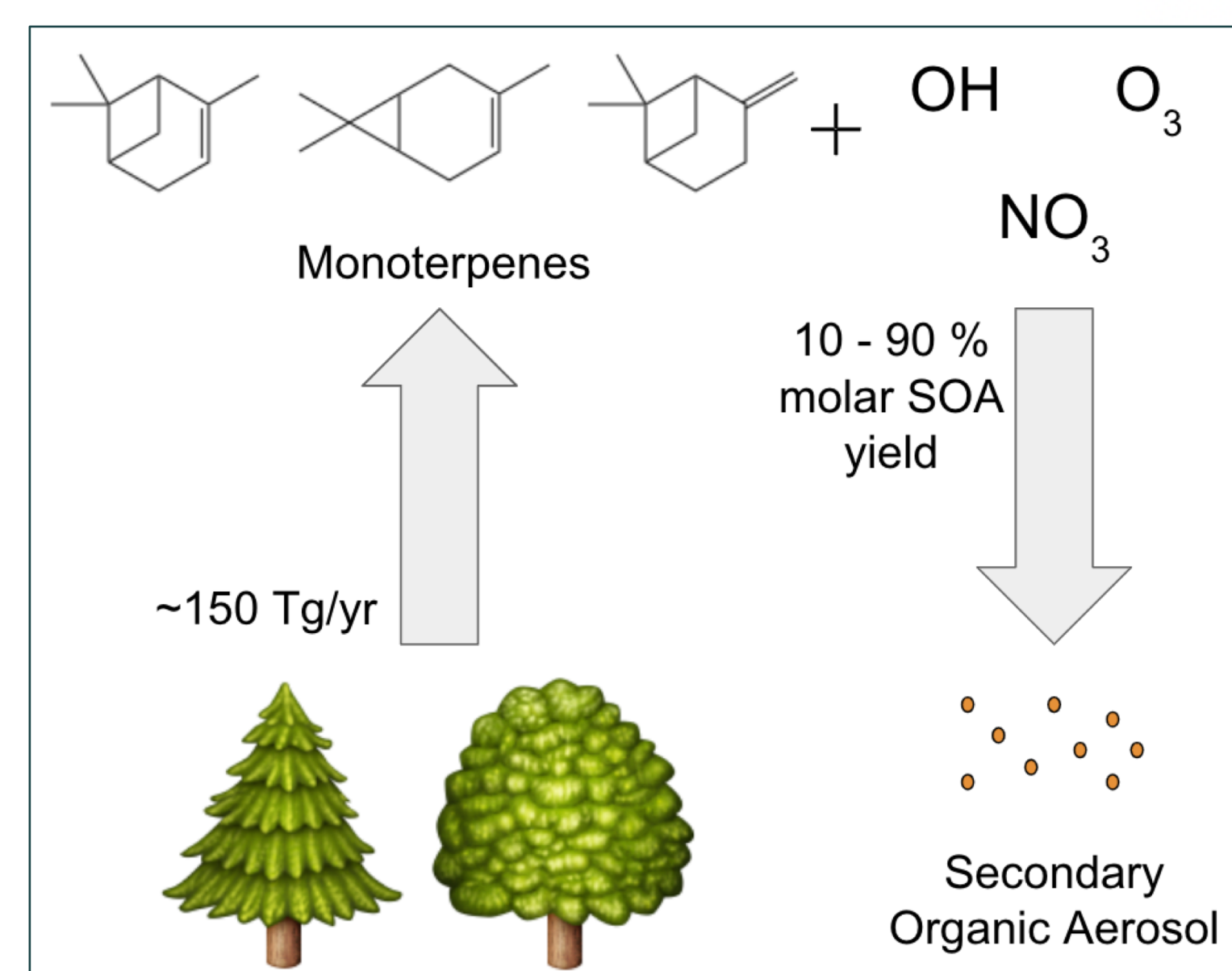
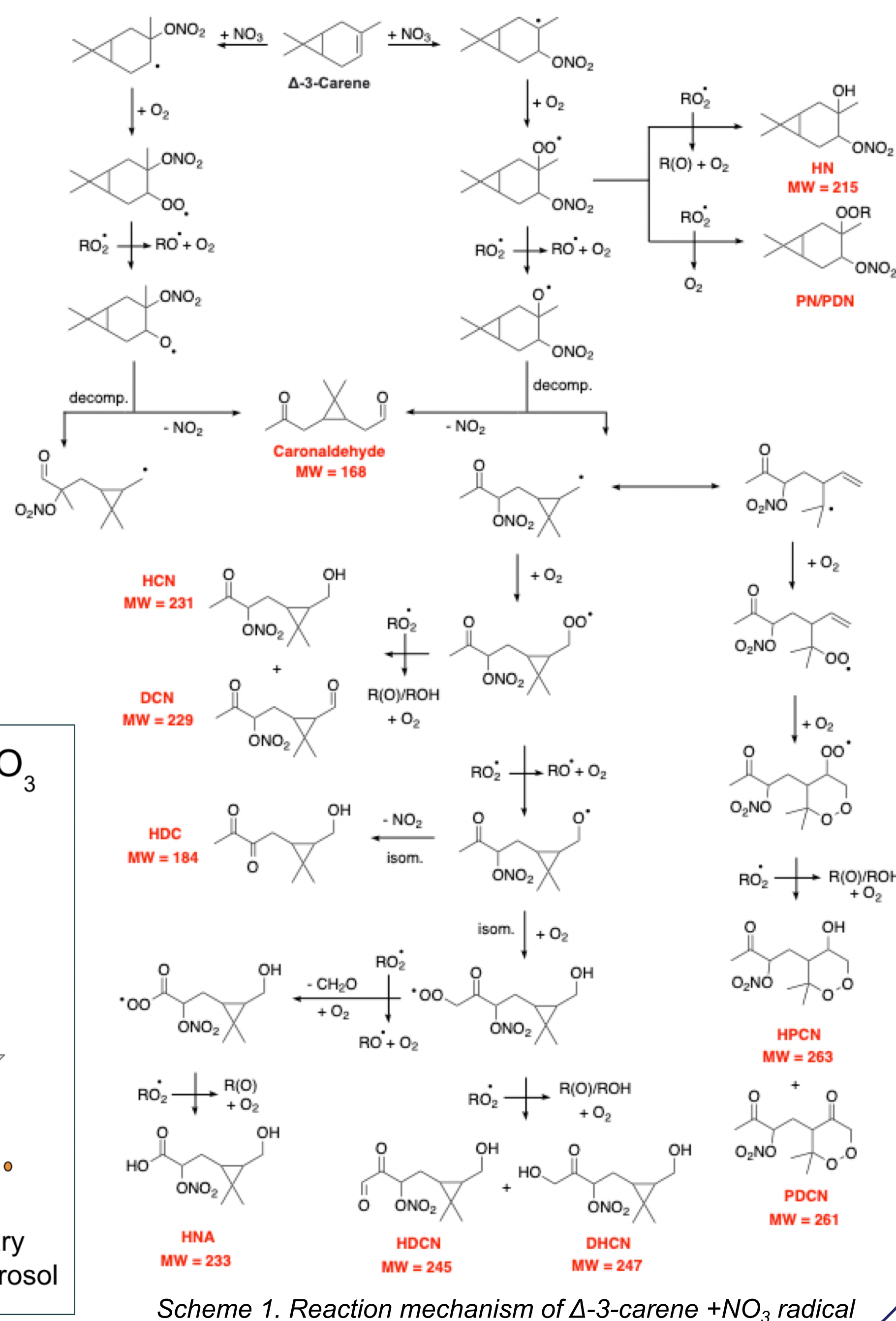


Introduction

- Monoterpenes can quickly oxidize in the atmosphere and contribute to secondary organic aerosol (SOA)
- Field studies have measured higher concentrations of organic nitrates in SOA than are currently accounted for in atmospheric models¹
- Δ -3-carene oxidation by nitrate radical is a potential source for these organic nitrates



Methodology

- We conduct environmental chamber experiments with clean air, at room temperature and 55% RH
- The amount of Δ -3-carene that reacts away is the same as the amount of N_2O_5 added

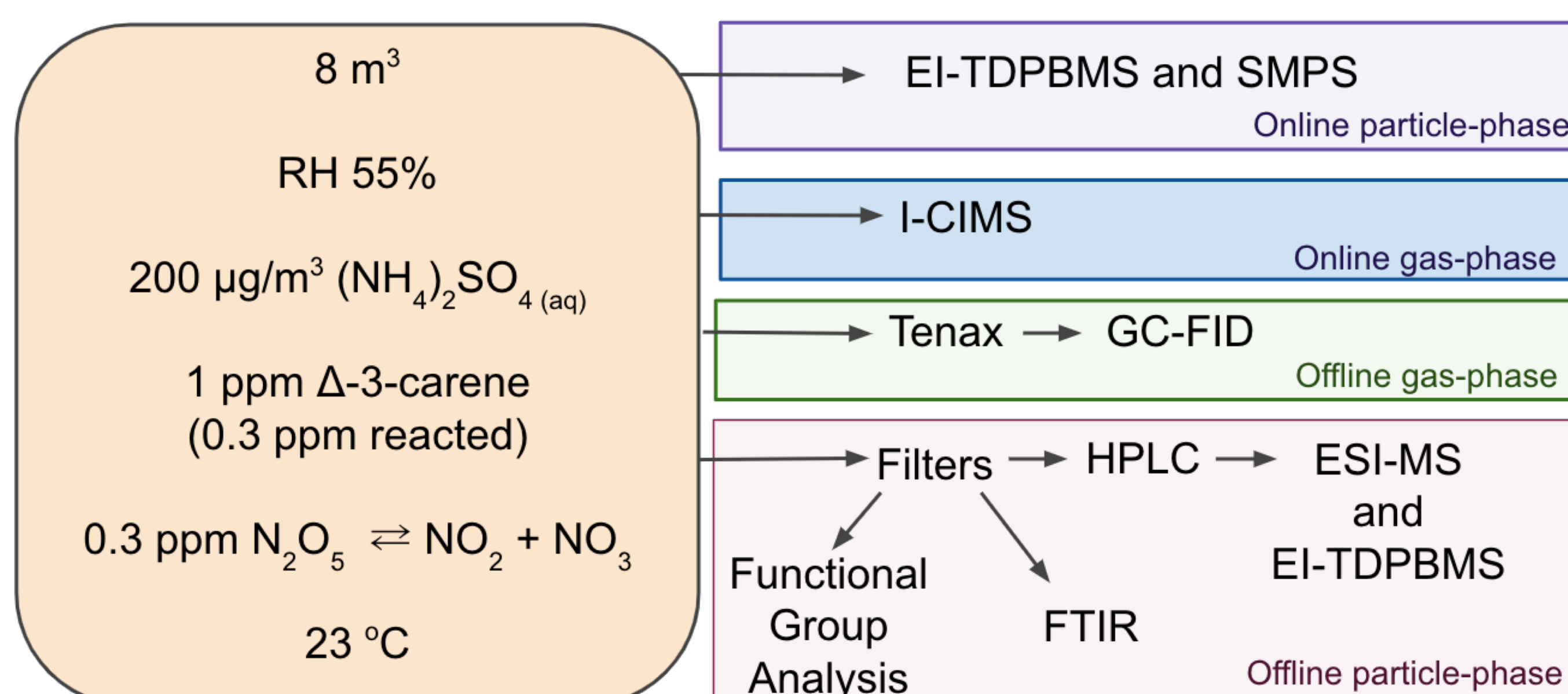


Figure 1. Diagram of a chamber experiment and analyses

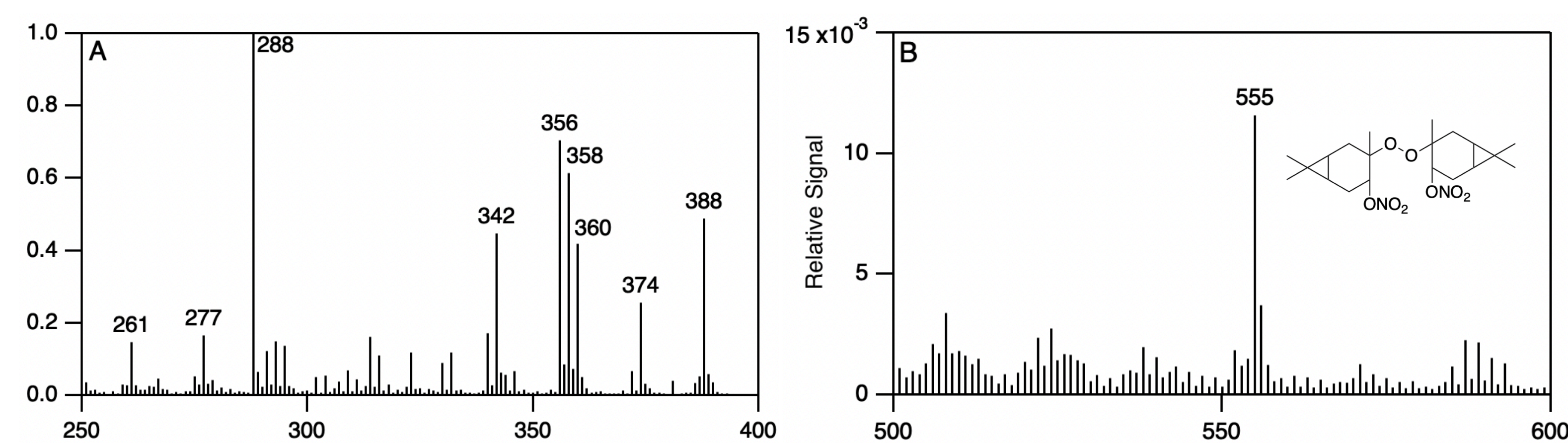


Figure 2. Gas-phase mass spectra showing expected monomers and an ROOR product

- After the reaction, we collect filters for two hours and extract the SOA

Identifying Products

- An HPLC separates out individual products in the bulk SOA, using the natural absorbance of nitrate groups (Figure 3)
- Then we put individual peaks onto an ESI-MS and ATR-FTIR

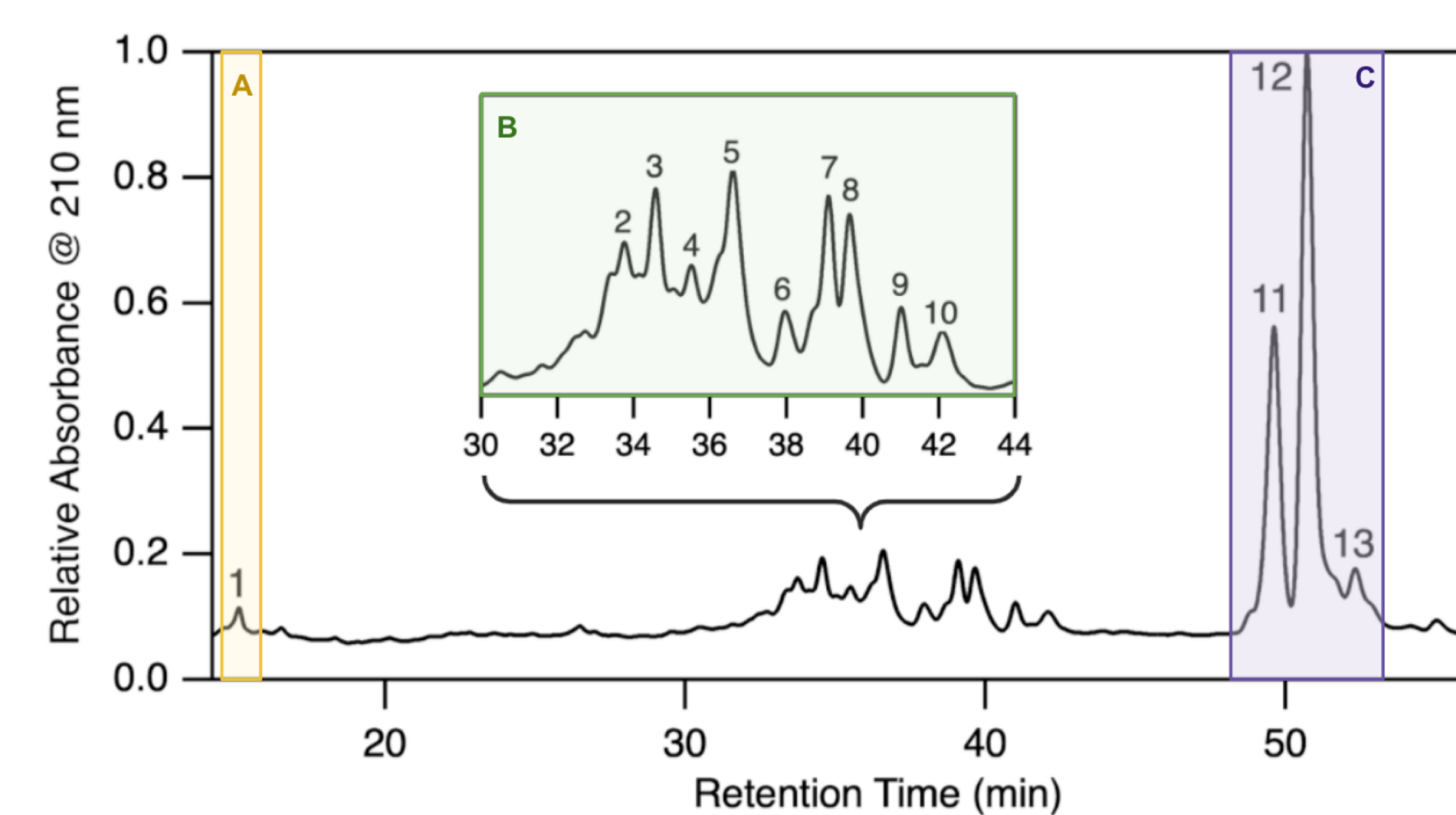
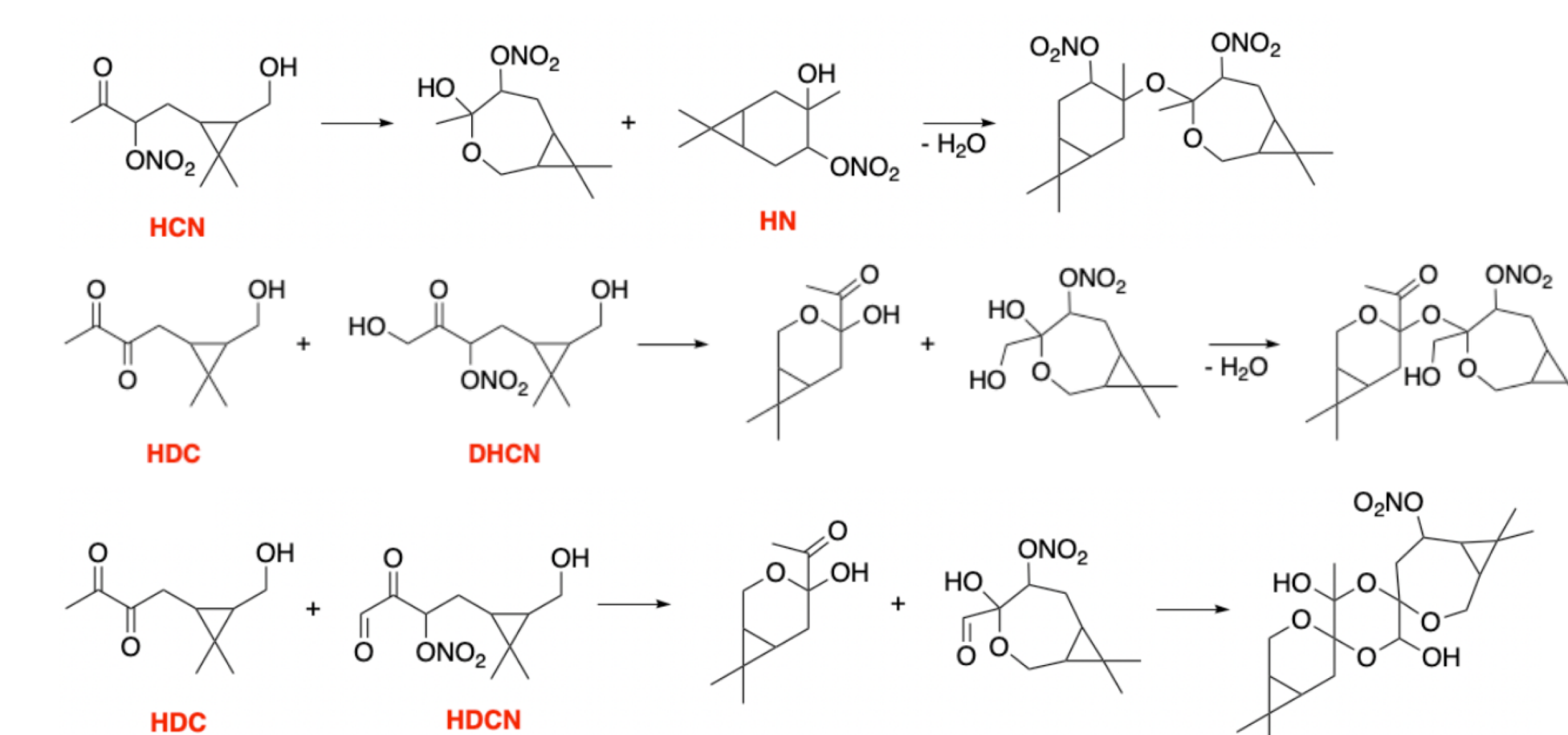


Figure 3. HPLC of SOA from Δ -3-carene + NO_3 radical



Scheme 2. Mechanism of acetal and hemiacetal dimers

- Only one monomer is present in the SOA- HNA shown in Figure 4a
- Most of the products are acetal or hemiacetal dimers, some of which are shown in Scheme 2
- The widest region on the chromatogram has many over-lapping peaks, which make it difficult to identify individual products, Figure 4b
- The largest peaks are 11 and 12, which we have identified as configurational isomers, Figure 4c
- Peak 13 was identified as the same gas-phase ROOR dimer seen in the I-CIMS. It has a similar structure to the isomers in peaks 11 and 12, so we verified the ROOR structure by selectively reacting away peroxides², which only affected peak 13

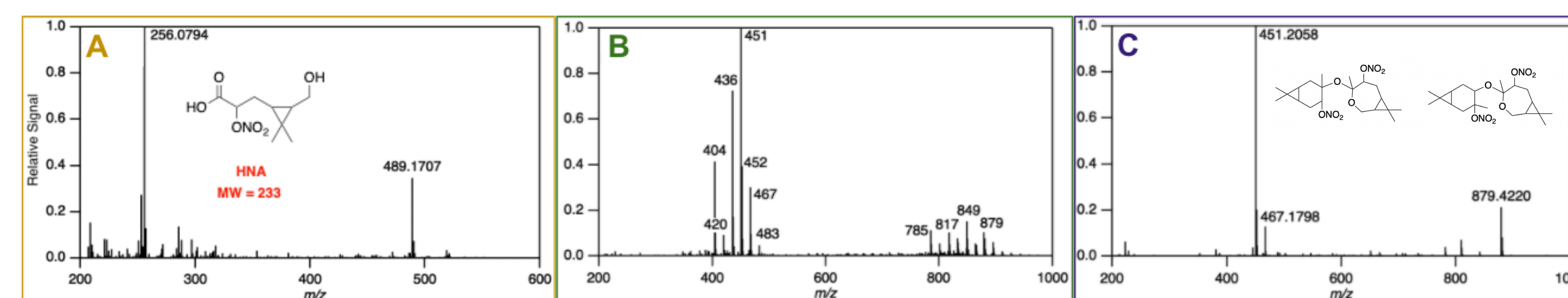
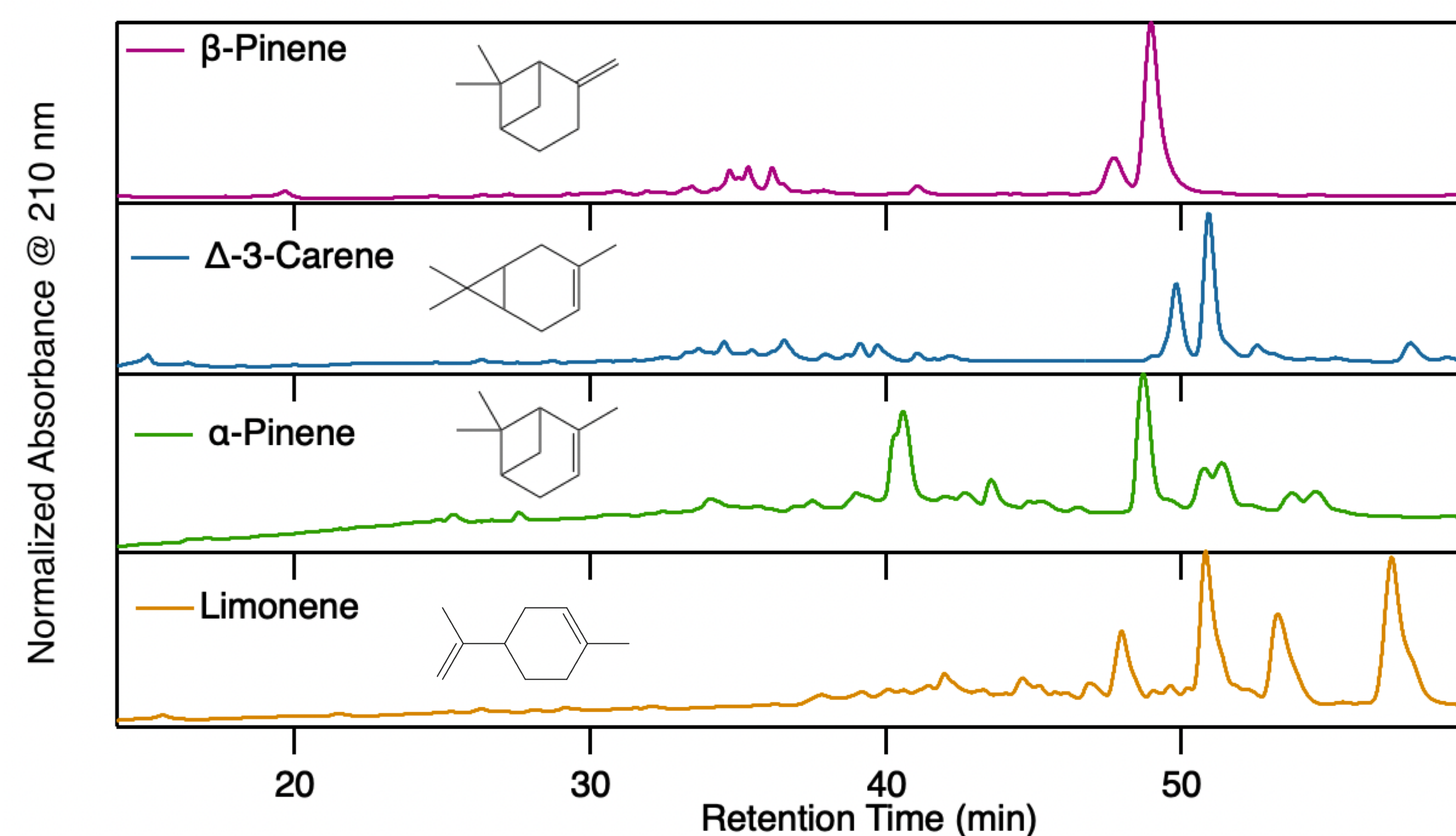


Figure 4. ESI-MS of different regions on the HPLC

Future Work: Comparing to Other Monoterpenes



Functional Group	Mol FG / C ₁₀			
	Δ -3-Carene	β -Pinene	α -Pinene	Limonene
Nitrate	0.87	1.12	0.71	1.05
Carbonyl	0.48	0.43	0.18	0.17
Hydroxyl	0.20	0.00	0.05	0.02
Carboxyl	0.23	0.06	0.00	0.00
Ester	0.20	0.01	0.04	0.17
Peroxide	0.12	0.02	0.01	0.03
Total FG	2.11	1.64	1.00	1.44
Methylene	7.89	8.37	9.00	8.56
Avg MW	221	217	188	213

Moving forward, we hope to expand this analysis to other high-emission monoterpenes and learn about the limits of acetal and hemiacetal formation in SOA. In addition, we are studying the mechanisms of OH/ NO_x oxidation of monoterpenes, since those reactions should generate similar organic nitrate products but take place under very different atmospheric conditions.

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