Presented at Yale-NUIST AE Center Video Seminar

# Mass spectrometric analyses of the airborne fine particles in a megacity of Yangtze River delta (YRD), China

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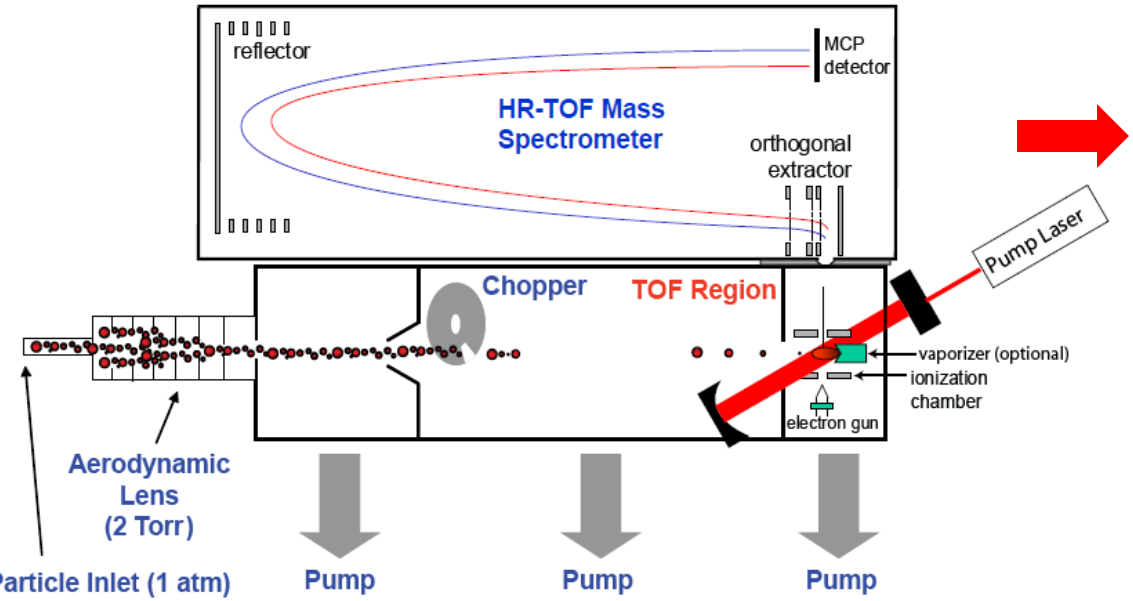
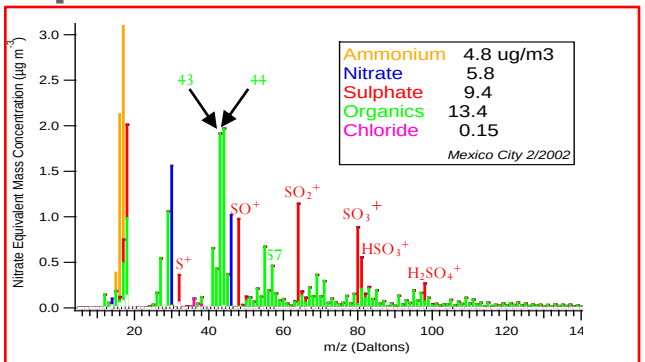
# Background – PM chemistry

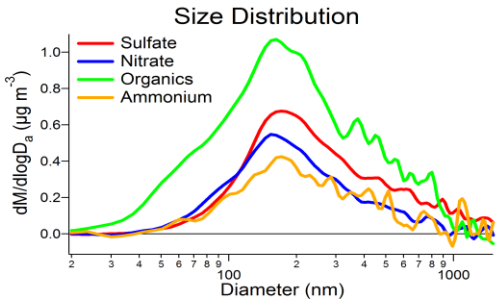
- Filter sampling and off-line analyses:
  - Coarse time resolution (daily sample, etc.), thus very limited to capture the details of fast atmospheric processes,
  - May introduce artifacts during sample storage and analyses
  - Possible loss of semi-volatile species.
- Online analyses:
  - Don't require sample preparation
  - Real-time display
  - fine time resolution
  - Capture detailed mechanisms

# Soot Particle-Aerosol Mass Spectrometer (SP-AMS)

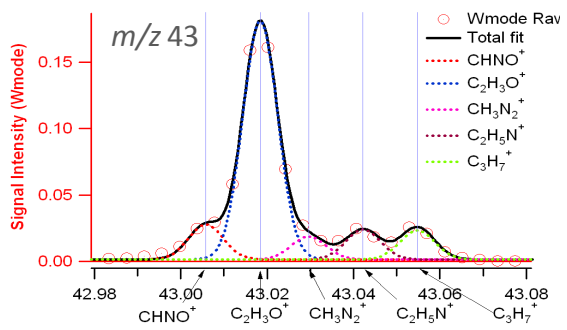



1. Quantitative composition

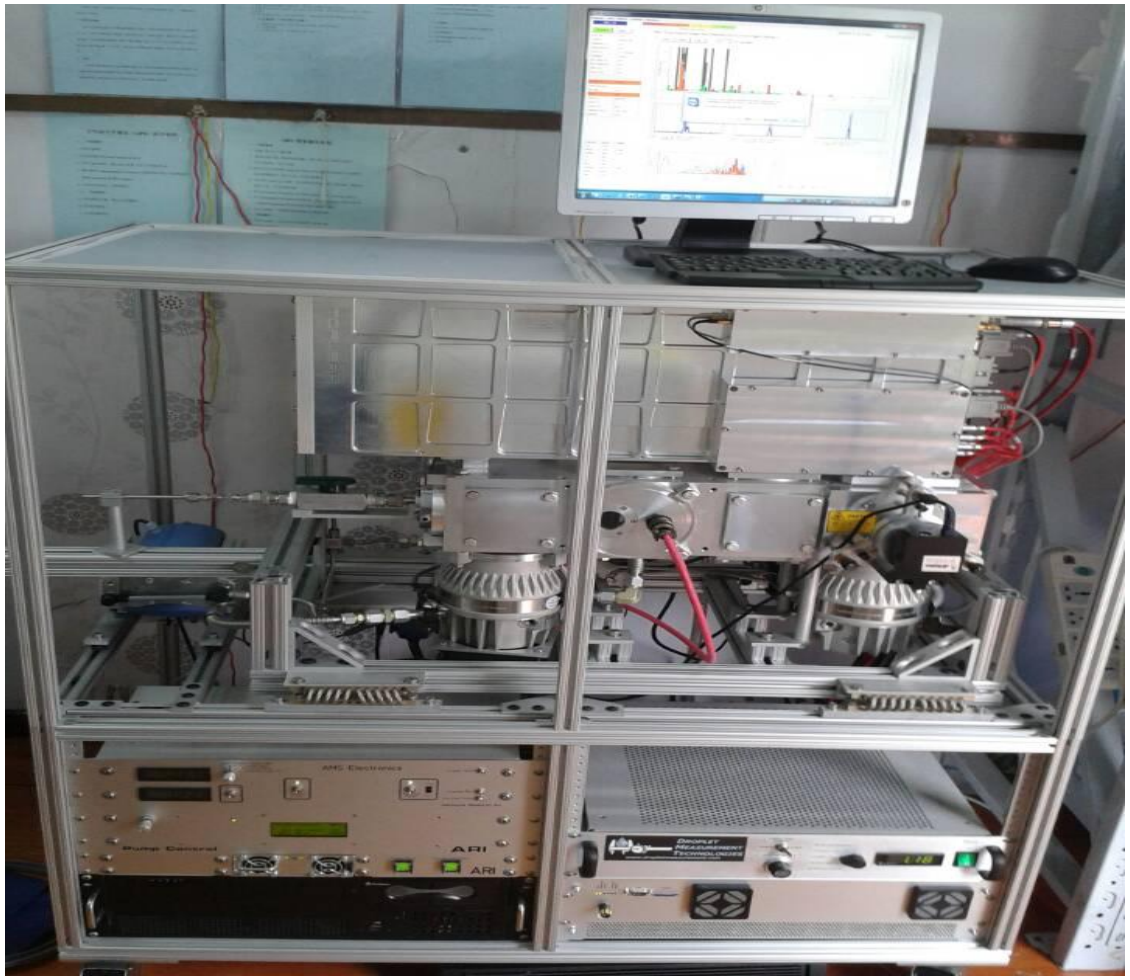



2. Size-resolved composition




3. Elemental comp. ($C_nH_mN_pO_zS_w$)

- Real-time and online measurements of inorganic (sulfate, nitrate, chloride, ammonium) and organic species of $PM_1$
- High chemical resolution (~6000 under W mode)
- Fine time resolution (a few mins or secs. each sample)
- Upgraded with a laser vaporizer → able to detect Black carbon (BC) and associated refractory species




For field on-line measurement

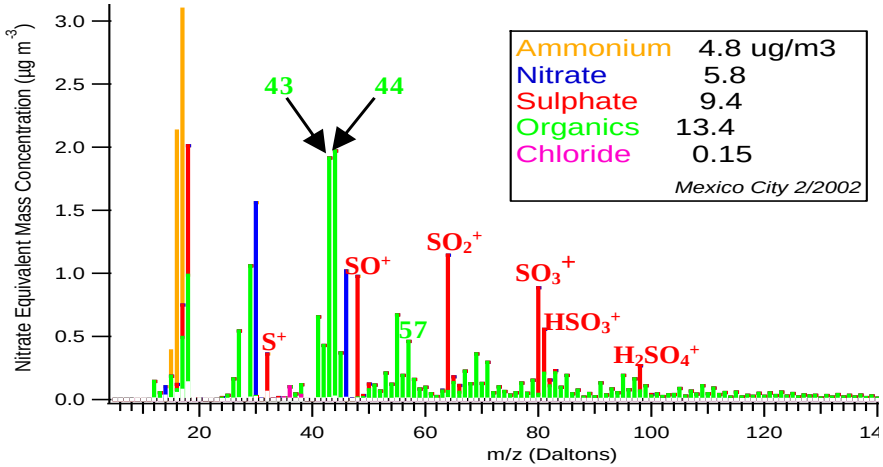
For chamber study

For off-line analyses of liquid samples

# How does an AMS work?

Likely every 5 min, an averaged mass spectrum (an ensemble of all fragments from all particle-phase species) is obtained

The Mass spectrometry analysis is to sort out each species from the fragments (The Game of Puzzles!) → chemical composition of the aerosols

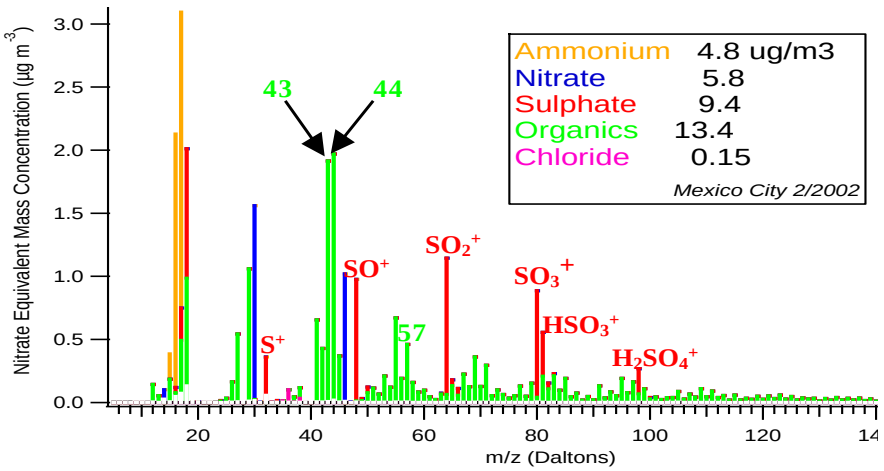



Certain species has its unique, reproducible fragmentation pattern, which can be used to apportion the total signals.

MS analysis

Courtesy: Q. Zhang

# How does an AMS work?



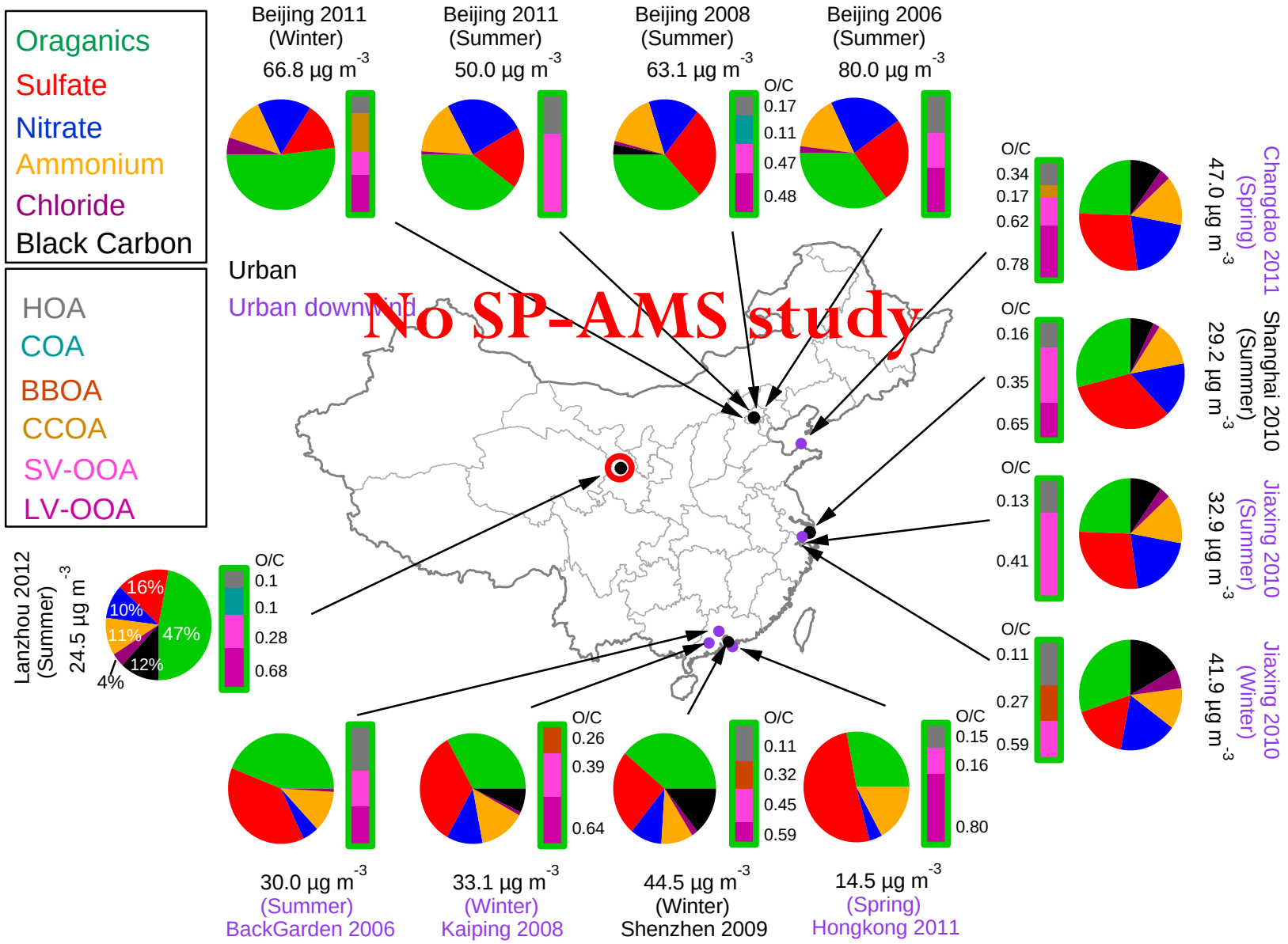

Inorganic species (sulfate, nitrate, chloride and ammonium )are easy to quantify.

BUT organics can contain numerous species

It is almost impossible to quantify each individual organics molecules (perhaps unnecessary); BUT we Still want to know the characteristics, sources of the organics (OA). They can contain very toxic compounds!

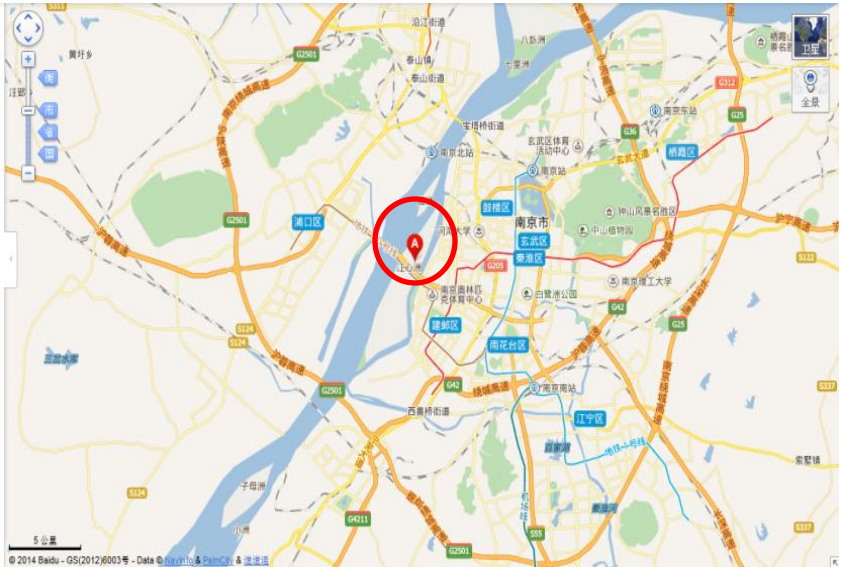
→ Factor analysis (segregate the total ORG into a finite number of factors)

# AMS field studies in China



# Field campaigns in Nanjing

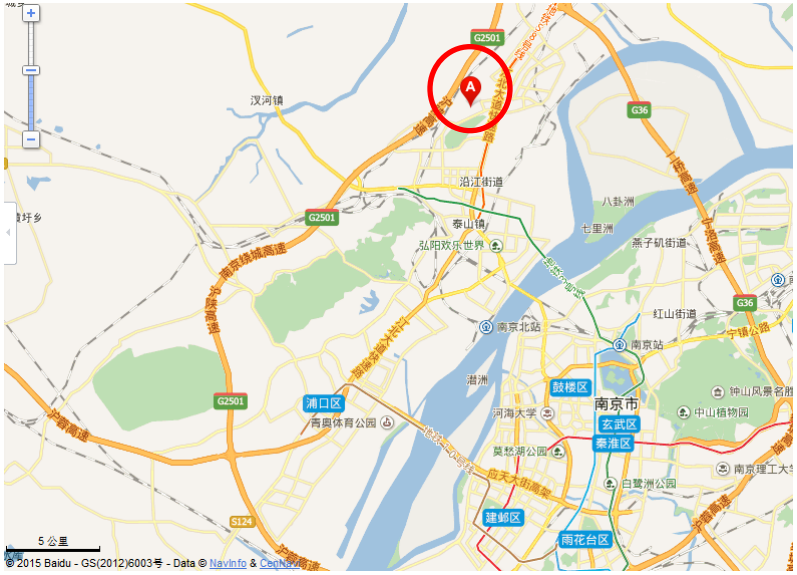
## 2014 Summer




2014.08.11-2014.09.18
(Nanjing Youth Olympic:
2014.08.16-2014.08.28)

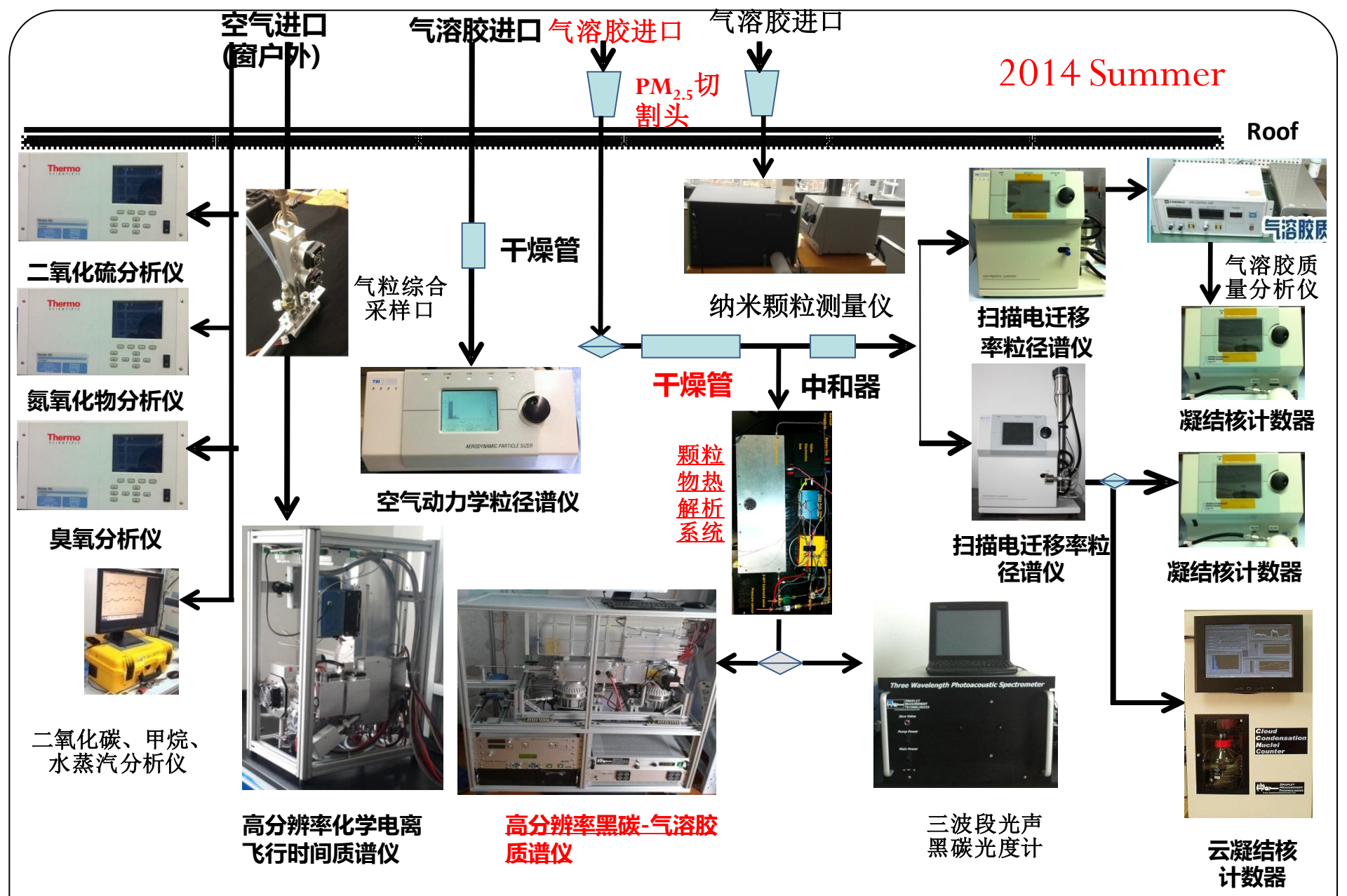
Nanjing Meteorological Bureau

## 2015 Winter




2015.02.16-2015.03.23
(Spring Festival:
2015.02.18-2015.02.24)

NUIST Campus

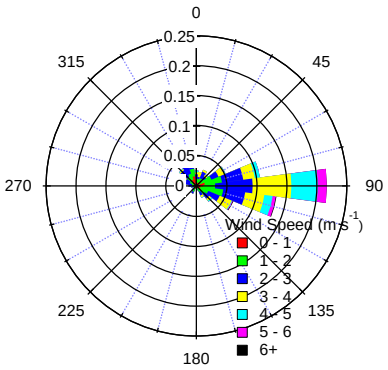


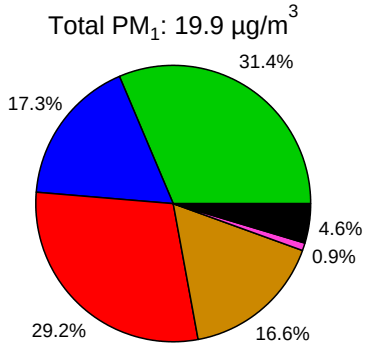

2014 summer instruments (MOUDI, high-volume sampleer not shown)

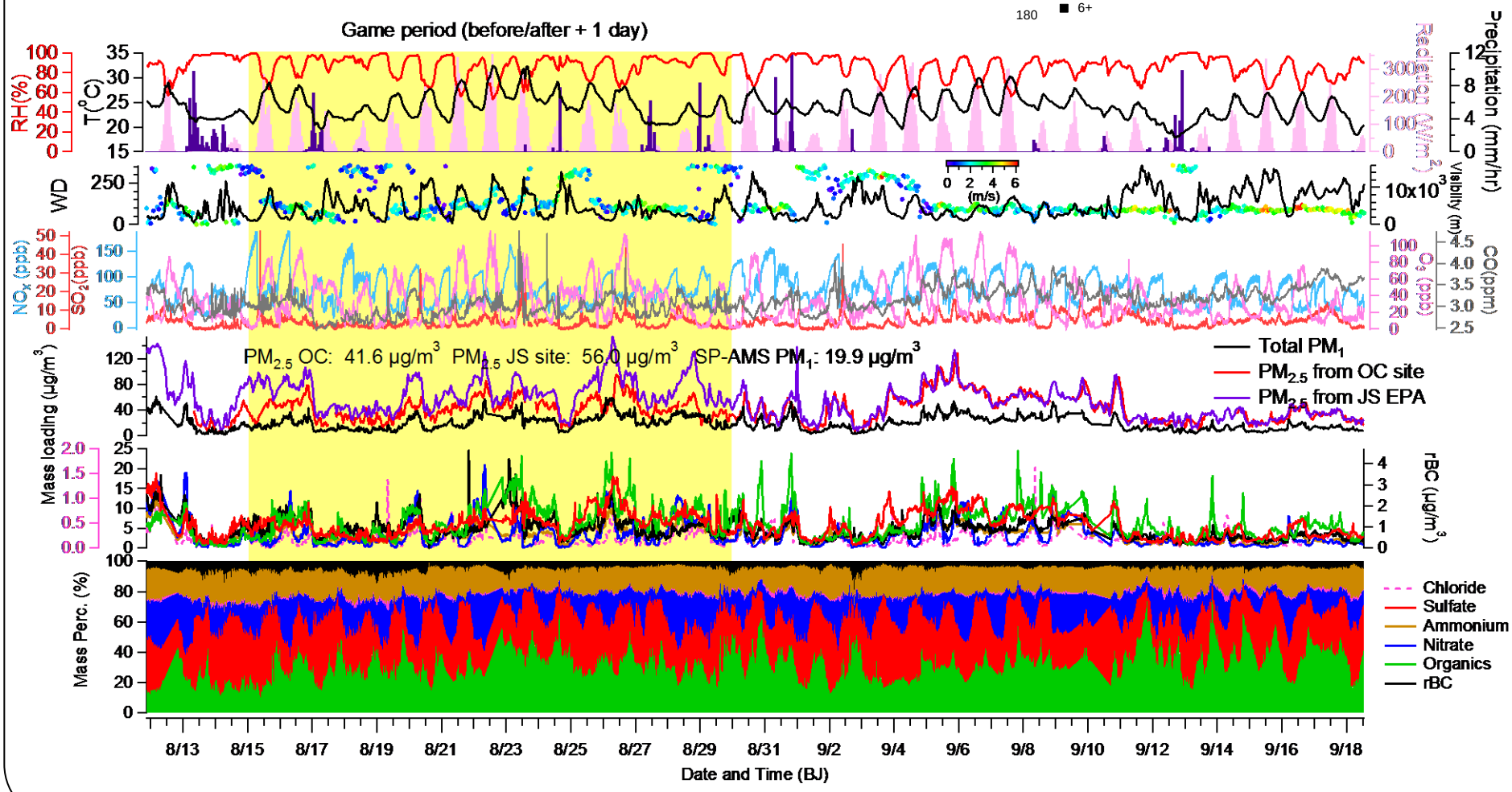
# Results and discussion

# 1. Overall characteristics

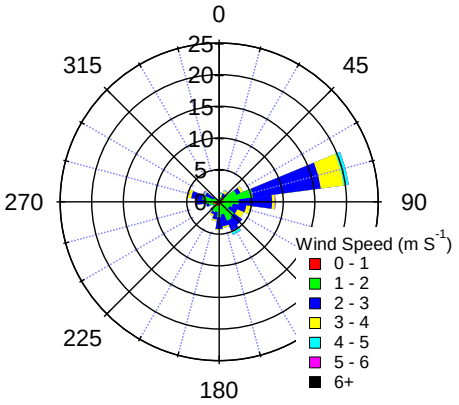
## 2014 Summer

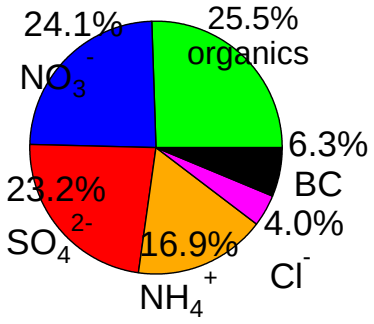


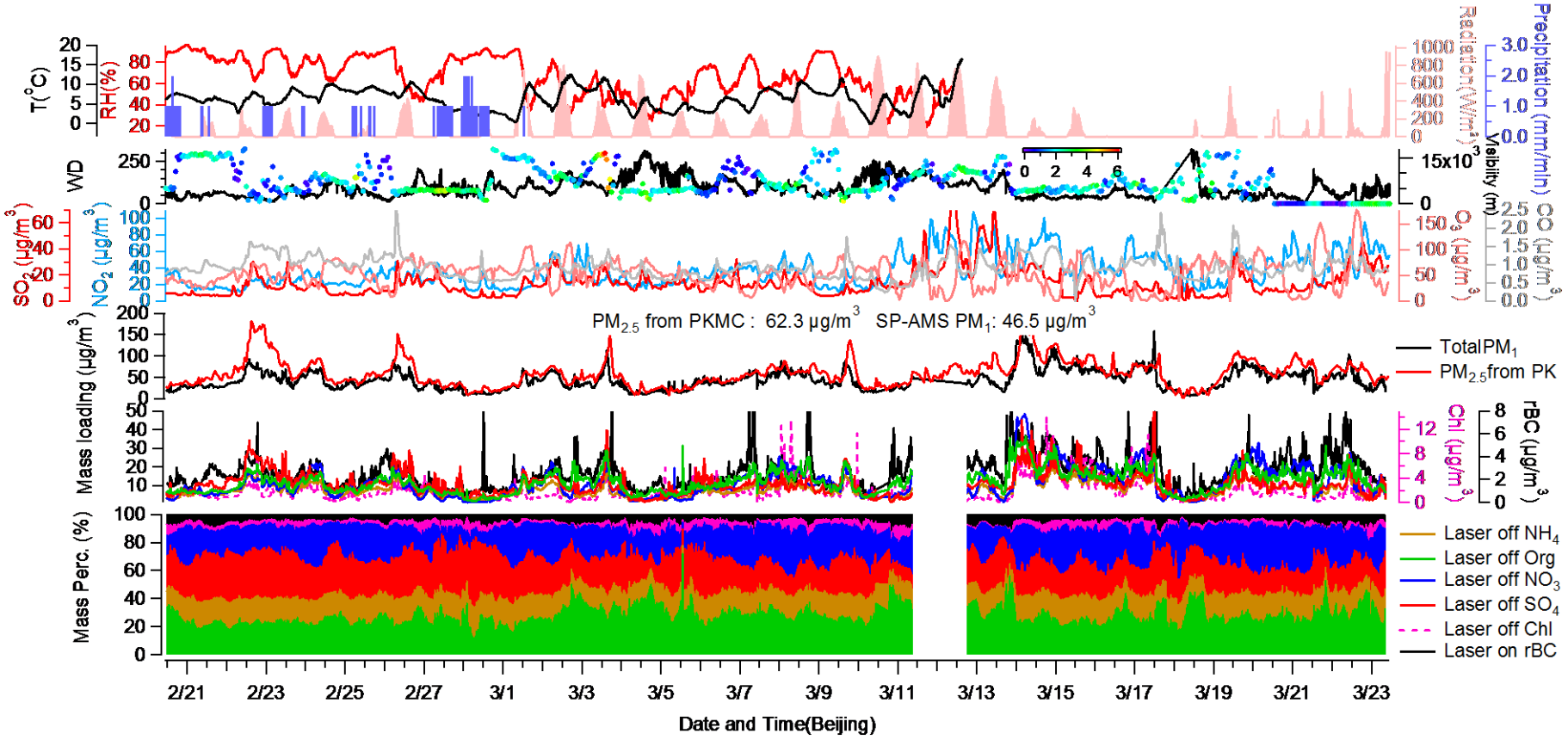



Prevailing eastern wind
both in summer and winter

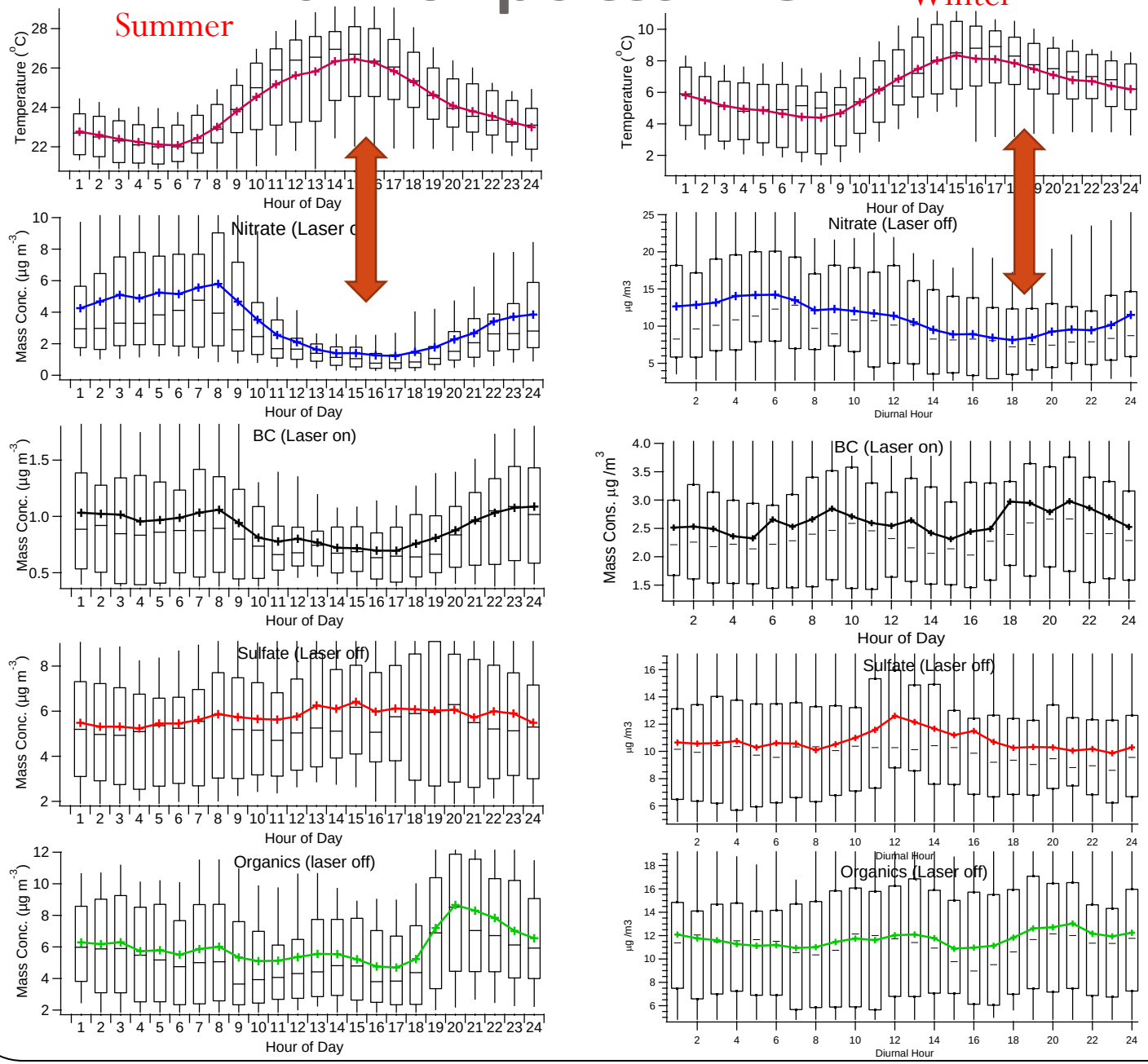



# 2015 Winter



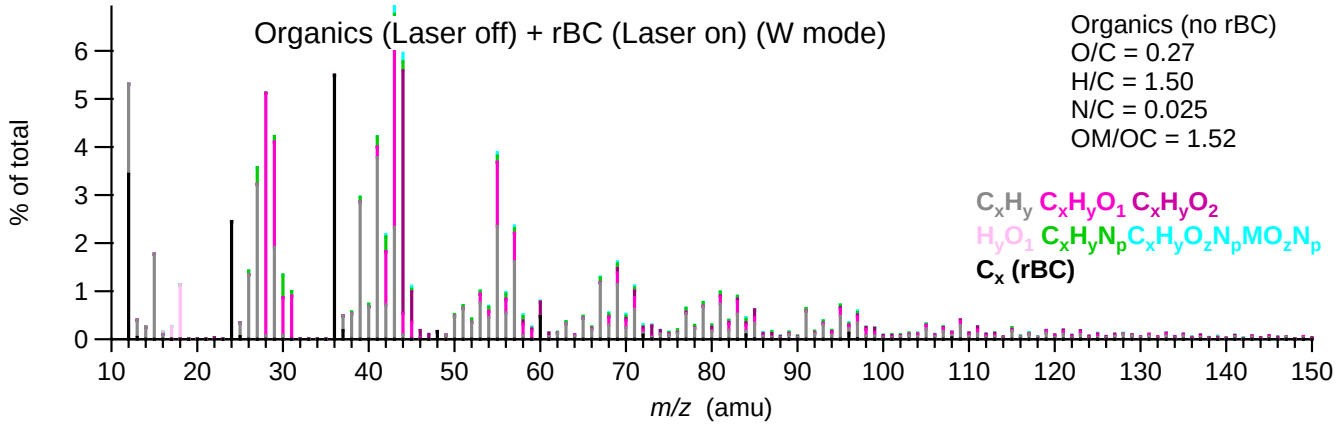
# 2. Diurnal patterns

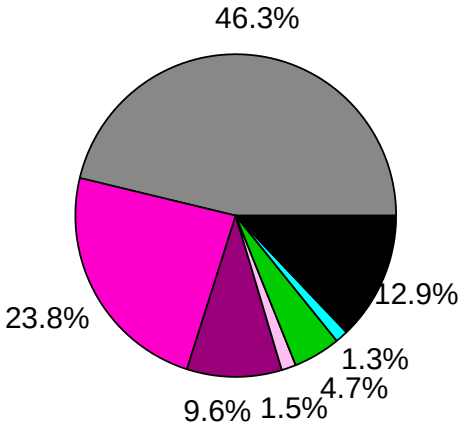



**Nitrate variations were mainly governed by Temperature in Nanjing!!!**

# 3. OA Mass spectra

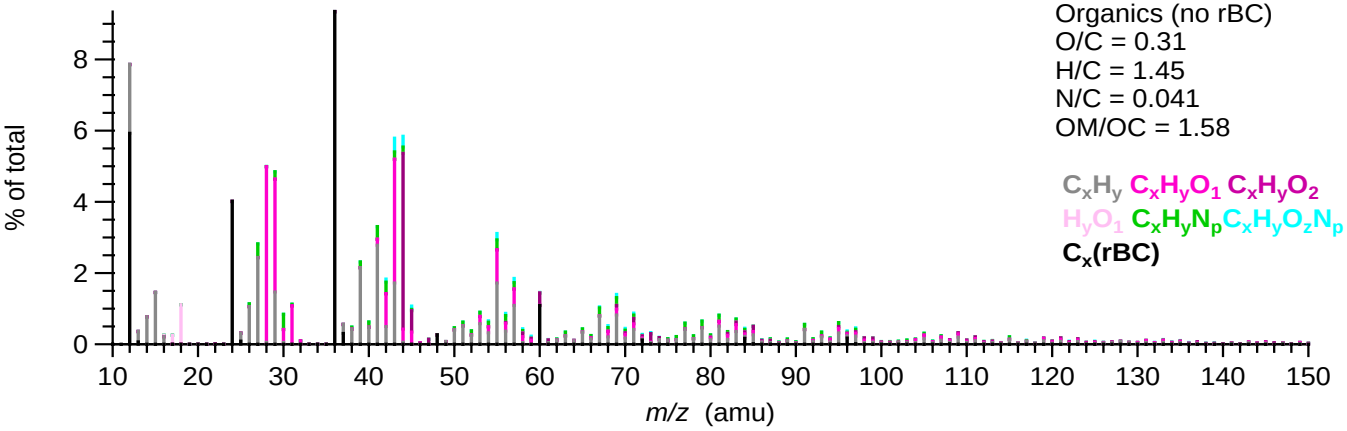
## 2014 Summer

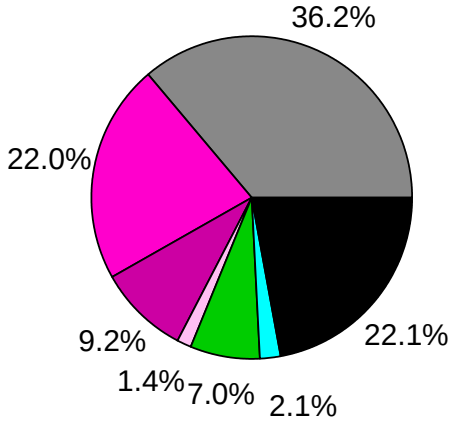



Higher ON species than other places → Presence of amino compounds

## 2015 Winter

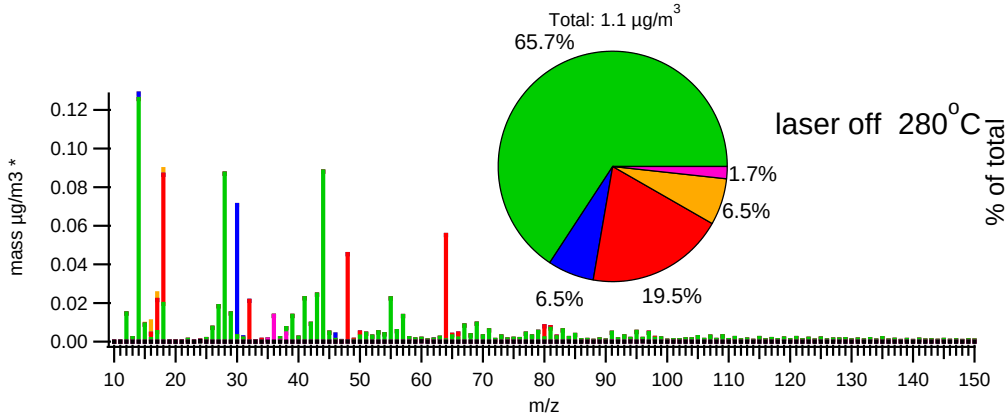


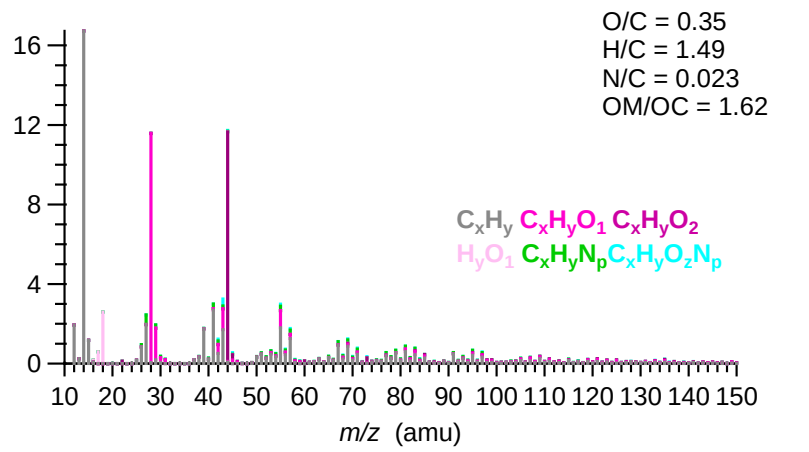



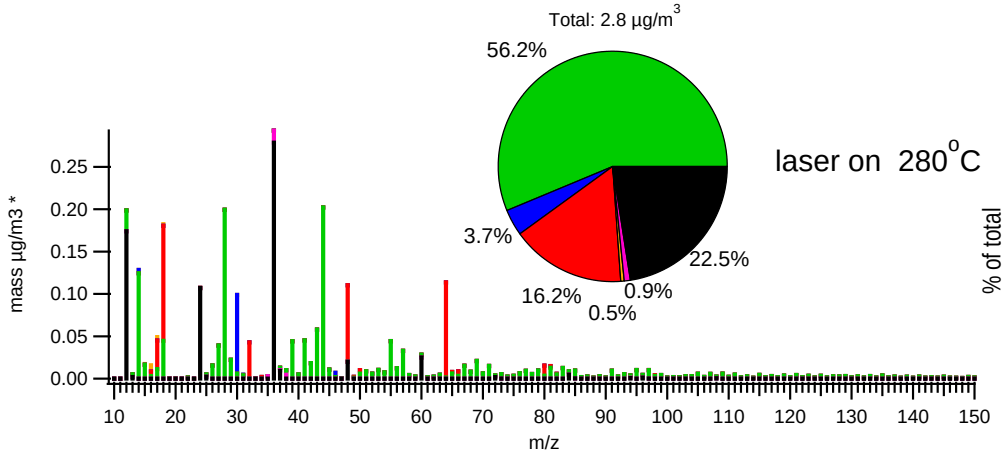

Higher ON and BC in suburban site → Likely Industrial emissions?

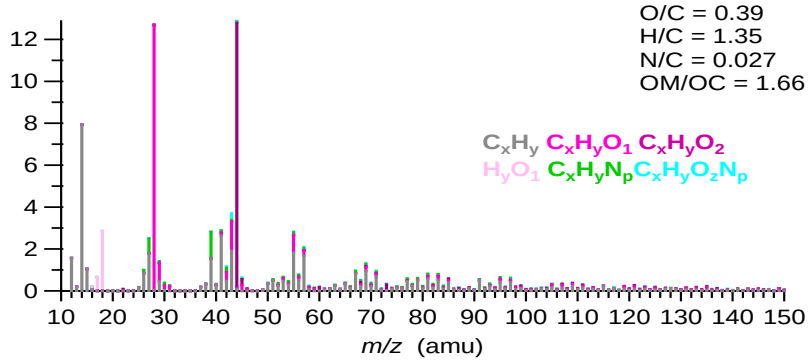
# 4. Volatility – PM spectra

2014 Summer



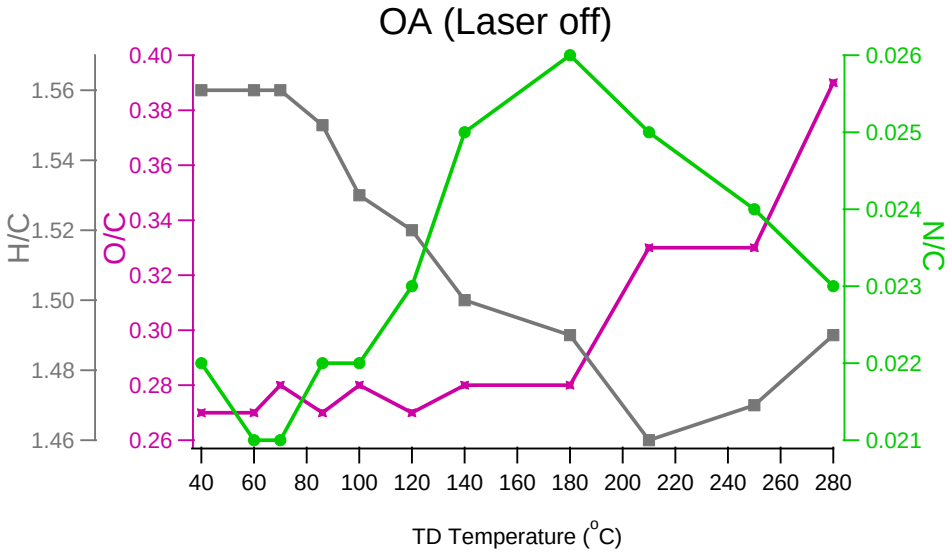



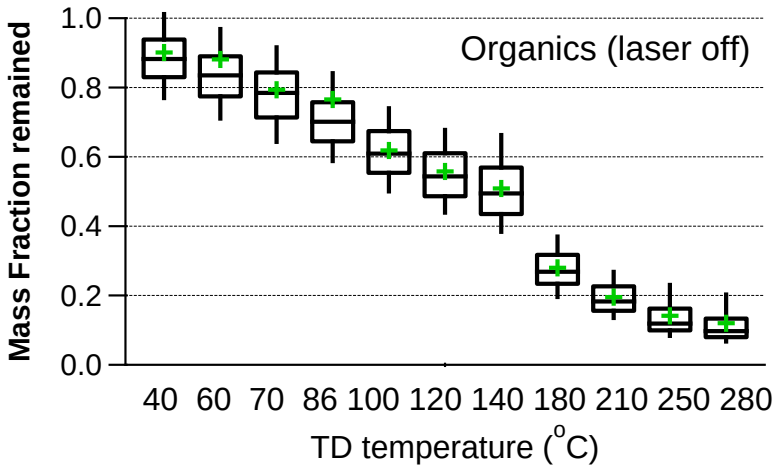



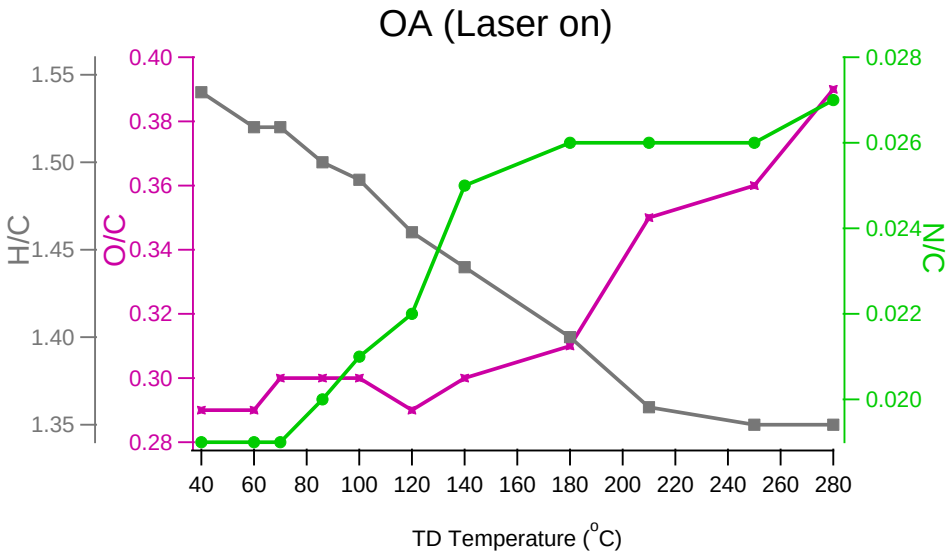

Significant amount of non-volatile organics remains in the particles under 280 °C, not only rBC

A portion of Nitrate and sulfate remains in the 280oC-denudered particles, indicating presence of other nitrate/sulfate salts.

# 4. Volatility – OA behavior



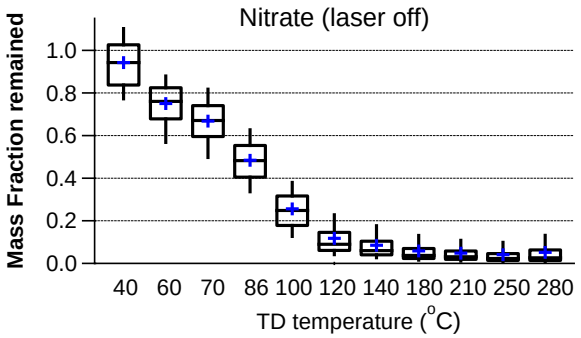



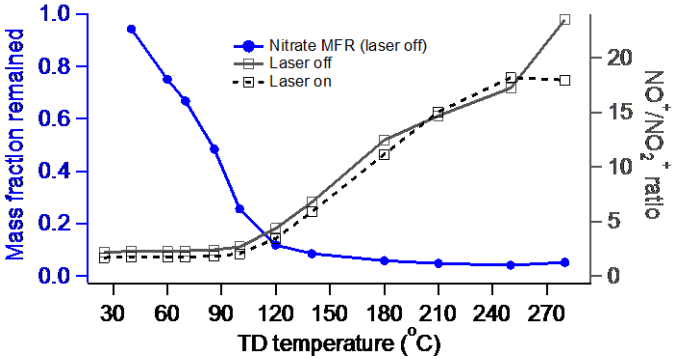



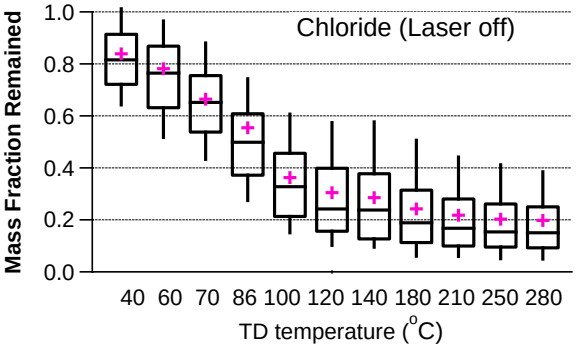

On average, 12% of organics remains even under 280oC, and these non-volatile organics tend to be more oxidized.

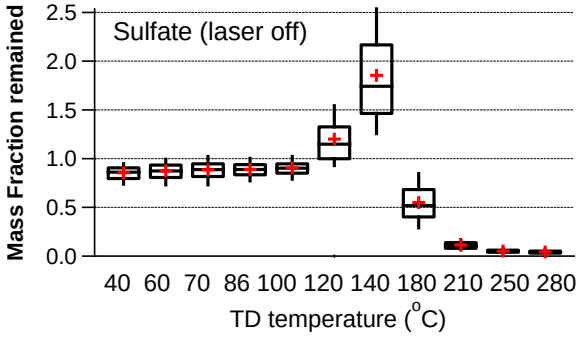
How does this relate to the Optical properties??

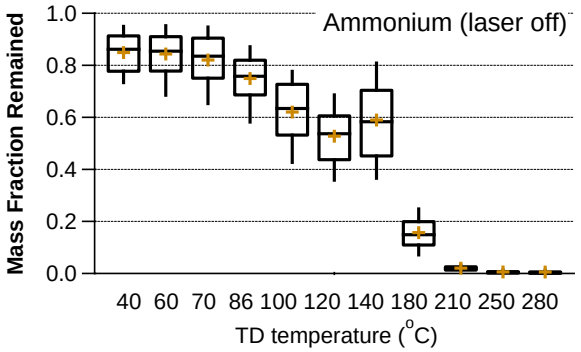
# 4. Volatility – Inorganics behavior

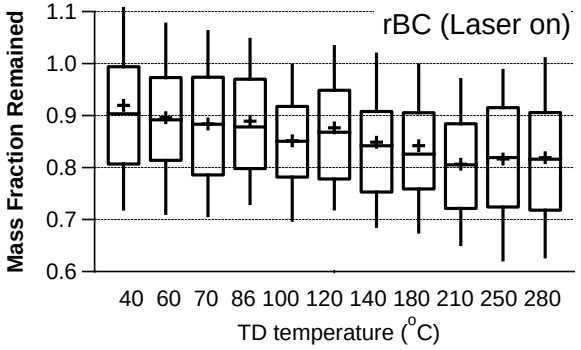


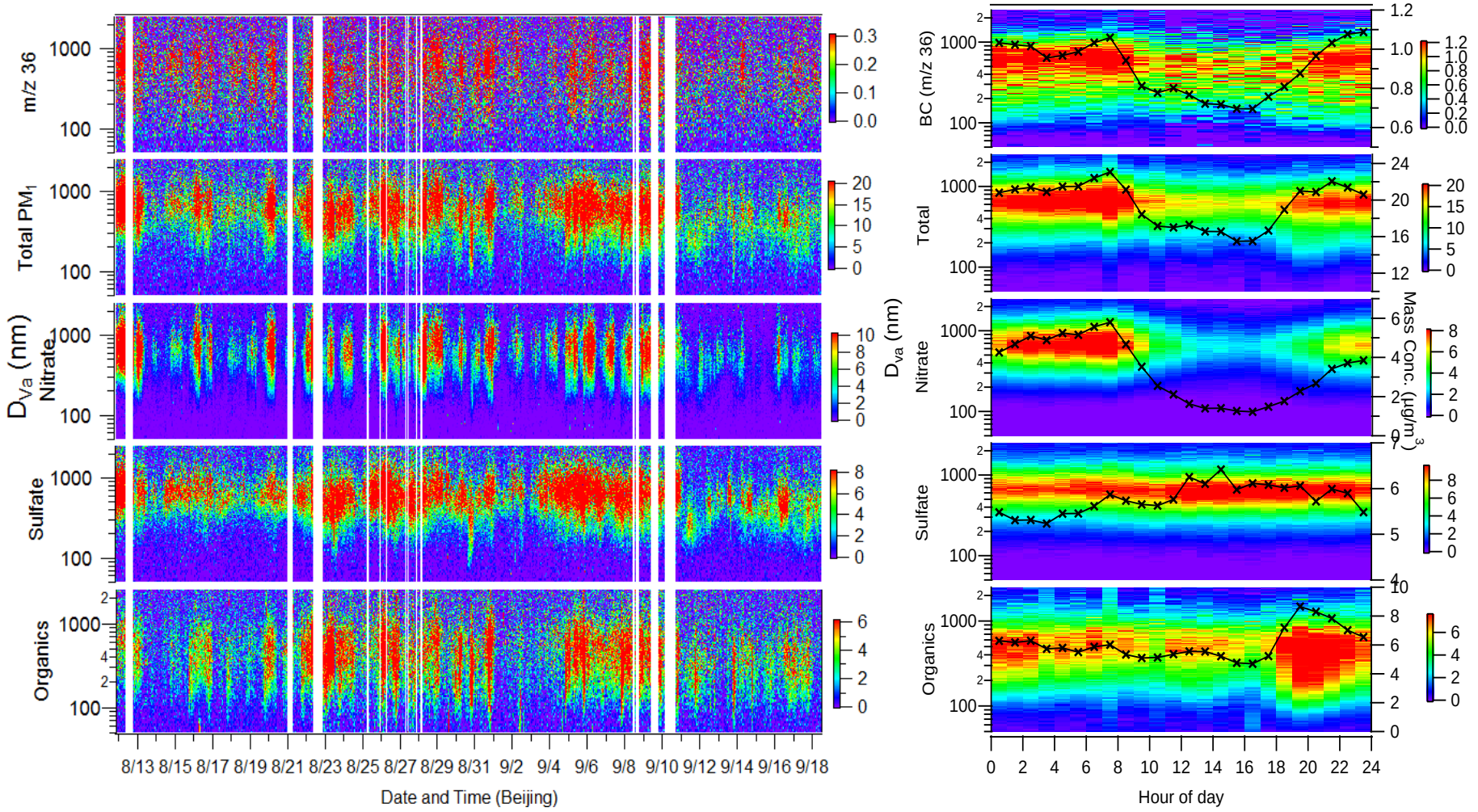



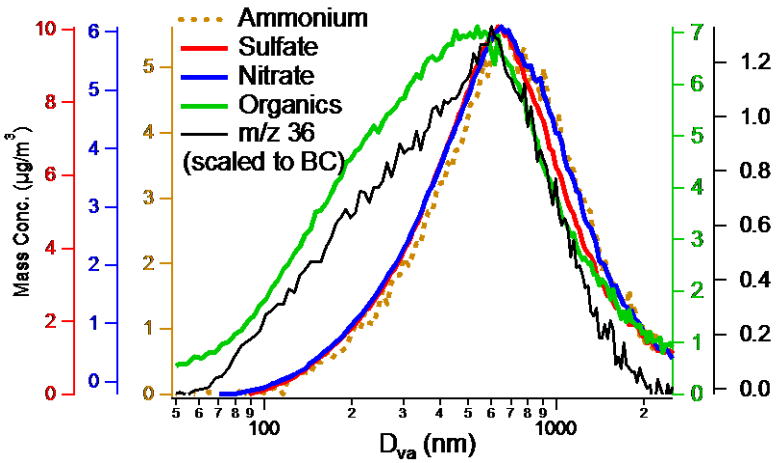



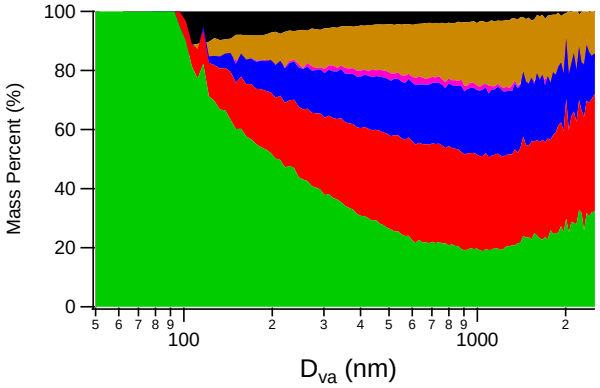
# 5. Size distribution

2014 Summer

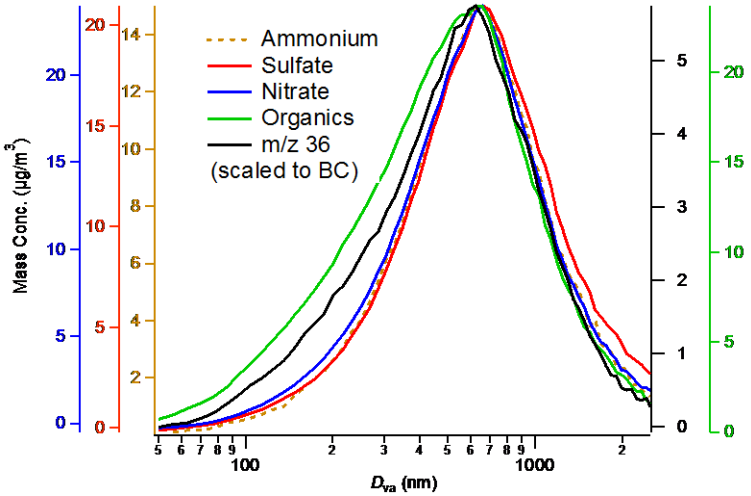


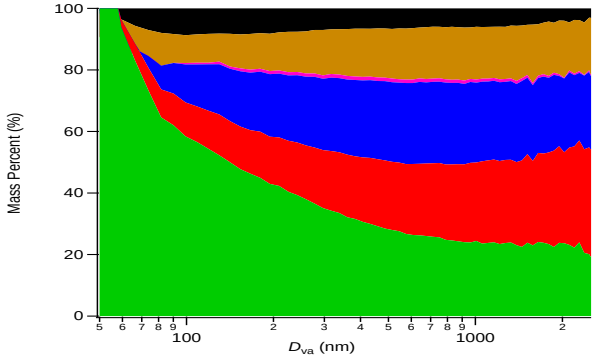
## 2014 Summer




## 2015 Winter



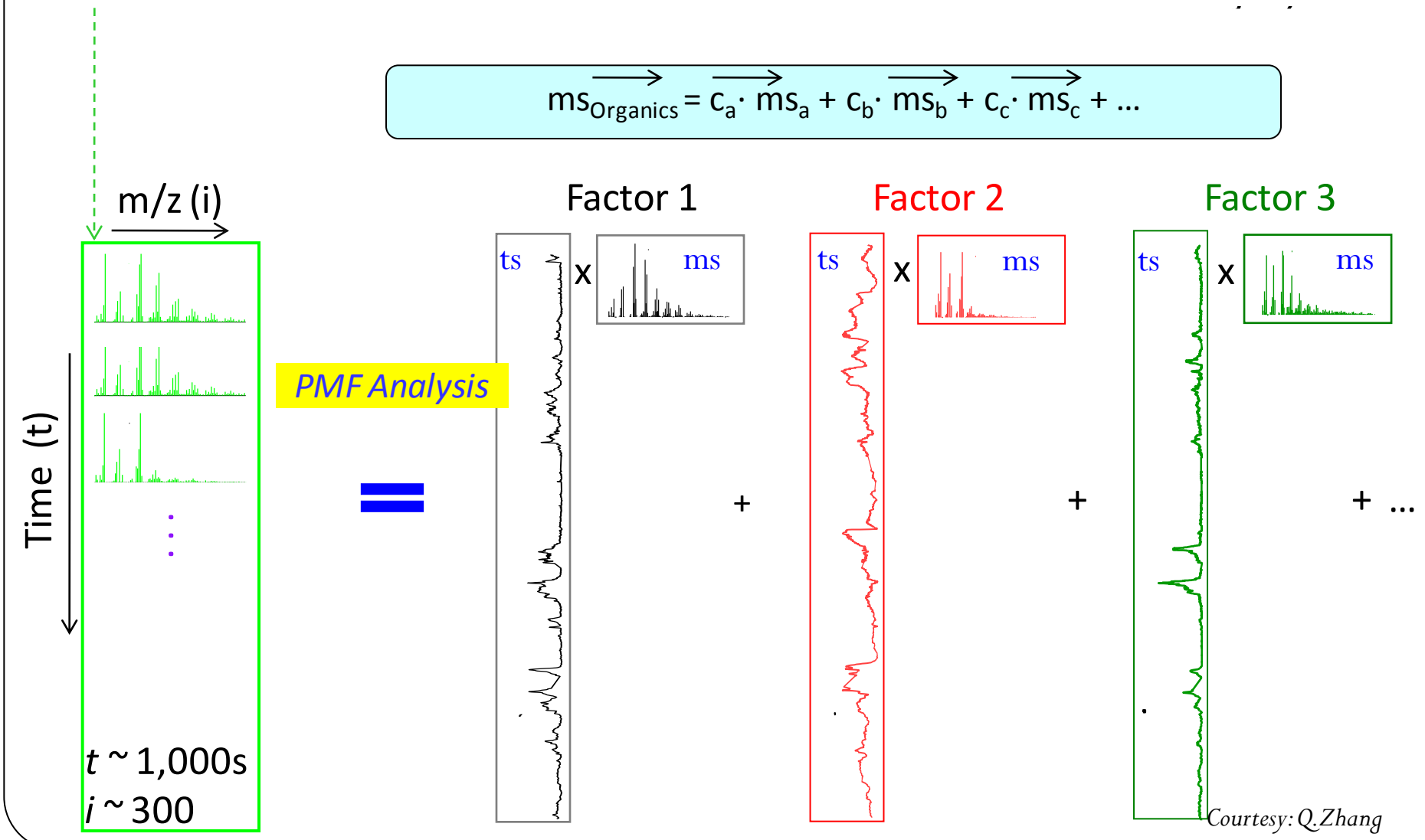



# 6. Source apportionment

Positive Matrix Factorization (PMF, 正矩阵因子分解)

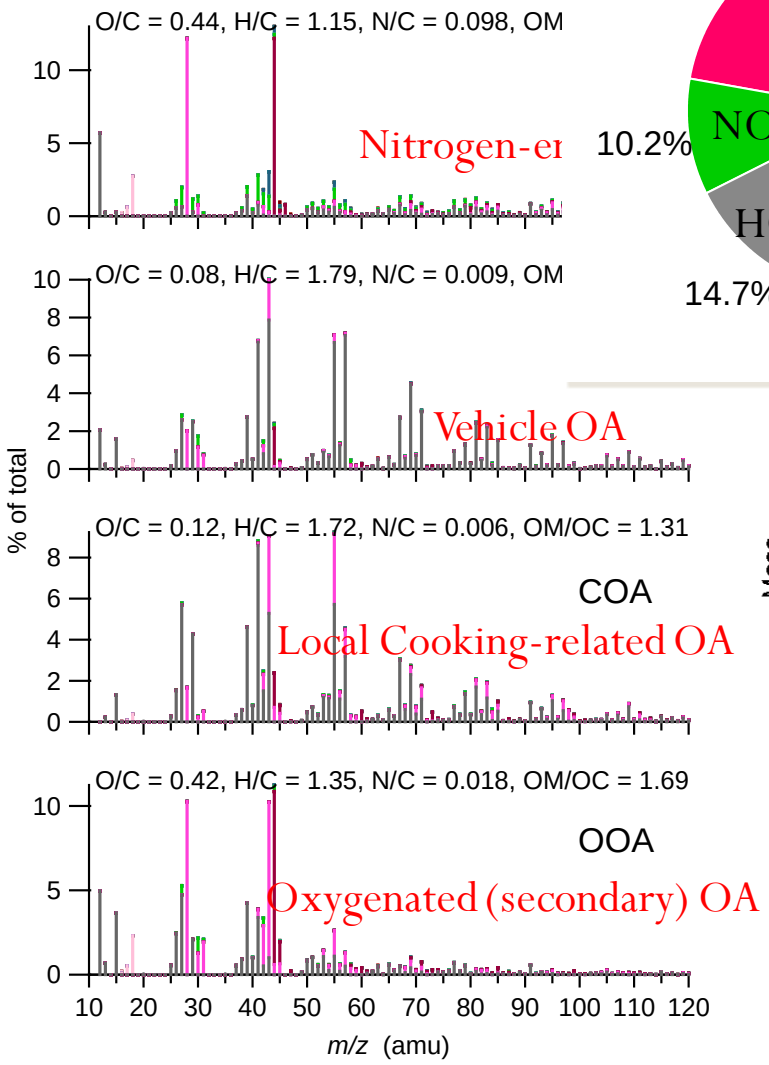
$ORG_{t\times i}$ =

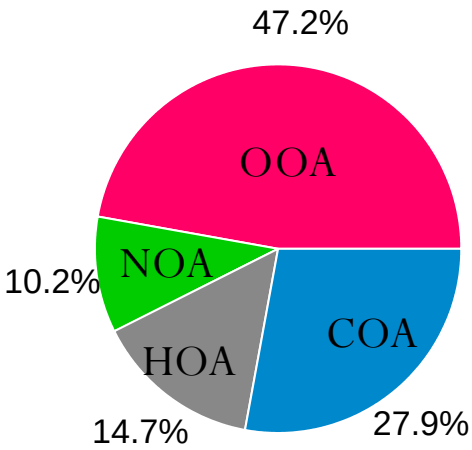
$$\overrightarrow{ms}_{Organics} = c_a \cdot \overrightarrow{ms}_a + c_b \cdot \overrightarrow{ms}_b + c_c \cdot \overrightarrow{ms}_c + \ldots$$

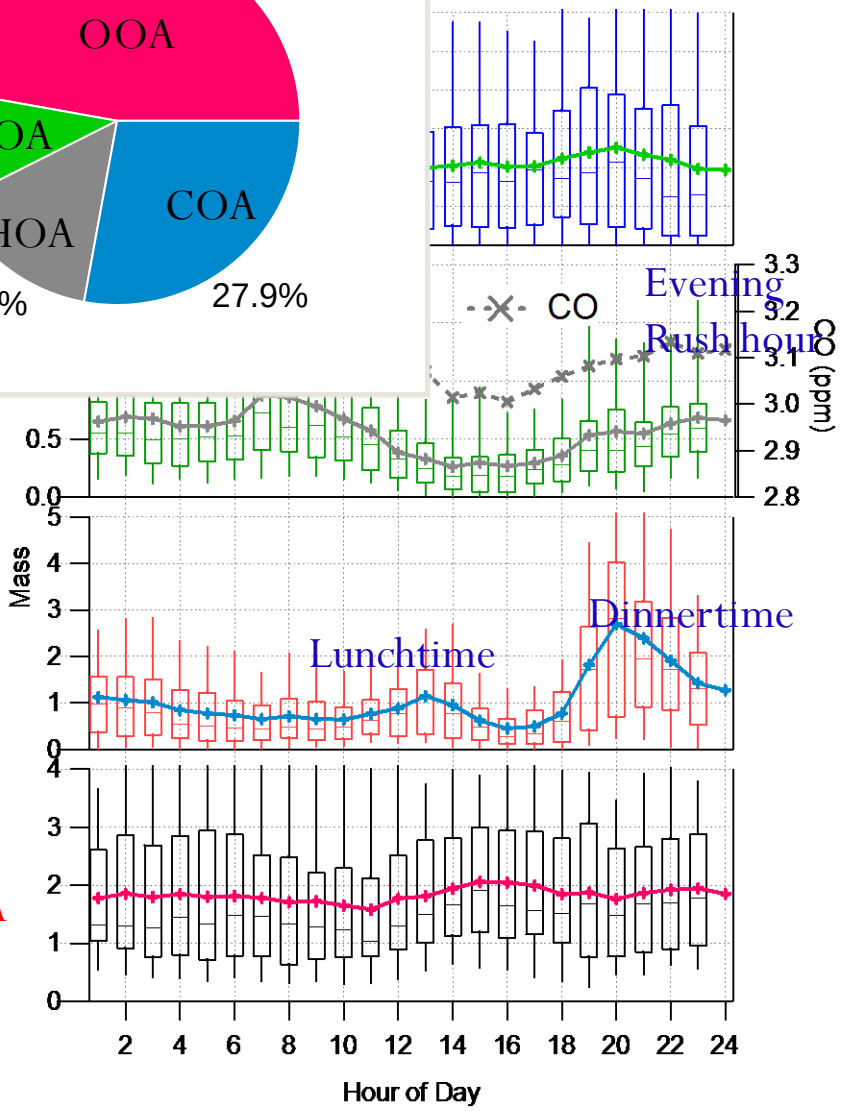



Courtesy: Q. Zhang

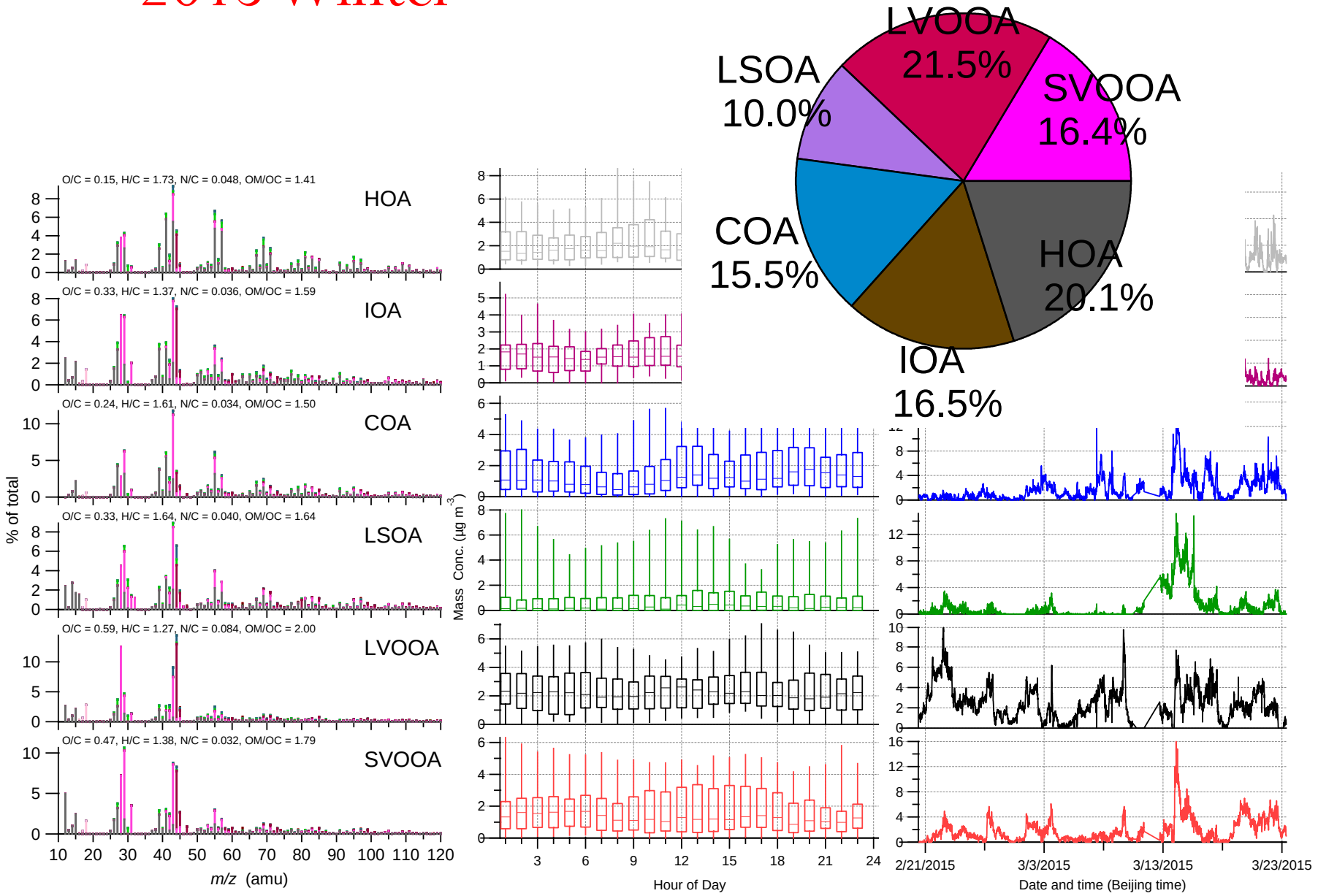
# 2014 Summer


O/C = 0.44, H/C = 1.15, N/C = 0.098, OM
Nitrogen-er
O/C = 0.08, H/C = 1.79, N/C = 0.009, OM
Vehicle OA
O/C = 0.12, H/C = 1.72, N/C = 0.006, OM/OC = 1.31
COA
Local Cooking-related OA
O/C = 0.42, H/C = 1.35, N/C = 0.018, OM/OC = 1.69
OOA
Oxygenated (secondary) OA
% of total
m/z (amu)


47.2%
OOA
10.2%
NOA
HOA
14.7%
COA
27.9%


CO
Evening
Rush hour
(ppm)
Mass
Lunchtime
Dinnertime
Hour of Day

# 2015 Winter


LVOOA
21.5%
SVOOA
16.4%
LSOA
10.0%
COA
15.5%
HOA
20.1%
IOA
16.5%
O/C = 0.15, H/C = 1.73, N/C = 0.048, OM/OC = 1.41
HOA
O/C = 0.33, H/C = 1.37, N/C = 0.036, OM/OC = 1.59
IOA
O/C = 0.24, H/C = 1.61, N/C = 0.034, OM/OC = 1.50
COA
O/C = 0.33, H/C = 1.64, N/C = 0.040, OM/OC = 1.64
LSOA
O/C = 0.59, H/C = 1.27, N/C = 0.084, OM/OC = 2.00
LVOOA
O/C = 0.47, H/C = 1.38, N/C = 0.032, OM/OC = 1.79
SVOOA
% of total
m/z (amu)
Mass Conc. (μg m-3)
Hour of Day
2/21/2015
3/3/2015
3/13/2015
3/23/2015
Date and time (Beijing time)

# Conclusions

- *For the first time*, we conducted the SP-AMS study in China……and got lots of interesting results…
- *For the first time*, we discovered the occurrence of fullerenes in the ambient particles, in China atmosphere.
- Only an overview, lots of in-depth analyses are needed……

*TO BE CONTINUED……*