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Analysis on the chemical composition of $PM_{2.5}$ and the effect of biomass burning combustion in Northern surburb of Nanjing

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Outline

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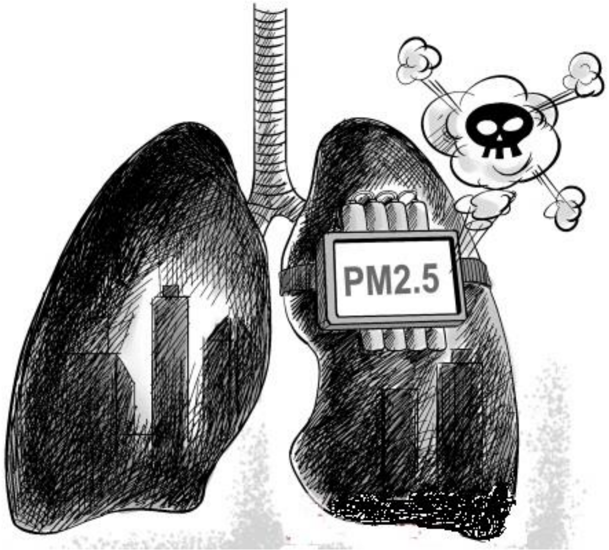
Introduction

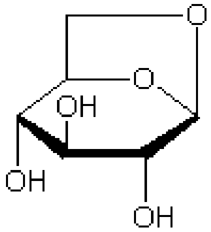
- Carbonaceous aerosols accounts for a high portion of $PM_{2.5}$, it includes organic carbon (OC) and element carbon (EC). Most of the EC derives from primary aerosol or incomplete combustion of fossil fuels or biomass; the origin of OC is relatively complex, it can exist in primary contaminant or it can developed from primary organic carbon (POC), which undergoes photochemical reaction and produces secondary organic carbon (SOC).OC and EC account for a high proportion in $PM_{2.5}$, and they have a great impact on environmental quality and human health. This topic is a hotspot in recent years at home or abroad.



Introduction

- In recent years, the reports of biomass burning increased a lot, which revealed many large-scale burning incidents in autumn. Although potassium may be useful as a biomass-burning tracer (Andreae,1983; Echalar et al.,1995), its application is limited by the fact that there are other important sources of this element such as soil and seawater. The monosaccharide levoglucosan released during the pyrolysis of cellulose at temperatures above 300°C, has been proposed as a specific tracer for biomass burning (Simoneit et al.,1999).

- Studies have found that, in addition to the effects of factories and motor vehicle emissions in suburban areas, influence of combustion due to exogenous biomass burning on $PM_{2.5}$ cannot be ignored. This research will explore for the first time the effect of biomass burning combustion on the northern suburb of Nanjing.



Levoglucosan($C_6H_{10}O_5$)

Experimental Method

➢ Experiment site

➢Observation data

Sampling time:
Mar 16th-Apr 15th 2015 Spring
May 25th-Jun 21th 2015 Summer
Oct 06th-Nov 05th 2015 Autumn
Dec 09th-Jan 07th 2015 Winter
Sampling place: Northern Suburbs of Nanjing
Samples: $PM_{2.5}$
Sampling frequency : 12 hours

OC and EC were analyzed by a Sunset Model 4 carbon analyzer with the Thermo optical transmission(TOT) method.

Water soluble ions and three kinds of dehydrated sugar were analyzed by ICS-5000^{+}.

Primary coverage

- Using the monitered data OC and EC of four seasons day and night to analyze the level and seasonal variation characters of pollution of OC and EC in the northern industrial area of Nanjing, and using the backward trajectory model and the analysis method of potential source contribution factor（PSCF）to explore the the influence of air mass from long distance and regional transportation on $PM_{2.5}$ in the northern suburb of Nanjing.

- Using data of water-soluble ions $PM_{2.5}$ monitored day and night in the characteristic months of four seasons to analyze the concentration level, seasonal variation, correlation of all kinds of water-soluble ions and $PM_{2.5}$ composition.

- Using the monitoring data of three kinds of sugar in $PM_{2.5}$ to study and explore on the contribution of biomass combustion to $PM_{2.5}$ to northern suburb of Nanjing.

Results and Discussion

➢Section 1 OC、EC Feature Analysis

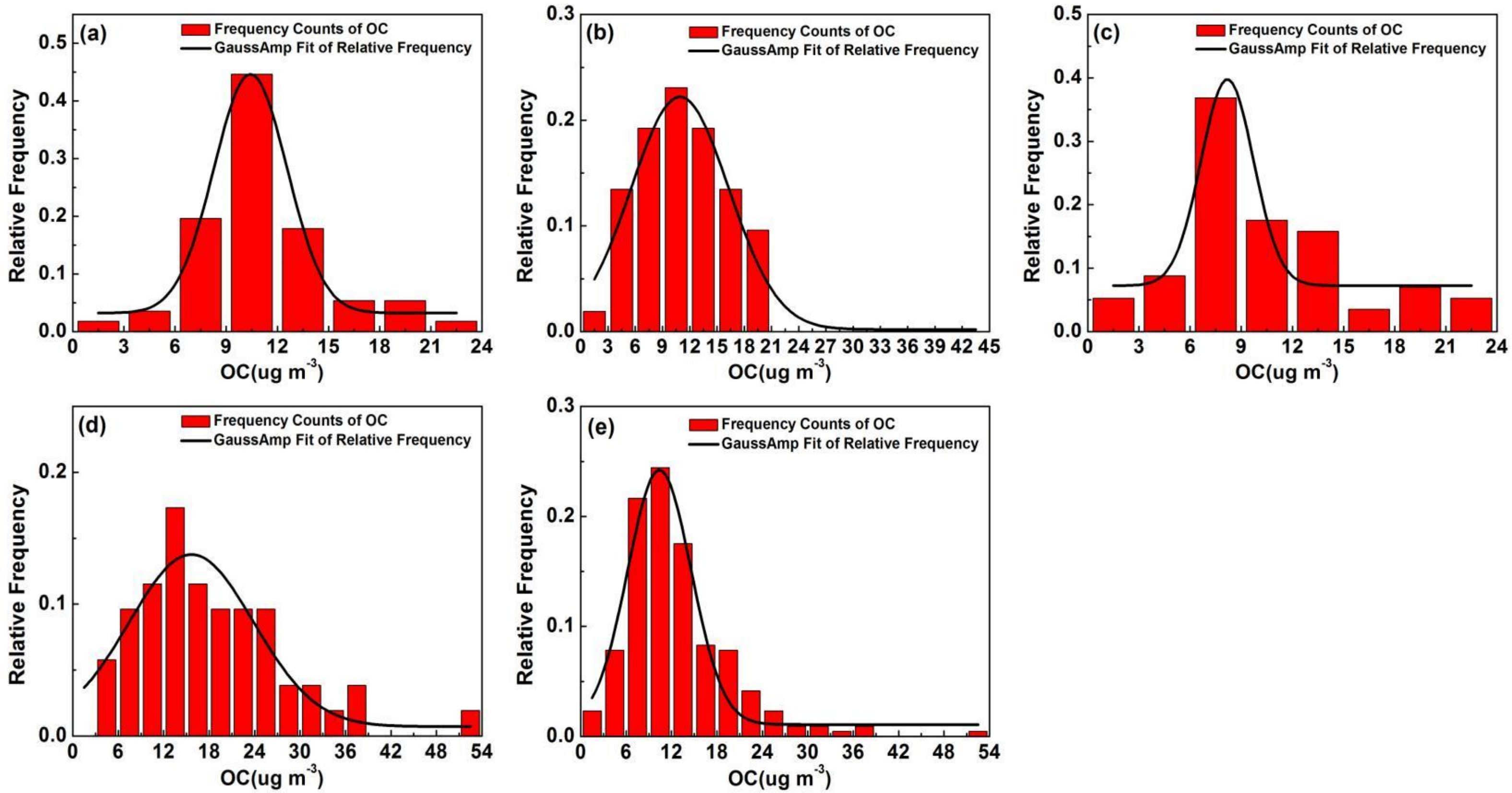


Fig 1. Gauss distribution of OC mass concentration during (a) spring, (b) summer, (c) autumn, (d) winter and (E) annual.

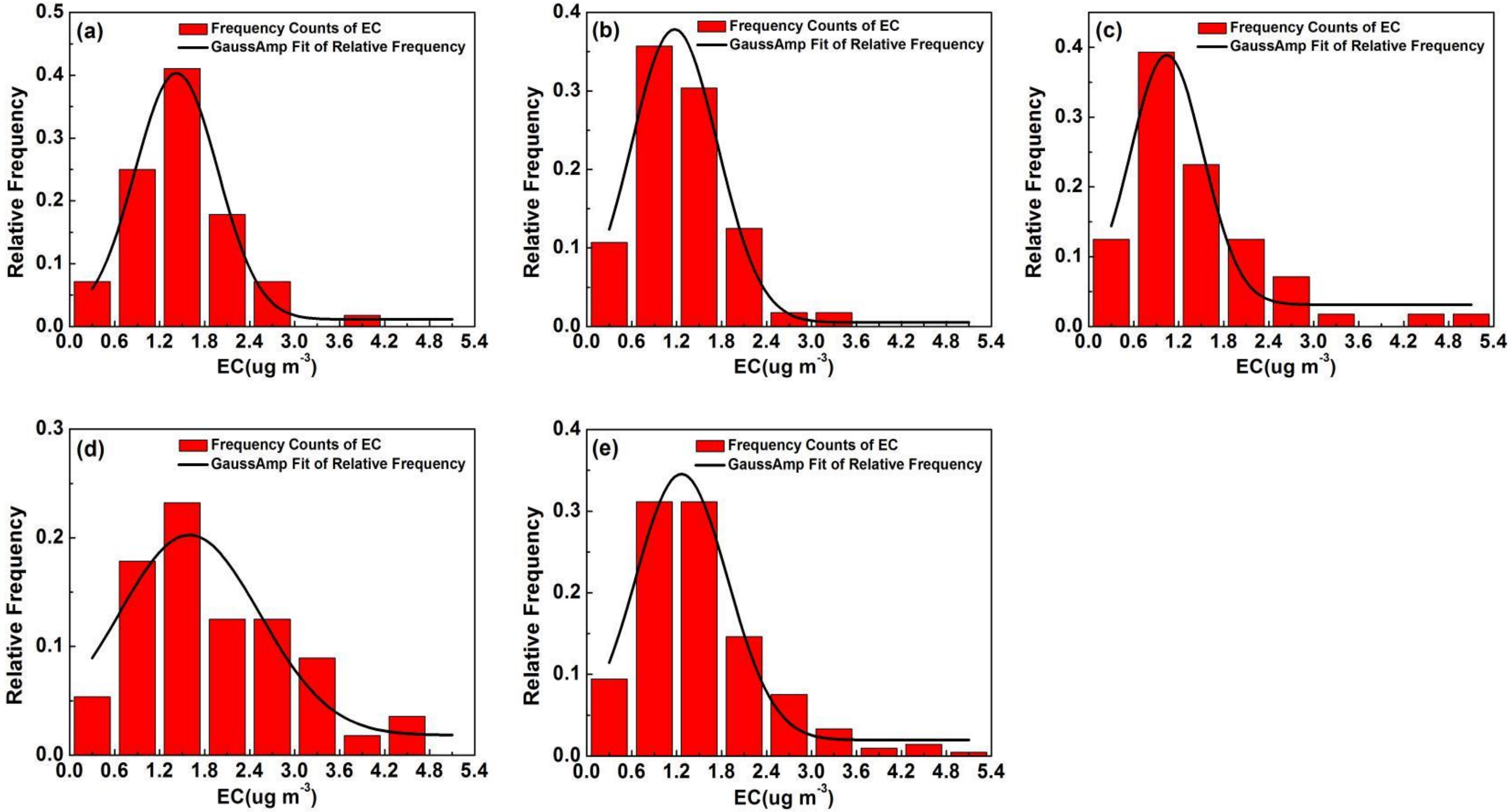


Fig 2. Gauss distribution of EC mass concentration during (a) spring, (b) summer, (c) autumn, (d) winter and (E) annual.

Table 1. Average mass concentration of OC and EC in each season

Season	OC ($\mu g\ m^{-3}$)		
	Average	Minimun	Maximun
Spring	11.0	2.8	23.0
Summer	11.2	3.0	20.9
Autumn	10.3	2.1	22.6
Winter	18.6	3.6	52.9
Annual	12.7	2.1	52.9

Season	EC ($\mu g\ m^{-3}$)		
	Average	Minimun	Maximun
Spring	1.48	0.40	3.91
Summer	1.26	0.38	3.26
Autumn	1.53	0.32	5.09
Winter	1.99	0.35	7.37
Annual	1.56	0.32	7.37

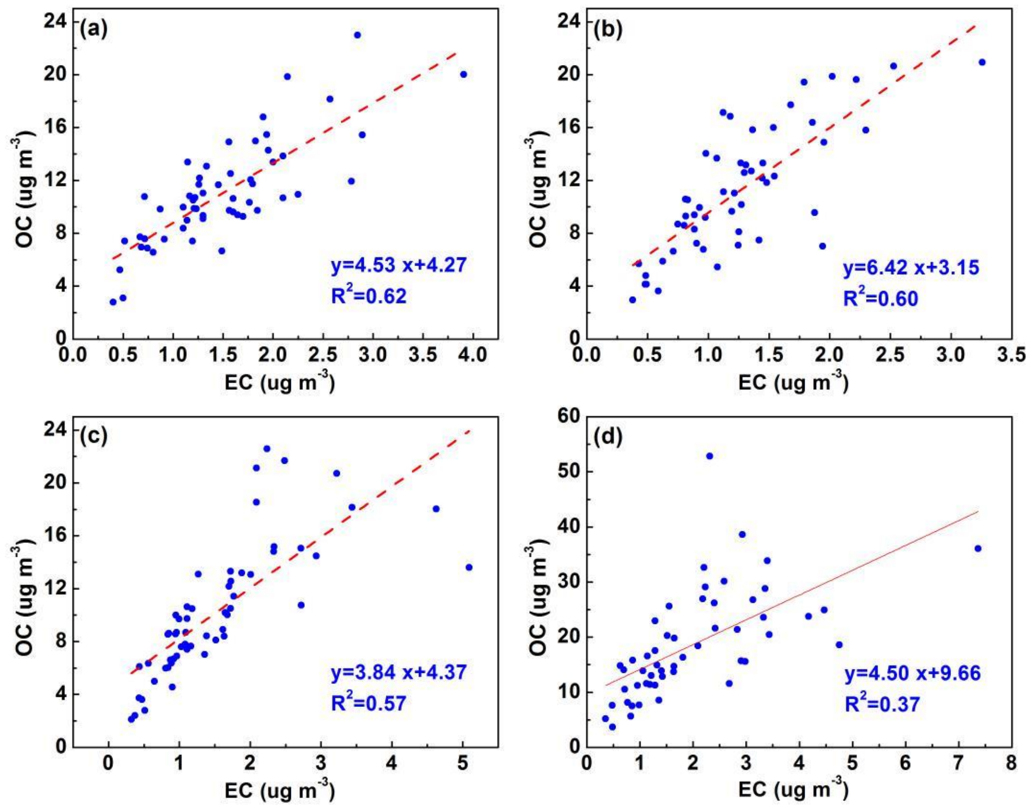


Fig 3. The correlation between OC and EC in (a) spring, (b) summer, (c) autumn, (d) winter.

This work uses empirical formula proposed by Turpin et al,. to make a quantitative description of SOC:

$$SOC=OC-EC\times(OC/EC)_{min}$$

$(OC/EC)_{min}$ in the equation seclected the minimum value during sampling period.

Table 2. SOC mass concentration and SOC/OC ratio in each season

Season	SOC (μg m⁻³)	SOC/OC (%)
Spring	4.33	40 %
Summer	6.09	50 %
Autumn	5.51	54 %
Winter	9.58	50 %

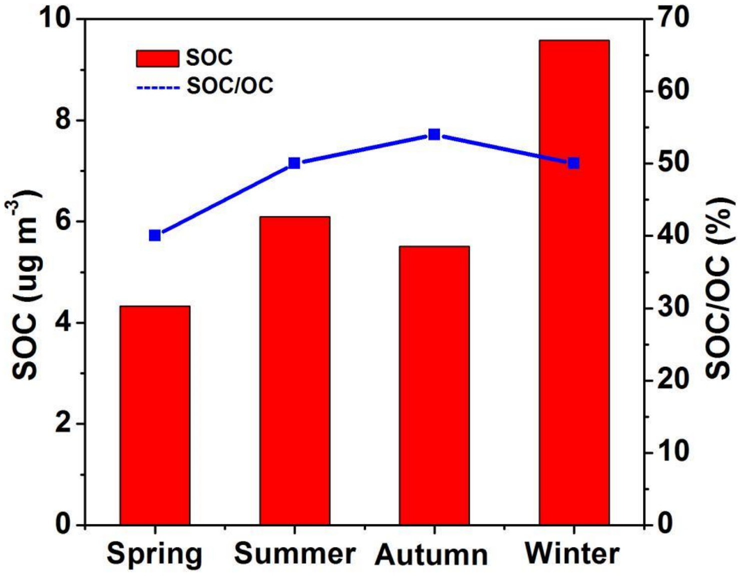


Fig 4. SOC concentration and SOC/OC ratio in each season

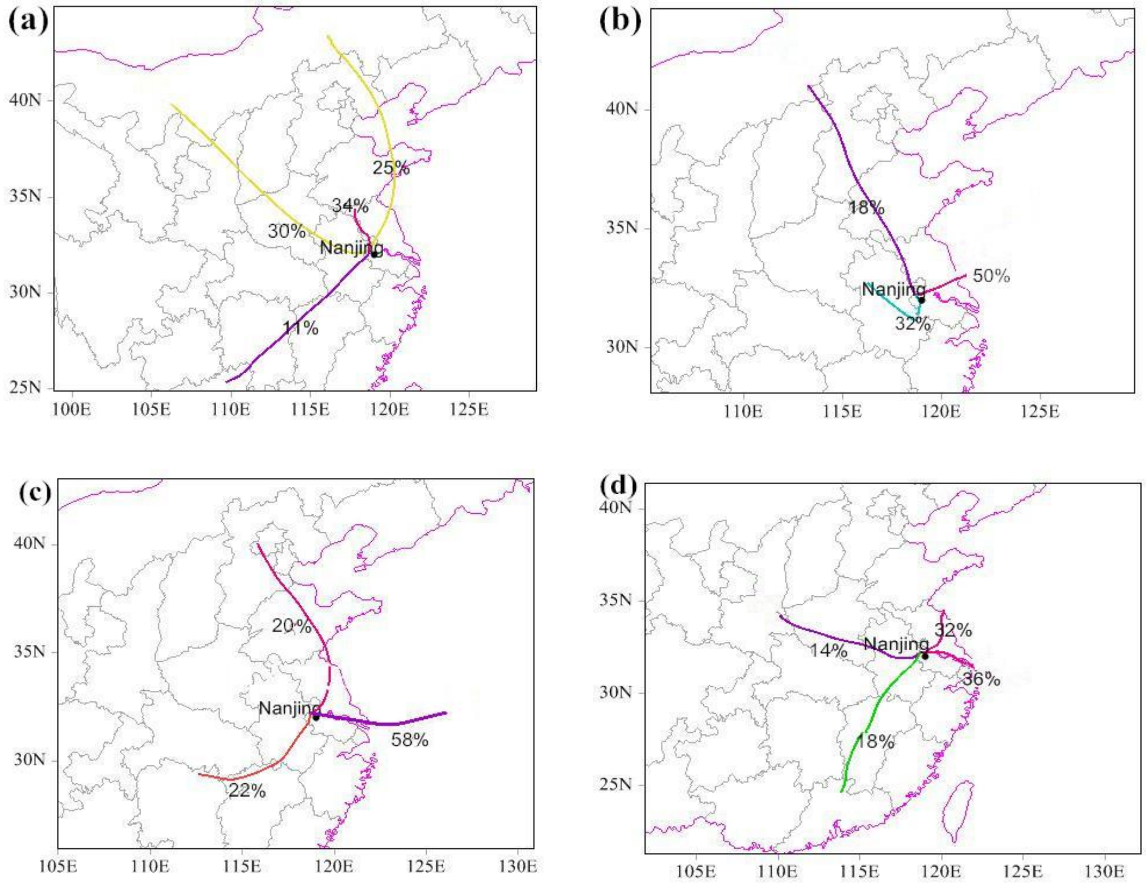


Fig 5. The trajectory of air flow at 500m in (a) spring, (b) summer, (c) autumn, (d) winter.

➢Section 2 Characteristics of water soluble ion pollution

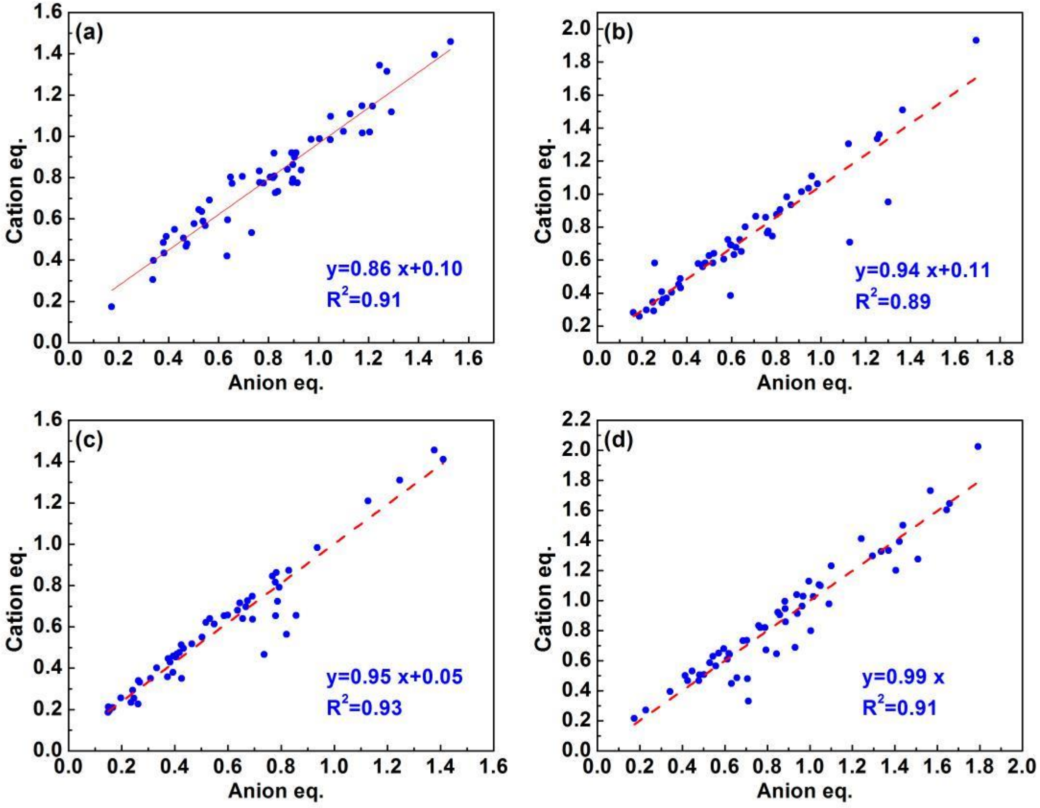


Fig 6. The correlation between anions and cations in (a)spring, (b)summer, (c)autumn and (d)winter.

Table 3. Concentration of water-soluble ions in four seasons

Season	Water-soluble ions		
	Average ($\mu g \cdot m^{-3}$)	Minimun ($\mu g \cdot m^{-3}$)	Maximun ($\mu g \cdot m^{-3}$)
Spring	57.16	11.91	103.07
Summer	46.25	13.47	128.68
Autumn	42.75	11.07	99.25
Winter	62.67	13.05	132.43
Annual	52.10	11.07	132.43

	Spring	Summer	Autumn	Winter
Na^+	0.42	0.47	0.30	0.32
NH_4^+	13.02	11.22	9.48	14.72
K^+	1.05	1.50	0.89	1.20
Mg^{2+}	0.10	0.12	0.05	0.05
Ca^{2+}	0.52	0.43	0.43	0.30
F^-	0.02	0.03	0.02	0.02
Cl^-	2.22	1.31	1.30	3.75
NO_2^-	0.07	0.33	0.05	0.06
NO_3^-	18.99	11.23	14.66	22.65
SO_4^{2-}	20.75	20.22	15.57	19.61
Total	57.16	46.86	42.75	62.68

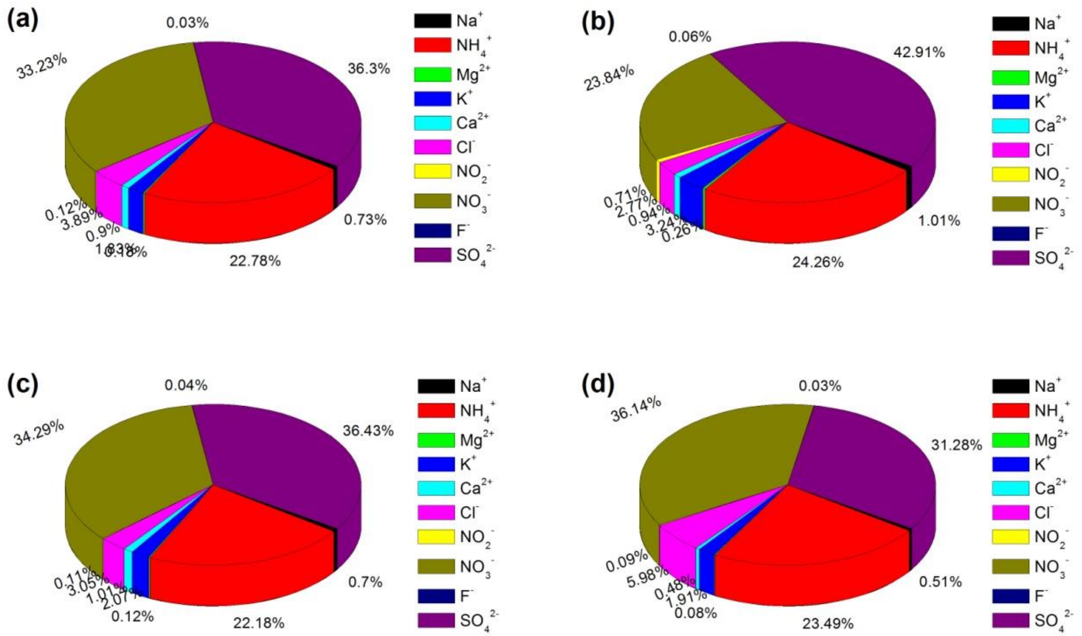


Fig 7. The proportion of each ion in (a)spring, (b)summer, (c)autumn, (d)winter.

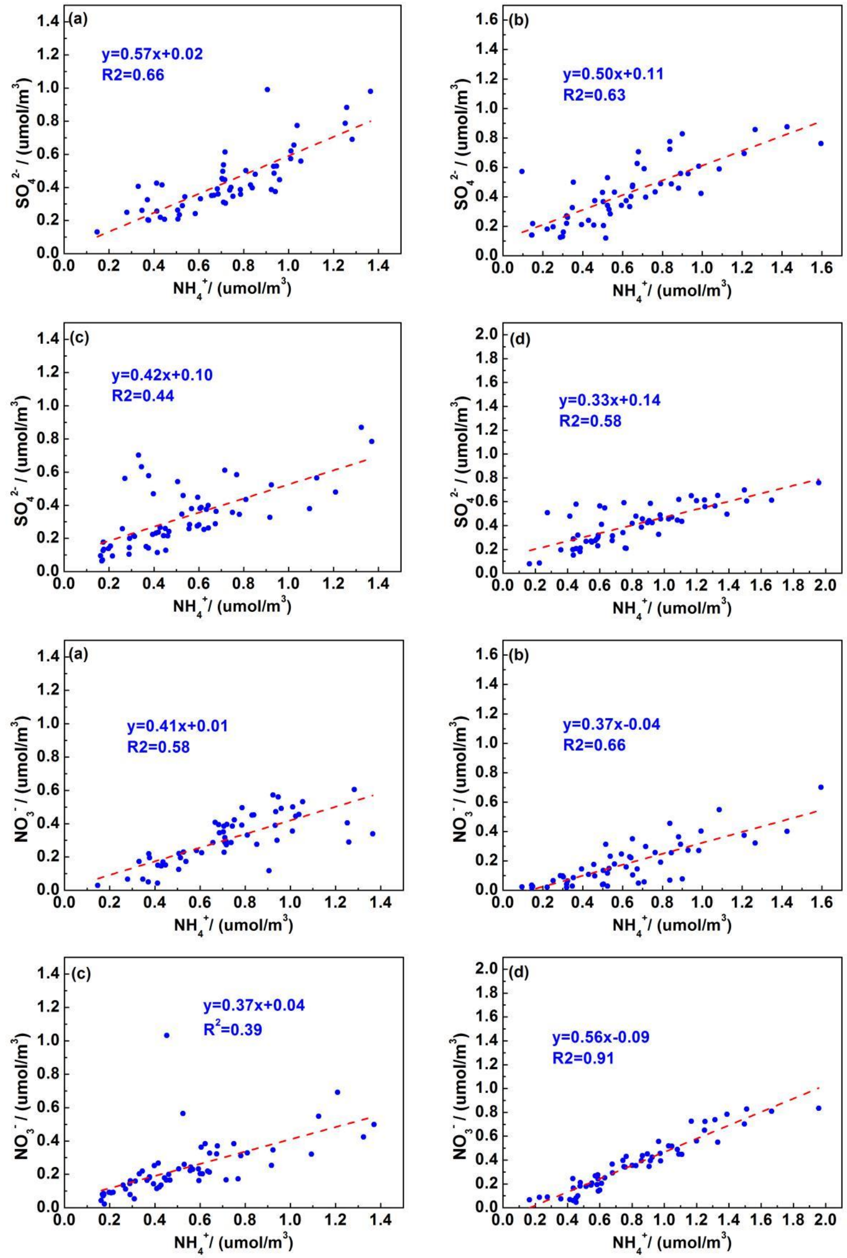


Fig 8. The relationship between SO_4^{2-}、NO_3^- and NH_4^+ molar ratio in (a)spring, (b)summer, (c)autumn, (d)winter.

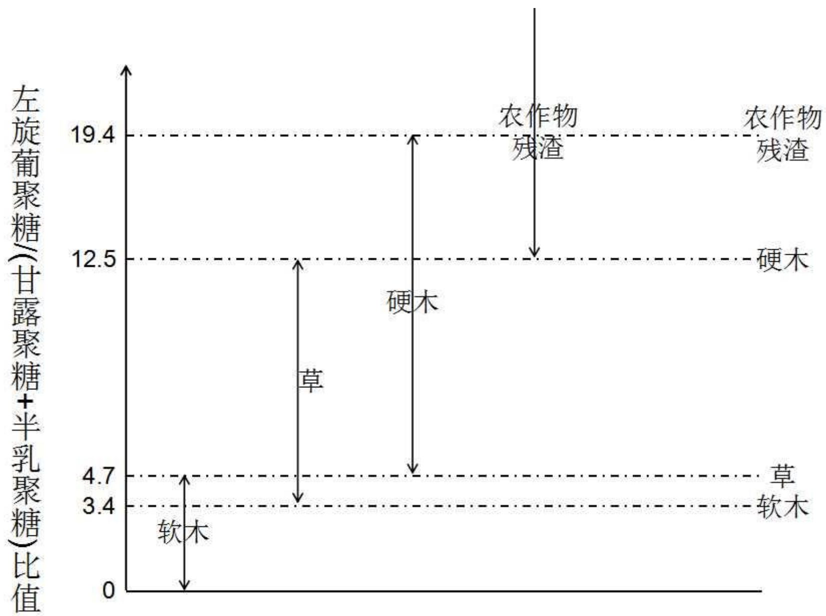
The correlation between NH_4^+ and SO_4^{2-} and NO_3^- is relatively better, and the amount of NH_4^+ is relatively high.

When the mole ratio of SO_4^{2-} to NH_4^+ is 1：2, it tends to form $(NH_4)_2SO_4$, and tends to form NH_4HSO_4 when the molar ratio of SO_4^{2-} to NH_4^+ is 1:1.

The proportion of SO_4^{2-} and NH_4^+ in the four seasons is generally between 1:1,and1:2, which is close to 1:2, indicating that in $PM_{2.5}$, sulphate is mainly $(NH_4)_2SO_4$, and there are also some NH_4HSO_4. The correlation between NO_3^- and NH_4^+ is also good, and tends to form NH_4NO_3. NH_4^+ mainly exists in NH_4HSO_4, $(NH_4)_2SO_4$ and NH_4NO_3.

➢Section 3　Analysis of Biomass Burning

Fig 11. Satellite remote sensing monitoring of biomass burning in mid October 2015.



The type of biomass burned can be judged to some extent with ratio (Levoglucosan/mannosan + galactosan).
The biomass burning is mainly cork when the ratio is 3.4;
The biomass burning is mainly grass when the ratio is 4.7;
The biomass burning is mainly hardwood when the ratio is 12.5;
The biomass burning is mainly crop residue when the ratio is 19.4.

The ratio average in autumn is 20.21 with the minimum 8.97 and the maximum 40.09, means then the biomass burning is mainly crop residue and some grasses and hardwoods in addition.

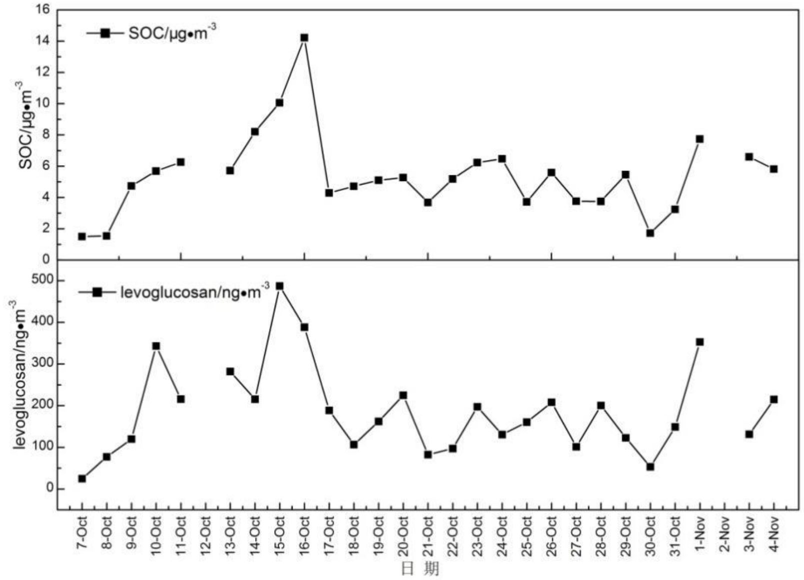


Fig. 12 Daily variation of levoglucosan and SOC mass concentrations

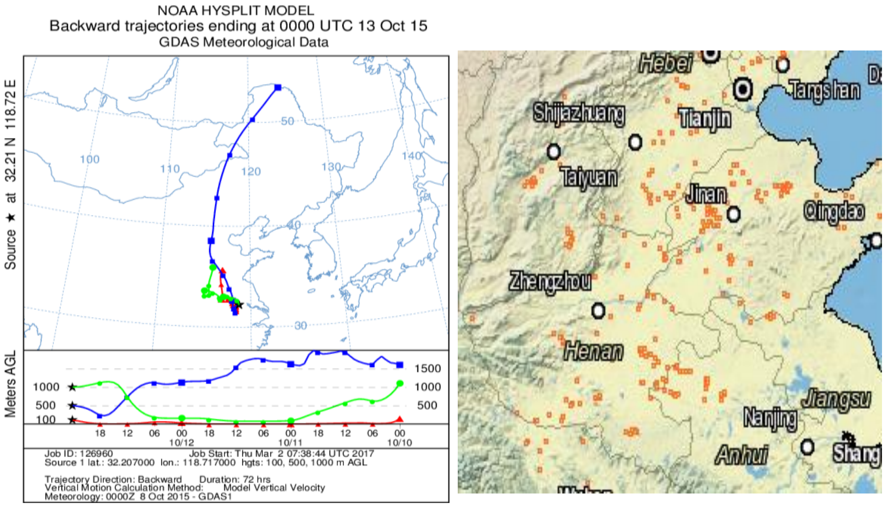


Fig. 13 The 72h backward trajectories of air mass arriving northern suburbs of Nanjing In October 13th and Fire point data during October 8th to October 10th

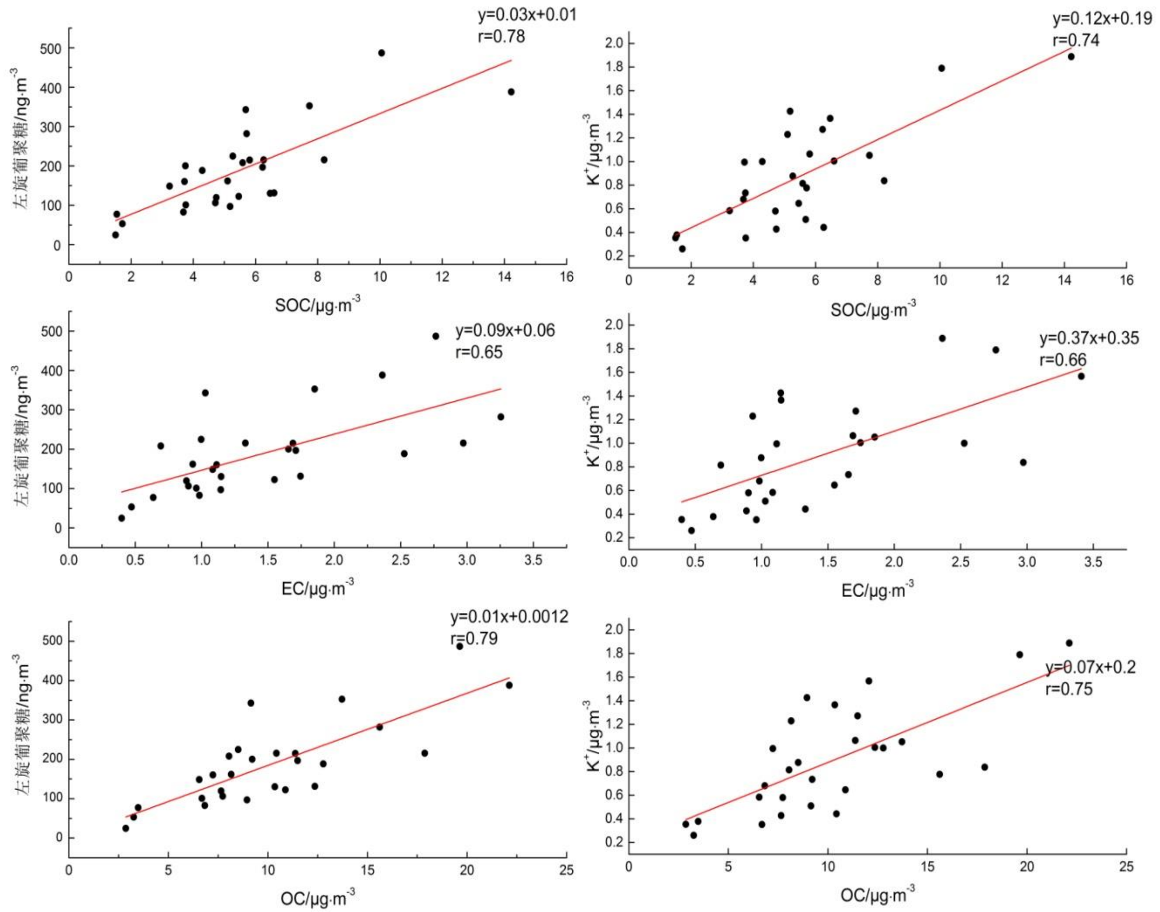


Fig.14 Correlation between potassium, levoglucosan and SOC, OC, EC

Through the receptor tracer method and the Levoglucosan and OC concentration as the tracer to estimate the biomass burning contribution as following:

$$\text{Biomass burning contribution (\%)} = (\text{Levoglucosan/OC})_{sample} / (\text{Levoglucosan/OC})_{source} \times 100\%$$

In the fomulation: $(\text{Levoglucosan/OC})_{sample}$ represents the average ratio of Levoglucosan of this sampling to OC is 1.8%;

$(\text{Levoglucosan/OC})_{source}$ represents the ratio of Levoglucosan to OC in the biomass burning source spectrum, referenced from 8.3%-average emission factor Levoglucosan/ OC in $PM_{2.5}$ studied by Zhang et al.in combustion emission of grain straw in China;

Autumn's estimated value is 21.9%, means that the biomass burning during sampling contributes more to OC in the northern suburb of Nanjing, thus it can be seen that the effect of biomass burning on the pollution in northern suburb of Nanjing in the autumn can not be ignored;

During days of 13~16, the average Levoglucosan/OC is 2.5%, the contribution of biomass burning to OC is estimated as 30.1%, which as well confirms that biomass burning is one of the important causes to this pollution.

Conclusion

- The average annual mass concentration of OC is 12.7 $\mu g \cdot m^{-3}$; The average annual mass concentration of EC is 1.6 $\mu g \cdot m^{-3}$; The correlation of OC to EC in spring, summer and autumn is relatively good, the correlation between OC and EC is relatively poor in winter. The source of carbonaceous aerosols is more complex, may be affected by a emission source, may be affected by regional polluted air mass, and may also be affected by the photochemical reaction of organic gases.

- The average concentration of water soluble ions in the annual monitoring period is 52.10 $\mu g \cdot m^{-3}$; the average concentration of water soluble ions in order: winter >summer > autumn > spring; The water soluble ions is mainly SO_4^{2-}、NO_3^-、NH_4^+, these ions account for 91.73% of all ions; NH_4^+, SO_4^{2-} and NO_3^- in $PM_{2.5}$ present in the form of NH_4HSO_4, $(NH_4)_2SO_4$ and NH_4NO_3.

- In autumn, Levoglucosan has good corralation with SOC and OC; The pollution from biomass burning comes mainly from northeast Nanjing, by way of Hebei, Shandong and other places finally reaches the Northern Suburb of Nanjing; The estimated contribution of biomass burning to OC in autumn is 21.7% and 30.1% during the heavily polluted date from October 13 to October 16. This exogenous biomass burning has a great influence on the pollution in the North Suburb of Nanjing in autumn.

Thank you