Yale-NUIST Center on Atmospheric Environment

# Biomass Burning Contribution to Haze Episode in Winter of Nanjing

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# Outline

- Introduction
- Material and method
- Result and Discussion
- Conclusion
- Other work

## 1月24日，雾霾给南京“颜色”看

2015年01月24日，江苏省南京市，双休日的第一天遭遇严重雾霾天气，晦暗压抑的天空，给这个大都市“颜色”看。
当日，南京9个空气质量实时监测点平均数值一直处于200以上。到18点，9个监测点中，有3个严重污染，其余6个都处在重度级别，仙林监测点数值一度达到316。



耶鲁大学-南京信息工程大学大气环境中心
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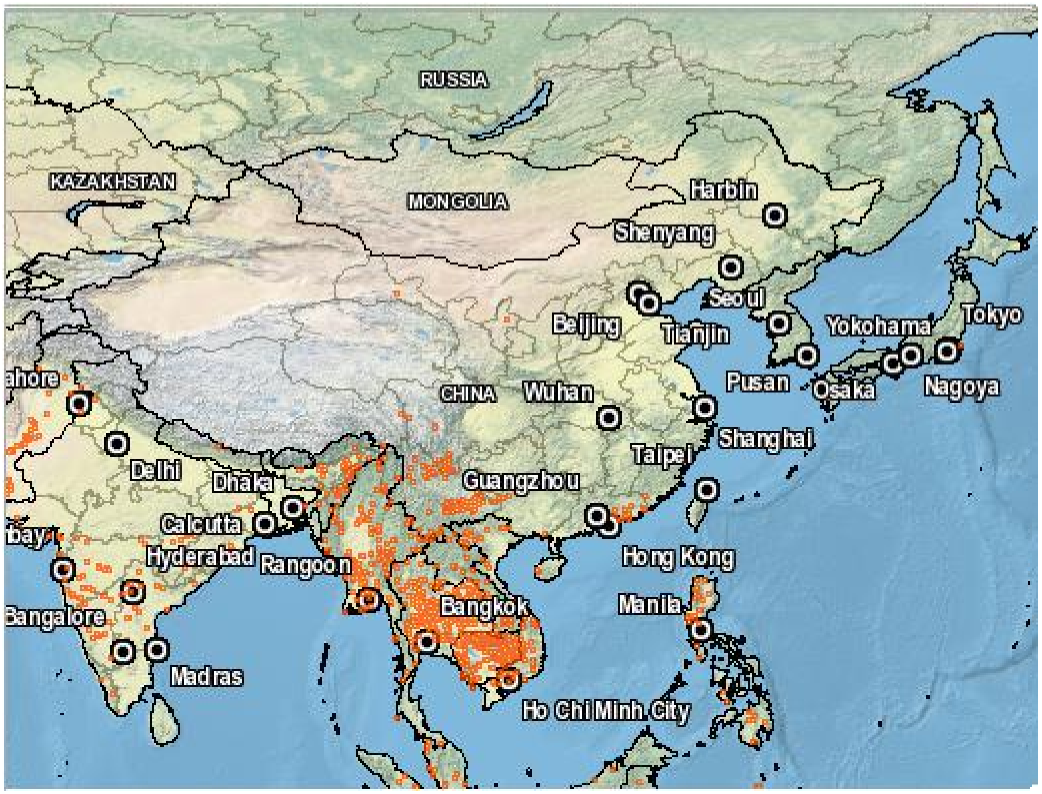
# *Yale-NUIST Center on Atmospheric Environment*




14-15

22-23

28-29

# Introduction

- Biomass Burning (BB)
- **what is BB?**
- Biomass burning includes the combustion of biomass fuels through either natural (e.g., wildfires) or planned processes (e.g., prescribed burning and residential wood combustion in fireplaces and wood stoves) .
- **Impact:** BB emit large amounts of air pollutants , which especially exists in fine particles.
- Fossil fuel burning has gained attention for about 2 centuries, but scientific interest in biomass burning grew when it had been suggested that for some atmospheric pollutants biomass burning could rival fossil fuel use as a source of atmospheric pollution *(Seiler and Crutzen, 1980; Crutzen and Andreae, 1990)* .The biomass burning contribution to seasonal ambient $PM_{2.5}$ mass is much higher in China, that is, 12-27μg $m^{-3}$ (15-24%) in Beijing *(Cheng et al., 2013; Song et al., 2007; Wang et al., 2009)*, 5.4-25.4 μg $m^{-3}$ (4-19%) in Guangzhou *(Wang et al., 2007), 37% in YRD (70% to OC)(Z. Cheng et al., 2014)*
- It became evident that these emissions could affect large areas of the world as a consequence of long-range transport *(Andreae, 1983; Fishman et al., 1990).*
- **Tracer:** Levoglucosan, $K^+$.

# Material and method

- Sampling site


- $PM_{2.5}$ Sampling instrument
  - Sampler: KC 1000
  - Sample collector: quartz filter（8×10 inch）

- Sampling frequency and time :

| Time | Frequency | Notes |
|---|---|---|
| 14th Jan 16:30-26th Jan 18:00 | Every 3 hrs | Afternoon of 14th : after light rain<br>Morning of 25th : light rain<br>9 a.m. to 1 p.m. of 25th :power failure |
| 26th Jan 18:00-29th Jan 00:00 | Every 6 hrs | 27th to 29th : rain and snow |

# Material and method

- Laborotary analysis of chemical species

| Chemical species | Instrument | Principle |
|---|---|---|
| Carbonaceous component | Sunset EC/OC analyzer | TOT |
| Water-soluble ion | ICS 5000+ | Ion Chromatography + Conductive Detector |
| Carbohydrate | ICS 5000+ | Ion Chromatography + Electrochemical Detector |

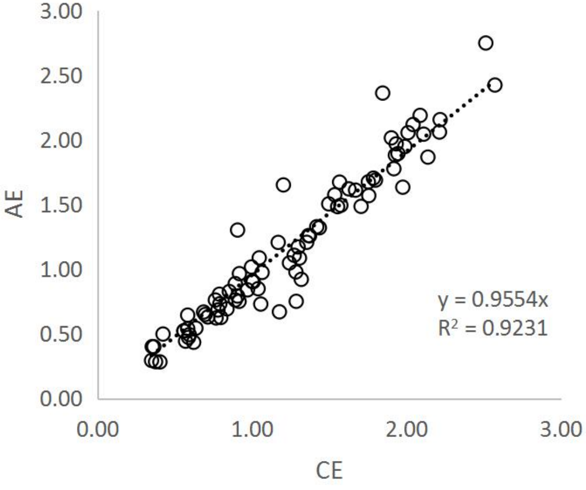
| | Cation | Anion | Carbohydrate |
|---|---|---|---|
| Column | IonPac CS12A<br>IonPac CG 12A | IonPac AS11-HC<br>IonPac AG11-HC | MA |
| Loop | 25 μ L | 25 μ L | 200 μ L |
| Elution Method | Flow:1mL $min^{-1}$<br>MSA:0-20min<br>30mM $L^{-1}$ | Flow:1.5mL $min^{-1}$<br>NaOH:0-3min 0.5mM $L^{-1}$,3-5min 0.5-5mM $L^{-1}$,<br>5-15min 5-30mM $L^{-1}$,15.1-20min 0.5mM $L^{-1}$ | Flow:0.4mL $min^{-1}$<br>NaOH:-15-34min 300mM $L^{-1}$,<br>34-45min 480mM $L^{-1}$,<br>45-60min 480-650mM $L^{-1}$ |

- QAQC

| Cation | Cal.Type | Points | Offset | Slope | Coeff.Det. % | RSD % | LOD ppb |
|---|---|---|---|---|---|---|---|
| glycerol | Lin | 5 | 0 | 0.0579 | 99.9712 | 2.5387 | 0.23 |
| threitol | Lin | 8 | 0 | 0.0804 | 99.996 | 0.9092 | 0.17 |
| xylitol | Lin | 8 | 0 | 0.0537 | 99.9657 | 2.7081 | 0.33 |
| levoglucosan | Lin | 8 | 0 | 0.0184 | 99.9842 | 1.8484 | 0.79 |
| arabitol | Lin | 6 | 0 | 0.0559 | 99.9964 | 0.773 | 0.28 |
| mannanson | Lin | 6 | 0 | 0.004 | 99.9765 | 1.965 | 5.90 |
| mannitol | Lin | 6 | 0 | 0.0549 | 99.9629 | 2.5023 | 0.42 |
| galctosan | Lin | 6 | 0 | 0.0297 | 99.922 | 3.6142 | 0.80 |
| mannose | Lin | 5 | 0 | 0.0398 | 99.9341 | 2.6905 | 0.69 |
| glucose | Lin | 5 | 0 | 0.0347 | 99.953 | 2.7181 | 0.65 |
| galactose | Lin | 5 | 0 | 0.0342 | 99.9592 | 2.0977 | 0.47 |
| fructose | Lin | 5 | 0 | 0.001 | 99.9779 | 1.603 | 19.94 |

- QAQC

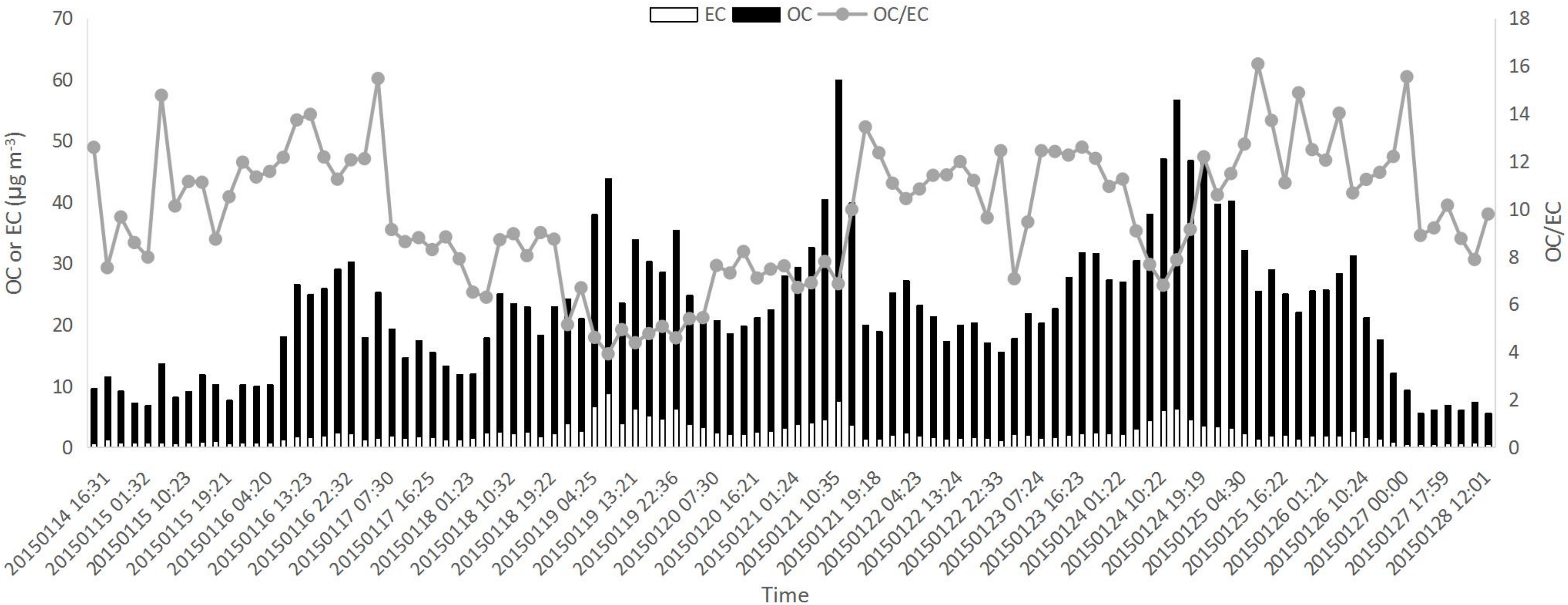
| Cation | Cal.Type | Points | Offset | Slope | Coeff.Det. % | RSD % | recovery % | LOD ppb |
|---|---|---|---|---|---|---|---|---|
| Na+ | LOff | 10 | 0.0108 | 0.2783 | 99.998 | 1.45 | 98.25 | 0.06 |
| NH4+ | Quad | 9 | 0.0000 | 0.1975 | 99.935 | 1.06 | 129.51 | 0.03 |
| K+ | LOff | 9 | 0.0025 | 0.1787 | 99.9985 | 0.72 | 95.72 | 0.12 |
| Mg2+ | LOff | 8 | 0.0037 | 0.5311 | 99.9984 | 1.75 | 97.25 | 0.08 |
| Ca2+ | LOff | 10 | 0.0113 | 0.3375 | 99.9985 | 1.09 | 111.95 | 0.13 |
| F- | LOff | 5 | -0.0037 | 0.3836 | 99.921 | 0.03 | 89.59 | 0.22 |
| MSA- | LOff | 6 | -0.002 | 0.0691 | 99.9321 | 0.01 | 107.29 | 1.62 |
| Cl- | LOff | 8 | -0.0003 | 0.2241 | 99.9494 | 0.72 | 95.75 | 0.64 |
| NO2- | LOff | 5 | 0 | 0.13 | 99.9298 | 0.06 | 104.48 | 1.11 |
| NO3- | LOff | 5 | -0.0254 | 0.1061 | 99.9254 | 0.08 | 111.85 | 2.67 |
| SO42- | LOff | 9 | -0.009 | 0.1481 | 99.8518 | 0.08 | 116.15 | 1.41 |

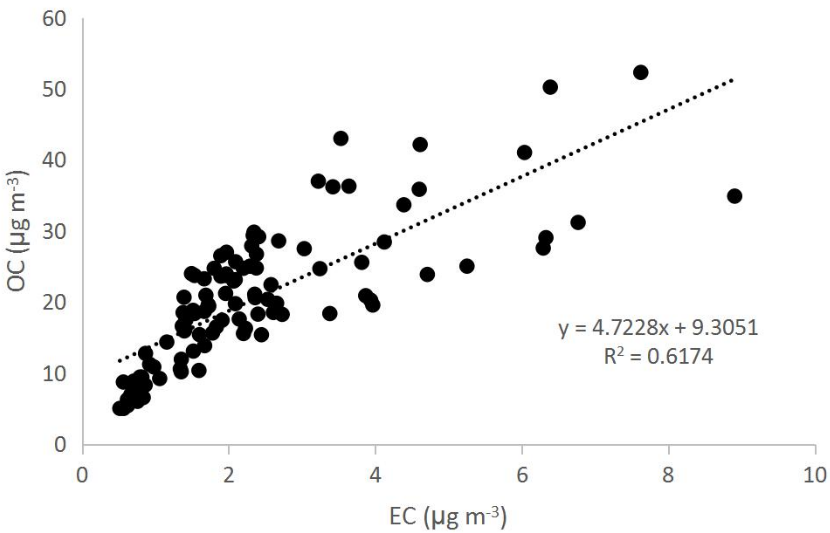



$$CE = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39.1} + \frac{2 \cdot Mg^{2+}}{24.3} + \frac{2 \cdot Ca^{2+}}{40}$$

$$AE = \frac{Cl^-}{35.45} + \frac{2 \cdot SO_4^{2-}}{96} + \frac{NO_3^-}{62} + \frac{MSA^-}{95.08} + \frac{F^-}{19} + \frac{NO_2^-}{46}$$

# Result and Discussion




| | OC | EC | SOC | OC/EC | SOC/OC |
|---|---|---|---|---|---|
| | | (μg m-3) | | | |
| min | | | | | |
| max | | | | | |
| average | | | | | |

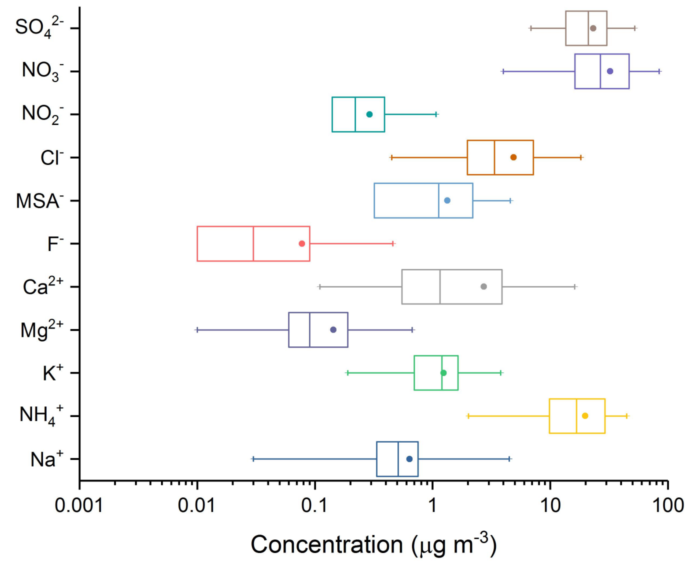
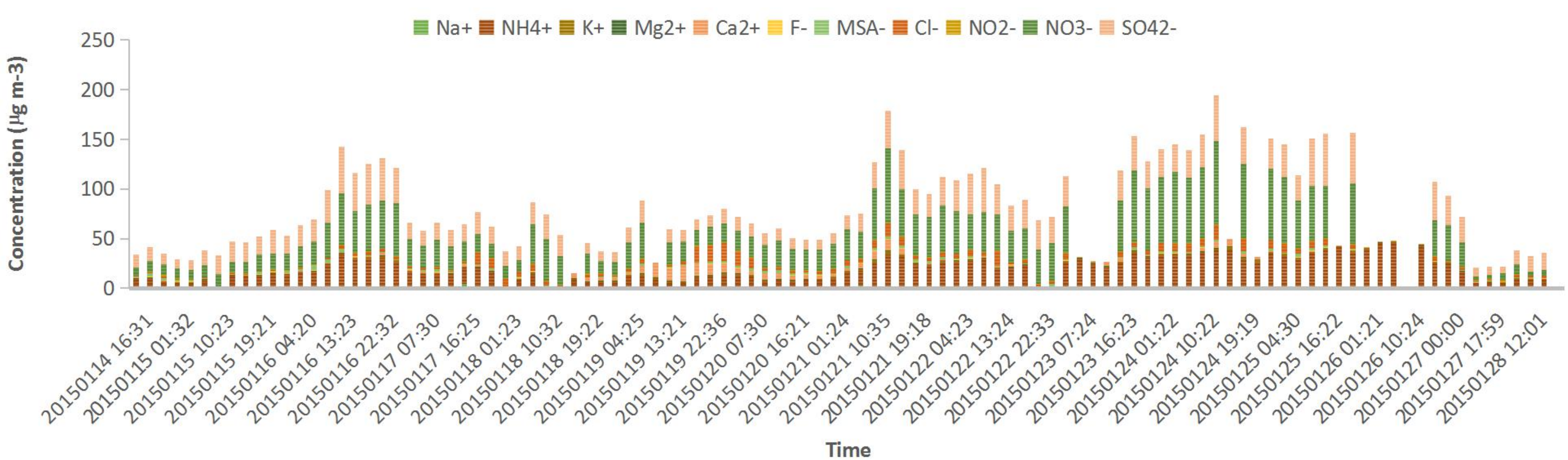


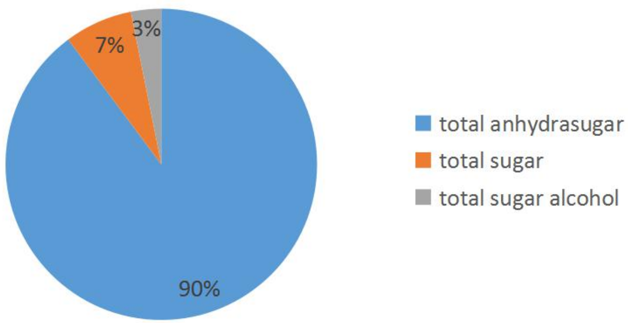

Figure 5. Concentration distribution of inorganic ion. The box represent the 25th (lower line),50th (middle line), 75th (top line) percentiles; the end of the vertical bars represent the 10th (below the box) and 90th (above the box) percentiles.The solid dots and stars represent abnormal value.

Table 3. The max, min and average value of inorganic ion in $PM_{2.5}$ and its ratio to $PM_{2.5}$.Ion in μ g $m^{-3}$

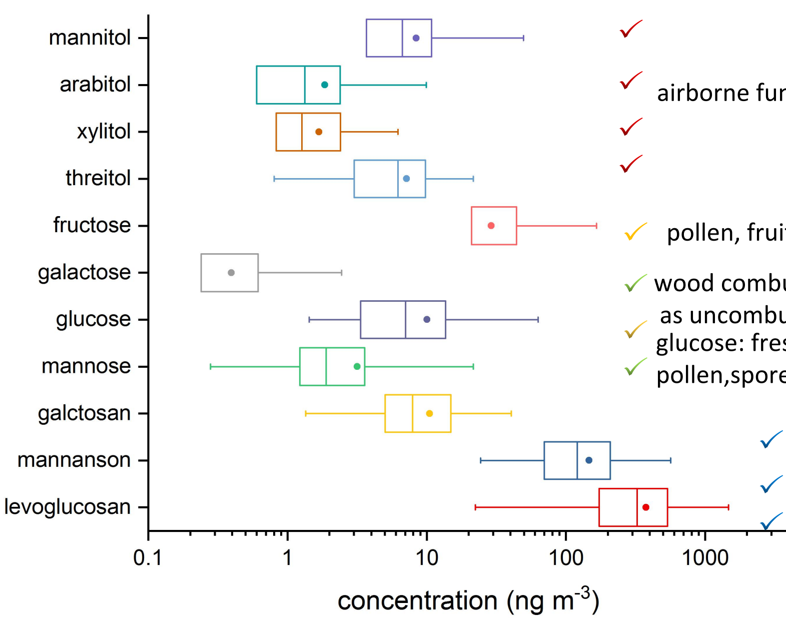
| | Average | SD | Max | Min |
|---|---|---|---|---|
| | ($\mu g\ m^{-3}$) | | | |
| $Na^+$ | 0.64 | 0.57 | 4.49 | 0.03 |
| $NH_4^+$ | 19.79 | 11.23 | 44.73 | 2.02 |
| **$K^+$** | **1.24** | **0.71** | **3.79** | **0.19** |
| $Mg^{2+}$ | 0.14 | 0.13 | 0.67 | 0.01 |
| $Ca^{2+}$ | 2.72 | 3.45 | 16.13 | 0.11 |
| $F^-$ | 0.08 | 0.10 | 0.46 | 0.00 |
| $MSA^-$ | 1.33 | 1.10 | 4.58 | 0.00 |
| $Cl^-$ | 4.89 | 4.22 | 18.21 | 0.45 |
| $NO_2^-$ | 0.29 | 0.22 | 1.07 | 0.00 |
| $NO_3^-$ | 32.30 | 20.05 | 84.14 | 3.98 |
| $SO_4^{2-}$ | 23.18 | 11.37 | 52.14 | 6.86 |



Total carbohydrate level in this study is higher than the mean level in urban area of Shanghai（503.7 ng $m^{-3}$） and Guangzhou（206.0 ng $m^{-3}$） during winter time（*Ma et al., 2009, Du et al., 2015*）。




| | average | SD | max | min |
|---|---|---|---|---|
| | | ng $m^{-3}$ | | |
| levoglucosan | | | | |
| mannanson | | | | |
| galactosan | | | | |
| **total anhydrasugar** | | | | |

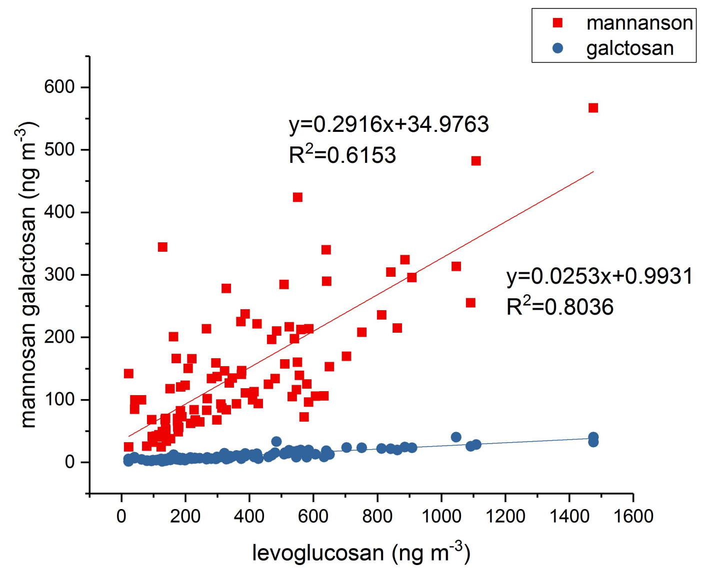


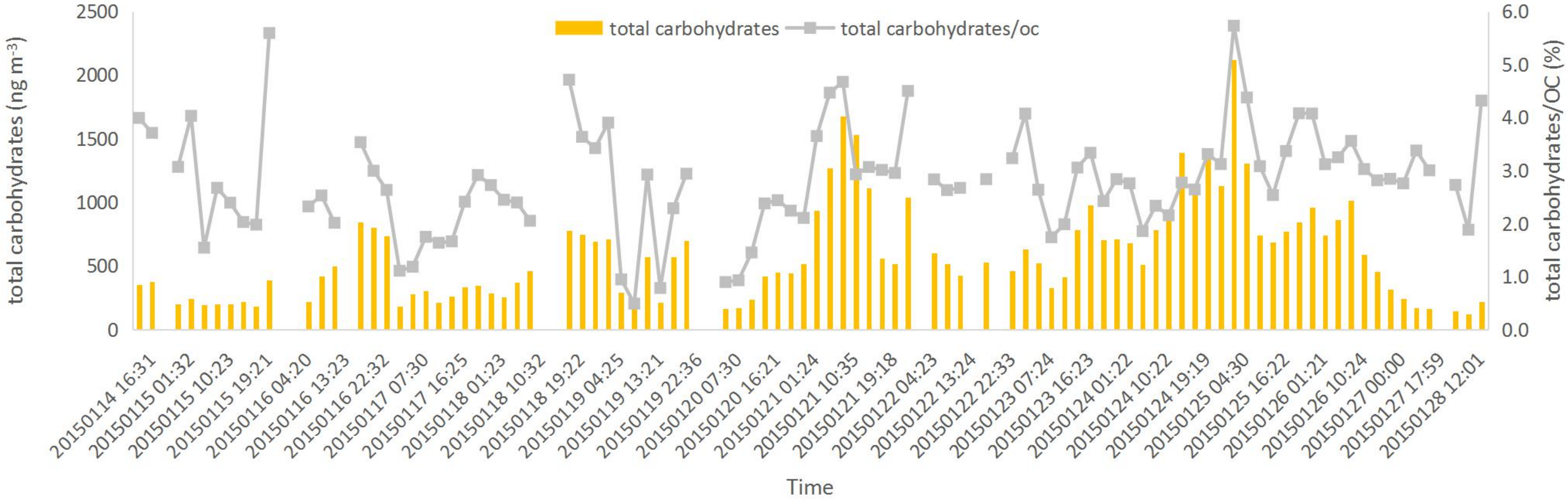

airborne fungal spores

pollen, fruit, debritus

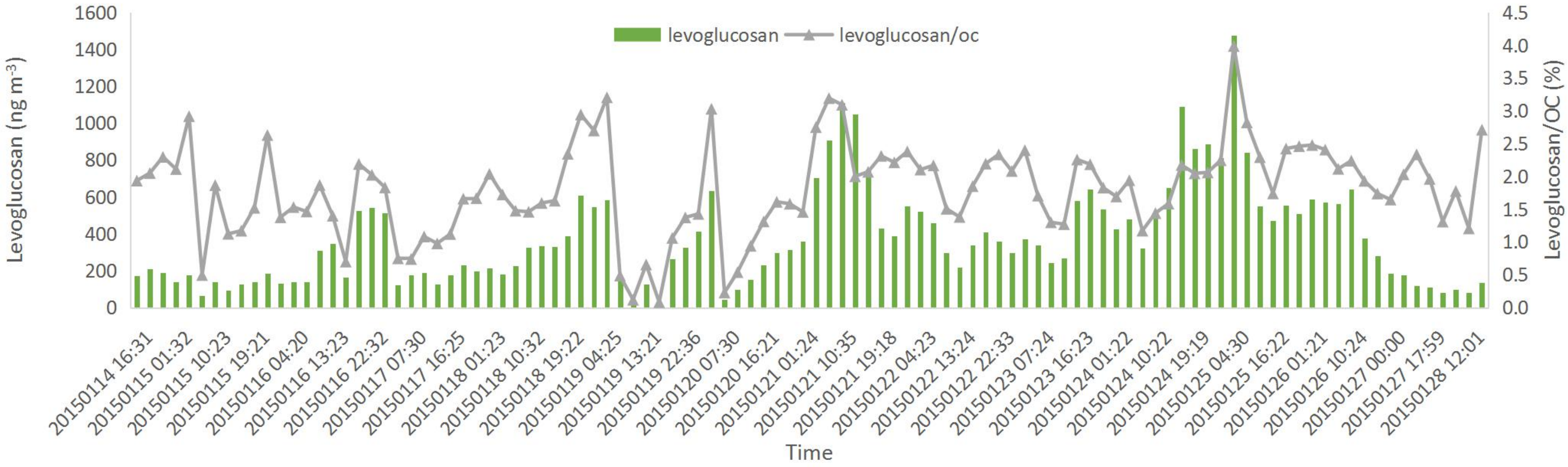
wood combustion, emitted as uncombusted material glucose: fresh leaf surfaces, pollen,spores,fungi,soil

biomass burning

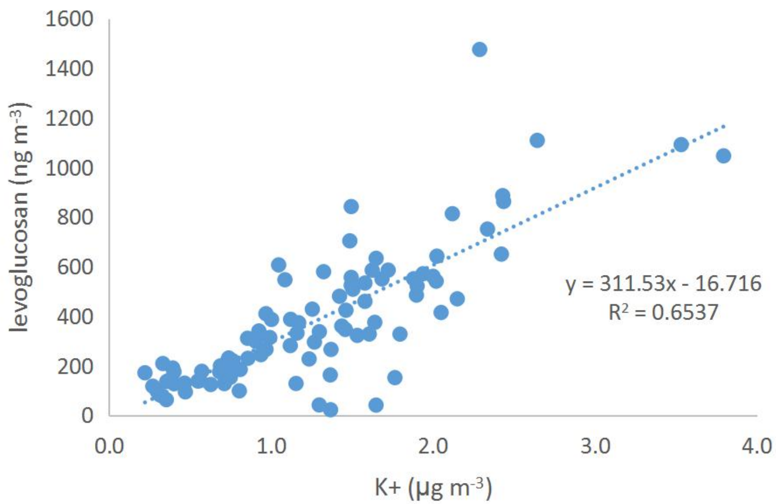


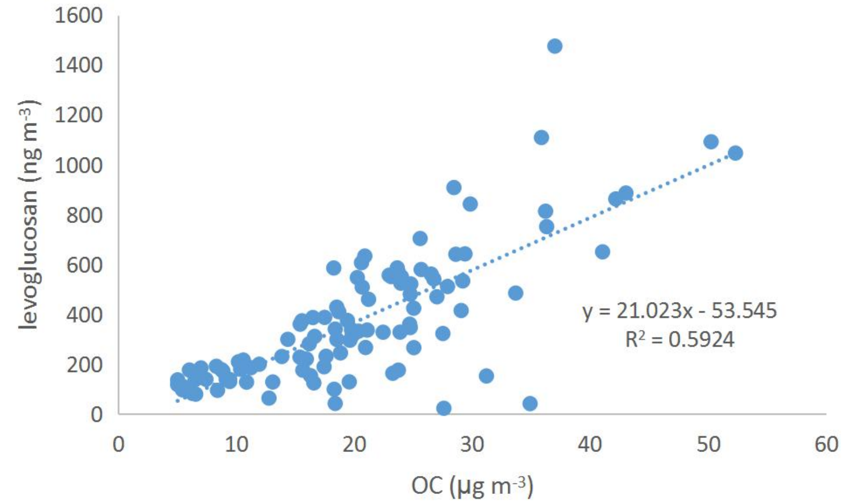



Total carbohydrate to OC ratio ranges from 0.54% to 5.31%， with a mean value of 2.86% which is higher than that of urban area in Shanghai during winter（X. Li et al., 2016）.



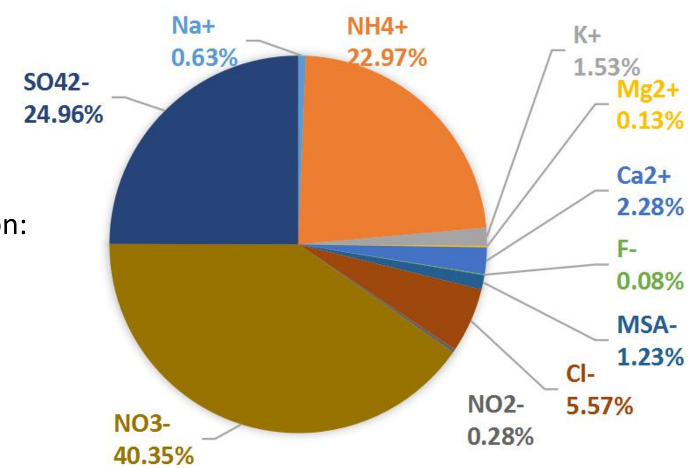

Levoglucosan is the most dominant component in total carbohydrate with a portion of 63%, indicating the significant contribution of biomass burning. Levoglucosan to OC ratio varies from 0.08% to 3.99%， with a mean level of 1.81% .



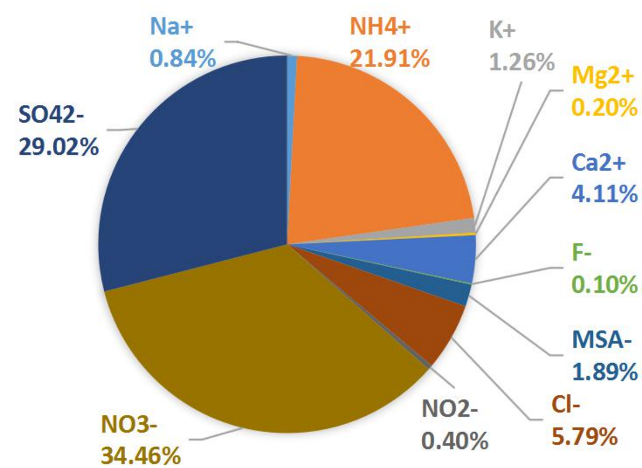

Good correlationship between levoglucosan and $K^+$ or OC suggested the important contribution of biomass burning.

Above mean amount of  levoglucosan

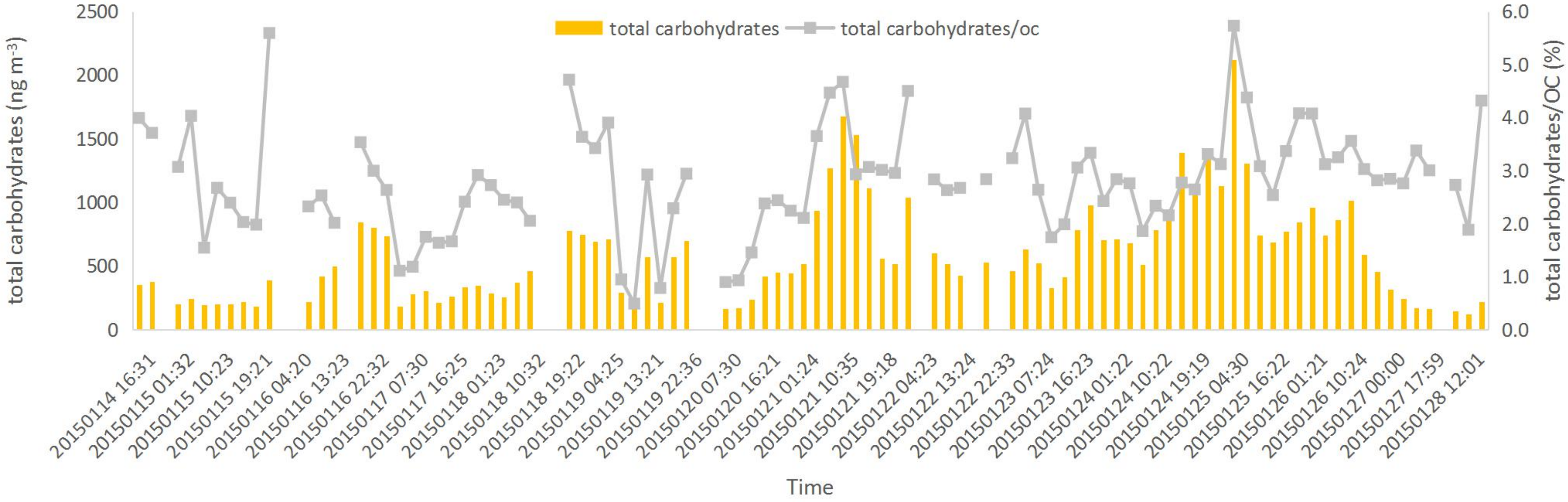



Second Ion: 88.28%

Below mean amount of levoglucosan




Second Ion: 85.39%

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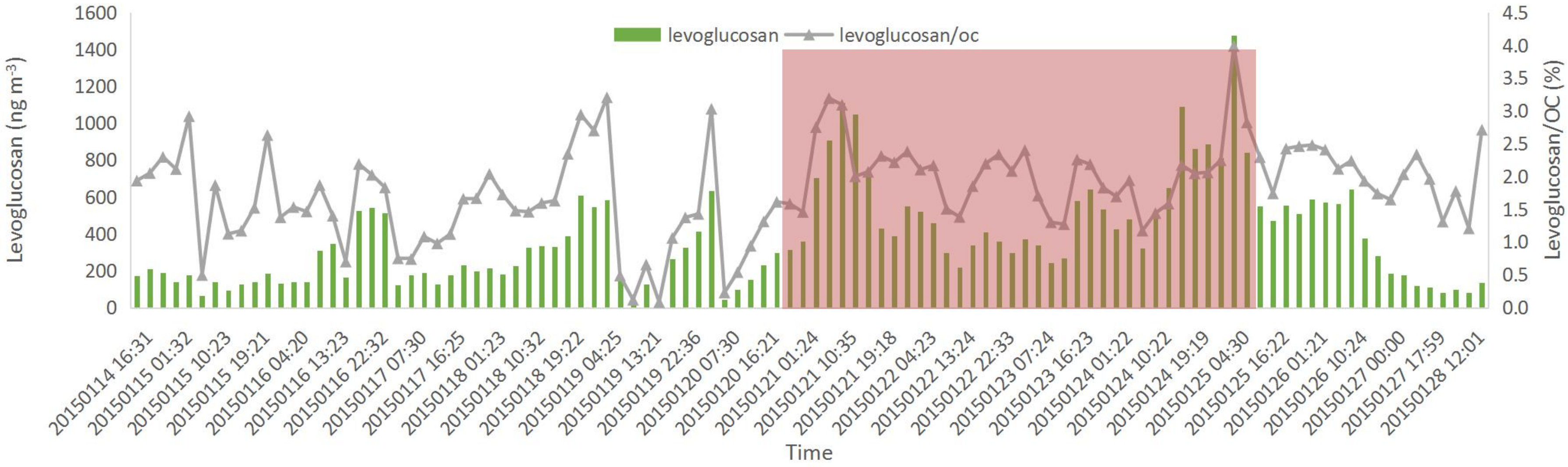


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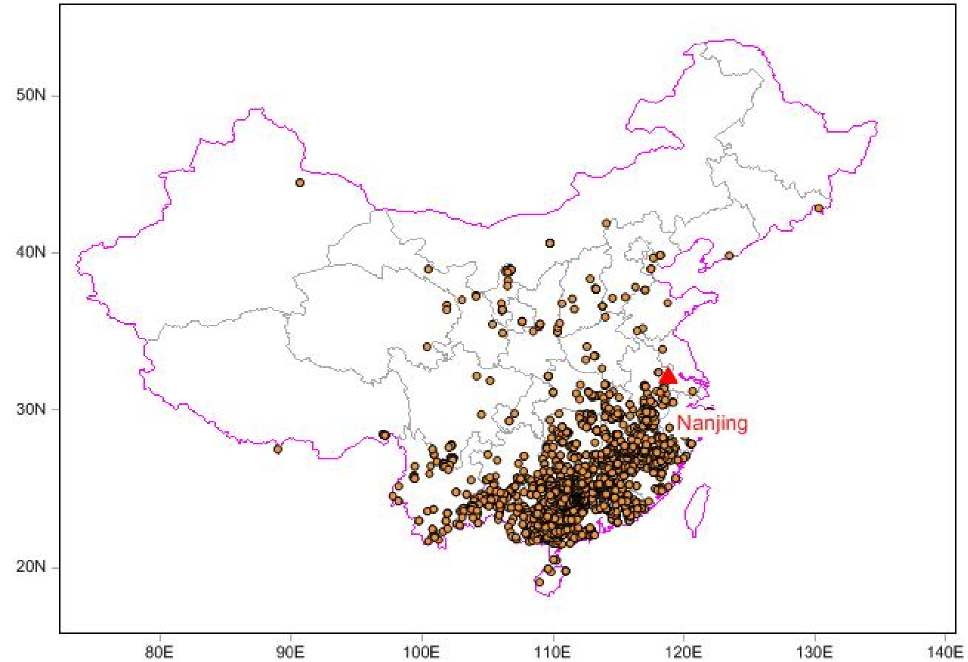
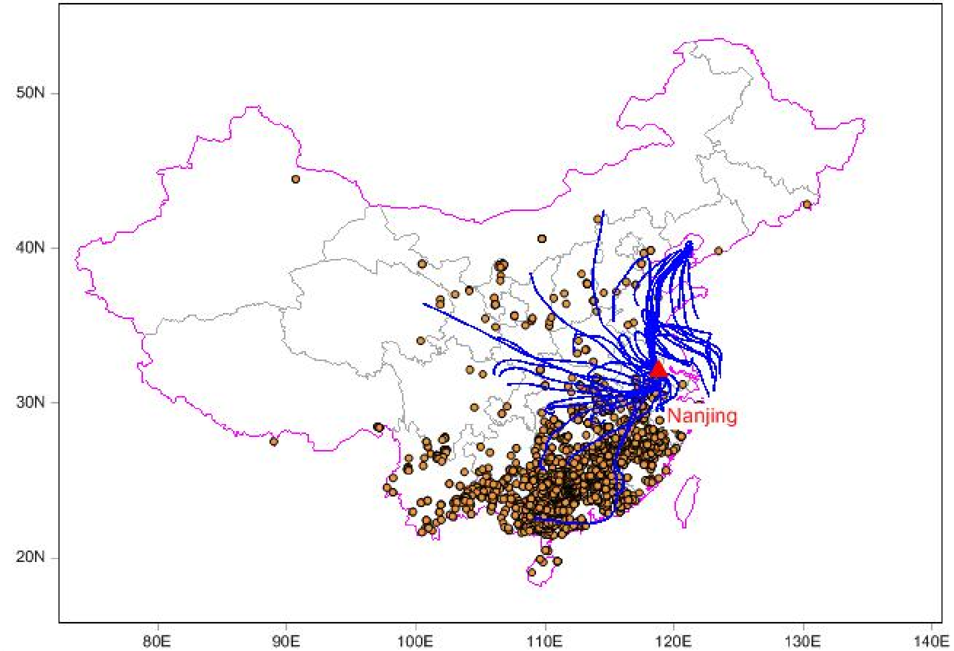
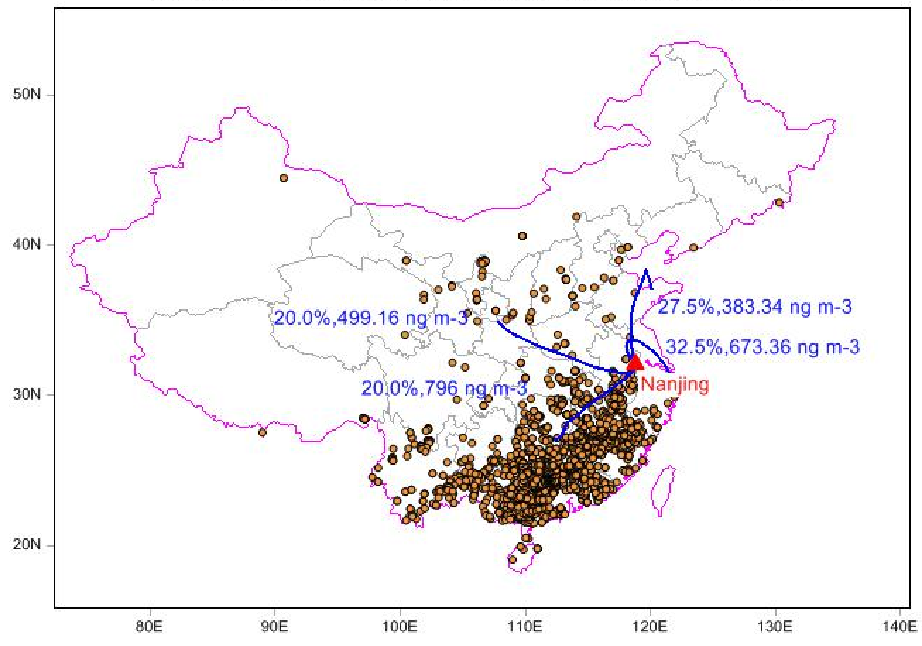
Air mass backward trajectory from Jan 21 to Jan 25




Air mass backward trajectory from Jan 21 to Jan 25



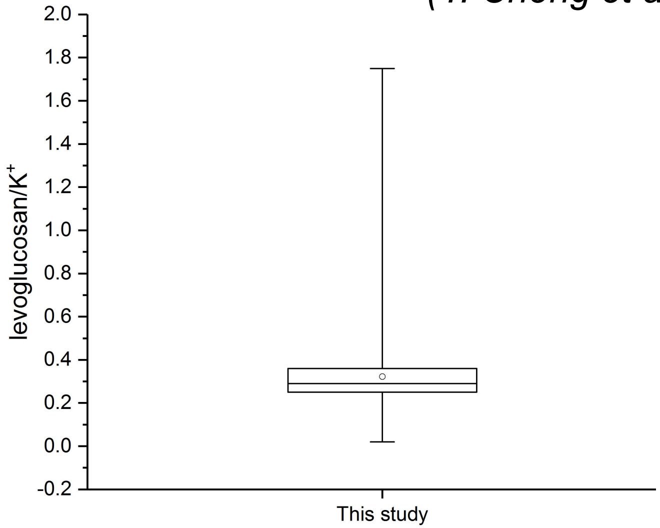

Air mass backward trajectory from Jan 21 to Jan 25

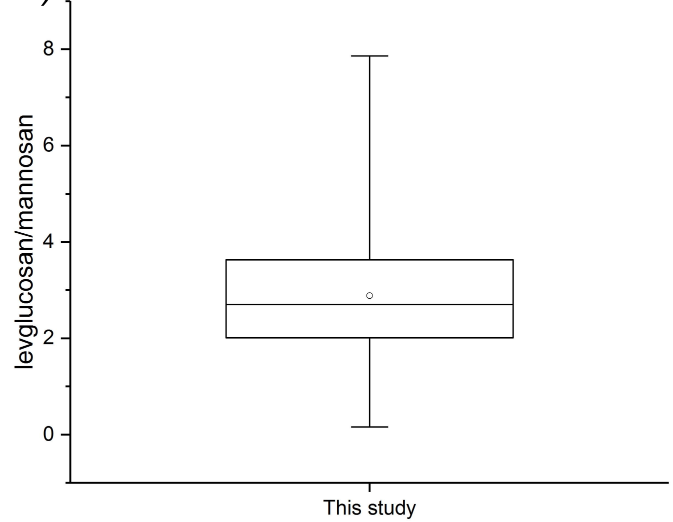


| | Ambient samples | | | |
|---|---|---|---|---|
| | BB episode | Typical summer | Firework episode | Typical winter |
| levo./$K^+$ | $0.11 \pm 0.06$ | $0.21 \pm 0.16$ | $0.16 \pm 0.09$ | $0.51 \pm 0.15$ |
| levo./manno. | $25.01 \pm 13.20$ | $12.65 \pm 3.38$ | $10.88 \pm 1.23$ | $9.01 \pm 1.47$ |
| | Source samples | | | |
| | Wheat straw | Corn straw | Pine wood | Poplar wood |
| levo./$K^+$ | $0.10 \pm 0.00$ | $0.21 \pm 0.08$ | $23.96 \pm 1.82$ | $5.89 \pm 0.53$ |
| levo./manno. | $12.71 \pm 1.53$ | $19.48 \pm 3.37$ | $2.69 \pm 0.03$ | $5.98 \pm 1.40$ |

| | levoglucosan/$K^+$ | levoglucosan/mannosan |
|---|---|---|
| average | 0.32±0.19 | 2.89±1.34 |
| max | 1.75 | 7.86 |
| min | 0.02 | 0.16 |

*(Y. Cheng et al., 2013)*




| | $K^+$/OC |
|---|---|
| average | $0.06 \pm 0.01$ |
| max | 0.11 |
| min | 0.01 |

Savanna burning emissions during their flaming phase $K^+$ /OC: 0.08–0.10
*by Cachier et al. (1991), (1995,）Echalar et al. (1995) , Maenhaut et al. (1996) .*
K/OC ratio for agricultural residues burning: 0.04–0.13
*by Andreae and Merlet (2001)*

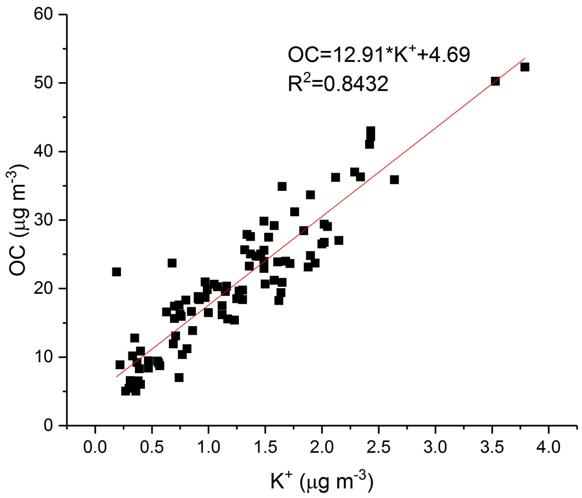
旋转成份矩阵a

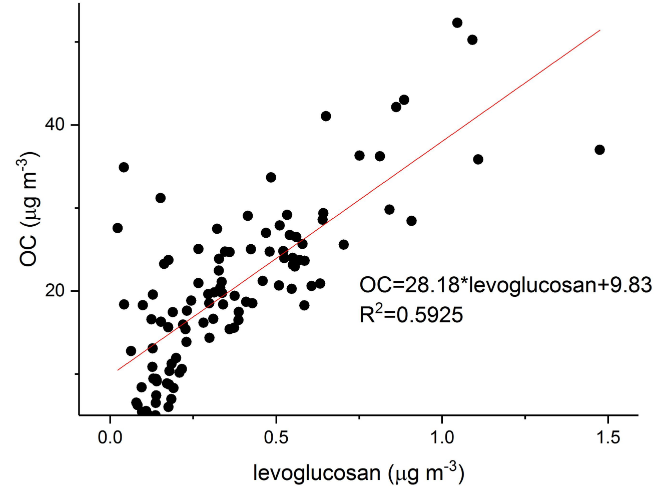
| | 成份 1 | 成份 2 | 成份 3 |
|---|---|---|---|
| OC | .800 | .494 | .026 |
| EC | .728 | .554 | .067 |
| Na | .165 | .438 | -.550 |
| NH4 | .935 | -.242 | .072 |
| K | .842 | .472 | .040 |
| Mg | -.006 | .957 | -.017 |
| Ca | -.031 | .955 | -.018 |
| F | .078 | .884 | .255 |
| MSA | .125 | .075 | .781 |
| Cl | .457 | .533 | .179 |
| NO2 | .097 | .251 | .459 |
| NO3 | .954 | -.003 | .065 |
| SO4 | .850 | -.238 | .082 |
| levoglucosan | .779 | .199 | .009 |

提取方法 :主成分分析法。 旋转法 :具有 Kaiser 标准化的正交旋转法。

- Factor 1:
  Biomass burning, fossil fuel burning
- Factor 2: Soil dust
- Factor 3: Marine emission

| | BB to OC_ $K^+$ | BB to OC_lev |
|---|---|---|
| | % | |
| average | 72.99% | 53.85% |
| min | 10.75% | 2.39% |
| max | 99.02% | 98.06% |

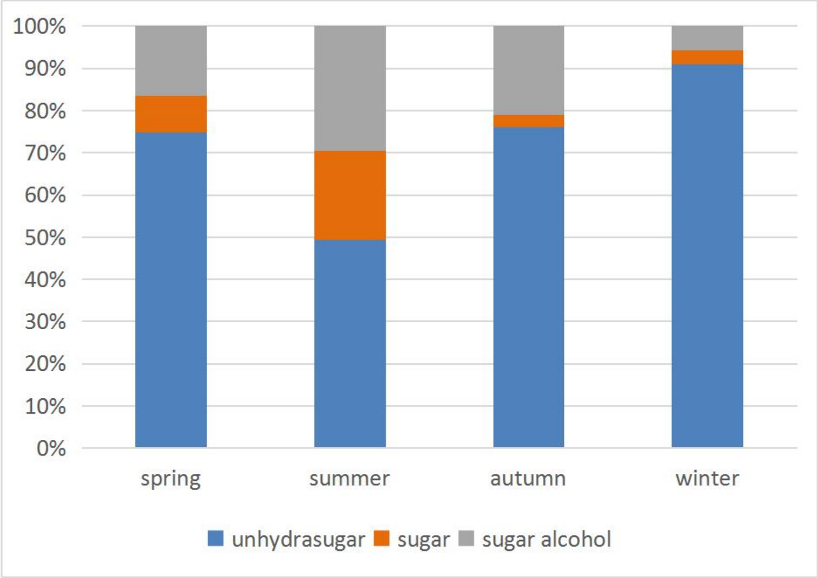


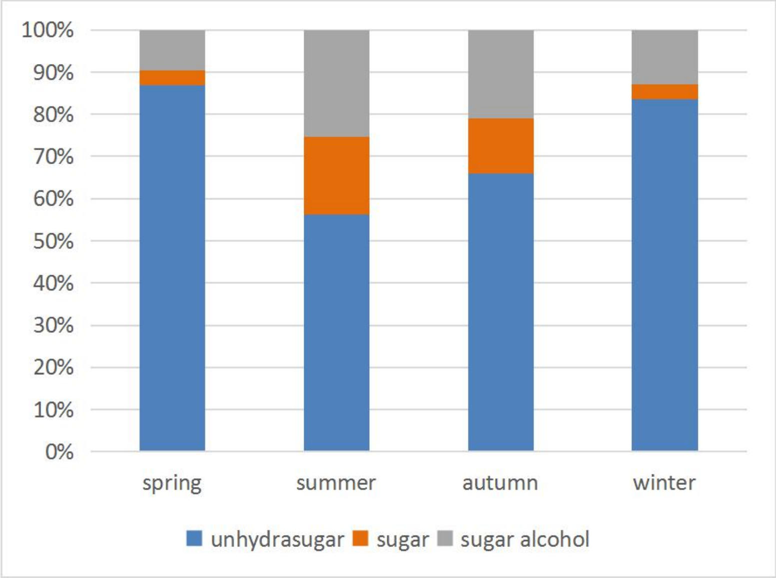



# Conclusion

- OC, EC mean concentration is 20.41 and 2.35 μg $m^{-3}$,with a mean OC/EC of in the ambient environment during this winter time pollution event in Nanjing. The good relationship between OC and EC indicates the important contribution of fuel combustion.
- The total carbohydrate concentration is 508.6 ng $m^{-3}$, including levoglucosan (375.6 ng $m^{-3}$) as its dominant component, with a high levglucosan/OC (1.81) illustrating the significant contribution of biomass burning to OC, which is estimited as 53.89%.
- It is identified that Nanjing has been influenced by open biomass burning in southeast China, through air mass long-range transport.
- Through PCA, main sources of emission are devided to biomass burning, fossil fuel burning, soil dust and marine emission.

# Nepal_$PM_{10}$


100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
spring
summer
autumn
winter
unhydrasugar
sugar
sugar alcohol


100%
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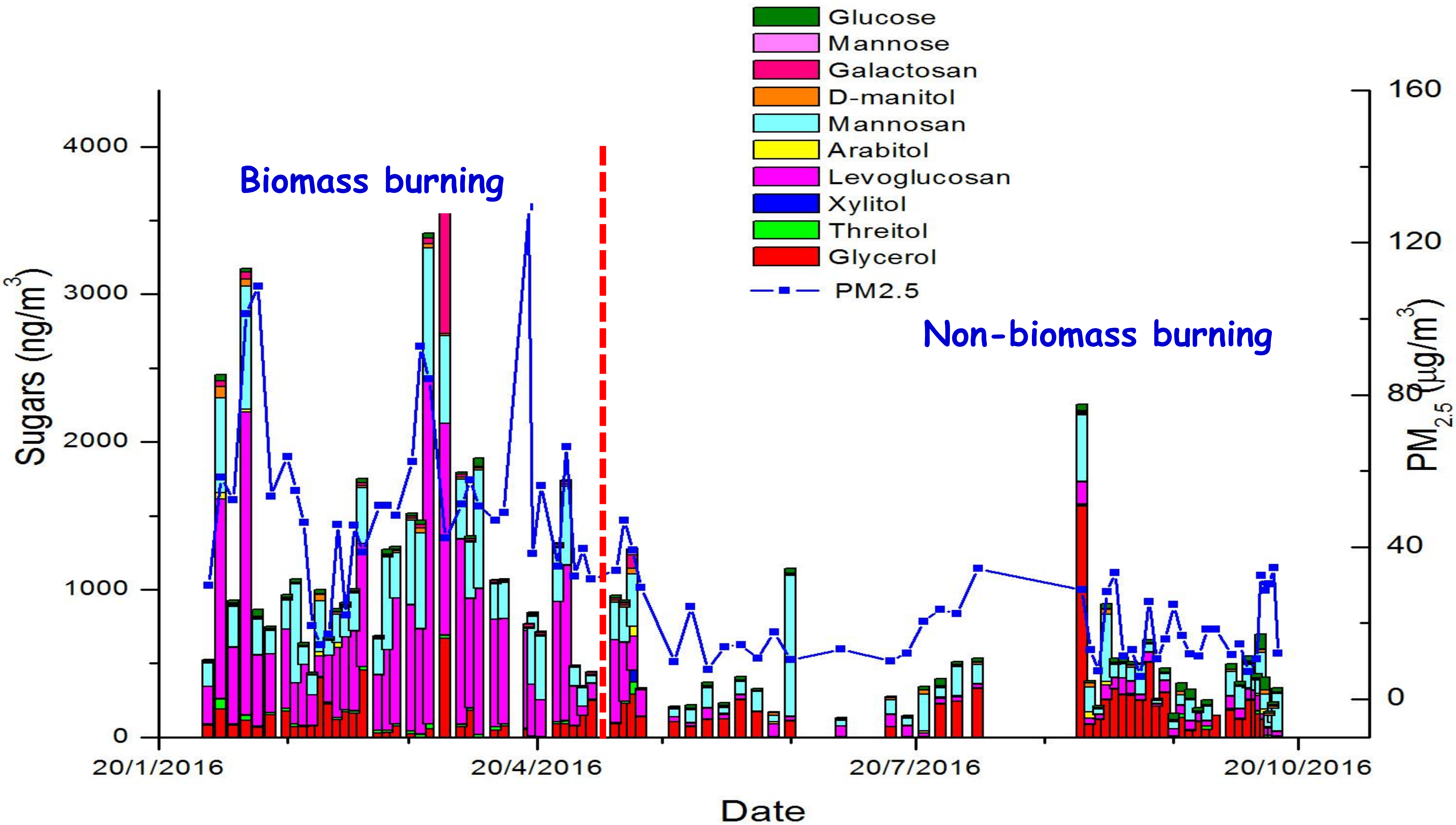
80%
70%
60%
50%
40%
30%
20%
10%
0%
spring
summer
autumn
winter
unhydrasugar
sugar
sugar alcohol

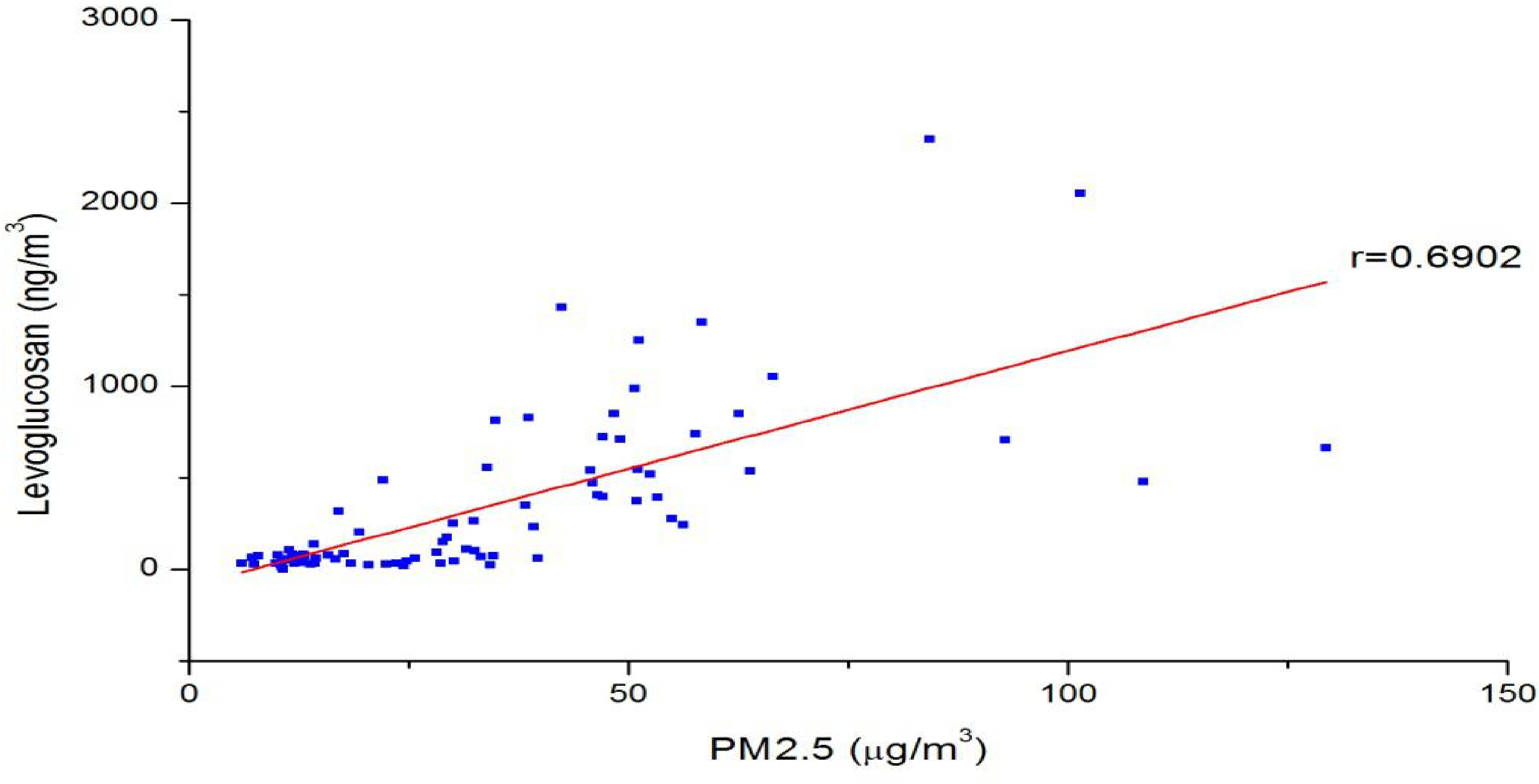
# Thailand

- The 10 sugars concentrations (ng/m$^3$) on PM$_{2.5}$ in BB and NBB




Research Institute for Health Sciences (RIHES), Chiang Mai University (CMU)

# The ratio of any sugars in total sugars on $PM_{2.5}$ in BB



# Outlook

- Looking for method to quantify contribution of biomass burning better.
- Investigate research method for various kinds of carbohydrates.
- Continue to improve seperation method for more sorts of target carbohydrate.

# Thank you