Development and Application of a Mass Spectra-Volatility Database of Combustion and Secondary Organic Aerosol Sources for the Aerodyne Aerosol Analysis Mass Spectrometer

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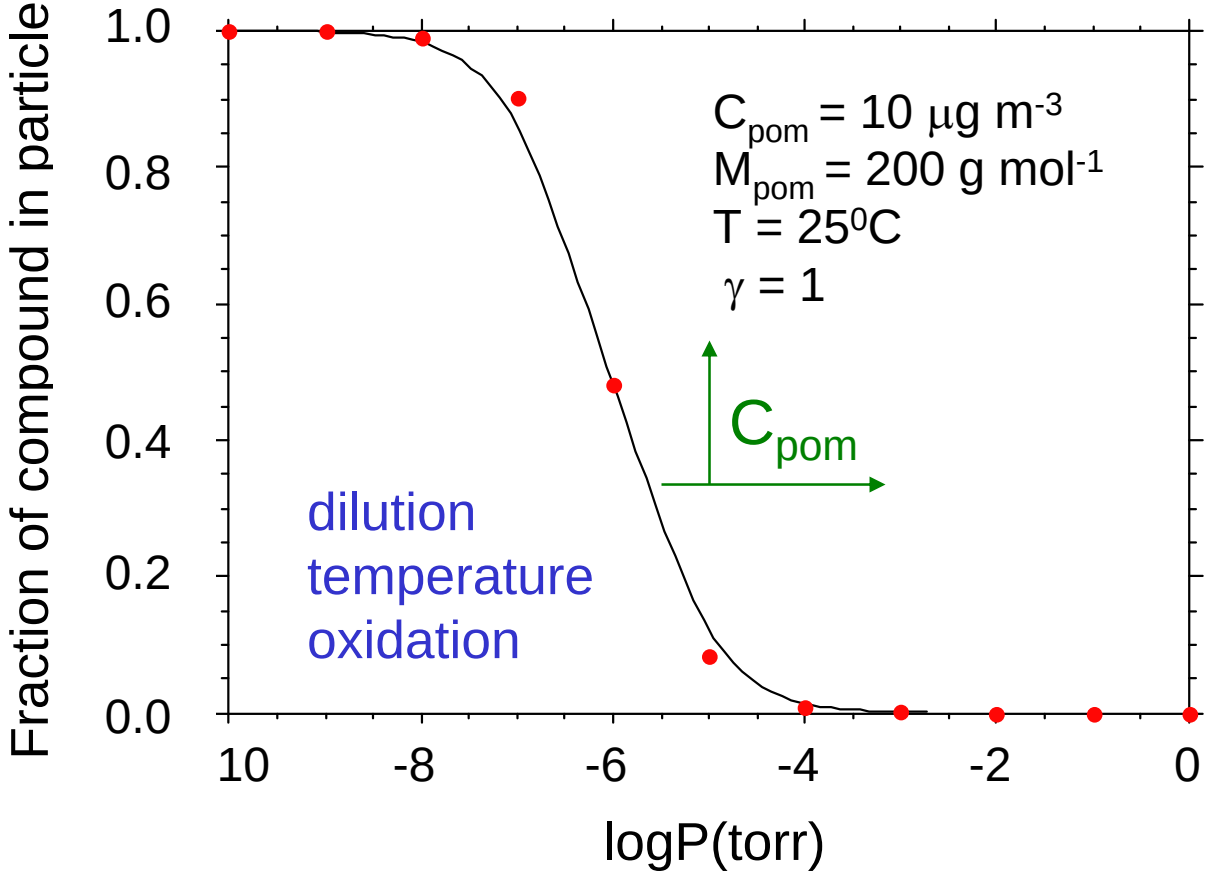
Outline

- Effect of gas-particle partitioning/volatility on organic aerosol formation
- Basis for proposed research
- Thermodenuder characterization
- Laboratory studies
- Field studies
- Conclusions
- Future plans

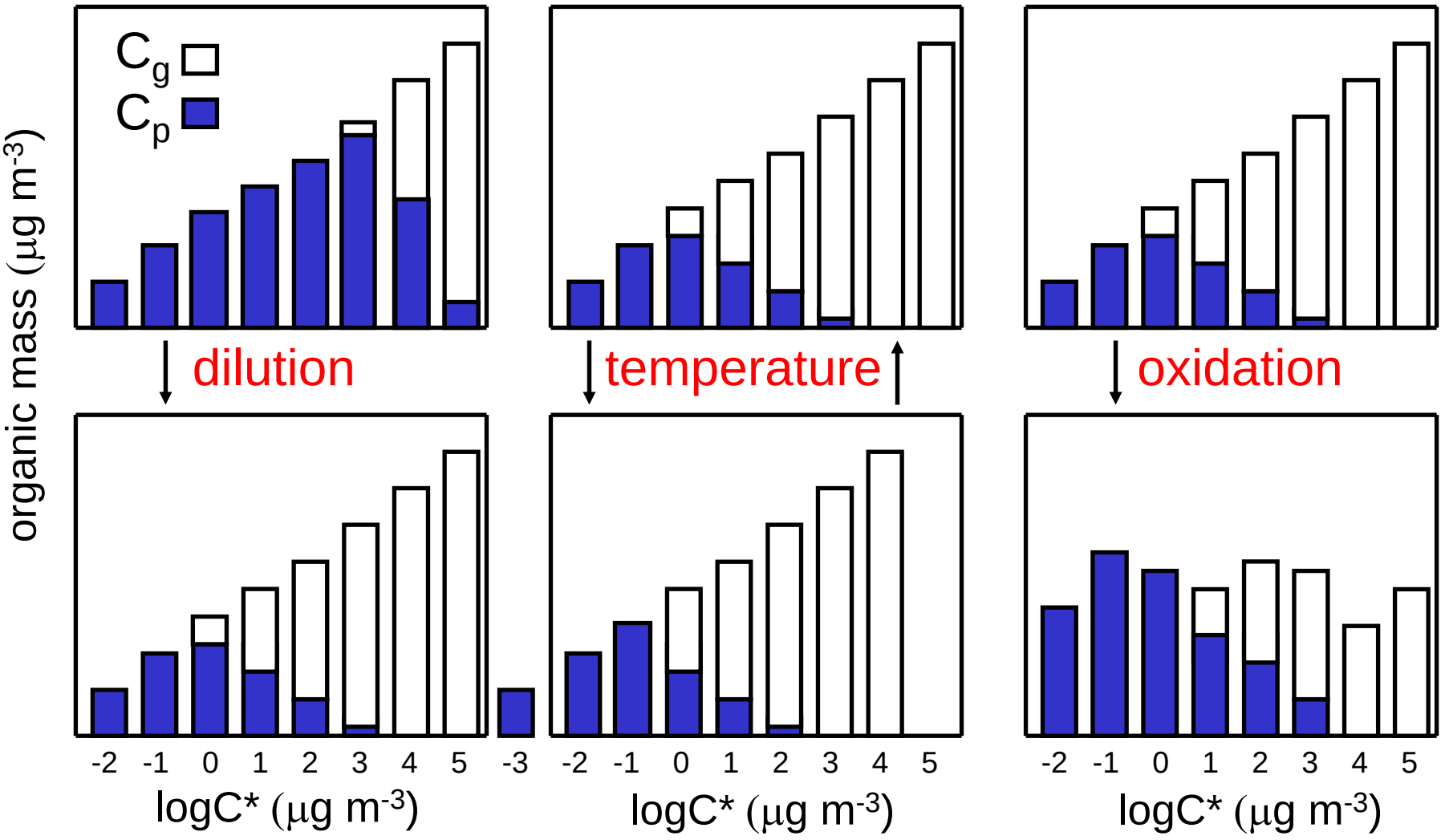
Organic Gas-Particle Partitioning

$$C_p/C_T = [1 + (M_{pom}\gamma P^o/RT)/C_{pom}]^{-1}$$

C^*

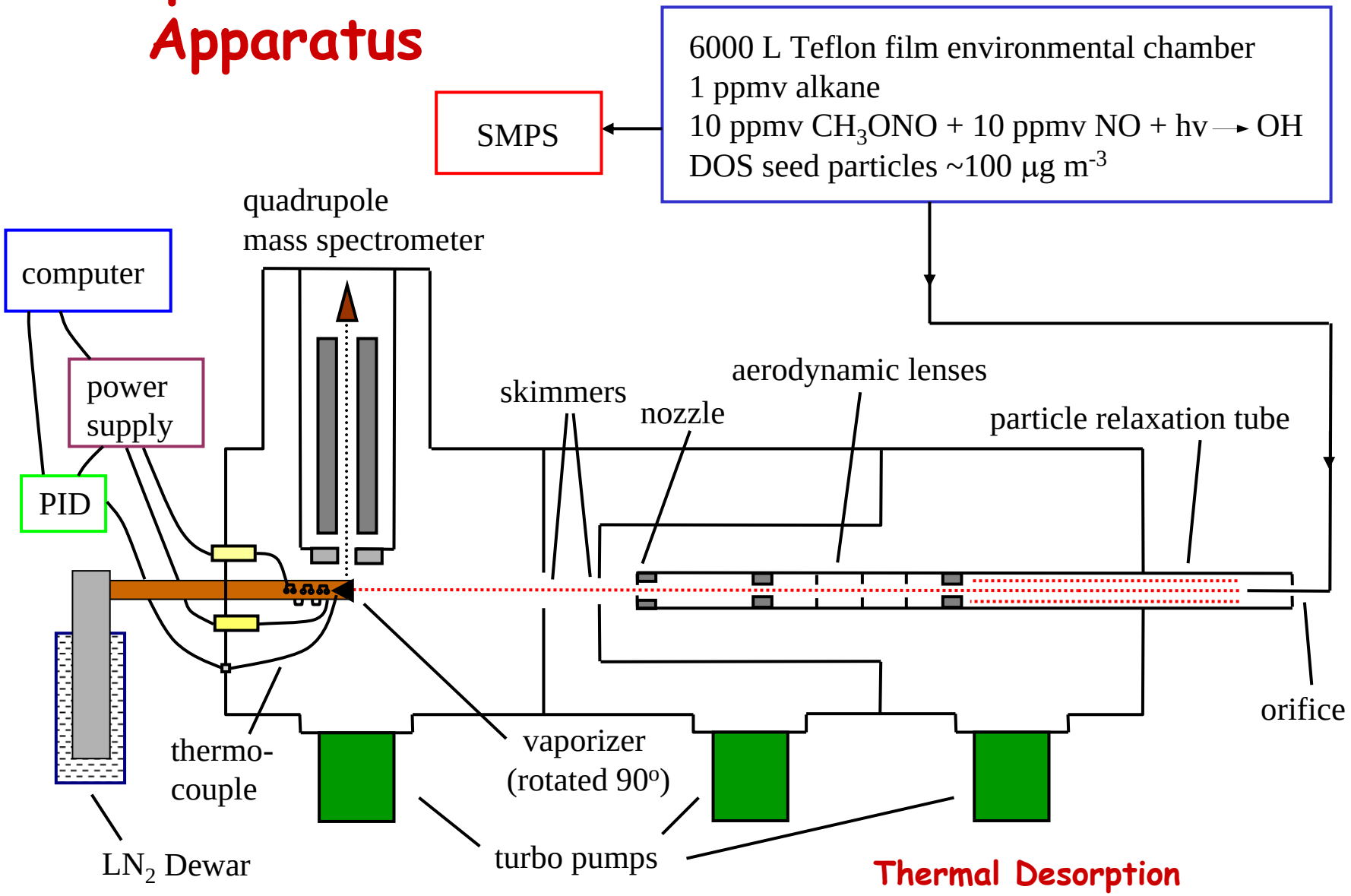


Effects of Dilution, Temperature, and Oxidation on Organic Gas-Particle Partitioning



Donahue et al. *Env. Sci. Technol*. 40, 2635 (2006)

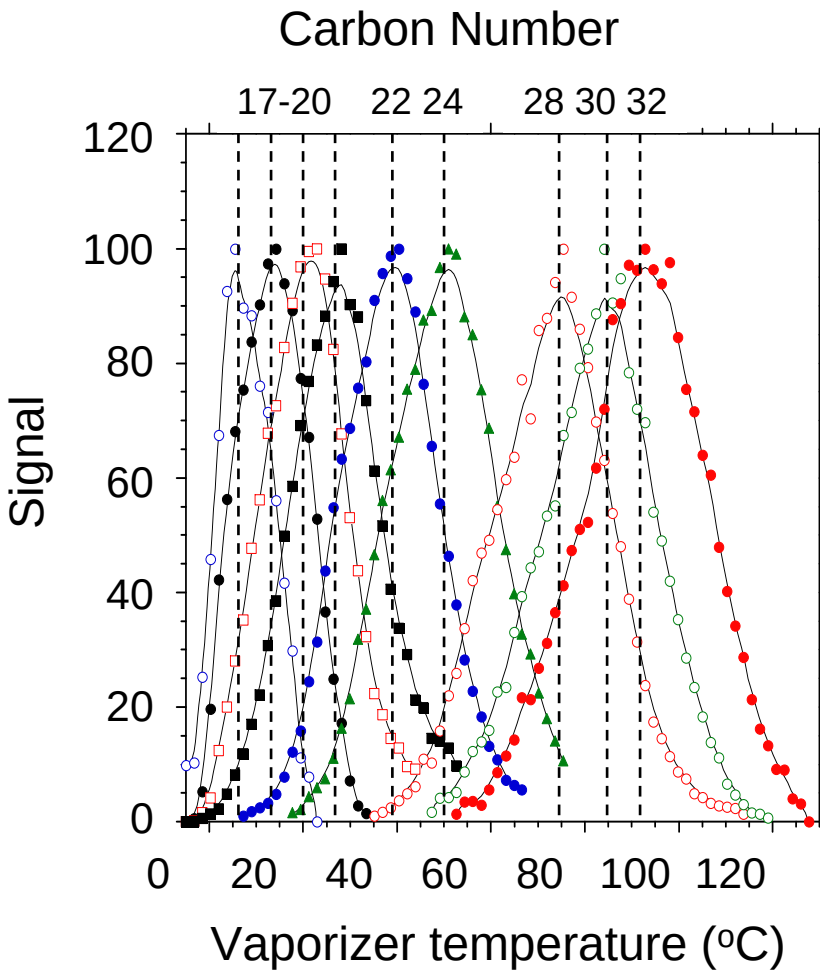
Experimental Apparatus



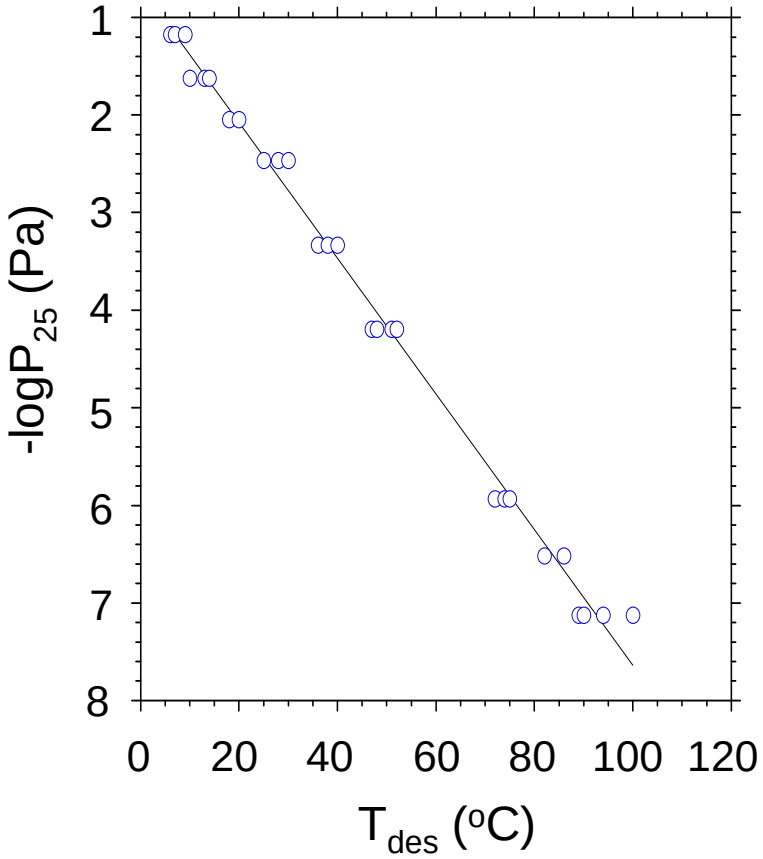
Thermal Desorption

Particle Beam Mass Spectrometer (TDPBMS)

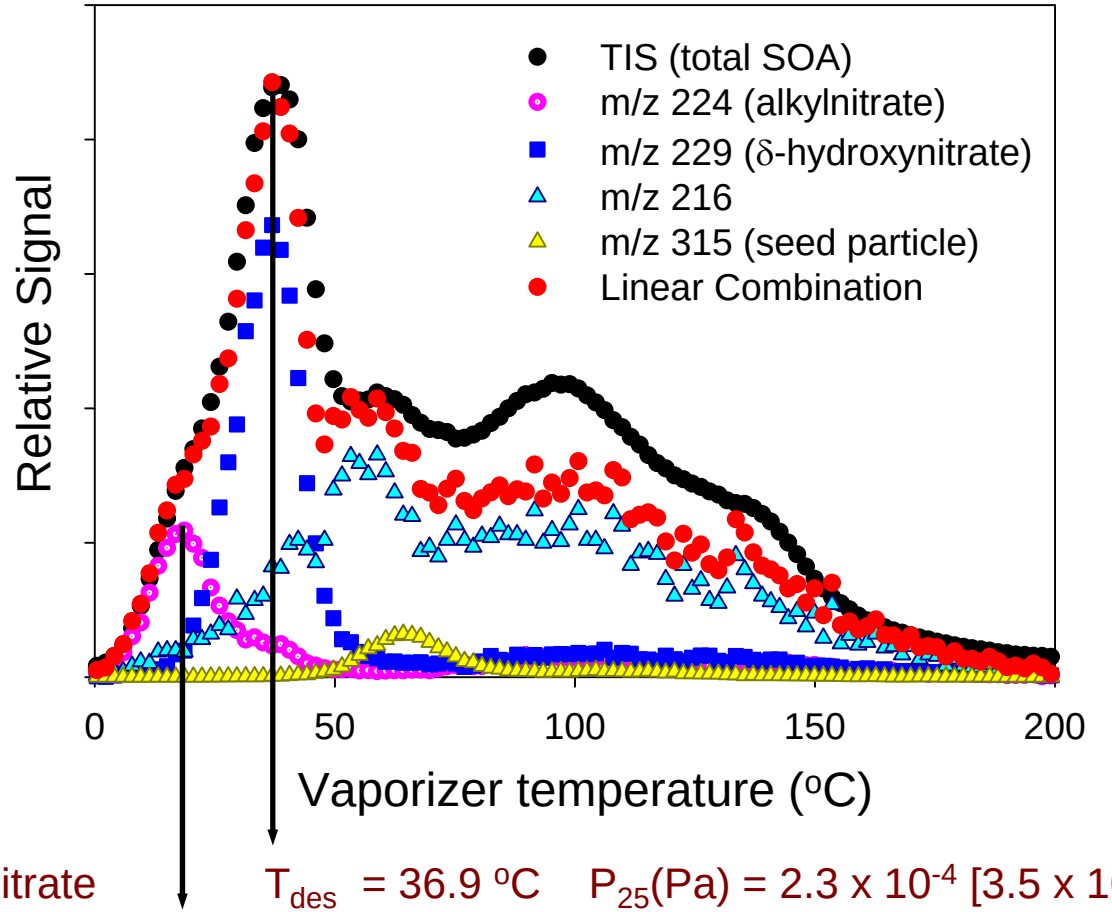
Temperature-Programmed Thermal Desorption of C_{17}-C_{32} *n*-Alkanes



$\log P_{25}(Pa) = -1.693 - 0.0694\ T_{des}(^{o}C)$



SOA Product Yield and Vapor Pressure from the Reaction of Hexadecane with OH/NO_x



δ-Hydroxynitrate T_{des} = 36.9 °C P_{25}(Pa) = 2.3×10^{-4} [3.5×10^{-4}]

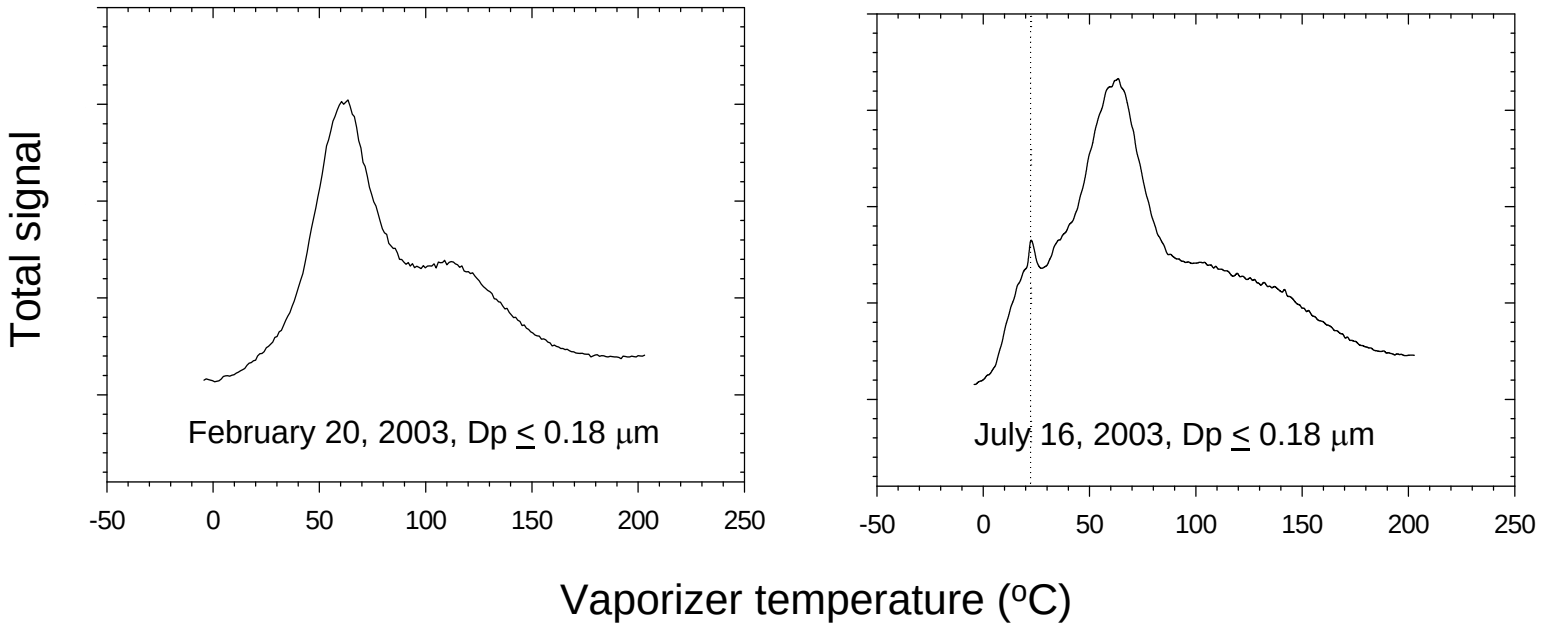
Alkyl nitrate T_{des} = 18.7 °C P_{25}(Pa) = 1.3×10^{-2} [8.3×10^{-3}]

$$\text{Mass fraction} = \frac{\text{Area under Single Ion Curve}}{\text{Area under TIS}} \rightarrow$$

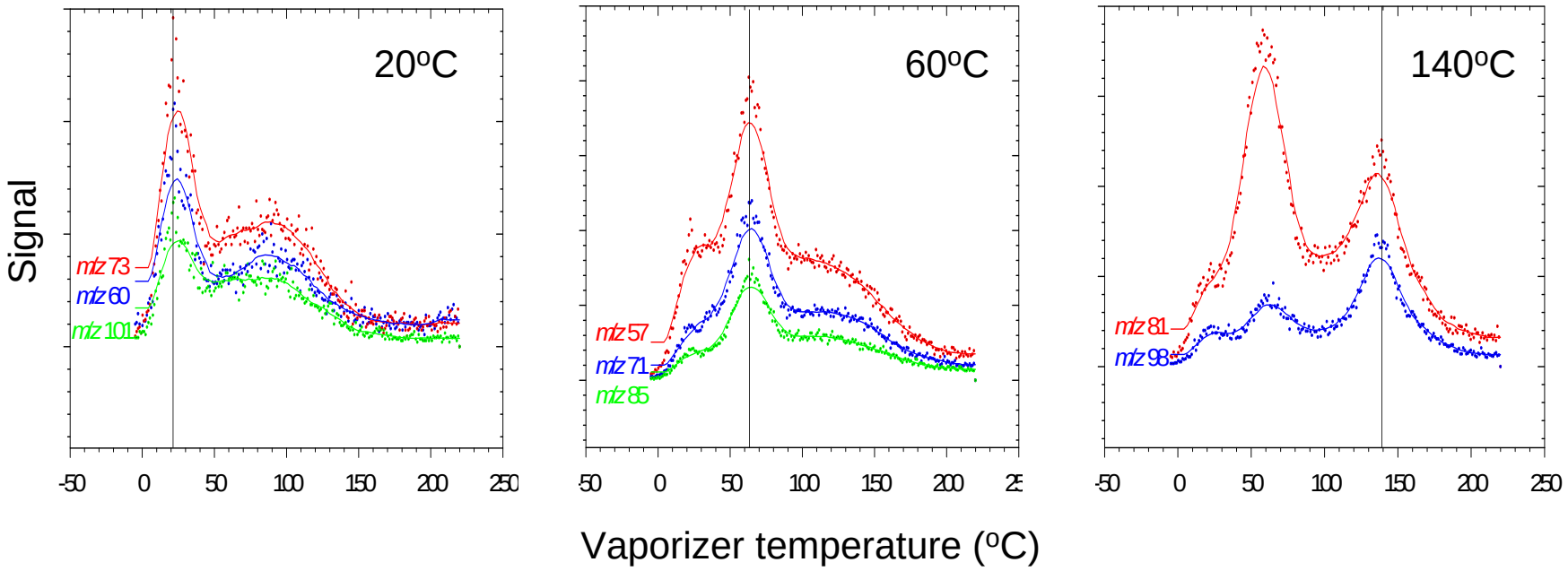
Alkynitrate = 0.08

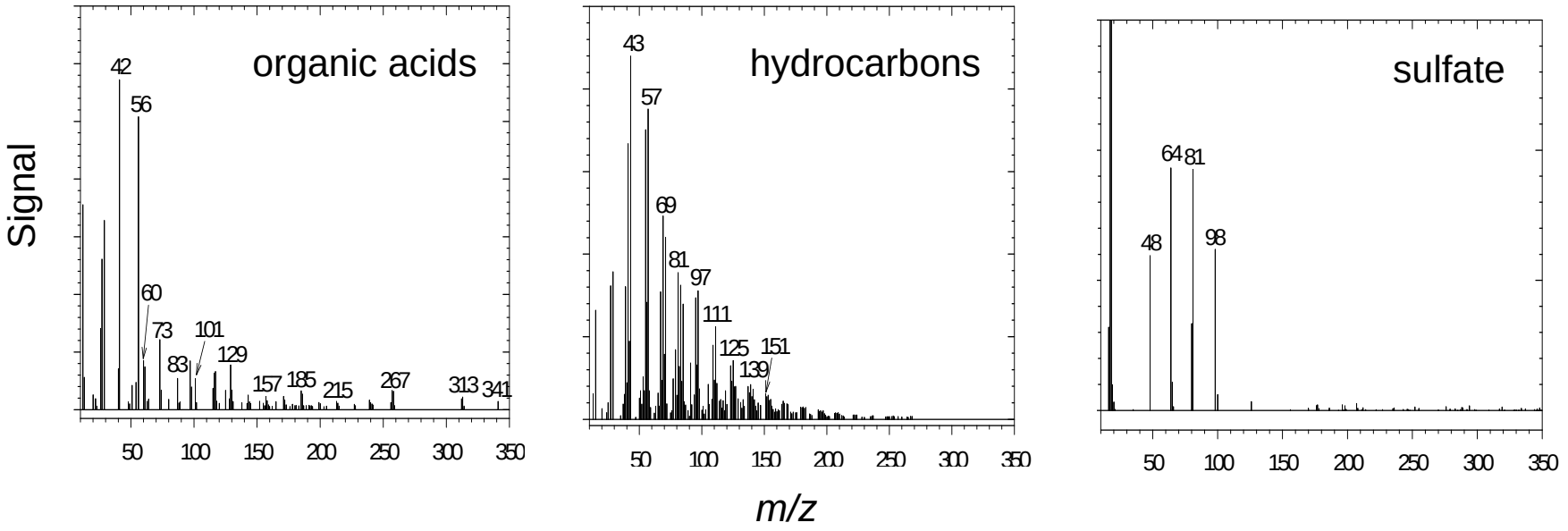
δ-Hydroxynitrate = 0.20

VACES-TPTD Ultrafines (D_p < 0.18 μm) Riverside, CA, February and July, 2003



VACES-TPTD, Ultrafines (<0.18 μm), Riverside July





Goal: Develop and apply a thermodenuder-Aerodyne Aerosol Mass Spectrometer (TD-AMS) technique for ambient organic PM-2.5 analysis

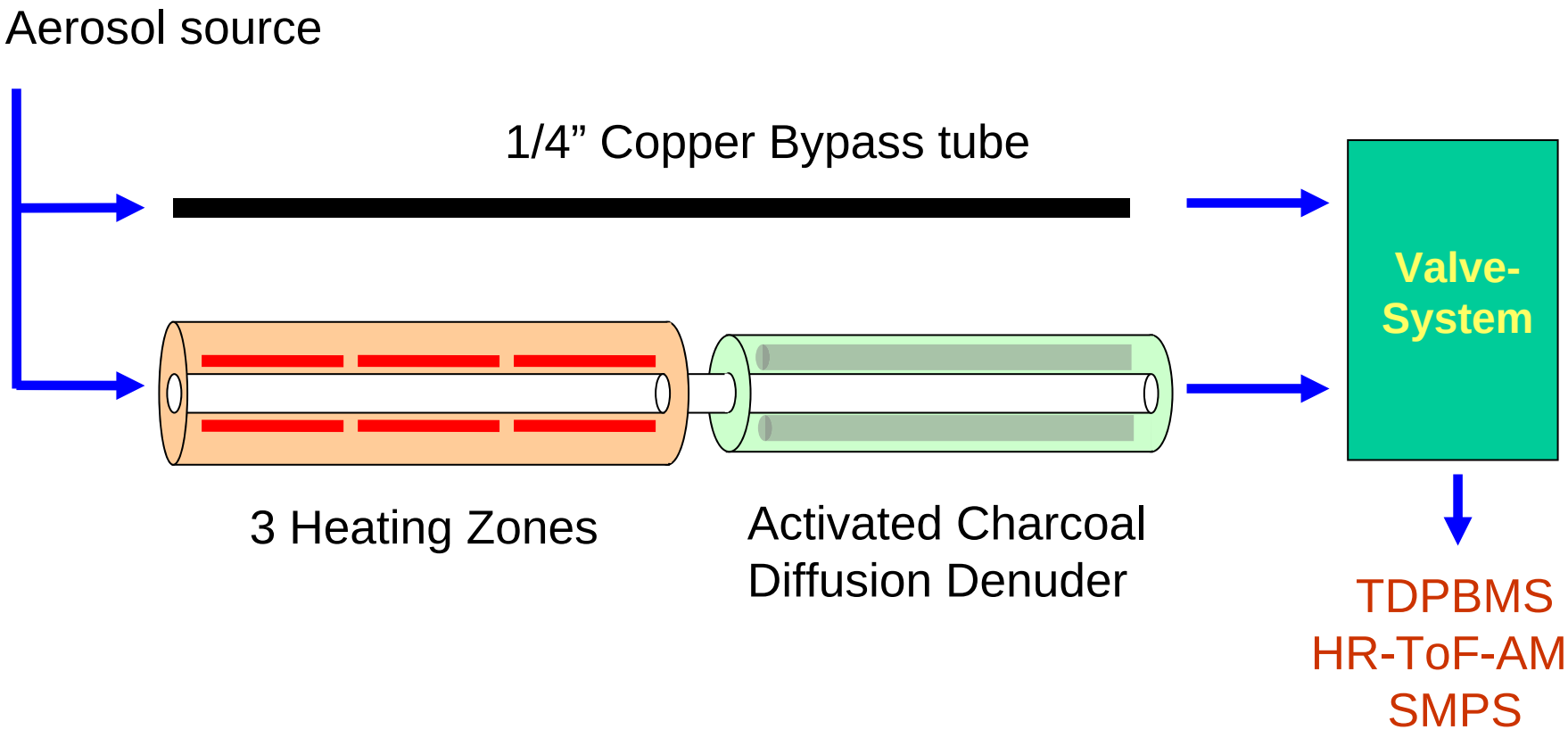
Specific Objectives:

1. Construct and couple a thermodenuder to the AMS and optimize and evaluate its performance.

2. Use the TD-AMS (and TD-TDPBMS) in laboratory studies to develop a mass spectral-volatility database for major atmospheric sources of secondary organic aerosol and combustion aerosol.

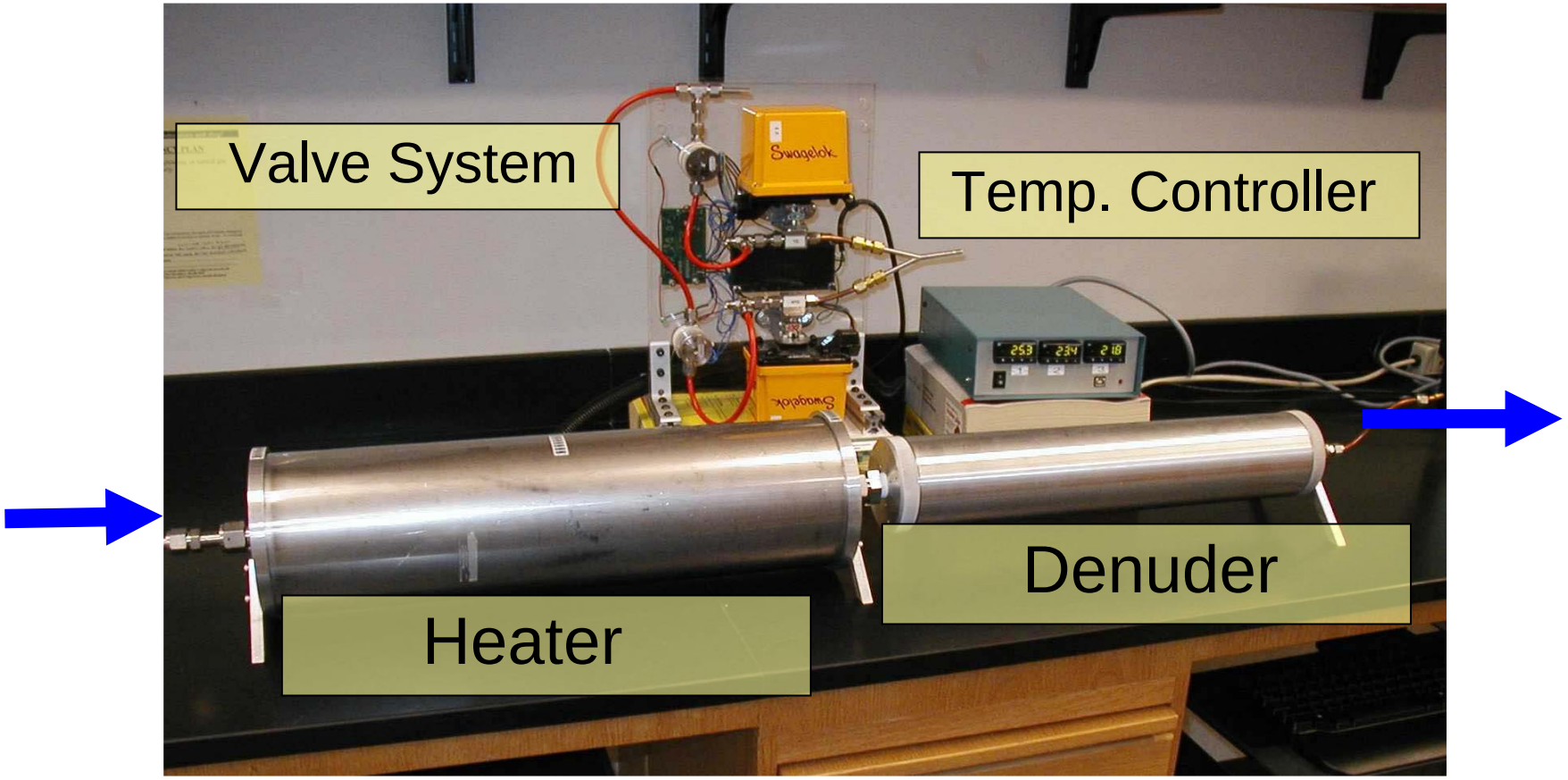
3. Apply the TD-AMS technique and database to a study of organic aerosol in the Los Angeles Air Basin (and other targets of opportunity).

Thermodenuder-AMS Apparatus

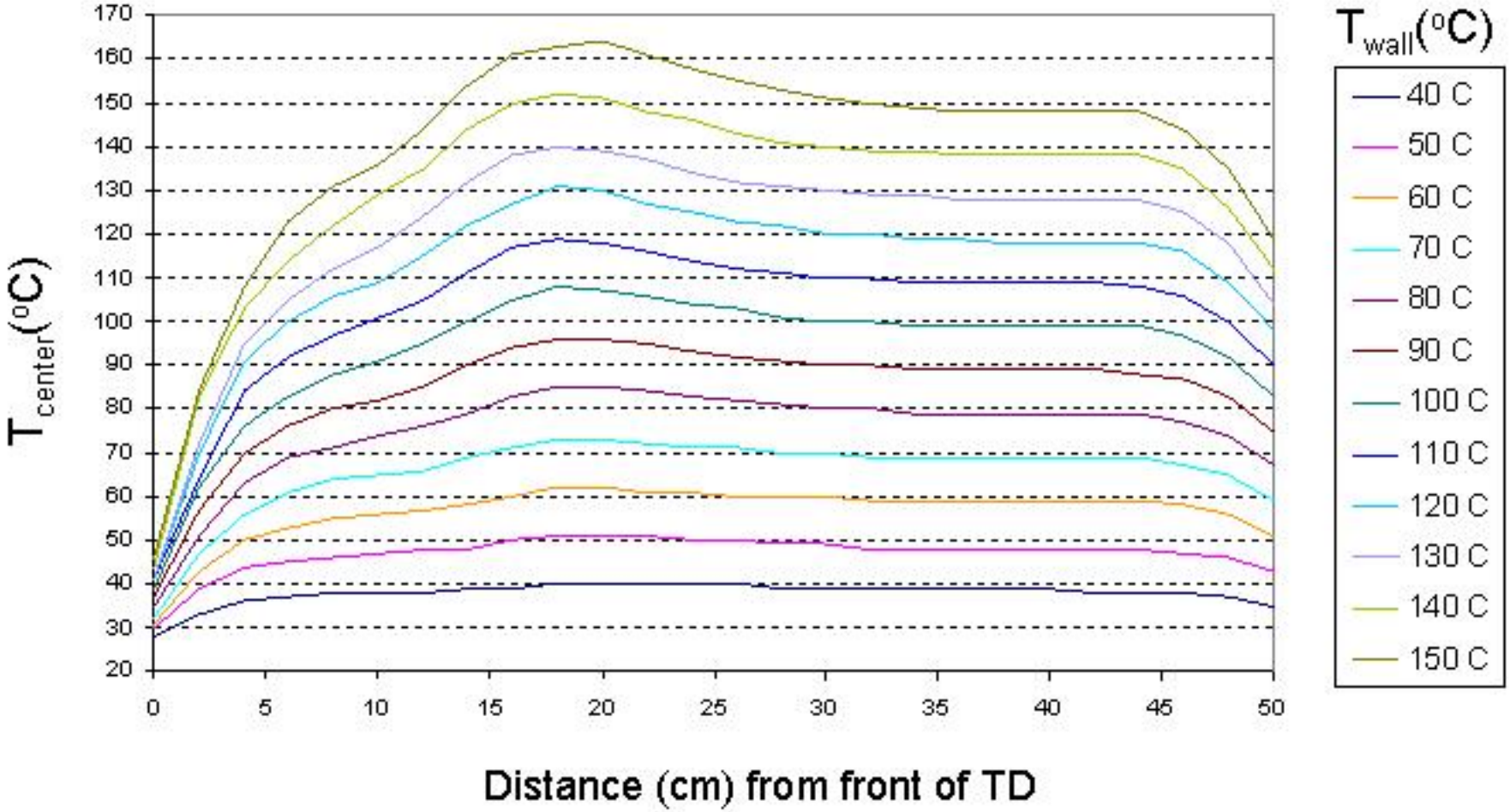


- AMS or TDPBMS detects remaining particle mass
- Ambient / TD alternately every 10 min
- Heater temp. ramps between 50 – 200 ^{o}C

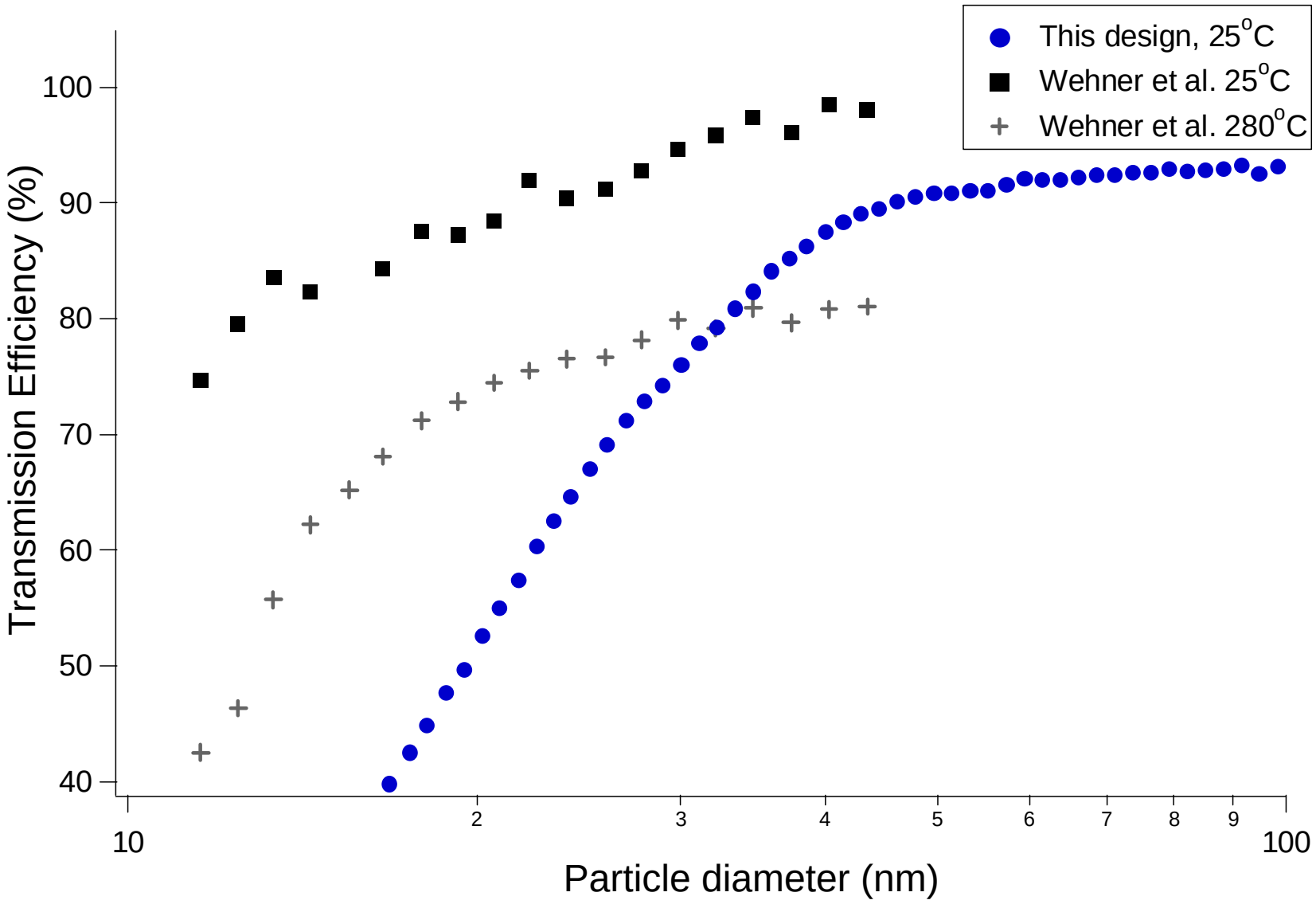
Thermodenuder



TD Temperature Profiles

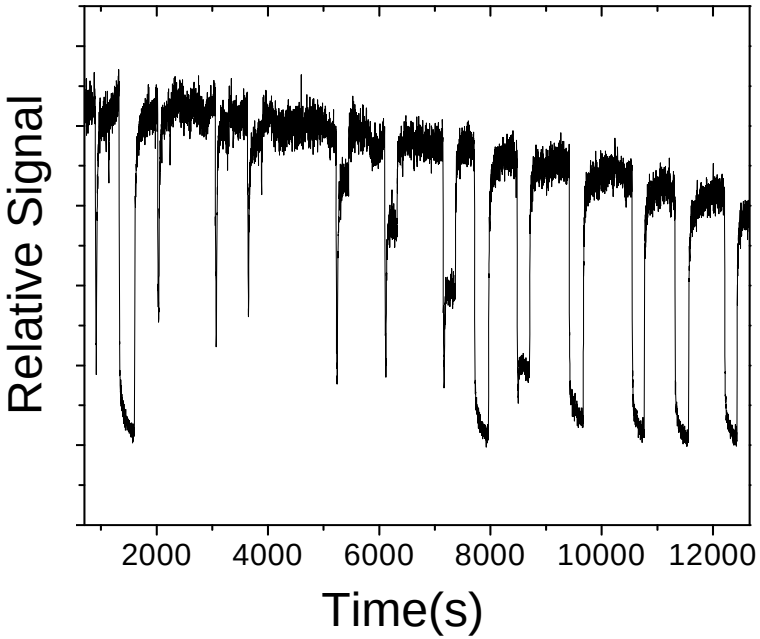


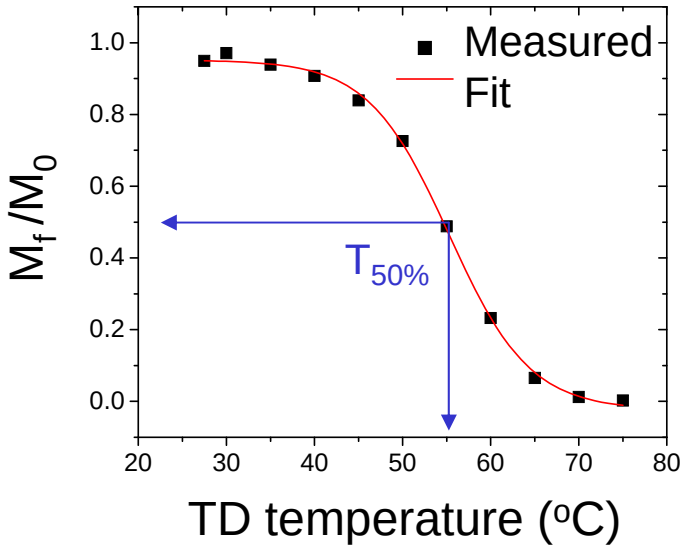
TD Particle Transport Efficiencies

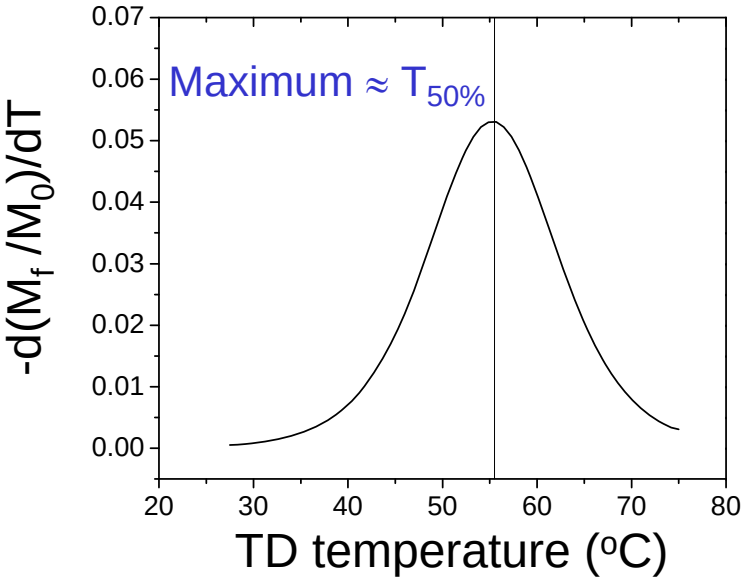


TD Measurement and Data Analysis

Adipic acid
C6 diacid

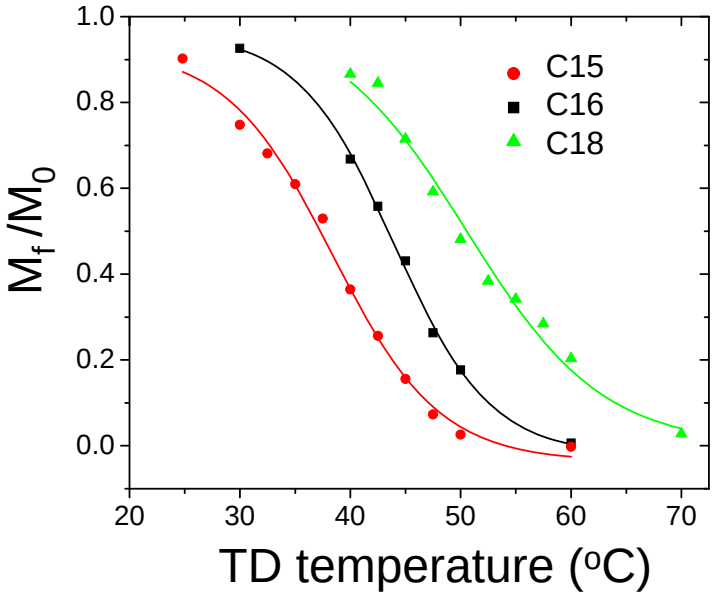




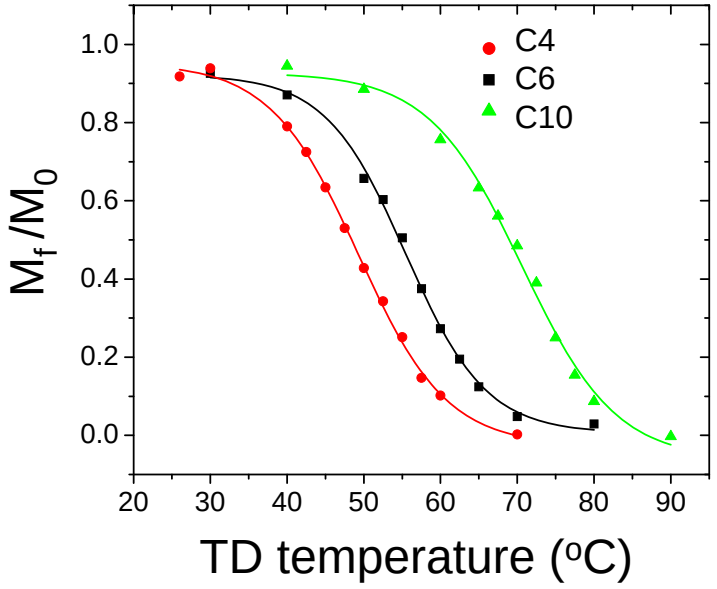


TD Evaporation of Standard Compounds

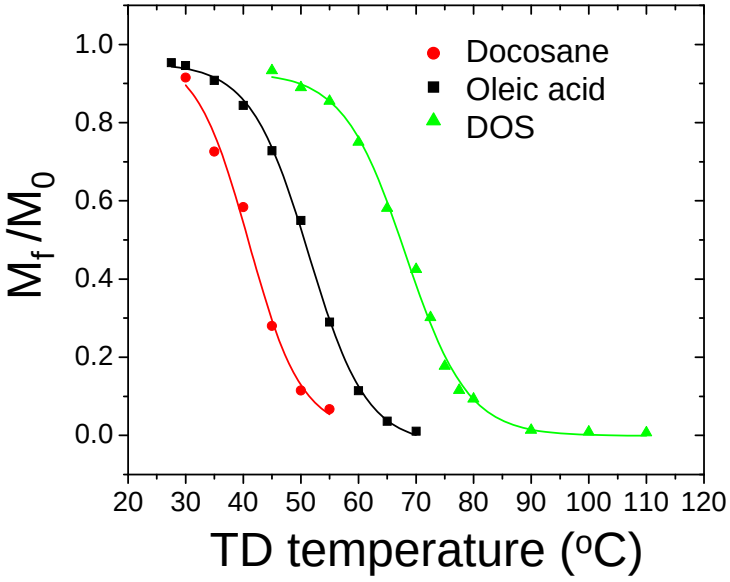
Monoacids



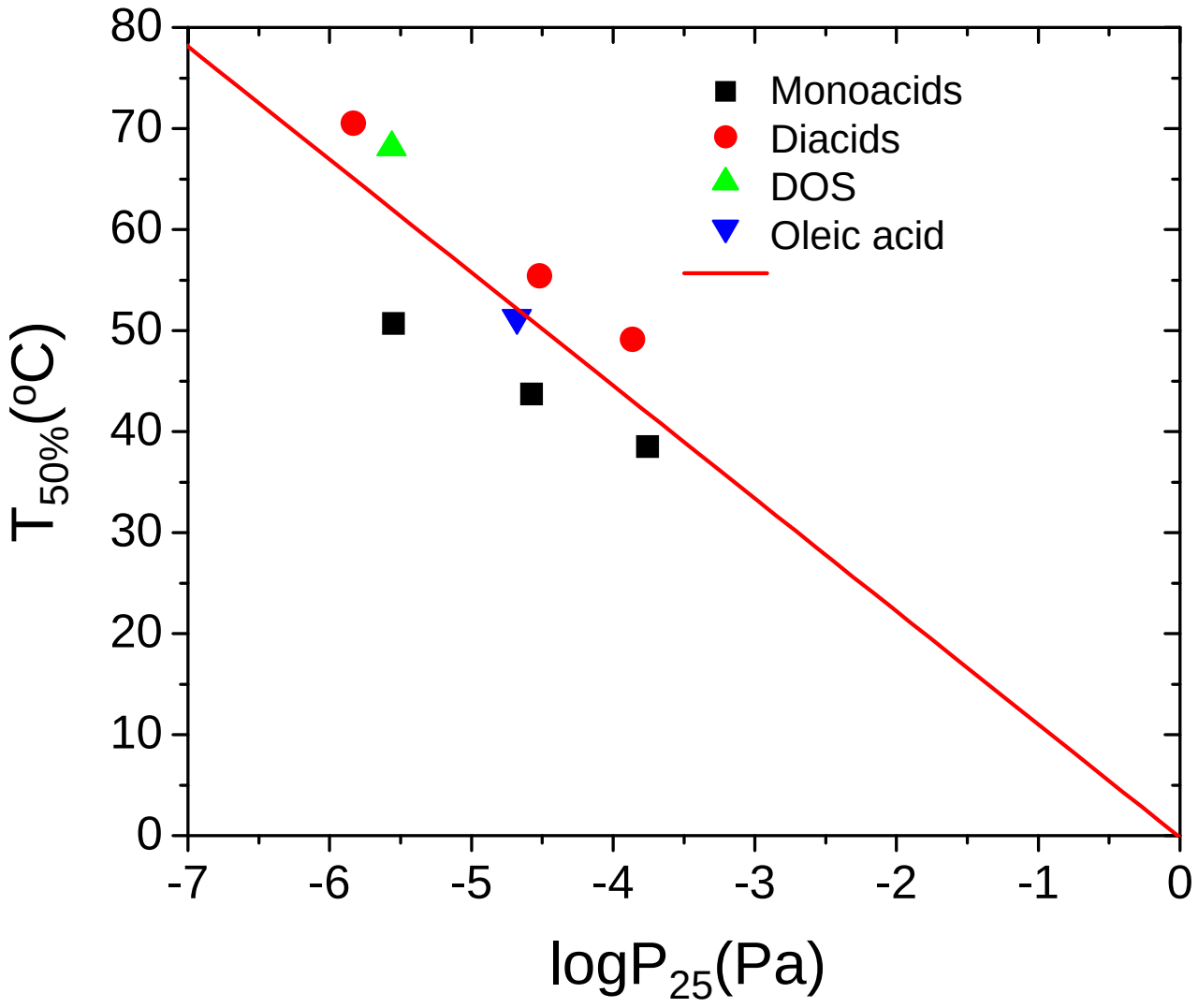
Diacids



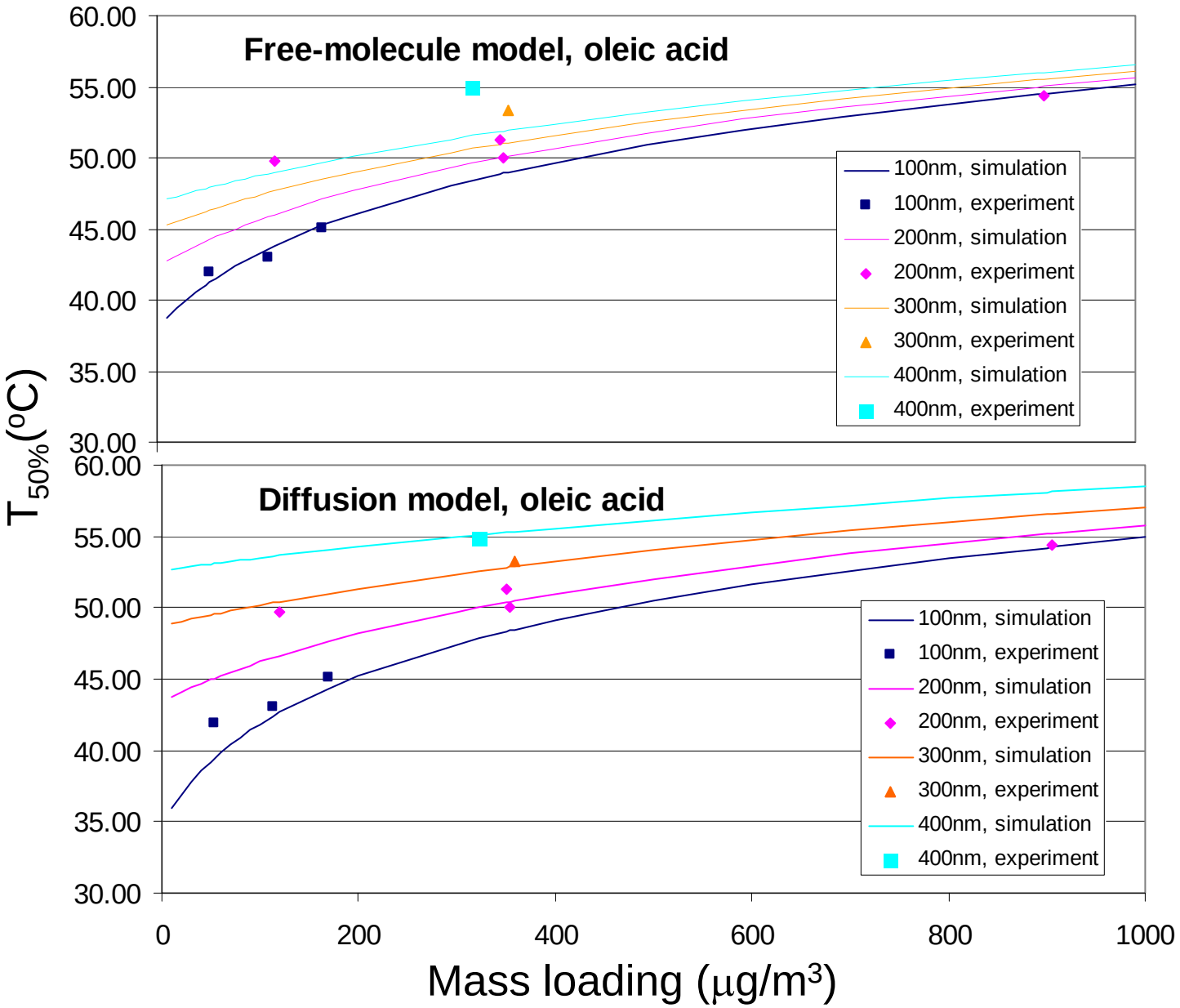
Liquid Alkane, Monoacid, Diester



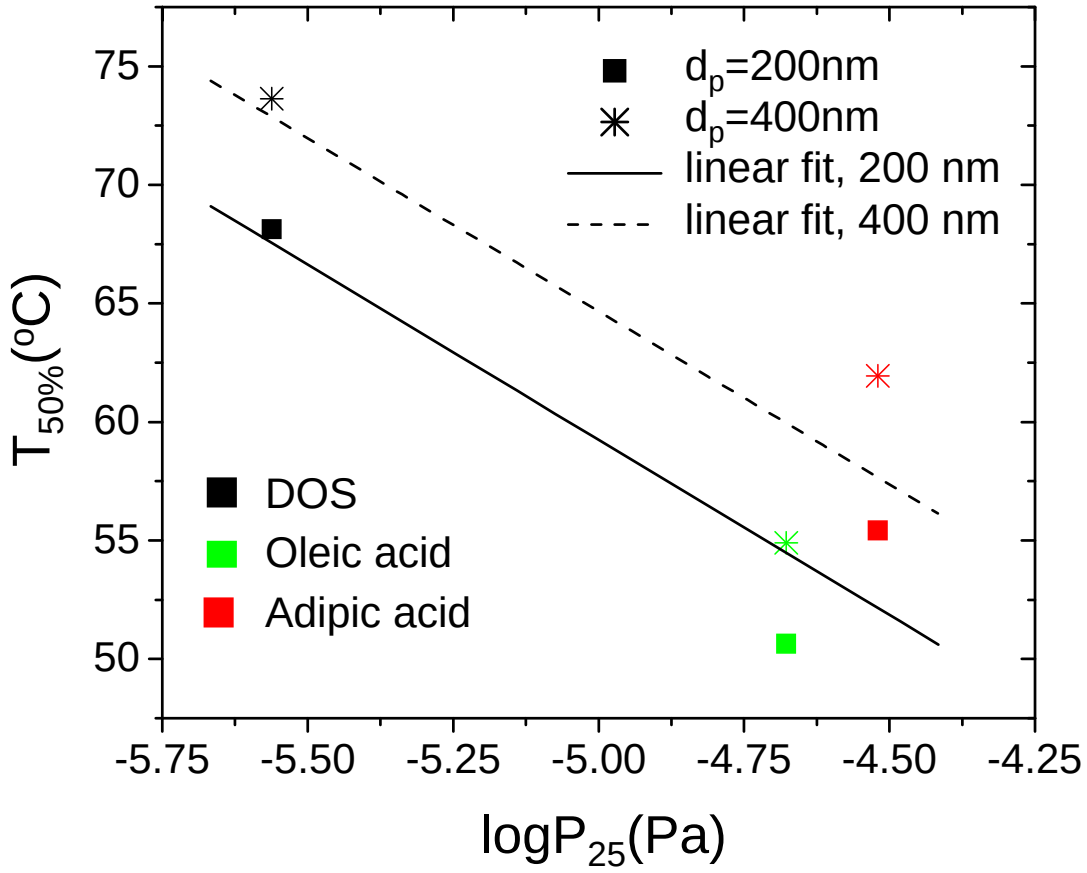
$T_{50\%}$ vs. $\log P_{25}$ Calibration Curve



Effect of particle diameter and mass loading on $T_{50\%}$

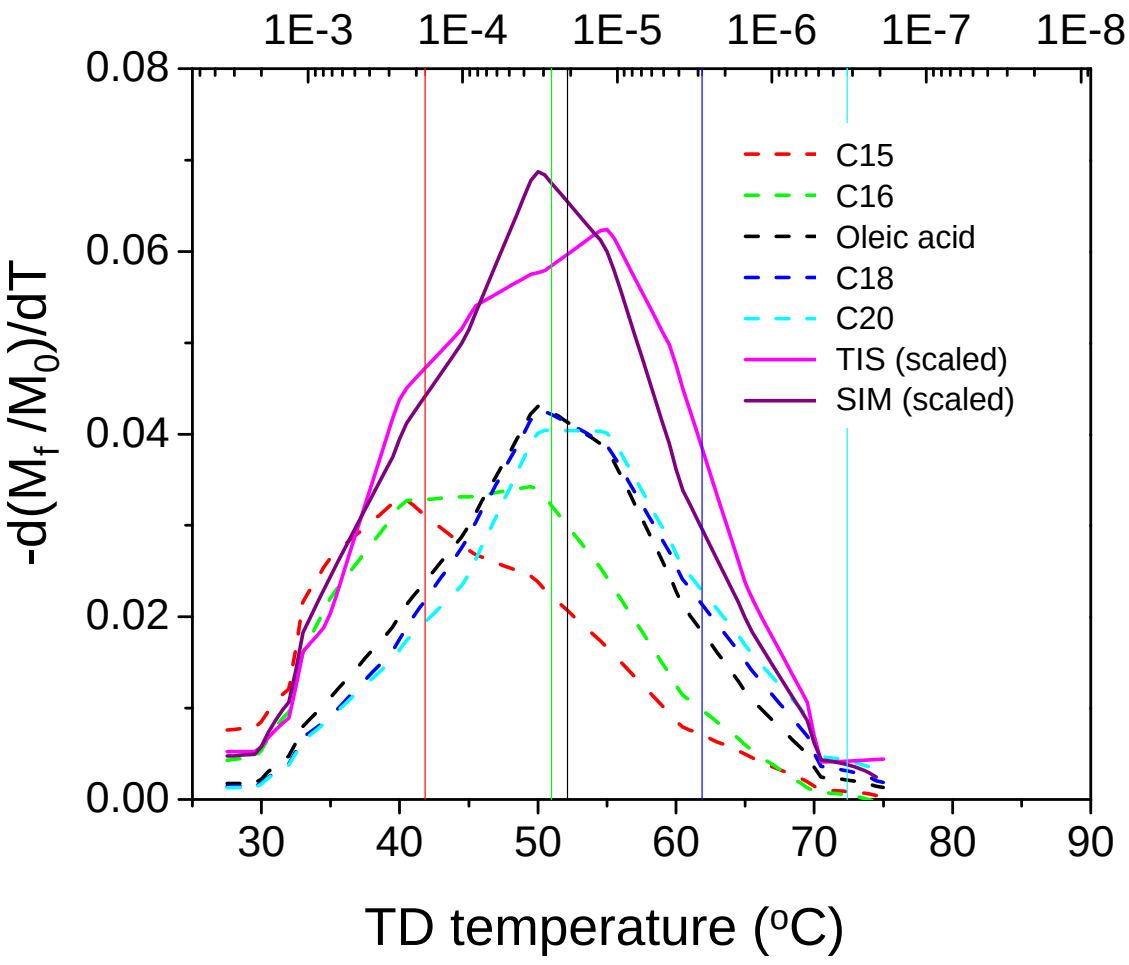


Effect of particle diameter on $T_{50\%}$ to log P_{25} conversion



mass loading
~300 μg/m³

Distribution of Vapor Pressures (P_{25}) Measured by TD for a Monoacid Mixture

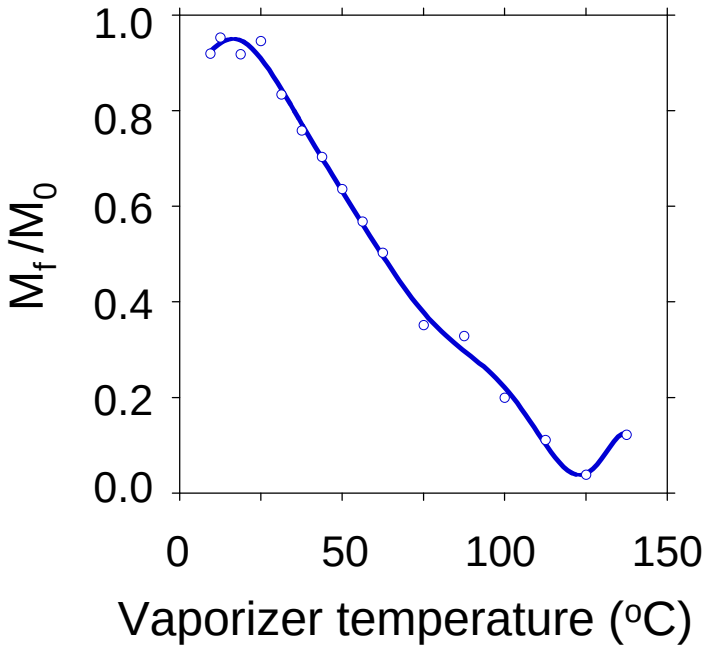


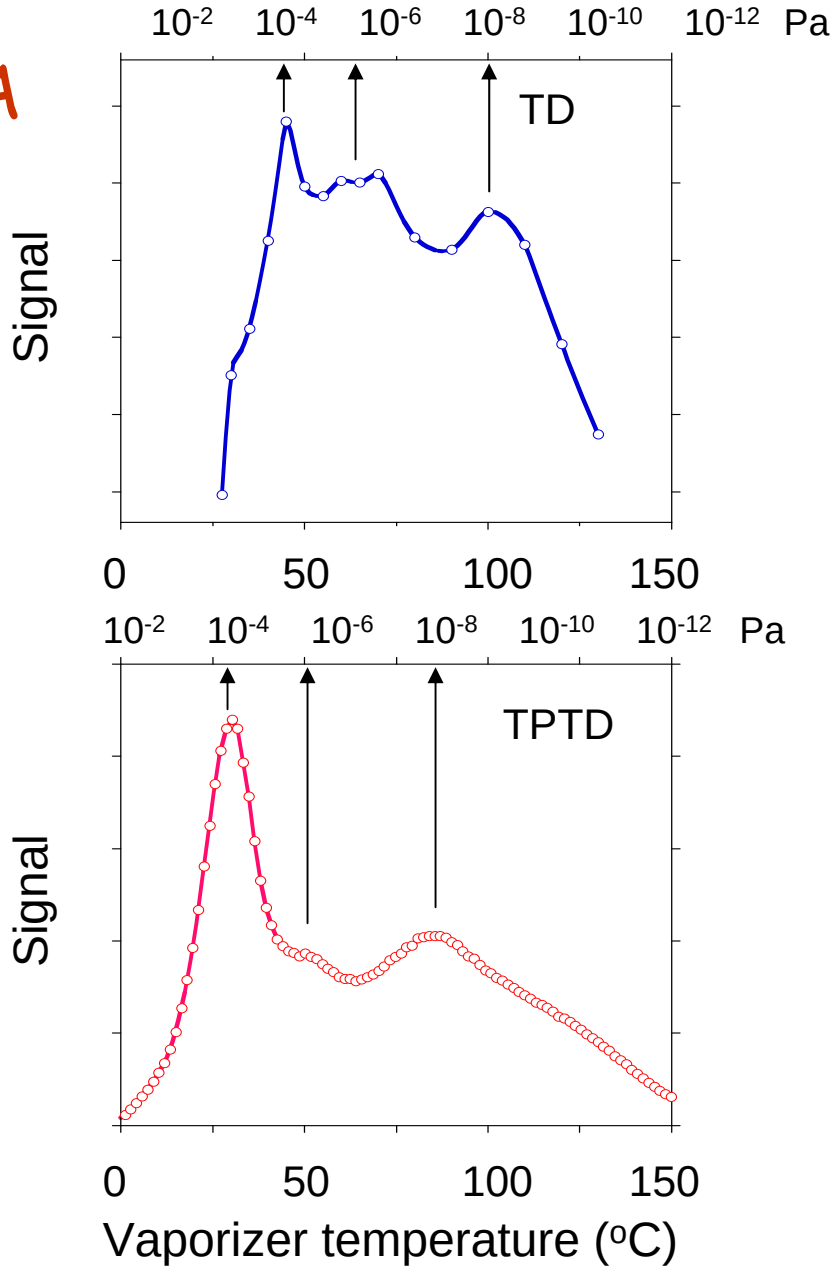
Particle properties

- oleic acid + C15, C16, C18, C20 saturated monoacids
- 0.5:4 x 0.125 mole fractions
- diameter = 200 nm

Vertical lines = P_{25} literature

TD and TPTD Analysis of Pentadecane + OH/NO_x SOA



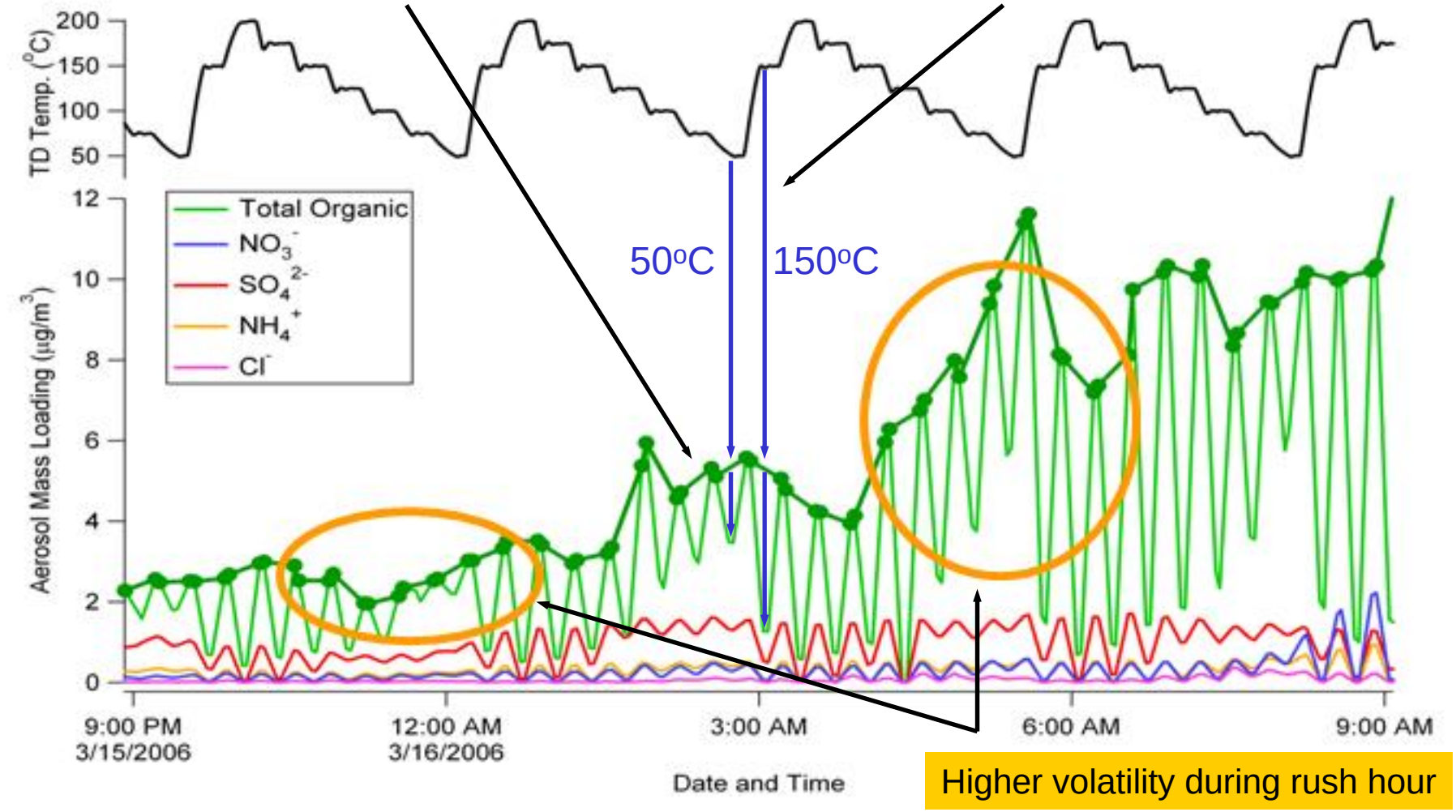



TD-AMS Applications and Field Studies

Rapid TD-AMS Analysis of Chemical Composition and Volatility

Ambient concentration not changing quickly

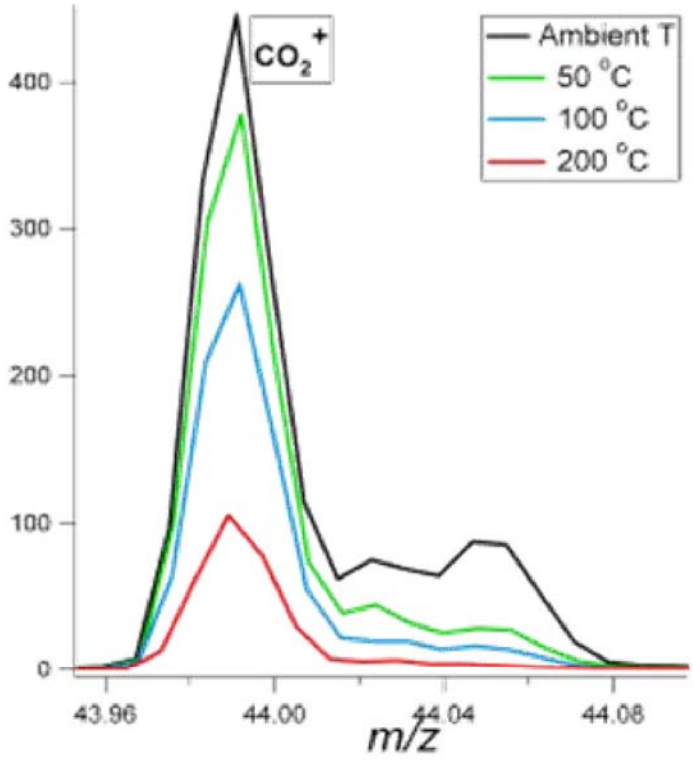
More mass lost at higher TD temperatures



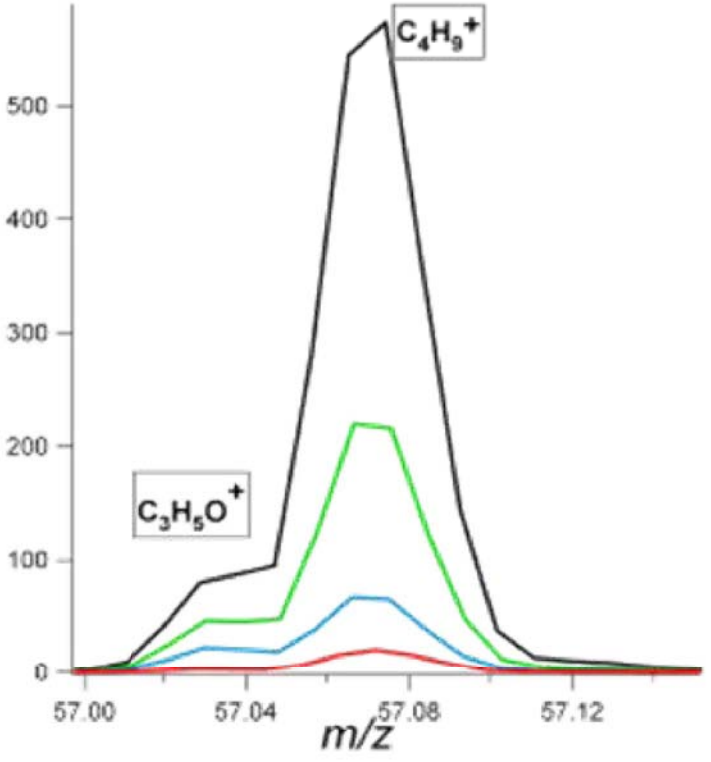
Higher volatility during rush hour

High Resolution AMS Tracers

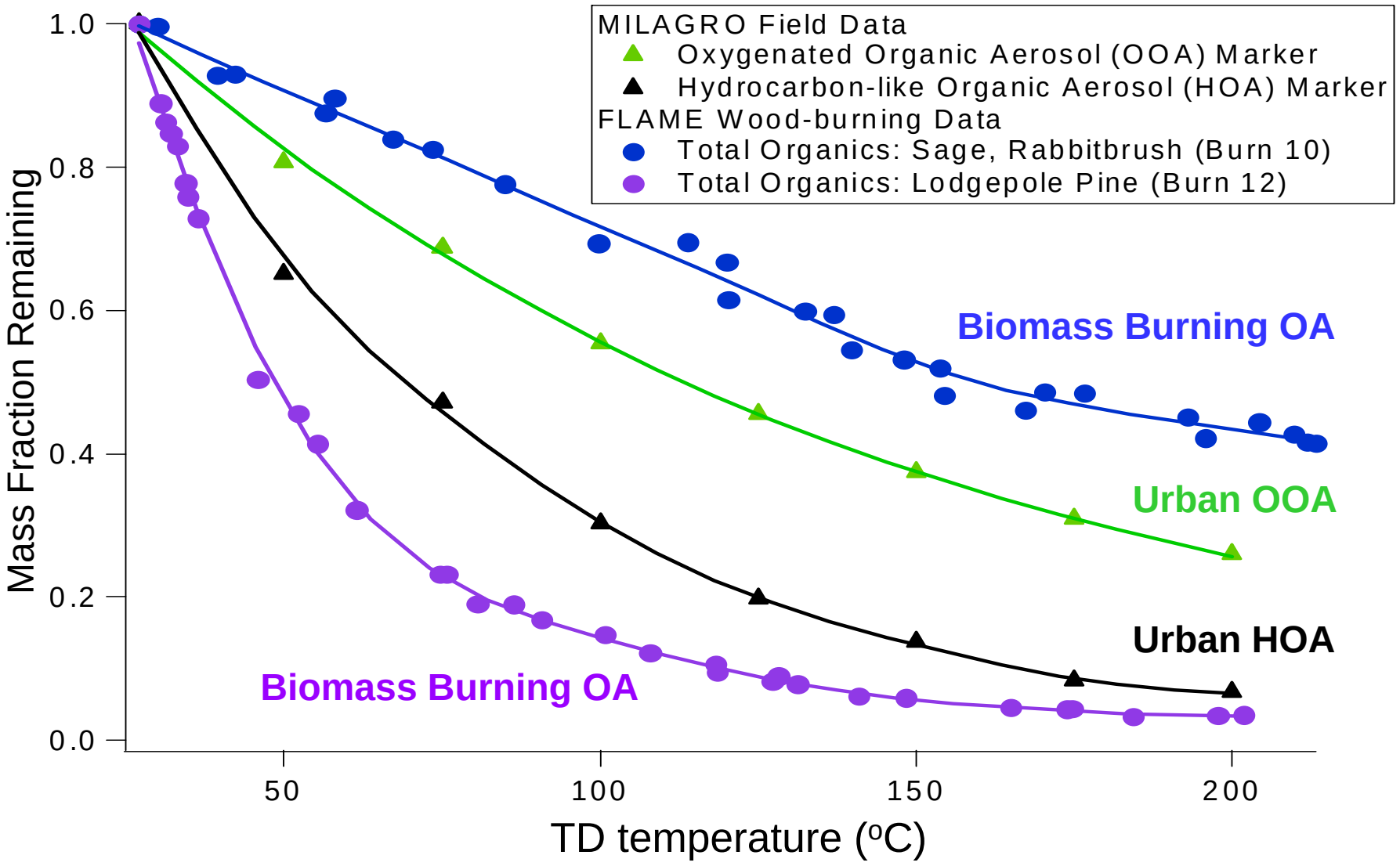
OOA



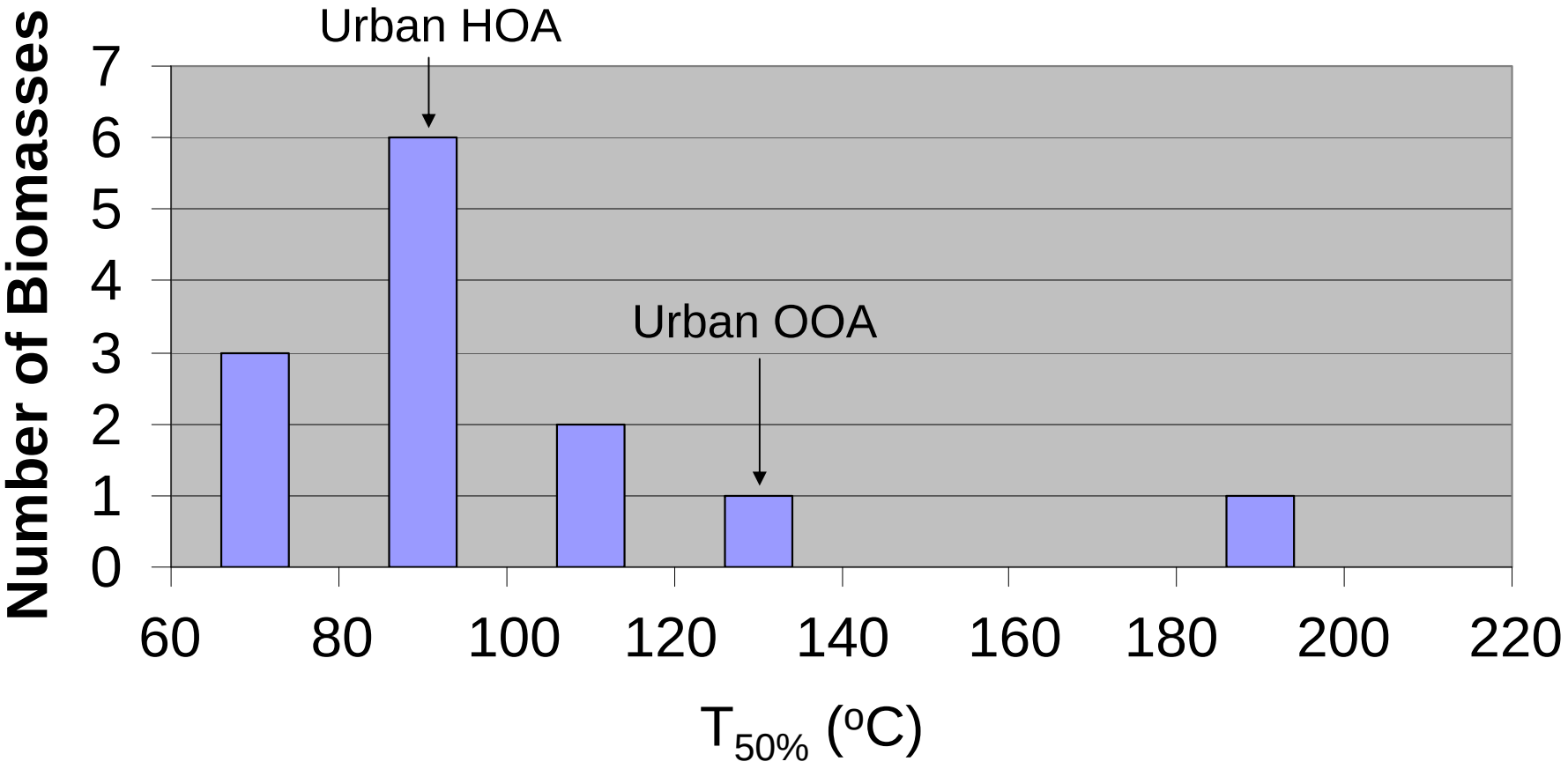
HOA



Volatilities of Biomass Burning Organic Aerosol (BBOA)



Distribution of Biomass Burning Organic Aerosol (BBOA) Volatilities ($T_{50\%}$)



If volatility of urban POA/HOA is important, then it also is for BBOA

Surprising Organic Volatility

- Volatility opposite of expectations
  - Models assume:
    - POA non-volatile
    - SOA semi-volatile
  - Thermodenuder results from MILAGRO (Also Riverside)
    - HOA quite volatile
    - OOA much less volatile
- POA may evaporate significantly upon dilution - consistent with Robinson *et al. (*Science, 2007)
- SOA may not evaporate significantly upon dilution

Conclusions

1. Addition of TD to AMS is a simple and powerful approach for obtaining both chemical and volatility information on aerosol
2. TD-AMS method can be used to measure organic aerosol volatility (vapor pressure) distributions of sources and atmospheric aerosol
3. TD volatility measurement provides a valuable new axis for identifying aerosol components (PMF)
4. TD-AMS database on SOA and combustion aerosol is a valuable (growing) resource for users
5. Study of Organic Aerosol at Riverside (SOAR) in Summer 2005 was a major success for testing TD-AMS methods and bringing together impressive group of scientists (~60 from 15 universities, institutes, and companies) to study organic aerosols

Future plans

1. Complete TD-TDPBMS SOA studies

2. Analyze available ambient TD-AMS data for volatility (vapor pressure) distributions

3. Finish compiling mass spectral-volatility database for SOA [alkanes, alkenes, monoterpenes, aromatics + OH/NO_x,O_3, NO_3, and combustion aerosol]
   Mass spectra/TD profiles/TPTD profiles

   http://cires.colorado.edu/jimenez-group/AMSsd/

   Spectra ID/Source/Group/Instrument/EI Energy Vaporizer Temp/Citation/Fig#/Comments/Data