Objectives

- FTIR analysis of OA functional groups in SOAS samples.
- Lab studies of effects of VOCs, NO_x, and sulfate, on functional group composition and FTIR spectra of SOA formed from biogenic VOCs.
- Identify and quantify contributions of biogenic and anthropogenic emissions to SOA formed during SOAS using FTIR spectra plus lab and field results.

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U.S. EPA - Science To Achieve Results (STAR) Program
Grant # 835408

Laboratory Apparatus & Methods

Blacklights

Environmental Chamber [8 m^3]

- VOC: isoprene, monoterpenes, alkanes (~0.1–1 ppmv)
- Seed particles: DOS, $(NH_4)_2SO_4/H_2SO_4$ (pH = 1, E-AIM)
- RH: 0 or 50% (SOAS ~ 75%)
- Oxidant & NO_x: OH (CH_2ONO/NO or H_2O_2 + UV), NO_3 (N_2O_5), O_3

Off-Line Analyses

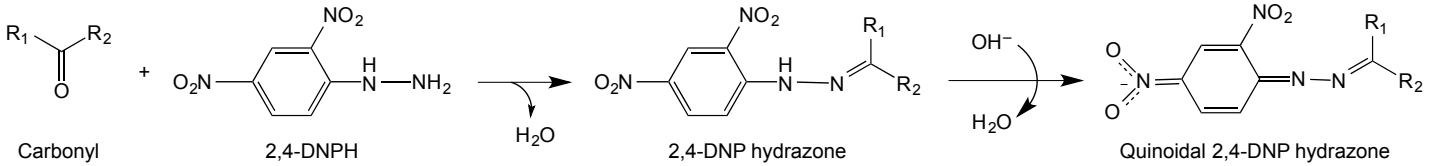
- Derivatization-Spectrophotometry, FTIR (extracts & filters) [particle functional groups]
- Gas & Liquid Chromatography & Mass Spectrometry [gas & particle composition]

On-Line Analyses

- Thermal Desorption Particle Beam Mass Spectrometer [particle composition & volatility]
- Scanning Mobility Particle Sizer [particle number and mass concentrations]

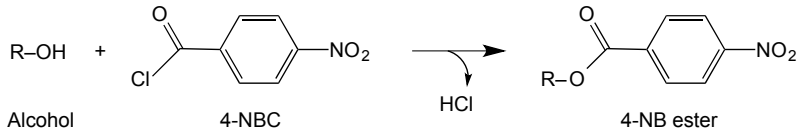
Derivatization-Spectrophotometric Methods for Functional Group Analysis

Carbonyl



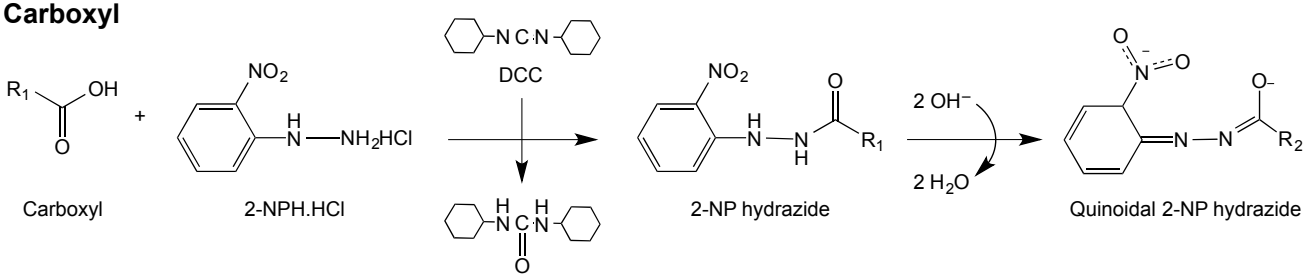
480 nm

Hydroxyl



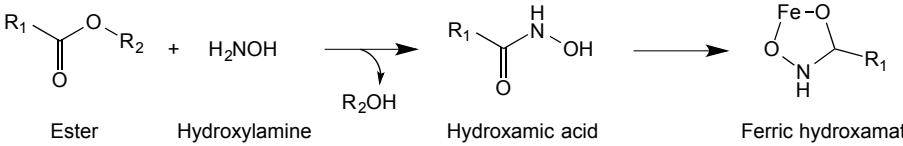
253 nm

Carboxyl



550 nm

Ester

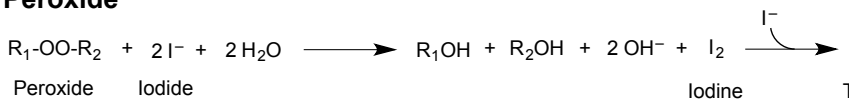


540 nm

Nitrate

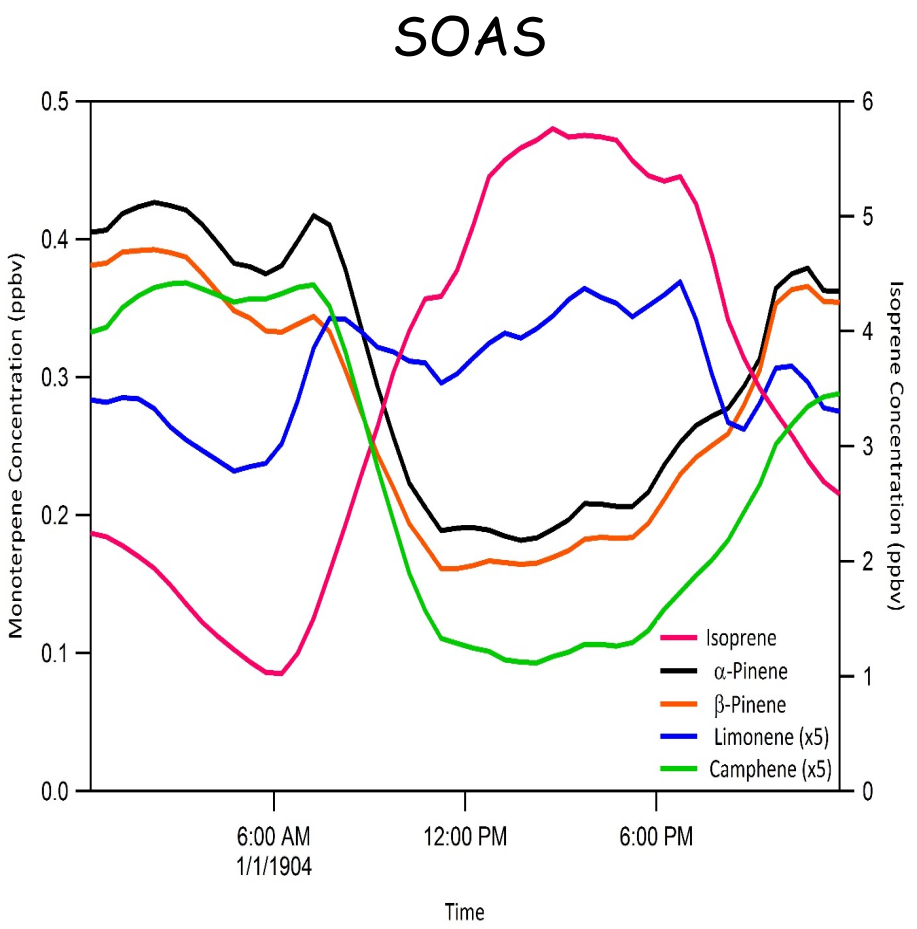
210 nm

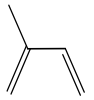
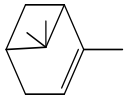
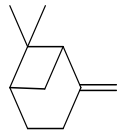
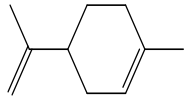
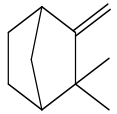
Peroxide



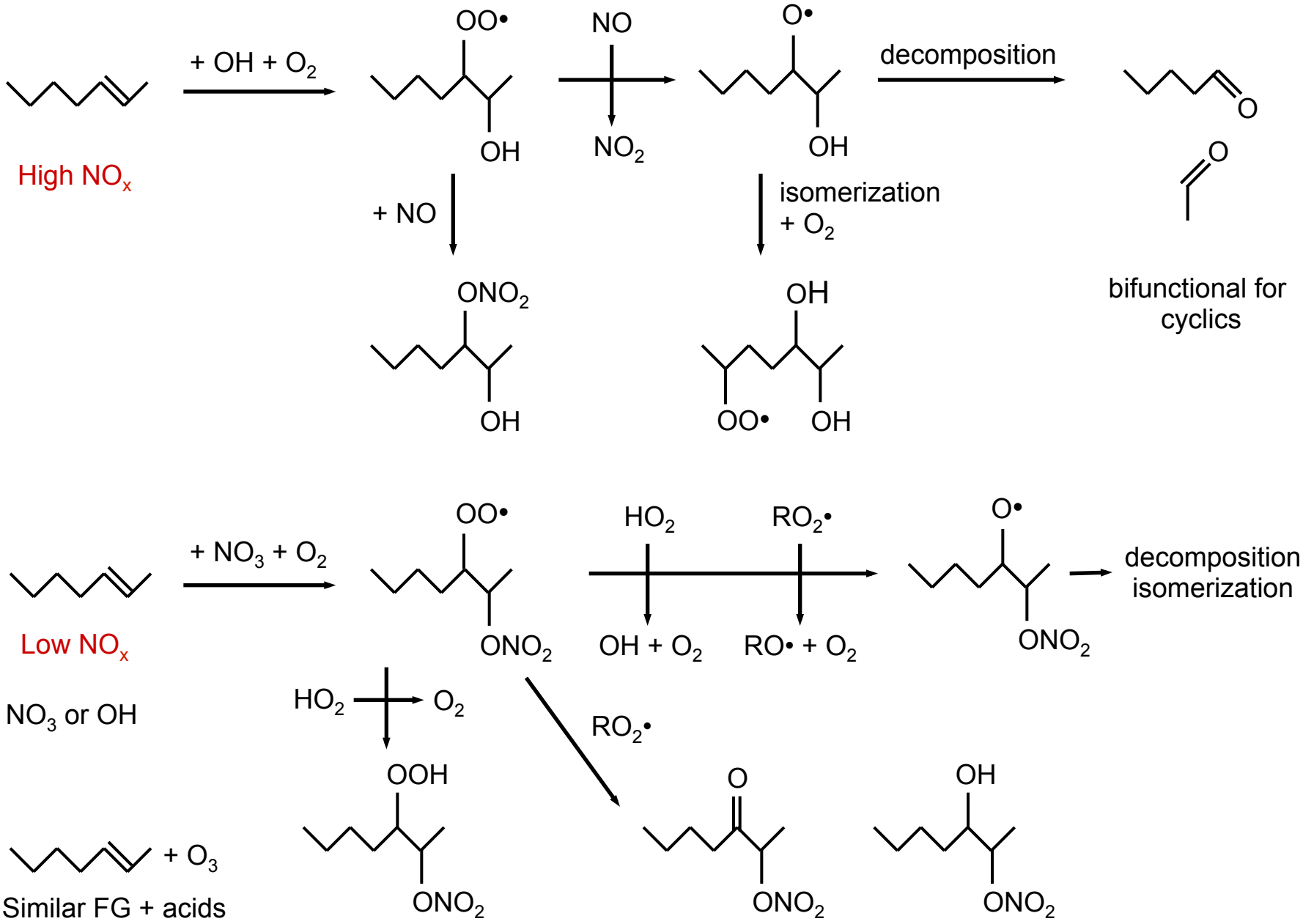
470 nm

Selected VOCs

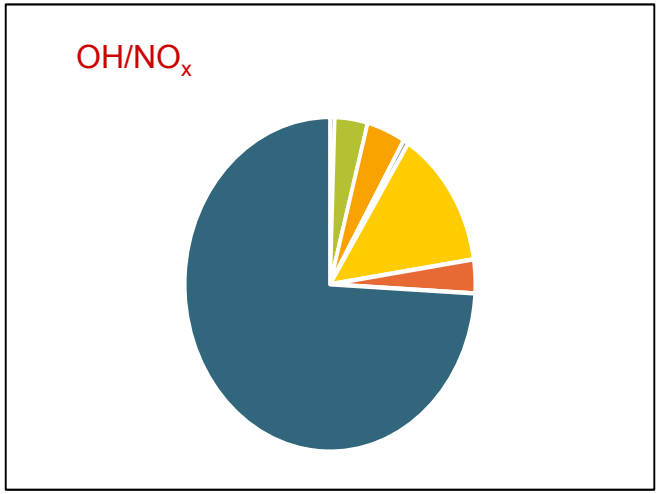


Compound	SOAS (ppbv)	Structure
Isoprene	3.5	
α-Pinene	0.31	
β-Pinene	0.28	
Limonene	0.06	
Camphene	0.05	

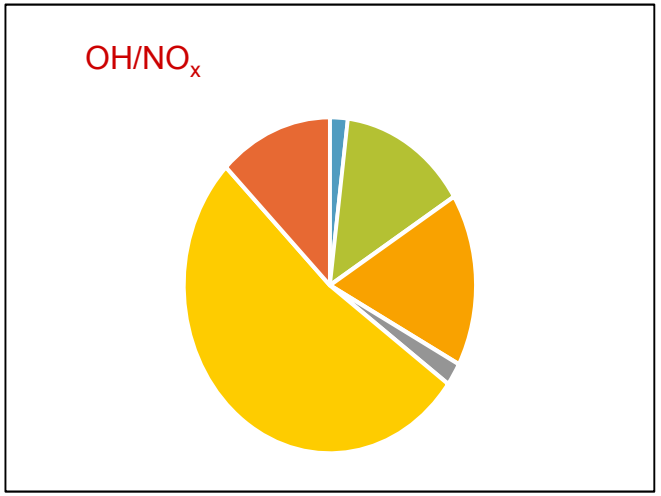
Reaction Mechanisms & Functional Groups



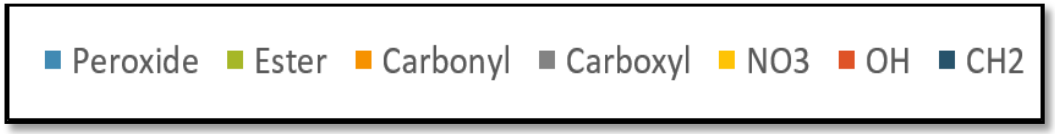
n-Pentadecane



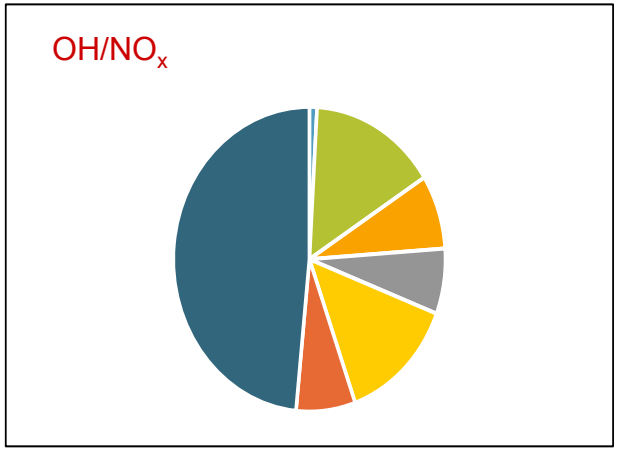
with CH_2



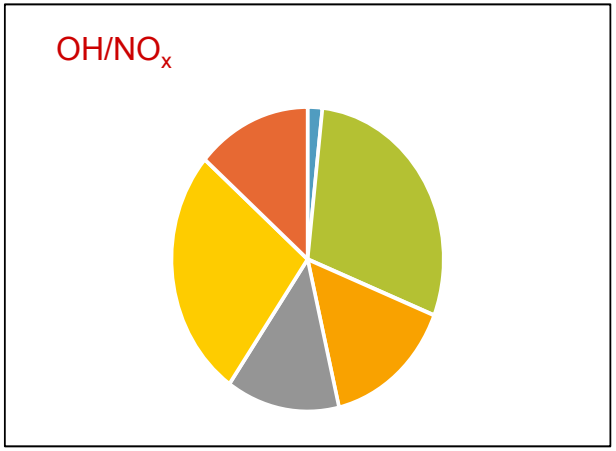
without CH_2



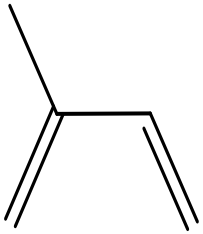
Isoprene



with CH_2

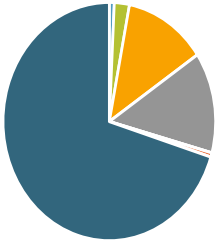


without CH_2

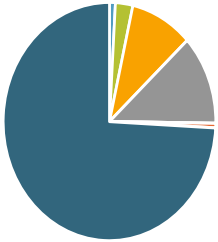


α-Pinene

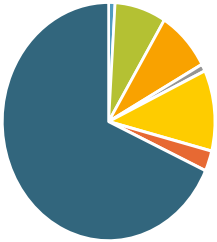
O_3



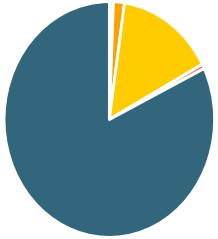
O_3 + AS seed + 50% RH



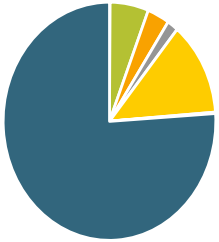
OH/NO_x + AS seed + 50% RH

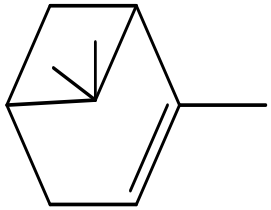


N_2O_5 + AS seed + 50% RH

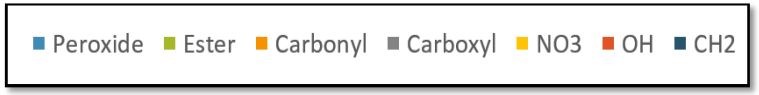


N_2O_5 + CH_2O + AS seed + 50% RH



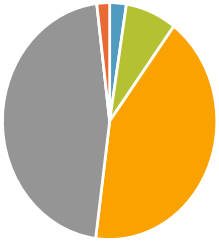


with CH_2



α-Pinene

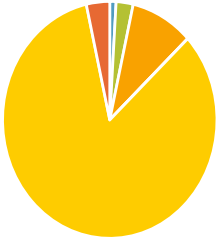
O_3



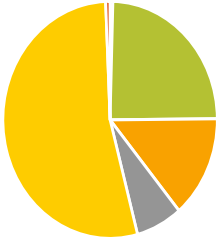
O_3 + AS seed + 50% RH

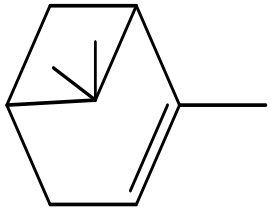
OH/NO_x + AS seed + 50% RH

N_2O_5 + AS seed + 50% RH

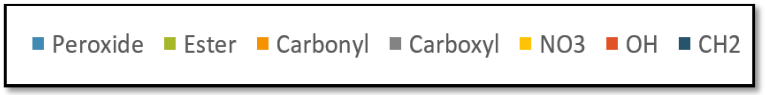


N_2O_5 + CH_2O + AS seed + 50% RH

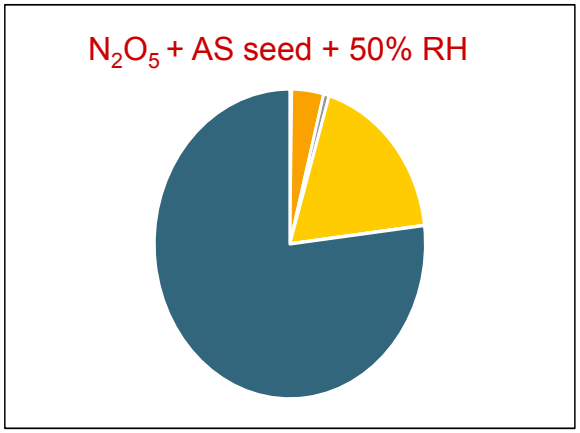


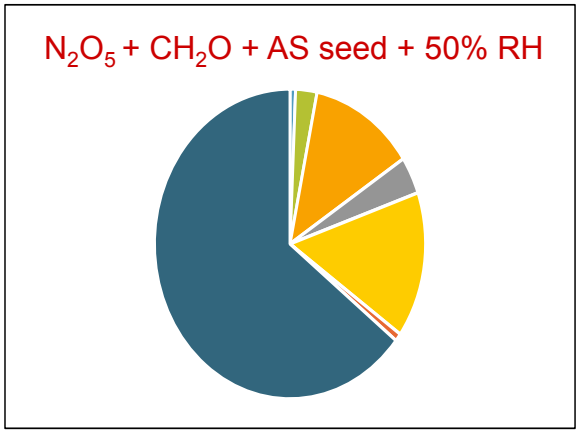


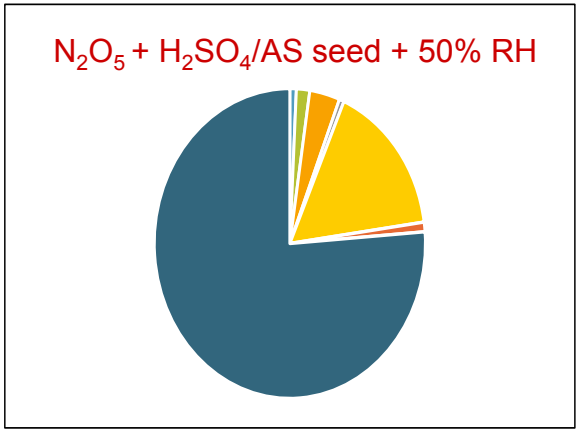
without CH_2

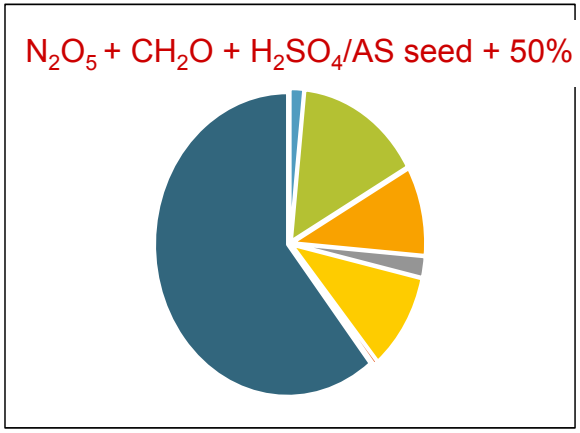


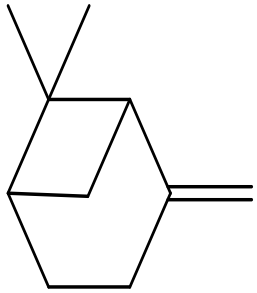
β-Pinene







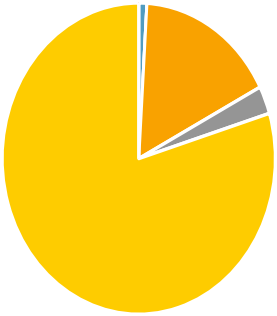




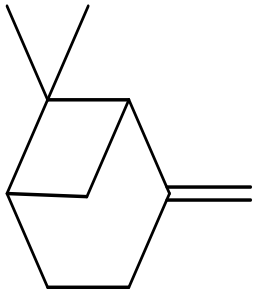
with CH_2

β-Pinene

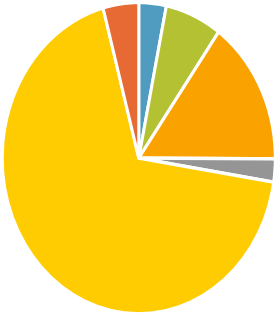
N_2O_5 + AS seed + 50% RH



N_2O_5 + CH_2O + AS seed + 50% RH

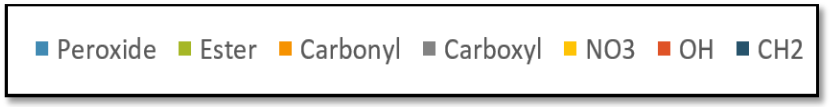


N_2O_5 + H_2SO_4/AS seed + 50% RH

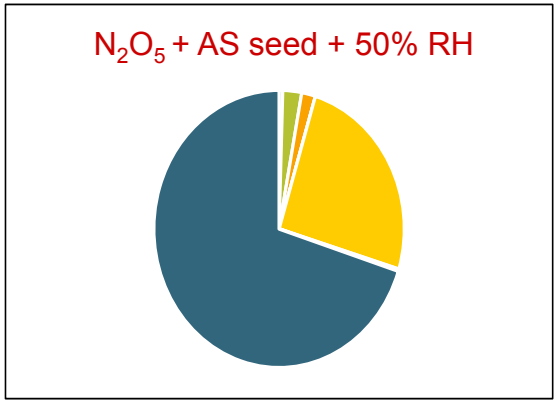


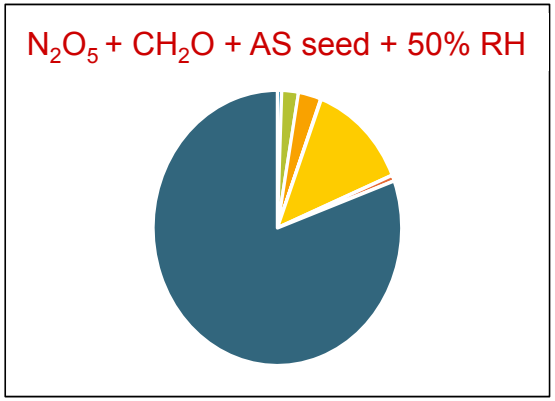
N_2O_5 + CH_2O + H_2SO_4/AS seed + 50% RH

without CH_2

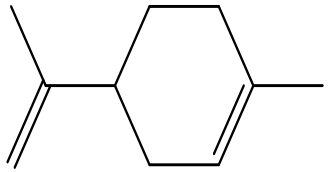


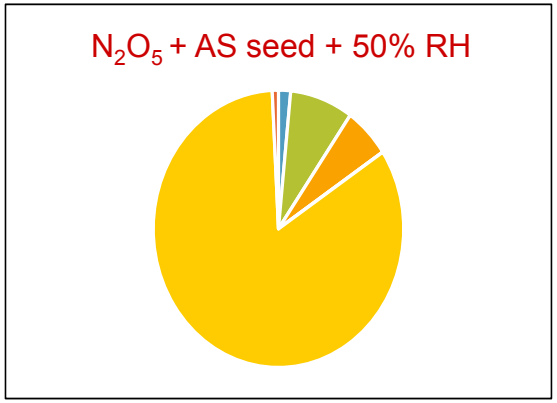
Limonene

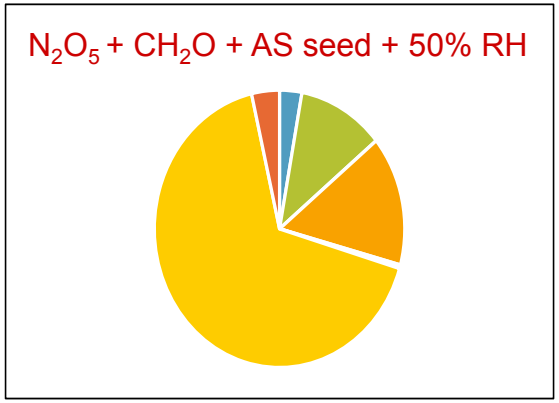




with CH_2



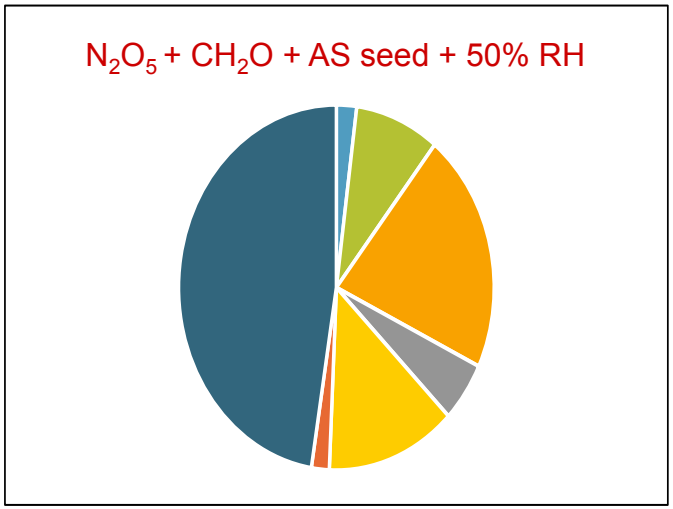




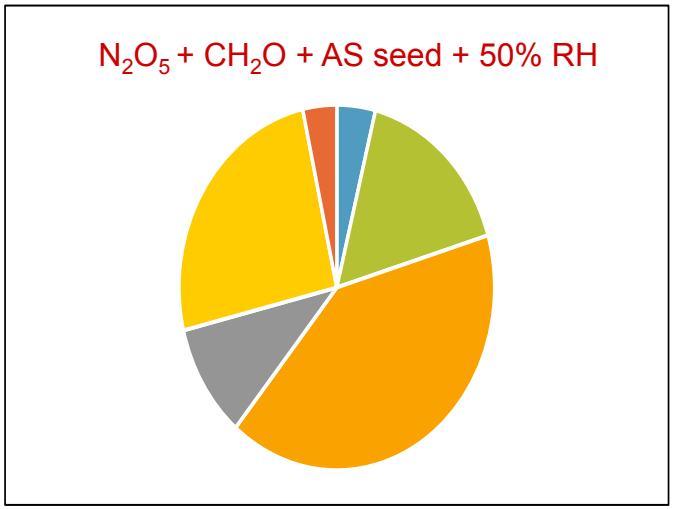
without CH_2

Peroxide Ester Carbonyl Carboxyl NO3 OH CH2

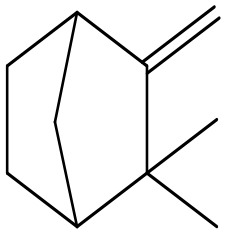
Camphene

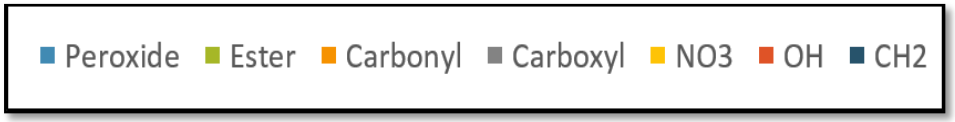


with CH_2



without CH_2





Conclusions & Future Plans

- Observe all functional groups
- Clear difference between high and low NO_x compositions
- Experiments at lower VOC concentrations
- Experiments with variable $HO_2/RO_2\cdot$ ratios
- Experiments with mixtures
- Molecular analysis
- Analyze SOAS filter samples with derivatization spectrophotometric methods
- Compare FTIR and derivatization-spectrophotometric methods