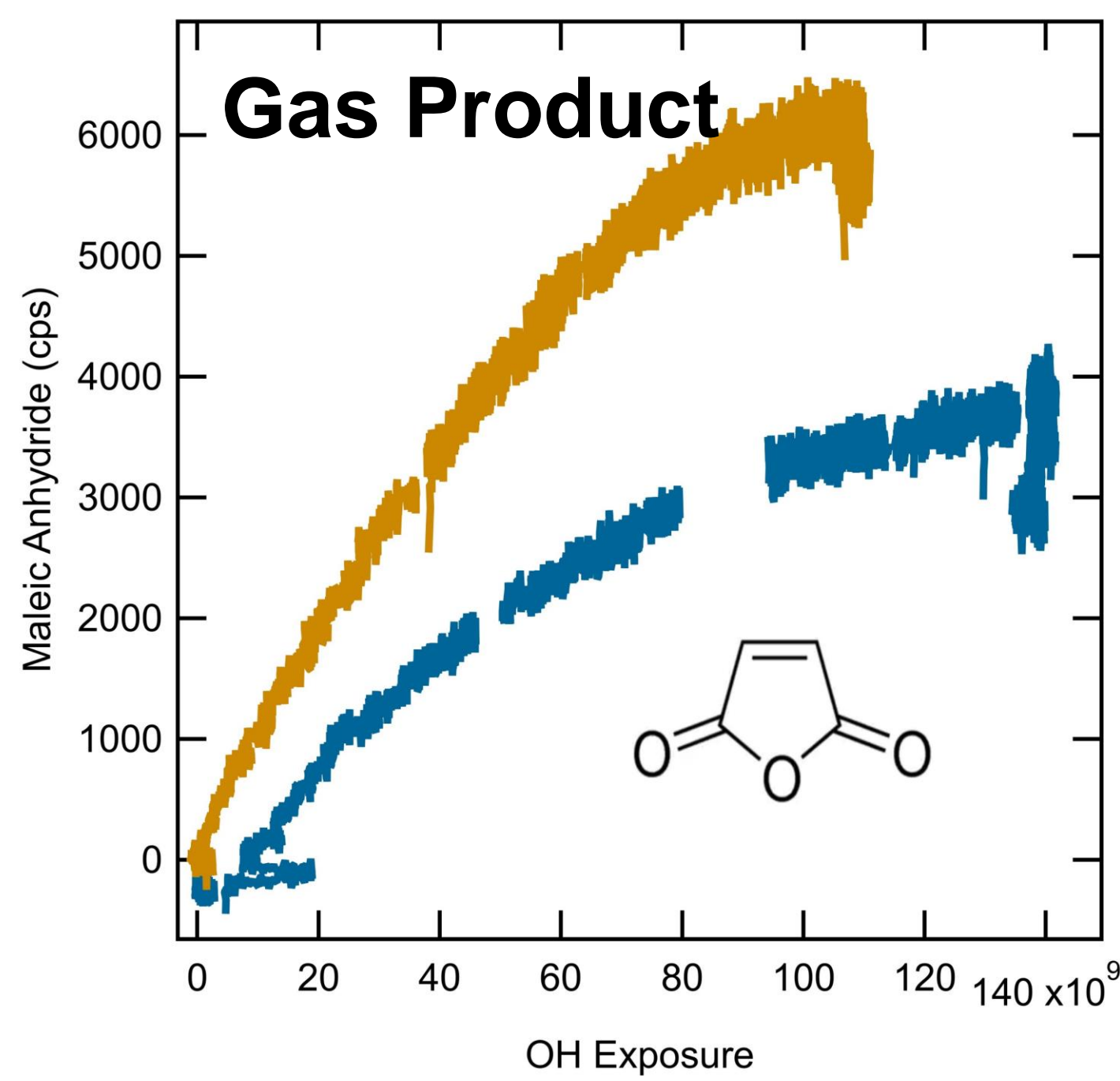
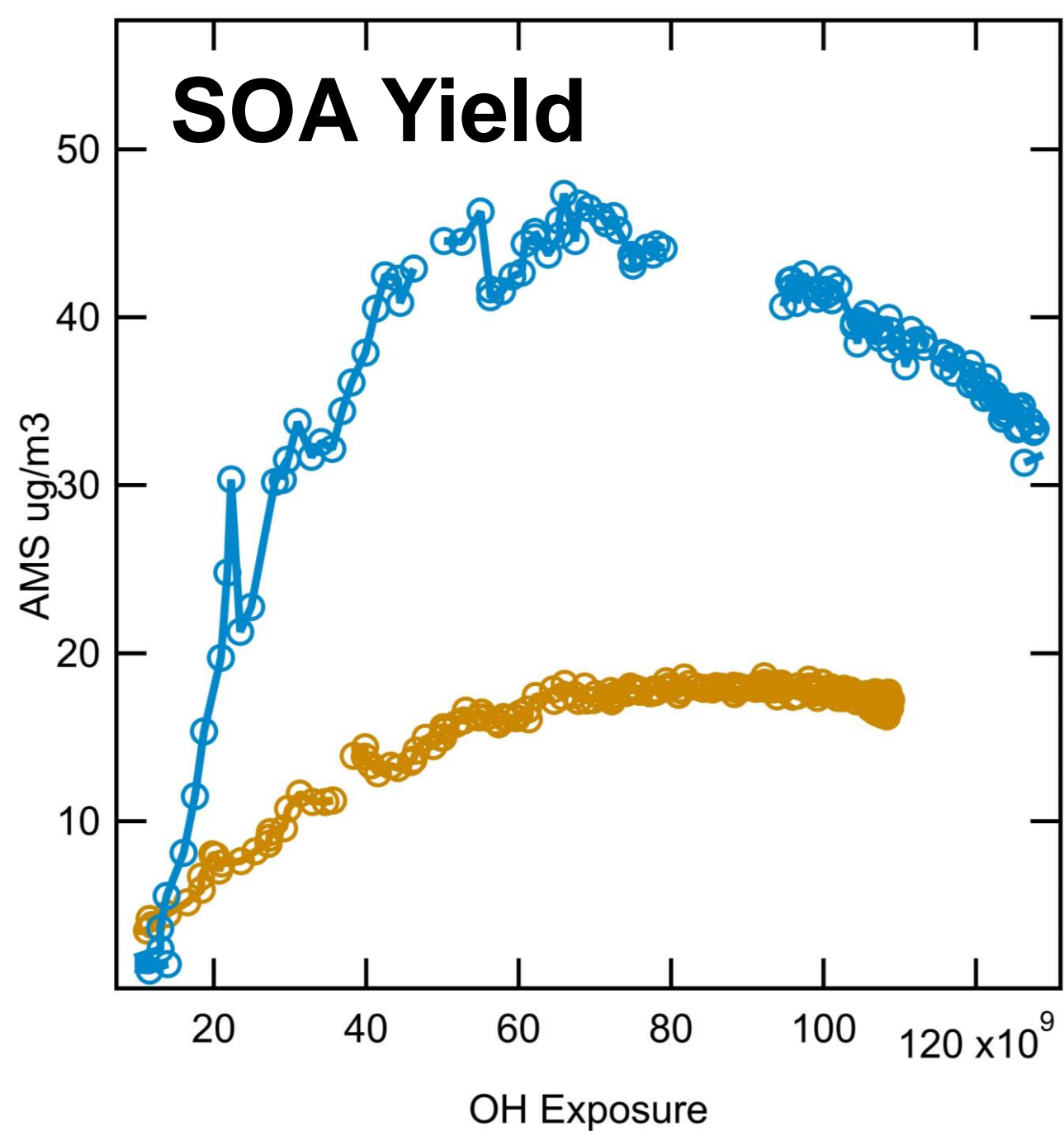
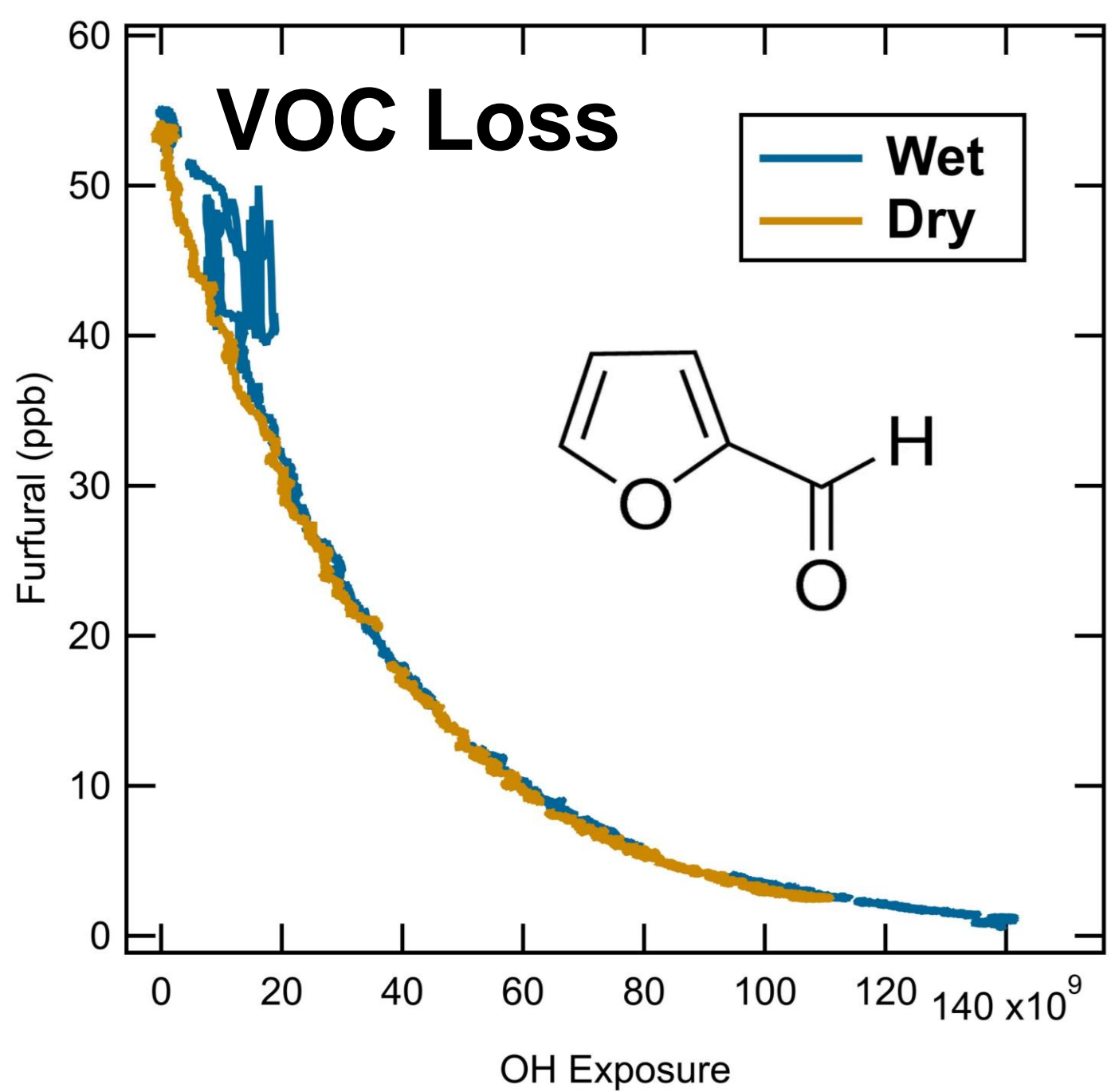
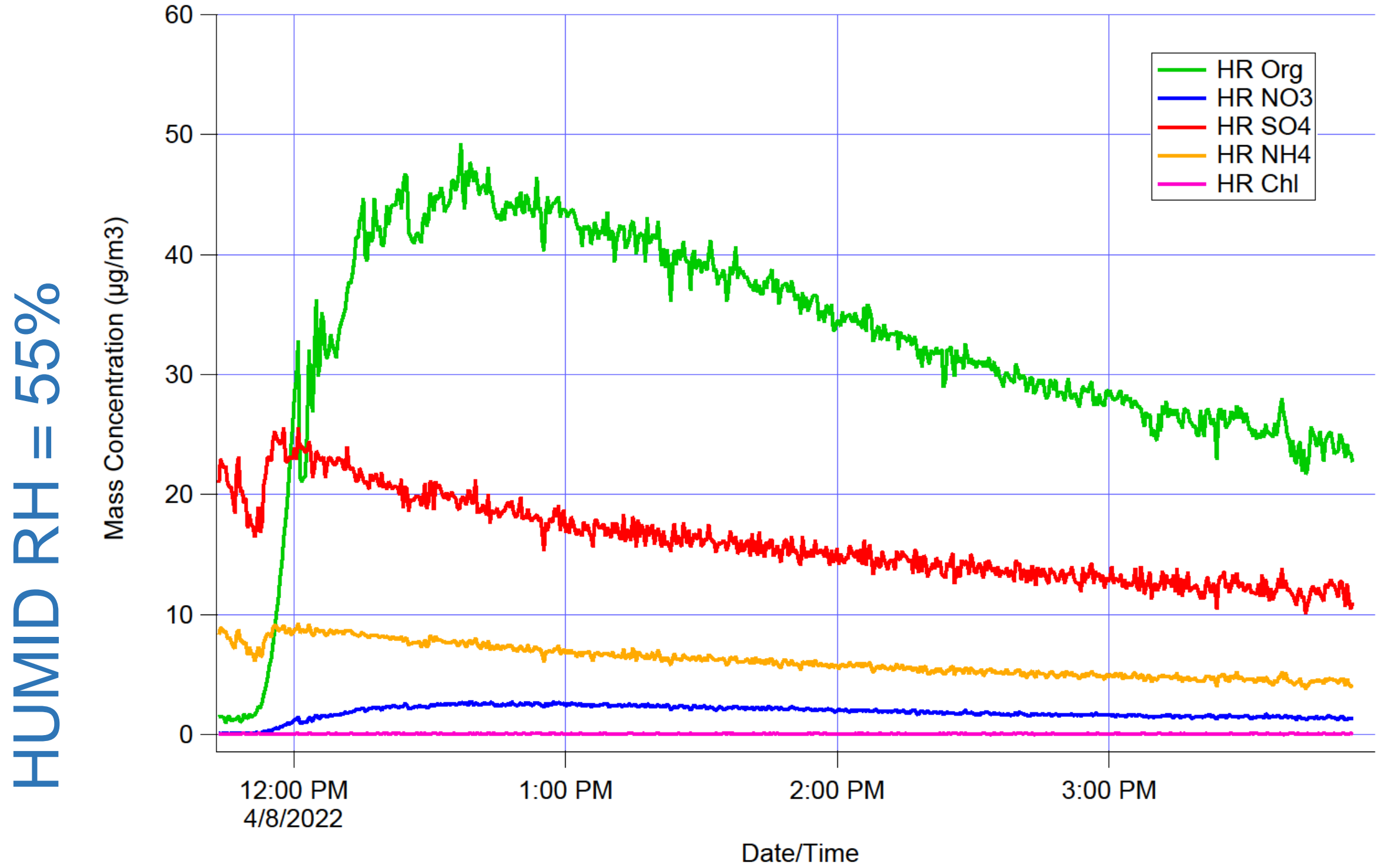
Abstract: Volatile chemical products (VCPs) have recently emerged as an important contribution to urban ozone generation and secondary organic aerosol (SOA) production which impact our understanding of radiative budgets and affect human health. Chamber experiments are an effective tool for probing specific chemical mechanisms in a more controlled environment than field measurements. The SCENTS (Secondary organic aerosol Chamber Experiments of Non-Traditional Species) project was specifically designed to constrain reaction rates and SOA generation of VCPs under urban conditions. Specifically, we seek to understand the evolving composition of both gas and aerosols in an urban environment, contribute to oxidation reaction rate constraints of VCPs, and constrain the rate of aerosol generation in urban environments. In collaboration CSU, we conducted chamber experiments under NO_x conditions characteristic of the urban environment to probe the atmospheric chemistry of VCPs and subsequent aerosol formation to ammonium sulfate seed. We measured the gas-phase chemistry and SOA formation of VCPs using a suite of instrumentation, including the high-resolution aerosol mass spectrometer (HR-AMS) and extractive electrospray ionization (EESI) mass spectrometer for aerosol composition and the proton transfer reaction (PTR) mass spectrometer and ammonium chemical ionization mass spectrometer for speciated gas phase VOCs. These results will provide new constraints that can be incorporated into air quality models and provide laboratory data to aid in interpretation of field measurements.

Experiments

Species	RH (%)	SOA Yield	O:C
Carbitol	55	High	1.1
Texanol	55	Low	0.75
D4 Siloxane	55	Low	0.8
Benzyl Alcohol	55	High	1.5
Dipropylene Glycol	55	Low	0.8
<i>Furfural</i>	55	<i>High</i>	<i>1.45</i>
<i>Furfural</i>	10	<i>Low</i>	<i>1.5</i>
Dipropylene Glycol Methyl Ether	55	Low	0.5
Dipropylene n-butyl	55	Low	0.75
Butyl Carbitol	55	Low	0.7
Butyl Acetate	55	Low	1.2

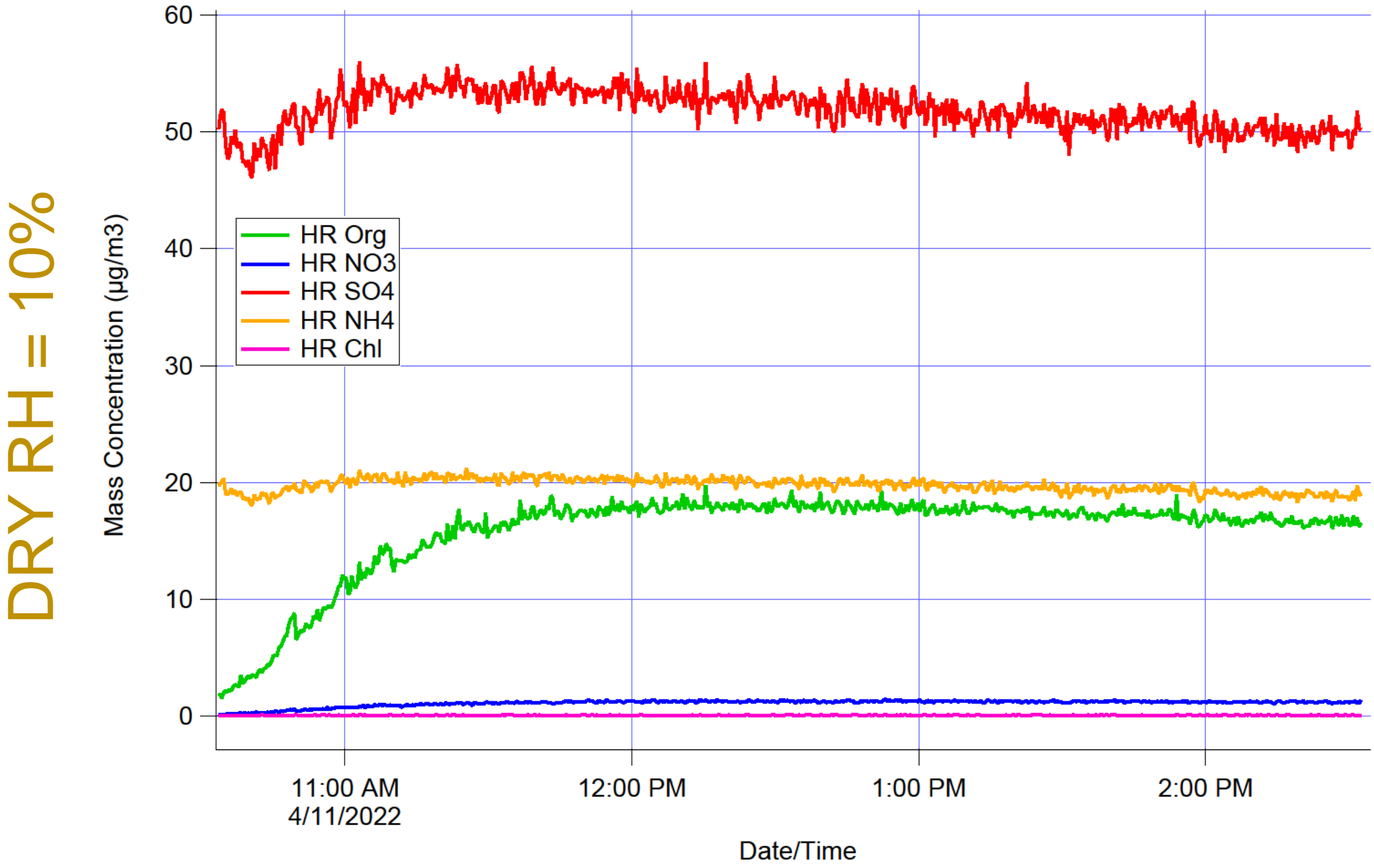
Results: Here we focus on the difference between wet and dry chamber experiments with furfural as the VOC. In general the wet has a higher SOA yield than the dry experiments. We believe this is due to a difference in oxidation pathway in the two systems yielding different products. Both sets of experiments are highly oxidized as seen on multiple instruments. We are able to track both the gas and particle phase data which validates earlier proposed mechanisms for VOC oxidation. The work will continue as we compare families of glycols.

Chamber: A picture of a similar chamber with Teflon bag, inlet and outlet, and UV light array to simulate atmospheric oxidation and generation of aerosol products.

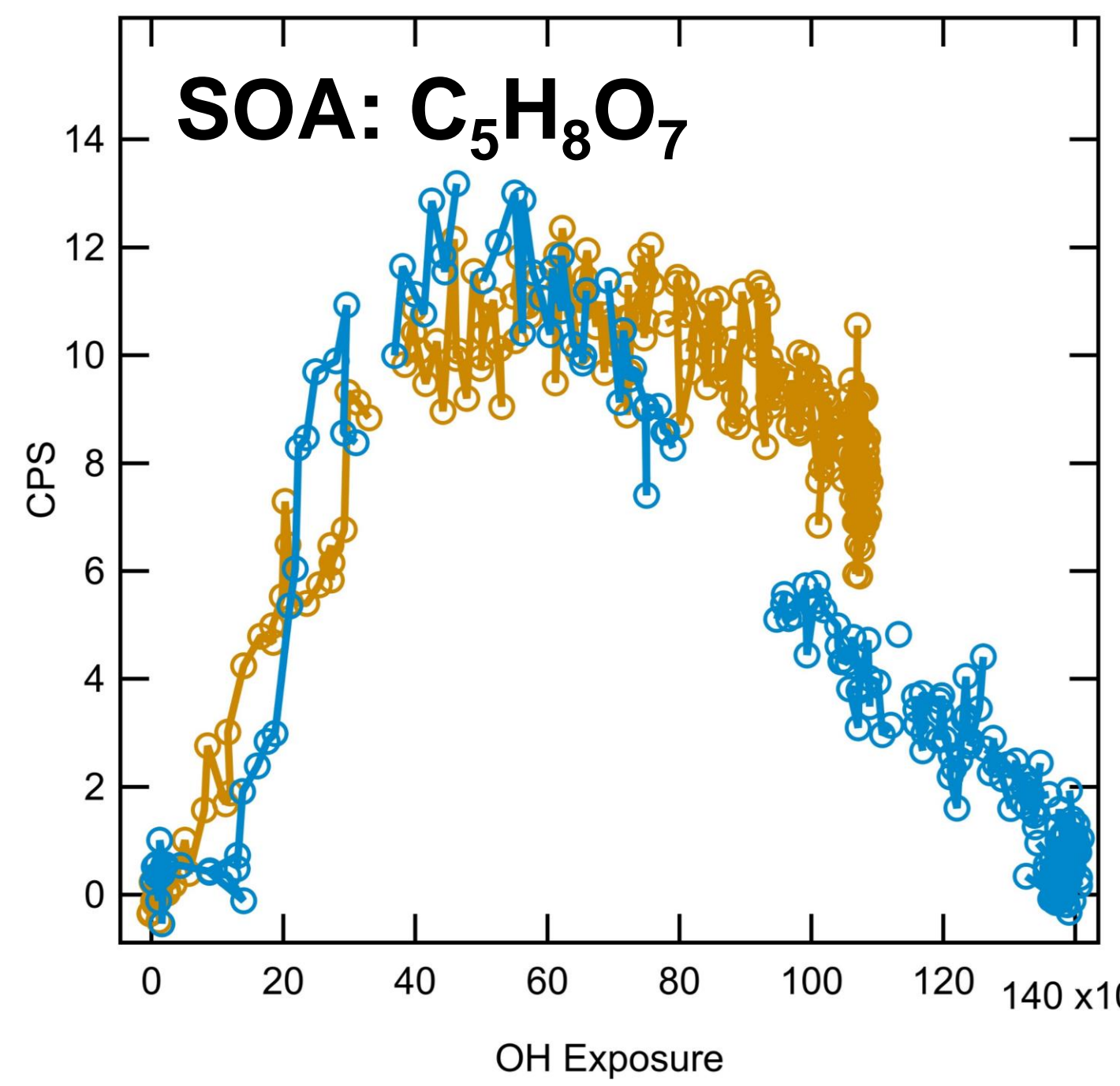
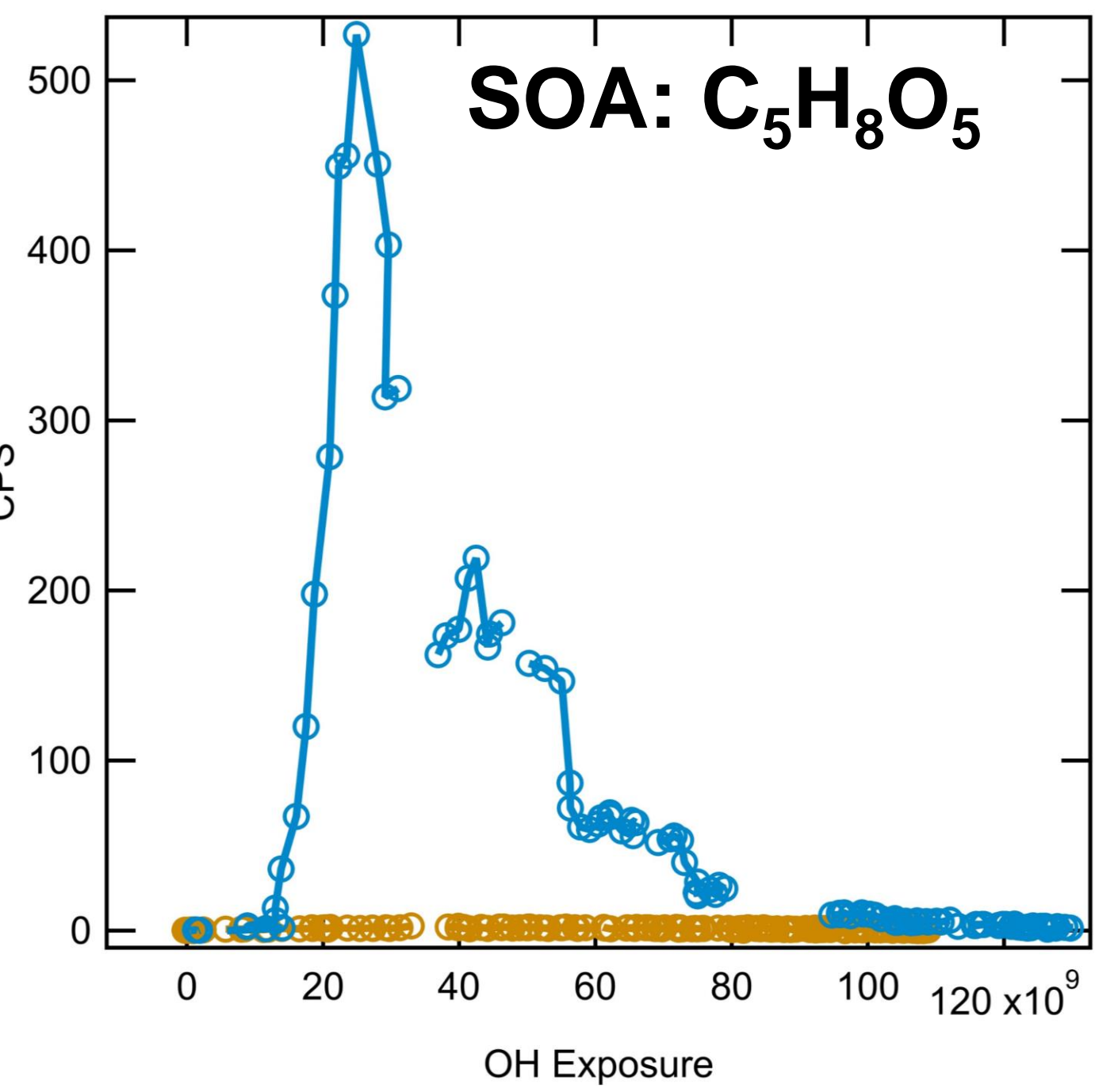
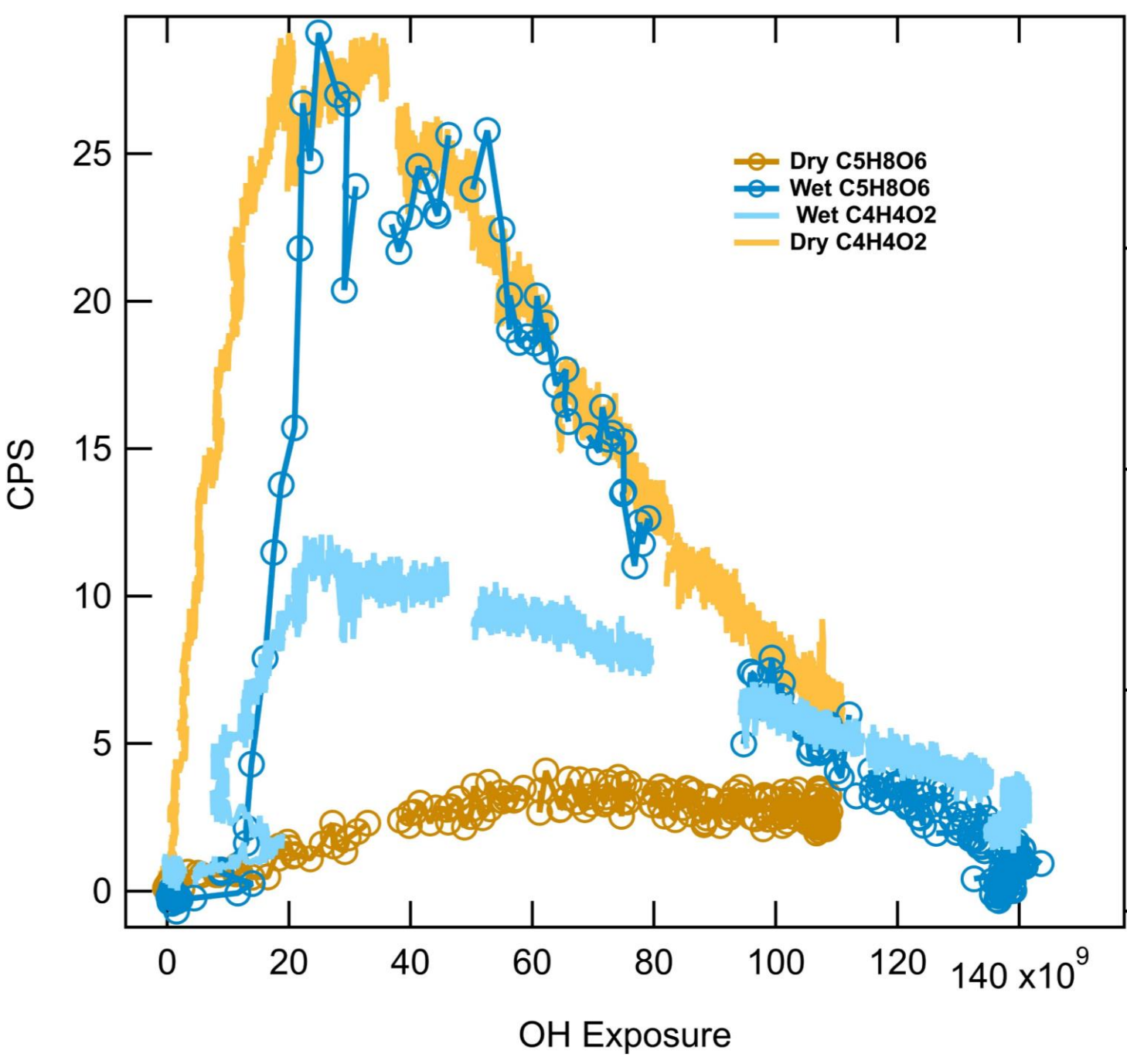


Zhao, X. and Wang, L., "Atmospheric Oxidation Mechanism of Furfural Initiated by Hydroxyl Radicals" *The Journal of Physical Chemistry*, 1017.

Relative Mass Yield: The relative yield of SOA from the wet vs dry experiments is different. There is much more generation of SOA under humid conditions, indicating a different pathway of formation. The data is not corrected for the increase in collection efficiency that occurs when the ammonium sulfate particles are coated in organic matter.



SOA Products: Using the EESI and the PTR the loss of VOC (Furfural, first panel) can be explicitly tracked while the SOA increases. The organic SOA yield from the HR-AMS normalized by OH exposure is shown in panel 2. The third panel shows the difference between wet and dry elucidating the different pathway of SOA generation under these different conditions. The lower three panels show different highly oxygenated species that are present in the two experiments. In general, the AMS sees a surprisingly high O:C ratio, but specific compounds with that ratio are seen in the EESI data. There are differences however in which compounds are more prevalent in the wet vs dry experiments consistent with the different pathway hypothesis.



Oxidation State: The upper figure shows two different proposed pathways for furfural oxidation. The lower figure shows the different O:C ratios for the different EESI species. There is a slight discrepancy in bulk O:C ratio between the AMS and the EESI which could be due to relative sensitivities between the two instruments.

