Yale 耶鲁大学-南京信息工程大学大气环境中心

Yale-NUIST Center on Atmospheric Environment

A discussion on the paper "The characteristics and origins of carbonaceous aerosol at a rural site of PRD in summer of 2006 "

By W. W. Hu, M. Hu, Z. Q. Deng, R. Xiao

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Chen Geng

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Outline

- Introduction
- Experimental
- Results and discussions
- Conclusions

1.Introduction

- Carbonaceous aerosol is the main constituent (20–80 % of fine particle) in the particulate matter . Recently, carbonaceous aerosol has become one of the most hot research topics due to its important role in climate and health effects.

- Pearl River Delta (PRD) region is the most developed city cluster, is located in southeast China and is heavily influenced by urban emissions. However, most of the previous studies were based on filter-sampling with low time resolution (12 h or 24 h) .Therefore, a higher time resolution research of carbonaceous aerosol in PRD region is needed to explore primary emissions and secondaryformation.

- The Program of Regional Integrated Experiments of Air Quality over Pearl River Delta 2006 (PRIDE-PRD 2006) was conducted in July 2006, in which both EC and OC were measured by online Sunset EC/OC instrument from 3 July to 31 July.

2.Experimental

2.1 Meteorology

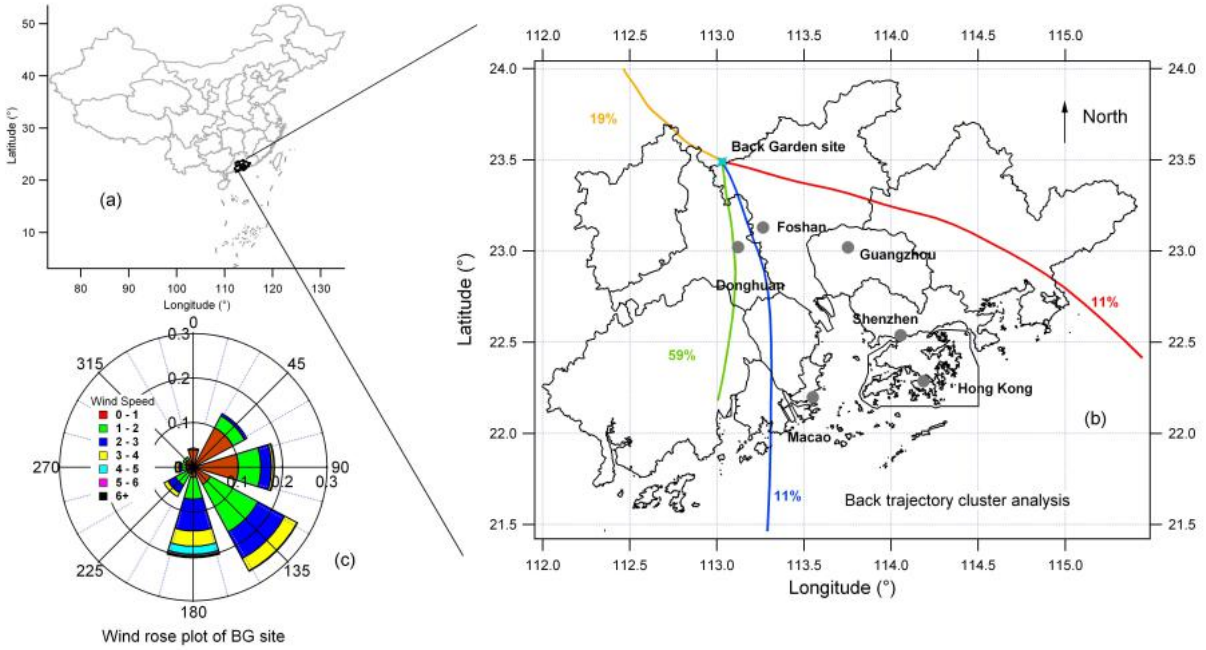


Fig. 1. (a) Map of the PRD area in China. **(b)** Location of Back Garden site (BG) and major cities related in this study, and also showed the back trajectory cluster analysis results. **(c)** Wind rose plot of BG site in July 2006.

Location:at the rural Back Garden (BG) site (23.49◦ N, 113.03◦ E) located about 50 km northwest to the Guangzhou City (Fig. 1)

Period:2006.7.3-2006.7.31

The meteorology parameters:T: 28.9±3.2° C RH:78.0±13.7%

P:997±4hpa

2.2 Measurement instruments

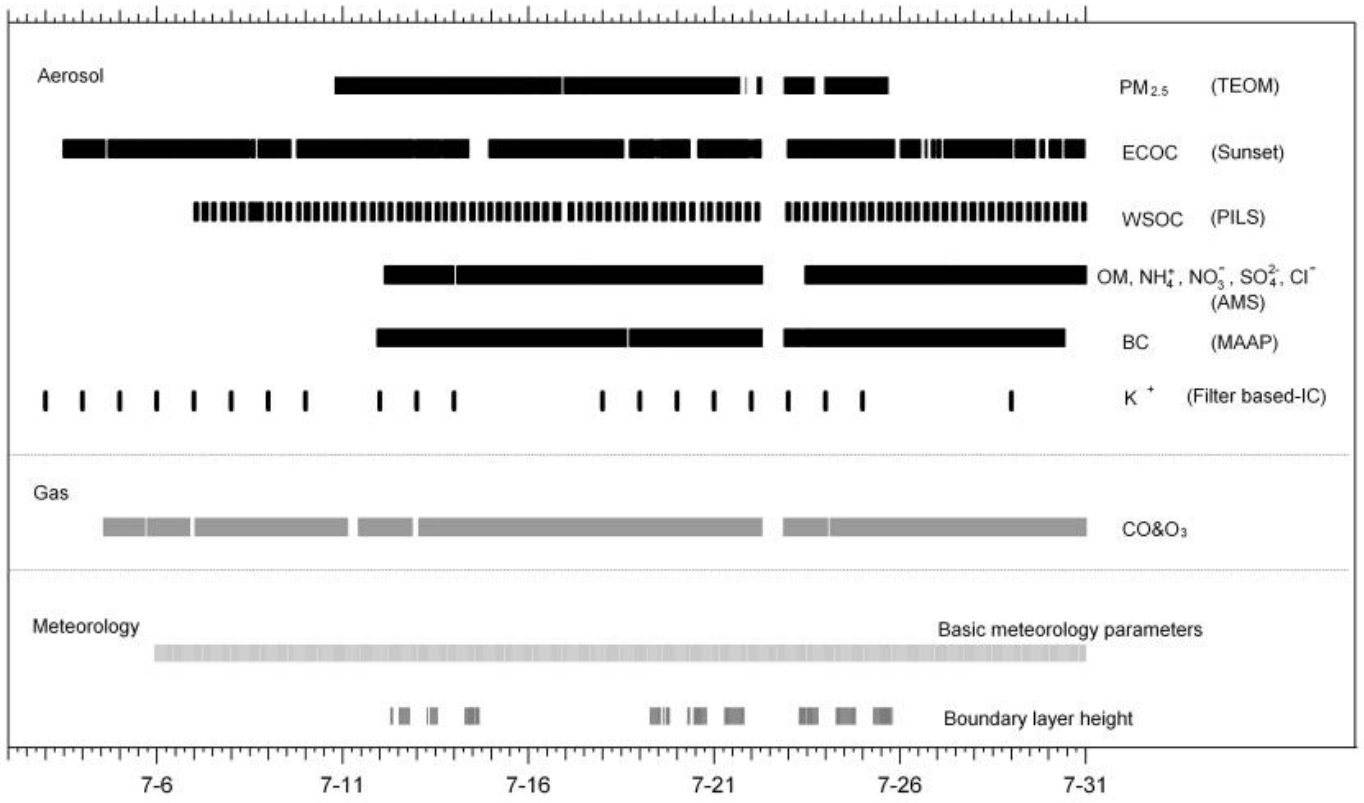


Fig. 2. The instruments used to measure aerosol and gas species at BG site in PRIDE-PRD 2006 campaign.

2.2 Measurement instruments

During the PRIDE-PRD 2006 campaign, a number of instruments were used to measure aerosol and gas pollutants.

- TEMO → PM2.5
- Sunset → ECOC
- PILS → WSOC
- AMS → OM、NH_4^+、NO_3^-、Cl^-

3.Results and discussion

3.1 The time series of carbonaceous aerosol

Table 1. Comparisons of carbonaceous aerosol concentrations in three typical periods in the PRIDE-PRD 2006 campaign.

Classification of measurement period (time periods)		OC (μgC m^{-3})	EC (μgC m^{-3})	TC*/$PM_{2.5}$ (%)
Typhoon and precipitation days	10–11, 15–18, 26–27 July 2006	4.0 ± 2.8	1.8 ± 1.2	12.5
Local emission influence days	23–25, July, 2006	28.1 ± 17.6	11.6 ±1 5.1	18.2
Normal days	except the two periods above	5.7 ± 4.5	3.3 ± 2.8	10.1
Total in average		7.6 ± 5.7	3.7 ± 5.7	13.6

* TC = OC + EC

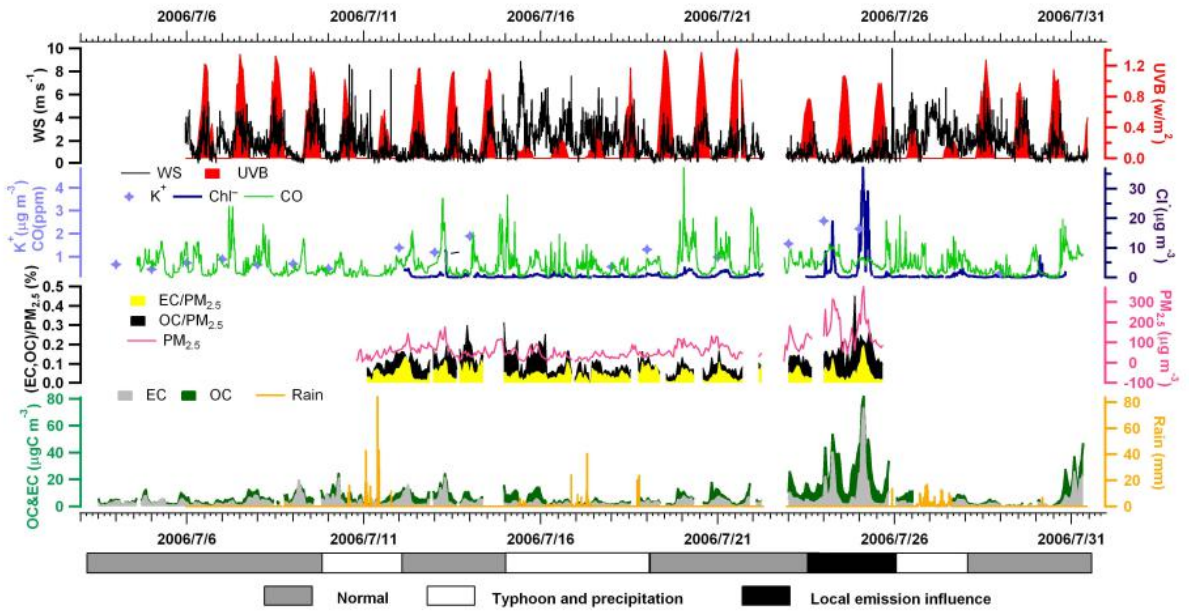


Fig. 3. The time series mass concentrations of $PM_{2.5}$, EC, OC, Cl^-, K^+ and meteorology conditions during PRIDE-PRD 2006 campaign. The whole campaign was divided into three typical periods: normal days (grey bar), typhoon and precipitation days (white bar), and local emission influence days (black bar).

- Local emission influence days (8 % of total days) were characterized by high concentrations of carbonaceous aerosol starting from noon, 23 July to midnight, 25 July.

- Typhoon and precipitation days (27 % of total days) were characterized by lower concentrations of carbonaceous aerosol.

- Normal days (65 % of total days): The remaining observational days are defined as normal days.

Table 2. Comparisons of carbonaceous aerosol concentration with other studies in China and other countries.

Location	Station types and mayor source	Period	Analysis Method	OC ($\mu gC\,m^{-3}$)	EC ($\mu gC\,m^{-3}$)	SOC/OC or WSOC/OC[g] (%)	Reference
BG, China	Regional site; Downwind of the Urban (Normal days)	July 2006 (normal day)	TOT	5.7	3.3	47	This study
BG, China	Regional site; Downwind of the Urban	July 2006	TOT	2.9[d]	1.36[d]	Not available	Yu et al. (2010)
Cong Hua, China	Regional site	Oct, Dec 2002; Mar, Jun 2003	TOT	8.1	1.4	Not available	Hagler et al. (2006)
Guangzhou, China	Urban site; Vehicle, industrial, domestic activities	July 2006	TOT	8.9[e]	4.7	Not available	Verma et al. (2009)
Guangzhou, China	Urban site	April 2007	TOR	14.8	8.1	29	Tao et al. (2009)
Beijing, China	Urban site	Summer 2006	TOT	10.0	2.2	45 (day); 17 (night)	Lin et al. (2009)
Hong Kong, China	Regional site	Summer 2006	TOR	1.5	0.4	69[g]	Ho et al. (2006)
Gwangiu, Korea	Urban site; motor vehicle emission	March–May 2001	TOT	15.7	5.7	62	Park et al. (2005)
T0, Mexico[a]	Urban site	March 2006	TOR	10.7[f]	4.2	46[h]	Aiken et al. (2008 2008, 2009)
T1, Mexico[b]	Suburb site; Downwind of the urban	March, 2006	TOT	6.4	2.1	63.6	Yu et al. (2009)
T2, Mexico[c]	Non-urban site; Downwind of the urban	March 2006	TOT	5.4	0.6	67.4	Yu et al. (2009)
Pittsburgh, USA	Regional site; No local emmissions	July 2001–August 2002	TOT	2.75	0.89	38	Polidori et al. (2006)
Barcelona, Spain	Urban background site; influenced by traffic emission transportation	Summer 2004	TOT	3.6	1.5	43/47[g]	Viana et al. (2007)

[a] T0 site was an urban site located in the center of Mexico City.
[b] T1 site was a suburb site in the down wind direction of Mexico City.
[c] T2 site was a regional background site of Mexico City.
[d] The concentrations of OC and EC were the sum of the values in condensation mode (0.36-0.46μm) and droplet mode (0.8-1.1μm).
[e] Personal communication.
[f] The concentration of OC is calculated by OM/1.71.
[g] Refer to the WSOC/OC.
[h] The data was calculated from OOA/OA.

TOT: thermal/optical transmission. TOR: thermal/optical reflectance.

3.2 The correlation of OM and WSOC versus OC

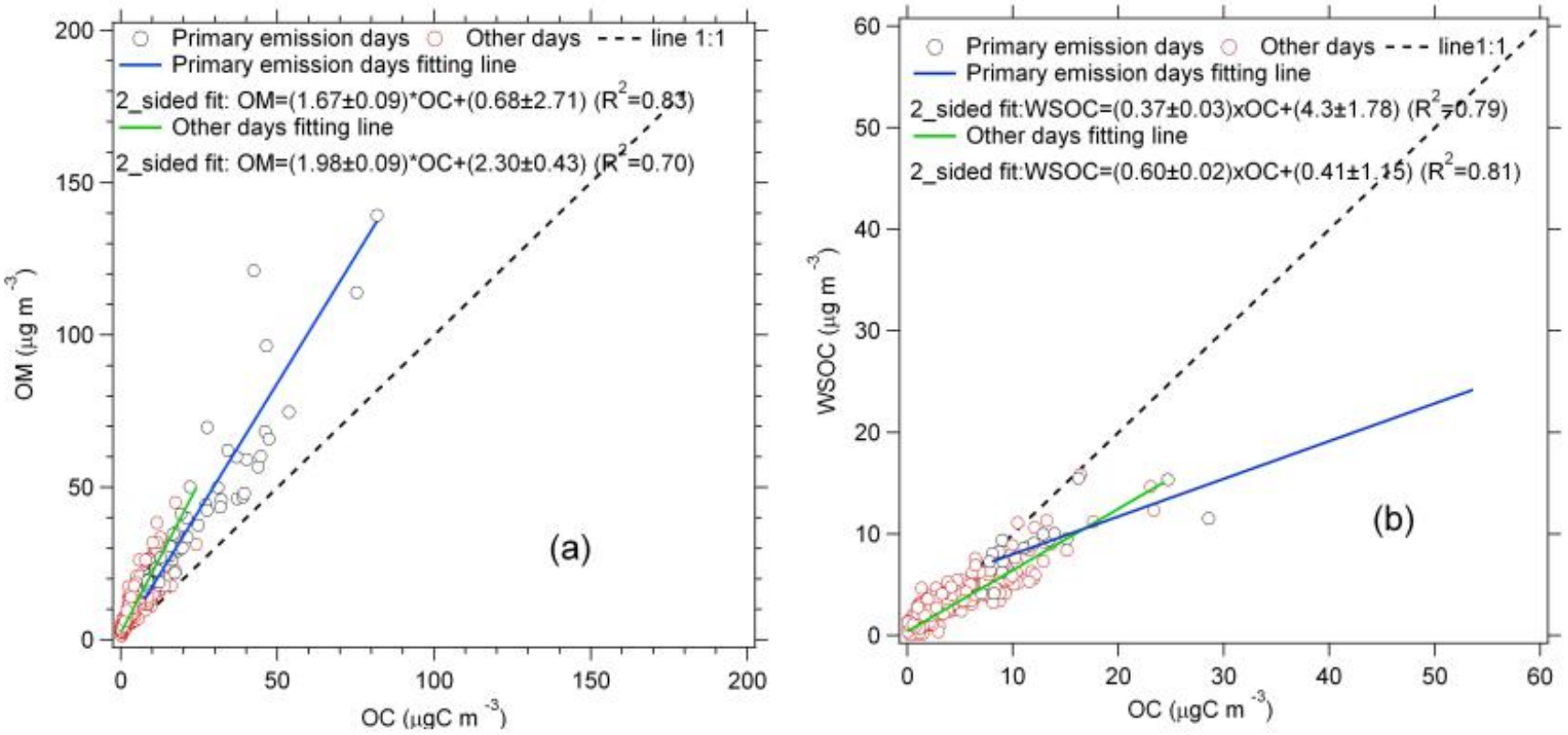


Fig. 4. The correlations of measured data between **(a)** OM and OC; **(b)** WSOC and OC.

- OM&OC
- WSOC&OC

3.3 Diurnal profile of carbonaceous aerosol

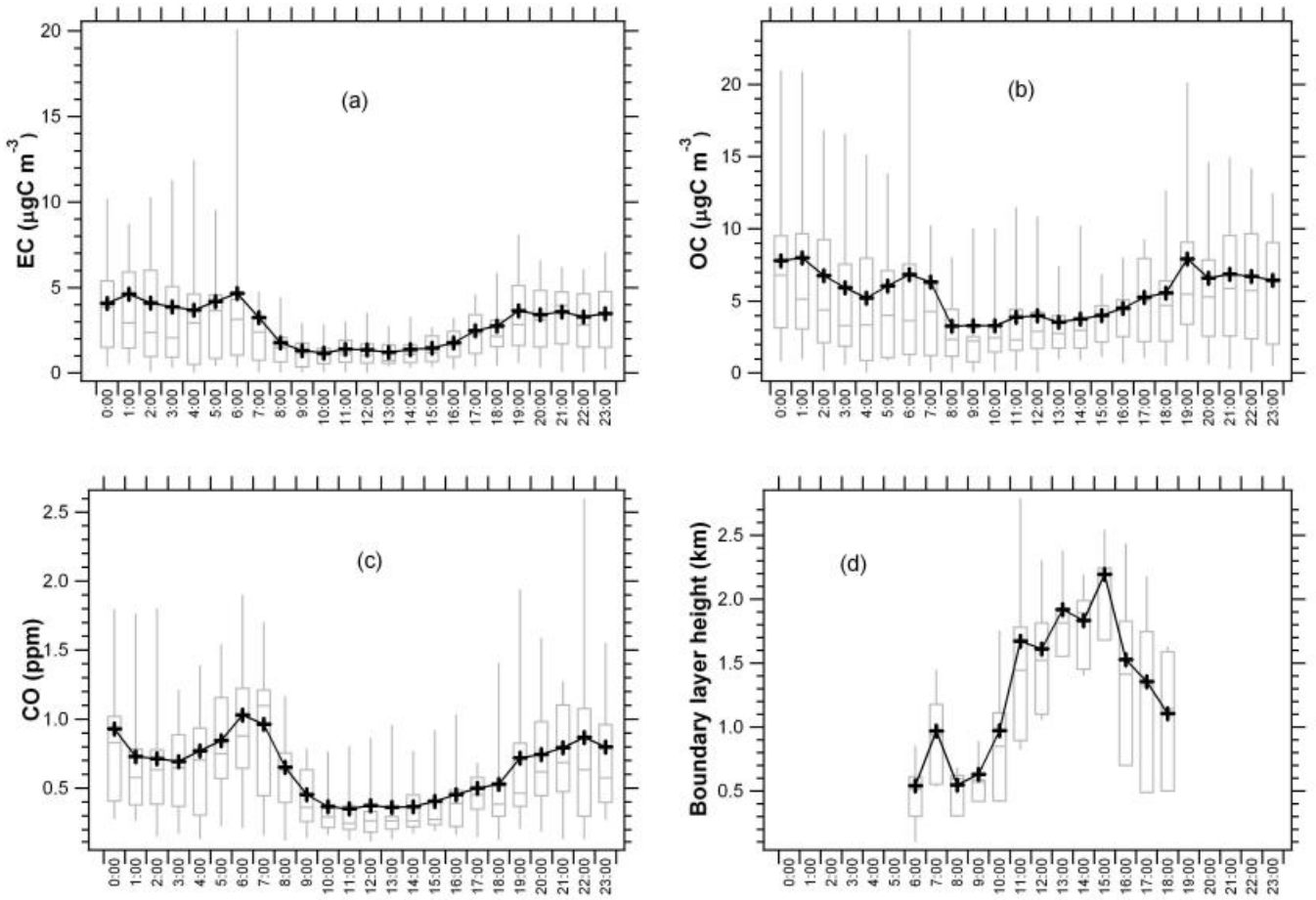


Fig. 5. Diurnal variation box plots of EC **(a)**, OC **(b)**, CO **(c)**, and boundary layer height **(d)**. The upper and lower boundaries of boxes indicate the 75th and 25th percentiles; the lines within the box mark the median; the whiskers above and below boxes indicate the 90th and 10th percentiles; and cross symbols represent the means.

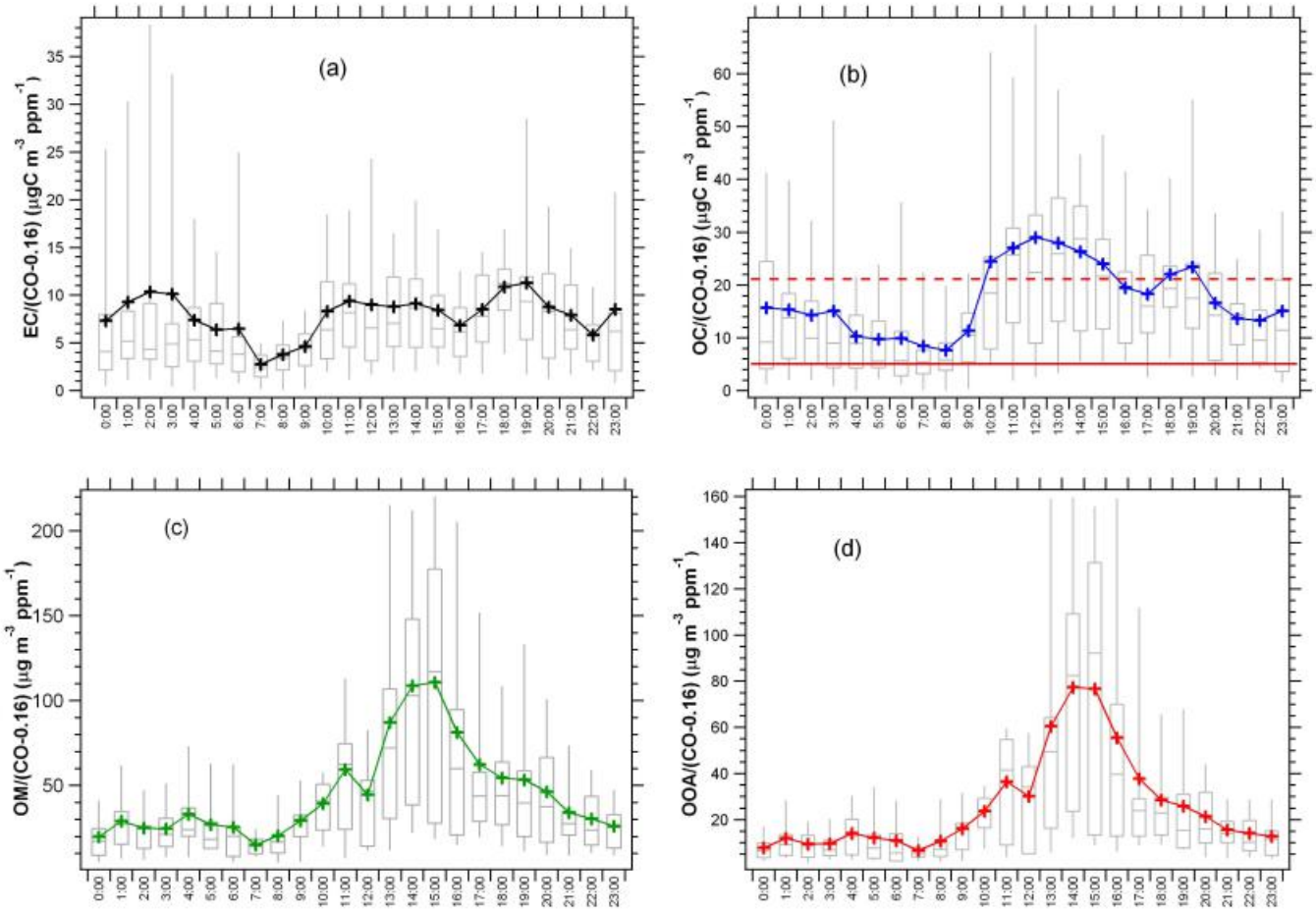


Fig. 6. Diurnal variations of different aerosol species EC **(a)**, OC **(b)**, OM **(c)**, OOA **(d)** versus (CO-0.16). The value of 0.16 ppm was CO background concentration. The box plot is the same meaning as Fig. 5 showed. The red lines in Fig. 6b indicate estimates for the direct emissions (solid) and secondary formation after half a day of processing (dotted) of organic aerosol in the northeastern US (de Gouw et al., 2009).

3.4 Estimation of secondary organic carbon by modified EC tracer method

- EC tracer method is usually adopted to estimate the SOC concentrations. This method assumes EC is a tracer of primary emissions and primary OC also comes from the same combustion sources with EC. Through calculating the emission ratio of primary OC to EC, we can calculate POC and SOC concentrations (POC + SOC = OC). So it is a key step to determine (OC/EC)pri for the SOC estimation by EC tracer method.

- Two methods to estimate (OC/EC)pri. (1) using the ratios between ambient OC and EC when primary source emissions dominate and the secondary organic aerosol formations are expected to be low. (2) using those ratios derived from emission inventories of OC and EC.

- Modified EC tracer method(combine traditional EC tracer method with source tracer ratio method)

$$OC_{total} = OC_{pri} + OC_{sec} + OC_{non} = EC_a * (OC/EC)_{pri} + OC_{sec} + OC_{non} \quad (1)$$

$$OC_{sec} = OC_{total} - EC_a * (OC/EC)_{pri} - OC_{non} \quad (2)$$

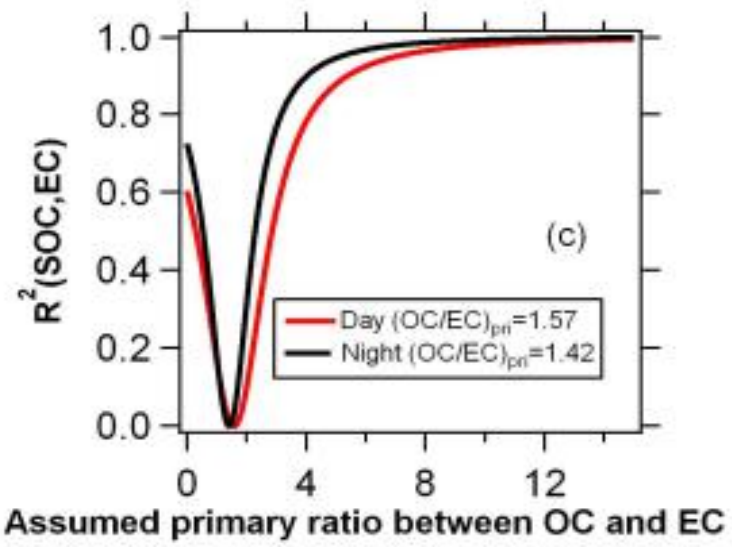
(OC_{non}:the non-combustion OC from biogenic primary OC or regional OC background.
EC_a :the measured ambient concentrations of EC.
$(OC/EC)_{pri}$:the initially emission ratio between OCpri and EC from combustion source.)

The OCnon in normal days was around -0.2, which suggested OC from non-combustion emissions was small and does not significantly affect our results. So the equation can be simplified to Eq. (3):

$$OC_{sec} = OC_{total} - EC_a * (OC/EC)_{pri} \quad (3)$$

In the Eq.(3),only OC_{sec} and $(OC/EC)_{pri}$ are unknow. So to calculate OC_{sec} concentrations, the key is to find out an exact $(OC/EC)_{pri}$.

- From the discussions of diurnal variation of carbonaceous aerosol in normal days, the sources of carbonaceous aerosol are different between day and night. So, the (OC/EC)pri calculation will be separated into two datasets: OC and EC in the day (06:00–18:00) and in the night (18:00–06:00). From the Eq. (3), A plot of the R^2 between OCsec and EC with the (OC/EC)pri values can be drawn.



- If we assume that OCsec and EC were from different sources, the proper (OC/EC)pri should be the one that corresponds to the minimum R^2 value or when OCsec correlated with EC worst.

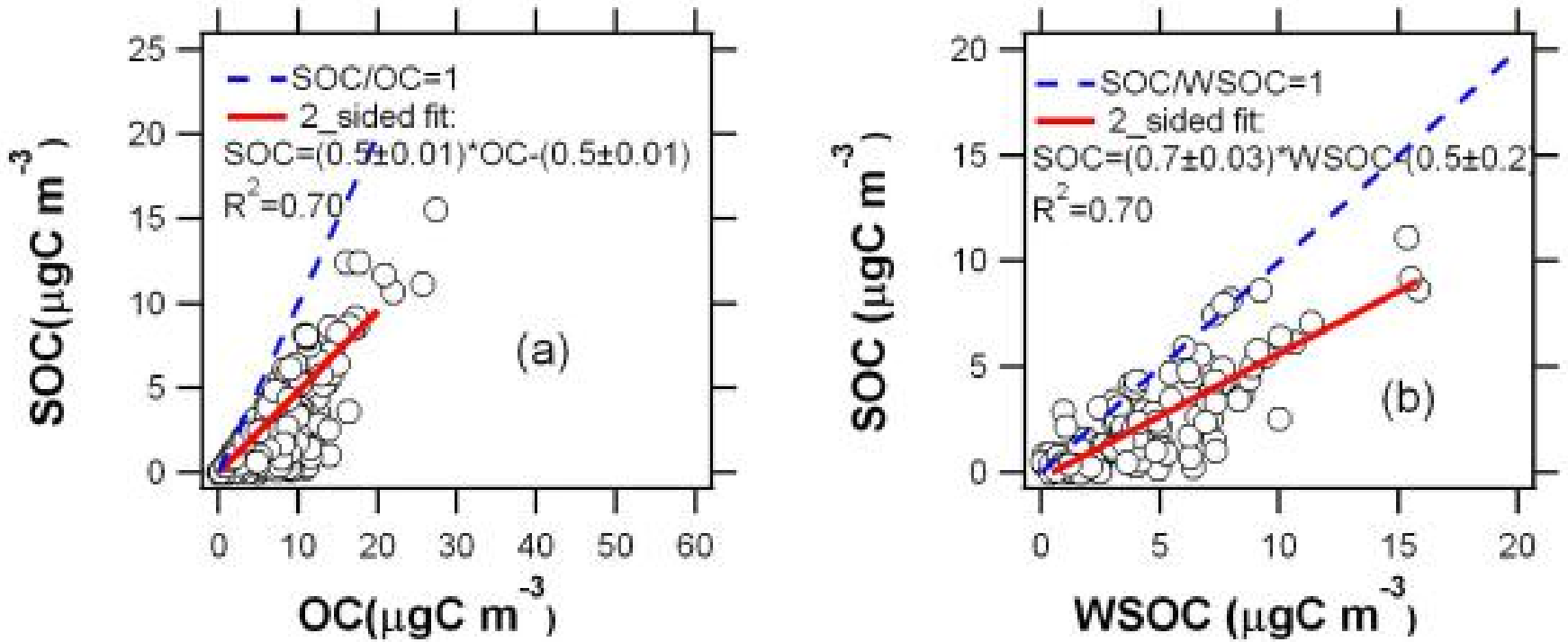


Fig. 8. Scatter plots of different organic aerosols at BG site, OC ***(a)***, WSOC ***(b)***

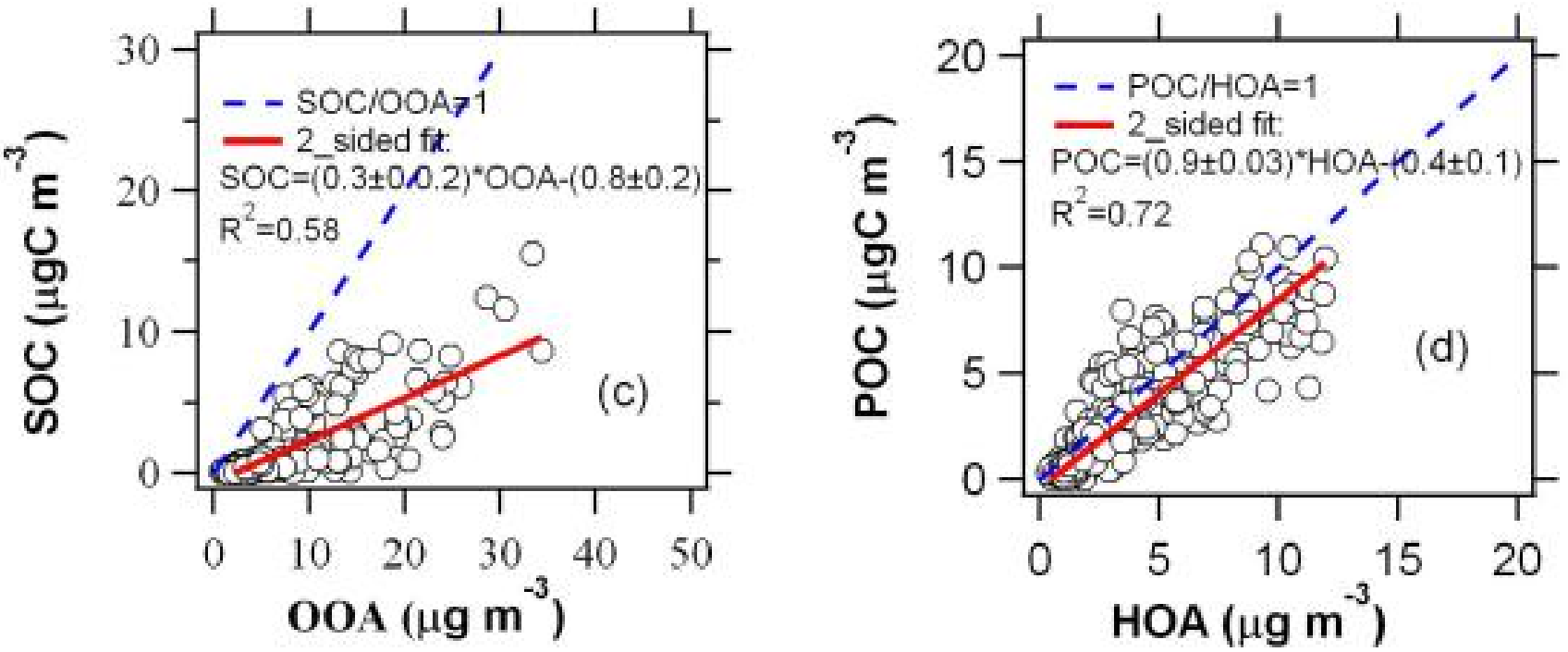


Fig. 8. Scatter plots of different organic aerosols at BG site, OOA **(c)** versus SOC and POC versus HOA **(d)**.

Conclusions

- Carbonaceous aerosol was measured at Back Garden (BG), a rural site of the PRD region during PRIDE-PRD 2006 campaign in July 2006. The concentrations of carbonaceous aerosol varied dramatically due to the effects from both extreme meteorology conditions (e.g. typhoon and precipitation) and anthropogenic emission sources (e.g. biomass burning) in the summer of PRD.

- The similar diurnal profiles for OC and EC were observed,with two peaks at night and in early morning, and were attributed to the local emissions accumulation in shallow boundary layer and rush hour emissions in the early morning. Minimum values were measured in the afternoon due to the dilution effect by the lifted boundary layer.

- The modified EC tracer method was adopted to estimate secondary organic carbon (SOC) concentrations. According to the distinct diurnal characteristic of carbonaceous aerosols, (OC/EC)pri was calculated for the data points in day and night, respectively. Good correlations were observed for estimated SOC with OOA and WSOC, and estimated POC with HOA, which proved the results by the modified EC tracer method are reliable in this paper.

Thank you