Hourly Measurements of Organic Molecular Markers in Urban Shanghai, China: Primary Organic Aerosol Source Identification and Observation of Cooking Aerosol Aging

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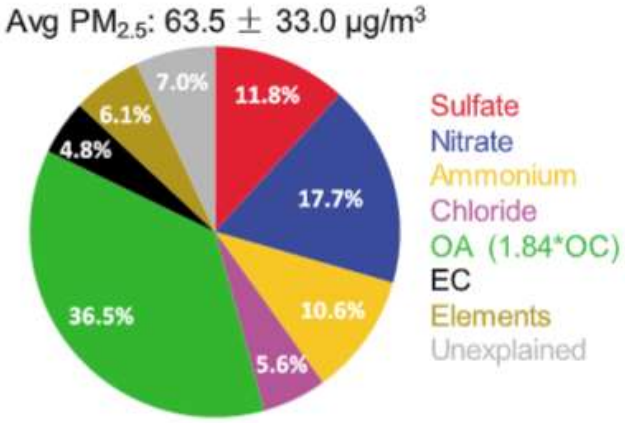
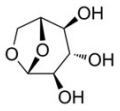
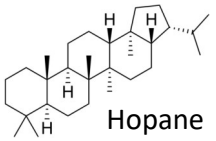
Importance of organic markers in OA



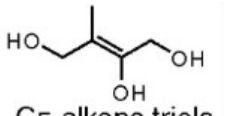


Levoglucosan

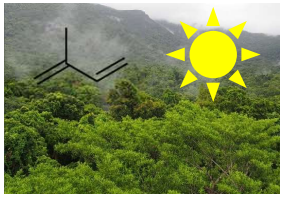
Stearic acid (C18:0)



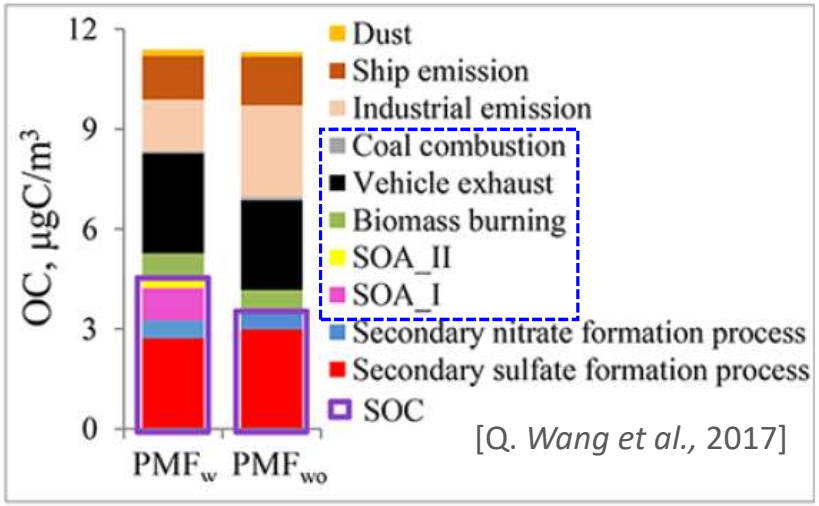
Hopane



C_5-alkene triols



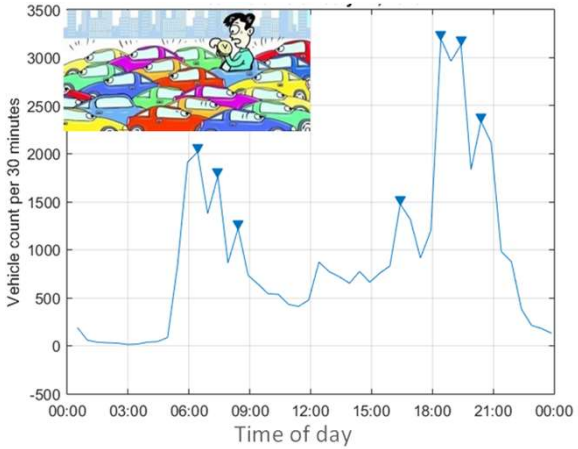
- Semi-volatile, ubiquitous in the atmosphere.
- Crucial to apportion various primary and secondary sources in PMF model.
- Technically demanding, mainly in offline analysis.



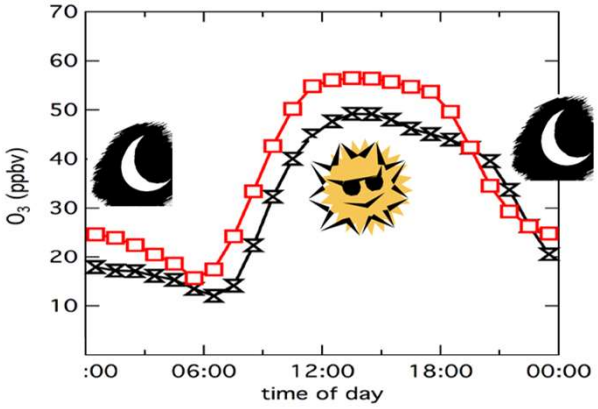
[Q. *Wang et al.*, 2017]

Rapid changing of PM sources & evolution in diel cycle

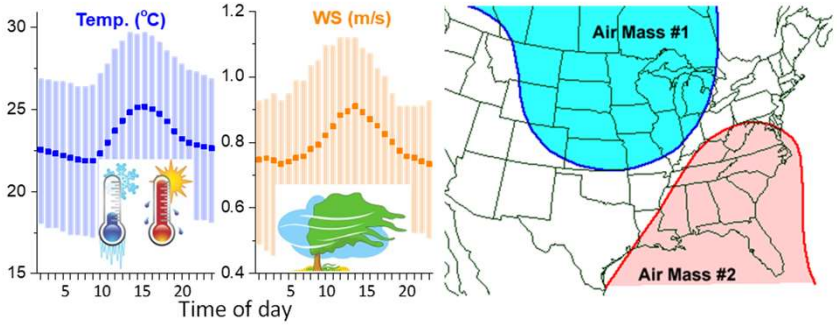
- Different diurnal pattern of emissions.



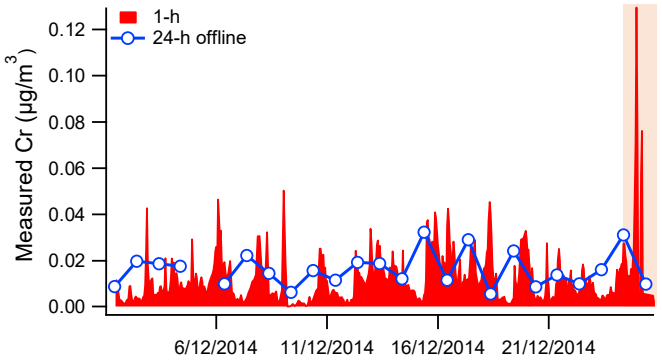
- Different dominant oxidants in day and night.



- Fast meteorology change:

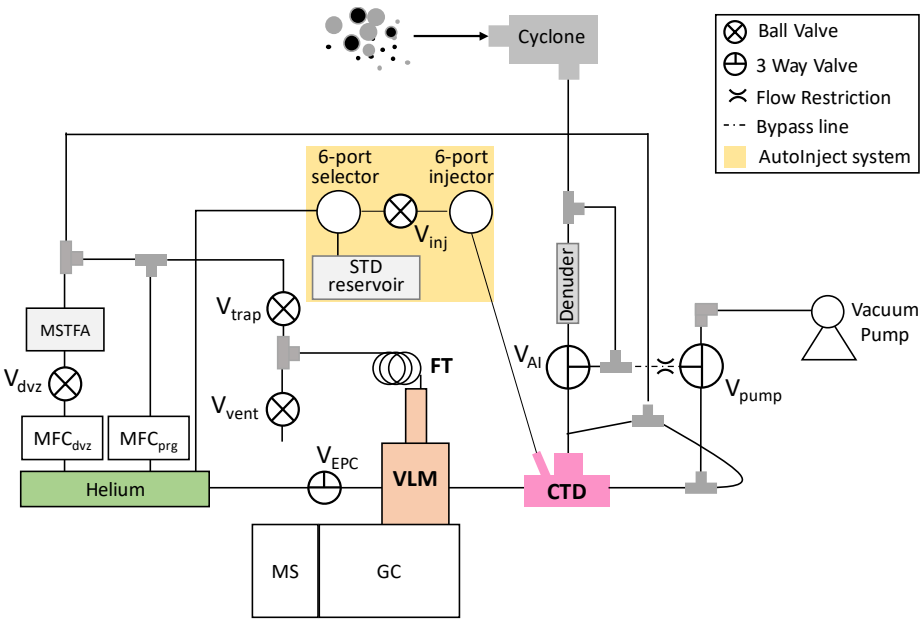


Online measurement is needed!

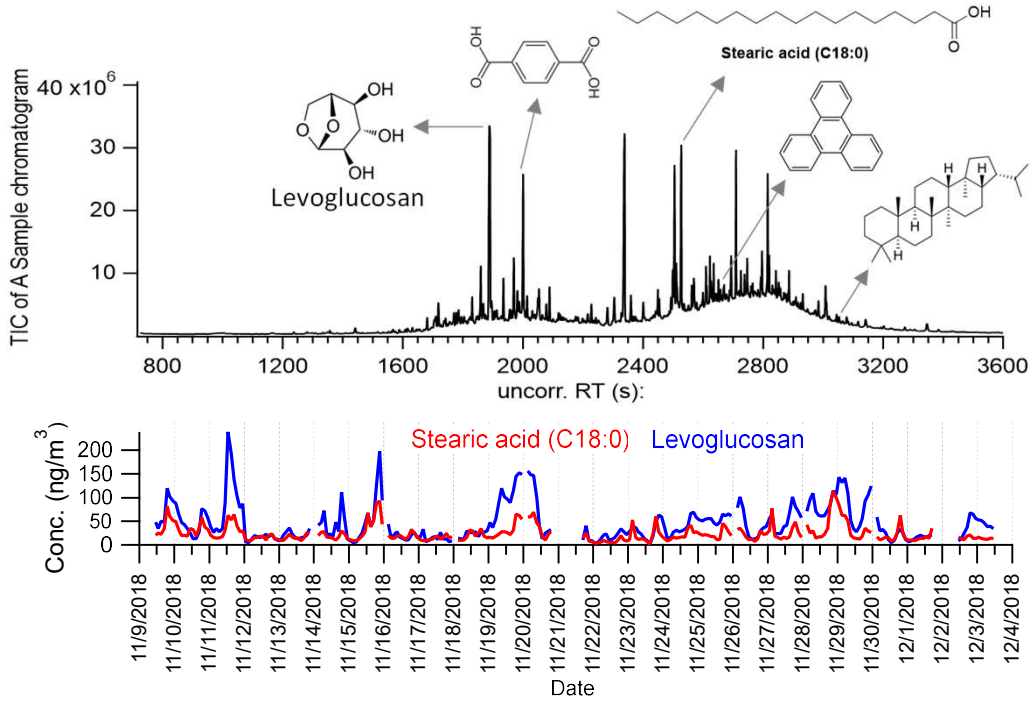


Hourly Organic Markers Measurement

Thermal desorption Aerosol Gas chromatography–mass spectrometry (TAG)



Schematic Diagram of TAG



- Online
- Time resolution: Bi-hourly
- Measured species: Individual organic species (>100 species) in OA

Sampling

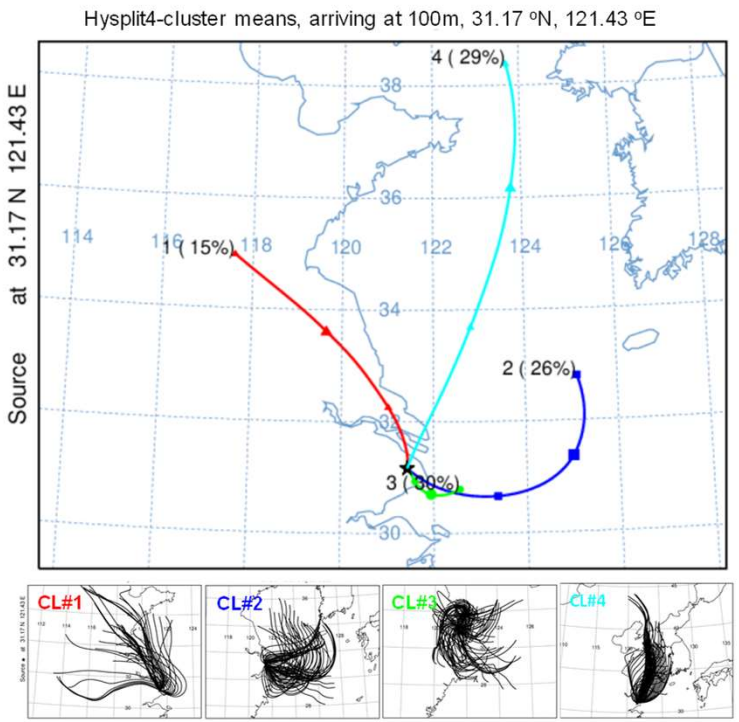
- Three-week campaign
  - 09 Nov. – 03 Dec. 2018

- Hourly measured species
  - $PM_{2.5}$
  - BC
  - Inorganic ions (MARGA)
  - Trace elements (online XRF)
  - Molecular organic species (TAG)

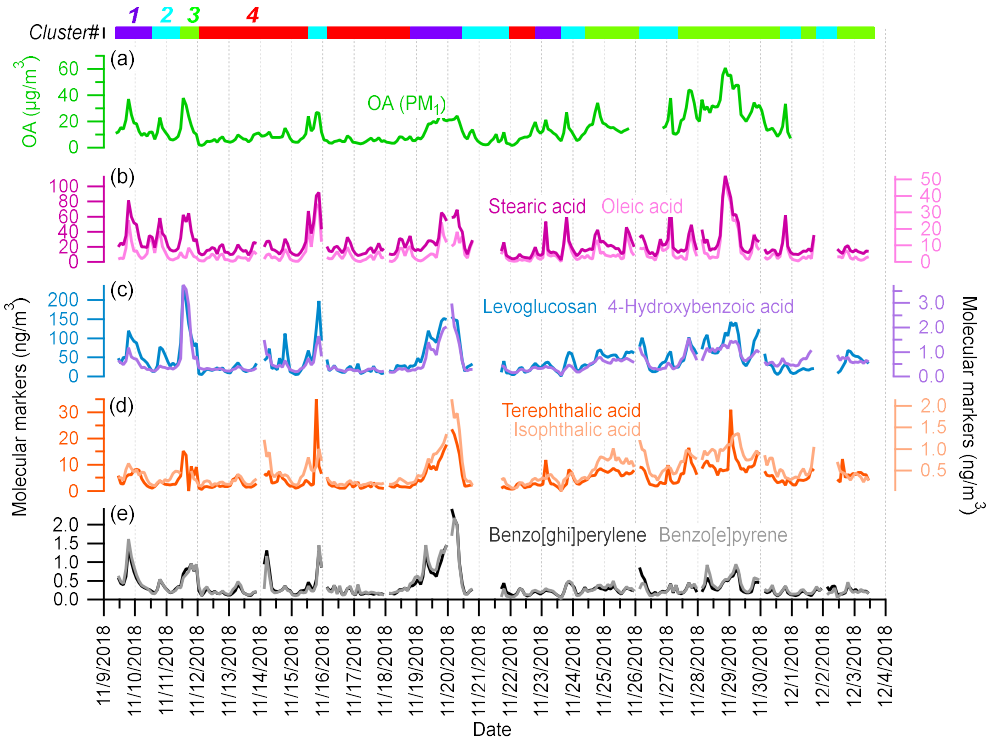
- Other hourly meteorological parameters and gas concentrations
  - RH, T, WS, WD
  - SO_2, NO_x, CO, O_3

Downwind from the downtown Shanghai, and mostly surrounded by commercial properties and residential dwellings.
→ A receptor site influenced by a wide mixture of emissions and their evolution.

General characteristics of OA and select organic markers

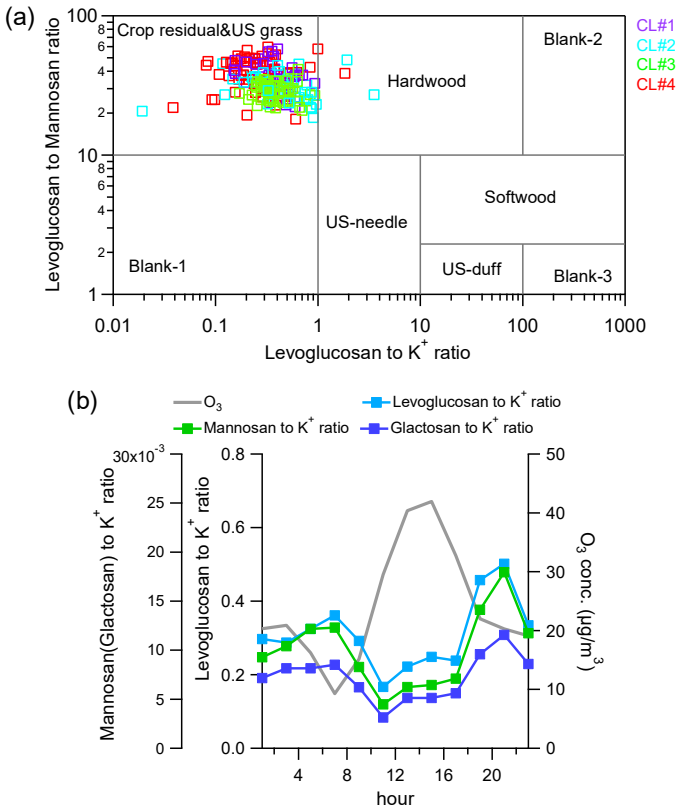


- Local air mass (CL#2&3) and long-range transport air mass (CL#1&4) impact the campaign.



- Campaign-wide temporal variations of total OA (PM_1) and select organic markers.

Biomass burning emission POA markers



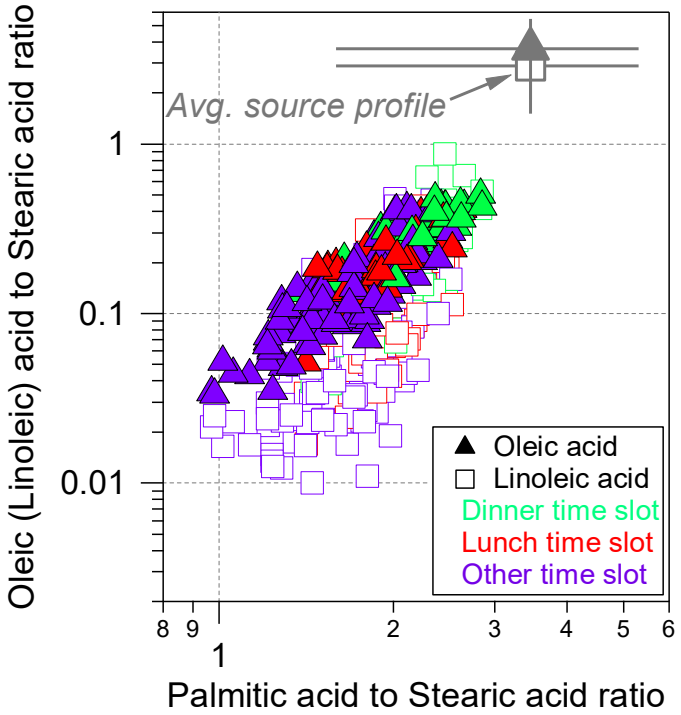
(a) Levoglucosan to K^+ and levoglucosan to mannosan ratios and (b) diurnal variation of levoglucosan, mannosan and glactosan to K^+ ratios of the ambient samples.

- Combustion of crop residuals such as rice straw, wheat straw and corn straw is a dominant BB source influencing Shanghai.
- Lower anhydrosugars/K^+ ratios in the daytime:

→ Different dominant combustion processes (flaming in the daytime vs. smoldering in the nighttime);

→ Degradation of the anhydrosugars in the day.

Atmospheric aging of cooking markers



Oleic and linoleic acid to stearic acid ratios vs. palmitic to stearic acid ratio of the ambient samples collected in Shanghai. Dinner time (17:00-21:00, green), lunch time (09:00-13:00, red) and other time slot (purple).

- The palmitic/stearic ratio had a narrow range, slightly lower than source profiles. While the oleic/stearic and linoleic/stearic ratios were much lower than source profiles.

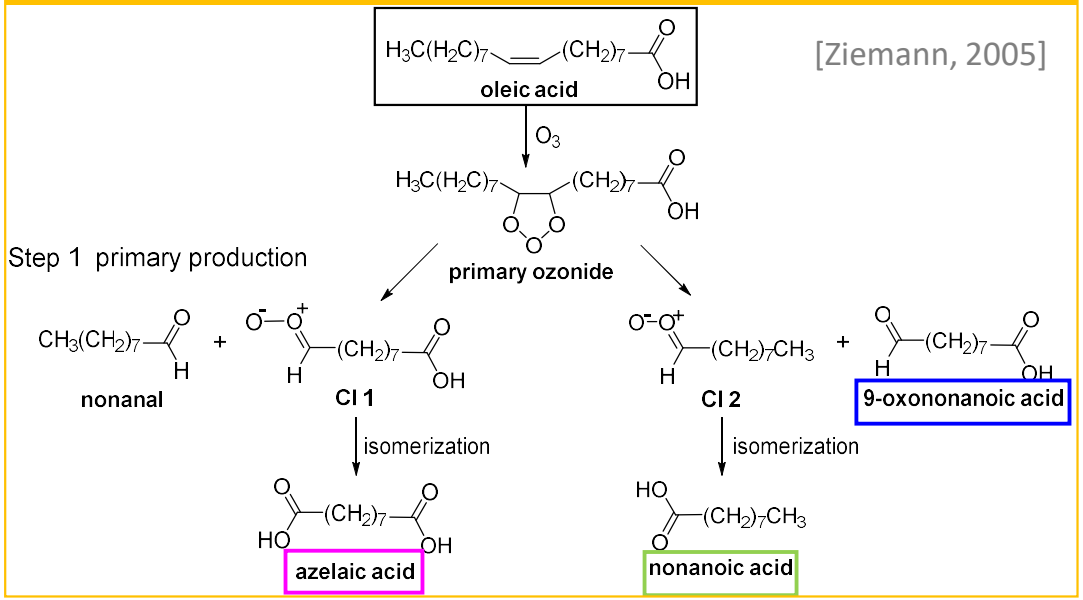
→ Degradation after emissions.

- Higher ratios during dinner and lunch time.

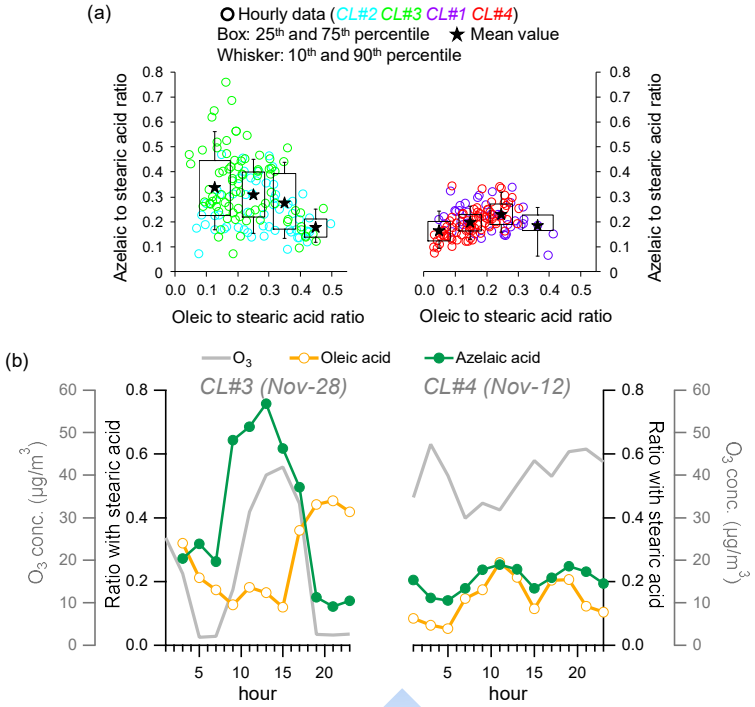
→ Local cooking emissions influence the sampling site.

Atmospheric aging of cooking markers

Oleic acid ozonolysis mechanism in chamber studies

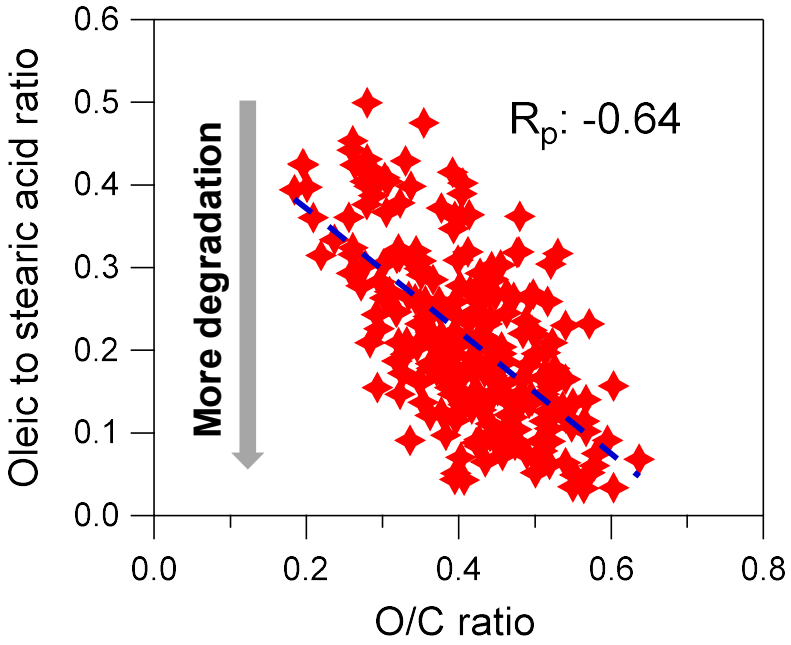


[Ziemann, 2005]



- Oleic acid ozonolysis C_9 products were detected in ambient samples.
- In-situ oxidation occur under local air mass influence (CL#2&3).

Atmospheric aging of cooking markers



Correlation of the oleic/stearic ratio from TAG measurements with the O/C ratio from AMS.

- The oleic/stearic ratio indicates the aging of cooking aerosols.
- The O/C ratio measured by AMS reflects the degree of oxygenation of OA.

→ The moderate correlation implies the heterogeneous reaction of particle phase unsaturated species such as oleic acid may represent a significant oxidation process of total OA in urban area.

Implication of hourly organic markers by TAG

- Effective in capturing the dynamic changes of the source contributions and their chemical evolution.
- Valuable in facilitating resolving bulk OA measured by AMS into more specific source types.
- Providing an opportunity to link observations made in chamber or laboratory studies with those in the real atmosphere, thereby informing the parameterization of OA aging in numerical modeling of air quality and climate.

All questions and comments are welcome !