Supporting Information for

NO_x-related Increases of Biogenic Secondary Aerosols (bSOA) in Summertime Southeastern U.S.

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Text S1.

Figure S1 shows the time series of AMS OM and organic functional group concentrations. The correlations of AMS and ACSM OM to FTIR OM are moderate to strong (r=0.68~0.80) at CTR and LRK (Figure S2). Emissions by county were available from Nation Emission Inventory (NEI). Both counties have vehicles as the most abundant source of NO_x. Figure S3 shows time series of FTIR PMF factors with nighttime marked on the figure. Figure S4 and Figure S5 show a consistent CCN pattern at both sites. Figure S6 shows BC and CO are likely largely driven by precipitation and transport that result in multi-day events that overwhelm the local diurnal cycles. The rose plot (Figure S7) suggests that NO_x at CTR was mostly from the north. The closest freeway is ~30 km north of the CTR site, consistent with the emission inventory of large vehicle emissions. Figure S8 shows the correlation of AMS OM to O_3 and NO_x at LRK and CTR. AMS and ACSM PMF factors at CTR and LRK are compared in Table S1. Time series correlations of FTIR PMF factors to tracers are shown in Table S2. The chamber generated bSOA FTIR spectra are compared with ambient biogenic factor spectra in Table S3. The threshold effect of NO_x on bSOA formation is shown in Table S4 and sensitivity analysis is shown in Table S5.

Text S2. FTIR PMF operation and factor selection

Factorization was applied to the baselined IR spectra from FTIR for both PM_1 and $PM_{2.5}$ samples at LRK and at CTR. Six factor spaces (1~6) were analyzed. Fpeak values were explored from -2 to 2 at 0.5 increments. Seeds of 1, 10 and 100 were used for each Fpeak and factor to examine the robustness of each solution. Figure S9 and Figure S10 and Table S6 show that the properties of the solutions are generally robust. The change of solutions with rotation values is small in all solutions. Q/Qexpected decreases smoothly when factor number increases in solutions with more than 3 factors (Table S6). The Q/Qexpected of PM_1 is lower than $PM_{2.5}$, which is consistent with the higher time resolution of the PM_1 samples, making PM_1 the stronger solution. The $PM_{2.5}$ solution is similar to that of PM_1, so only the PM_1 PMF solutions at LRK are reported here.
Two factors that contain a large amount of ammonium were identified from the PMF in the 2-factor space (Figure S9 and Figure S10). Those two factors are produced in almost all solutions with different factor numbers and rotations. However, with only these two factors, ~20% of the OM cannot be explained and is categorized as residual. A third factor with higher hydroxyl and carbonyl group is identified from the 3-factor solution and accounts for ~20% of the total OM. The 3-factor solution reduces the residual to less than 15%. The time series of the factors are independent, with the highest correlation coefficient of 0.72 in the 3-factor solution. Degenerate spectra appear in solutions with 4 or more factors. Two pairs of factors at LRK and one pair at CTR have similar cosine similarity (>0.80) in the 4-factor solutions.

Text S3. Group of model species in CMAQ model

The CMAQ model simulations are used here to show the regional uniformity of bSOA [Murphy et al., 2017; Pye et al., 2015; Pye et al., 2017]. CMAQ predictions for summer

2013 have been evaluated regionally with measurements from the SEARCH network, IMPROVE network, CSN network, and CASTNET for species including OA, nitrate (nitric acid + aerosol nitrate), sulfate, ammonium, NOx, VOCs, oxidants, and other atmospheric constituents [Pye et al., 2015; Pye et al., 2017]. The names of CMAQ model species are in Table S7 and can be found in the supplement of two recent CMAQ model papers [*Pye et al*., 2015; *Pye et al*., 2017]. The nitrate radical related species are ISOPNN, MTNO3 (gas phase), AISOPNN and AMTNO3 (aerosol phase). The chemistry processes were introduced in the introduction of main text. ASQT (sesquiterpene species) is not included since it's small (0.05 μg m^{-3}). The species from CMAQ model were simplified in Figure 6, and the simplified groups are defined in Table S7.

Figure Captions

Figure S1. Time series of AMS OM and FTIR functional group concentrations at (a) LRK and (b) CTR. Times when there was precipitation are marked on the plot.

Figure S2. Scatter plots of (a) AMS OM with FTIR OM at CTR (R=0.68, slope=1.33) and (b) AMS OM (R=0.80, slope=1.07) and ACSM OM (R=0.80, slope=1.26) with FTIR OM at LRK.

Figure S3. Time series of FTIR PMF factor OM at (a) LRK and (b) CTR.

Figure S4. Scatter plot of CCN/CN and number mean diameters at both sites for supersaturations of 0.1%, 0.2%, and 0.5%.

Figure S5. Scatter plot for CCN/CN ratio at both sites (r=0.22 and Slope=0.35 at 0.20% supersaturation; r=0.26 and Slope=0.47 at 0.37% supersaturation; r=0.37 Slope=0.45 at 0.58% supersaturation at LRK and 0.54% supersaturation at CTR) .

Figure S6. Time series of black carbon concentration and carbon monoxide mixing ratio at CTR and LRK.

Figure S7. Wind rose plot of NO_x concentration at LRK and CTR.

Figure S8. Scatter plots of AMS OM at CTR with (a) O_3 with r=0.42 and (b) NO_x with r=0.22, respectively. Scatter plots of AMS OM at LRK with (a) O_3 with r=0.61 and (b) NO_x with r=0.08.

Figure S8. Time series of black carbon concentration and carbon monoxide mixing ratio at CTR and LRK.

Figure S9. FTIR PMF factors for solutions with 2 to 5 factors and Fpeak values of -2 to 2 at LRK.

Figure S10. FTIR PMF factors for solutions with 2 to 5 factors and Fpeak values of -2 to 2 at CTR.

Table Captions

Table S1. Cosine similarity of AMS PMF factors at CTR and LRK. Numbers in bold are the highest numbers in each column (if above 0.7).

Table S2. Time series correlation coefficients of FTIR PMF factors with tracers. Numbers in bold are the highest numbers in each column (if above 0.4).

Table S3. Cosine similarity of FTIR biogenic factors and chamber isoprene and α-pinene bSOA. Ammonium absorption was removed.

Table S4. Correlation coefficients of NO_x to AMS and FTIR OM and factors for low NO_x (<0.5 ppb) and high NO_x (>1 ppb) regimes.

Table S5. The slope and correlation coefficients from the linear regression of OM concentration with NO_x mixing ratio as well as the normalized standard deviation of OM concentrations for in the high NO_x regime.

Table S6. Properties of FTIR PMF factor solution evaluation at LRK and CTR.

Table S7. Nomenclature of the bSOA categories from the CMAQ model.

Figure S1.

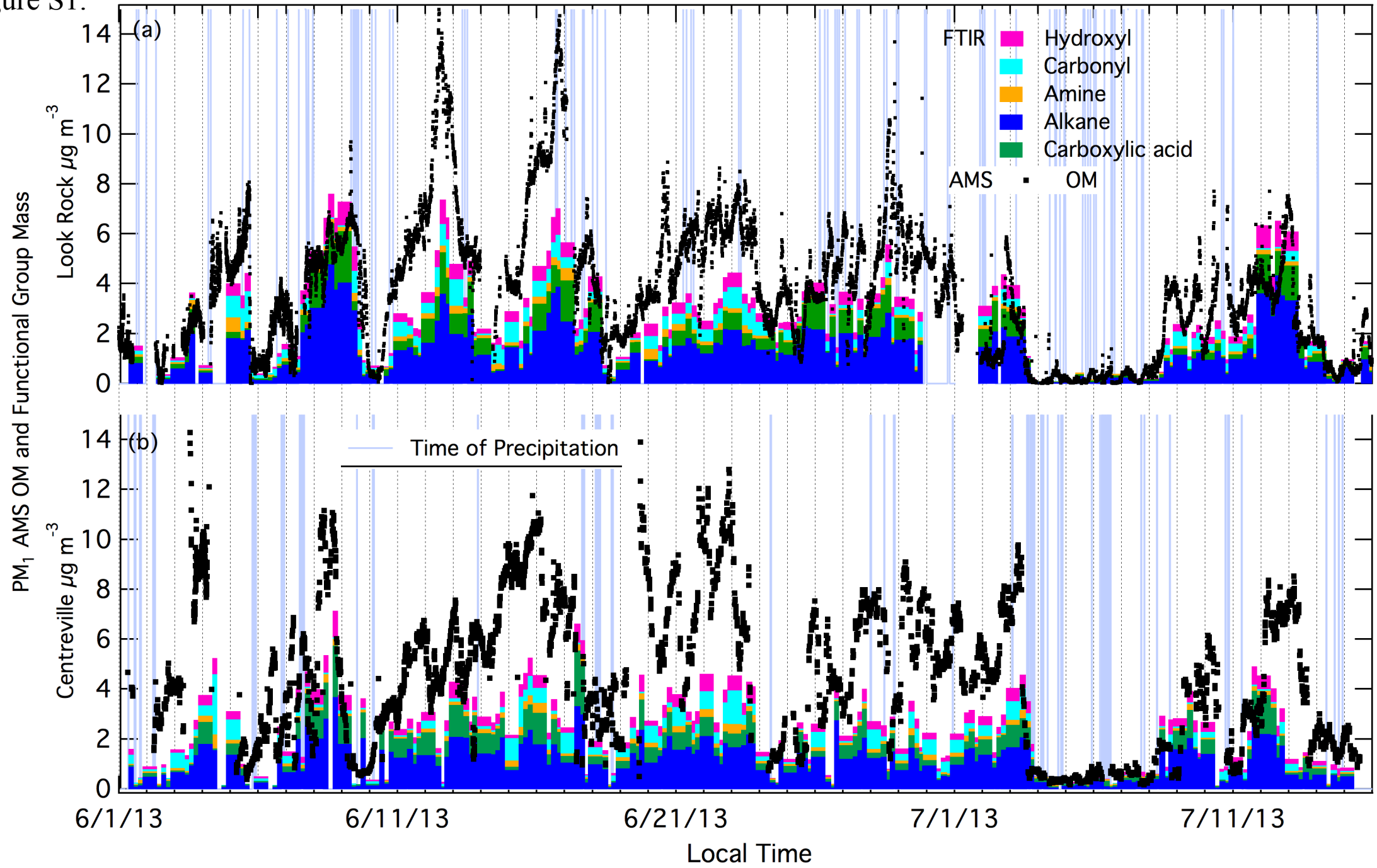
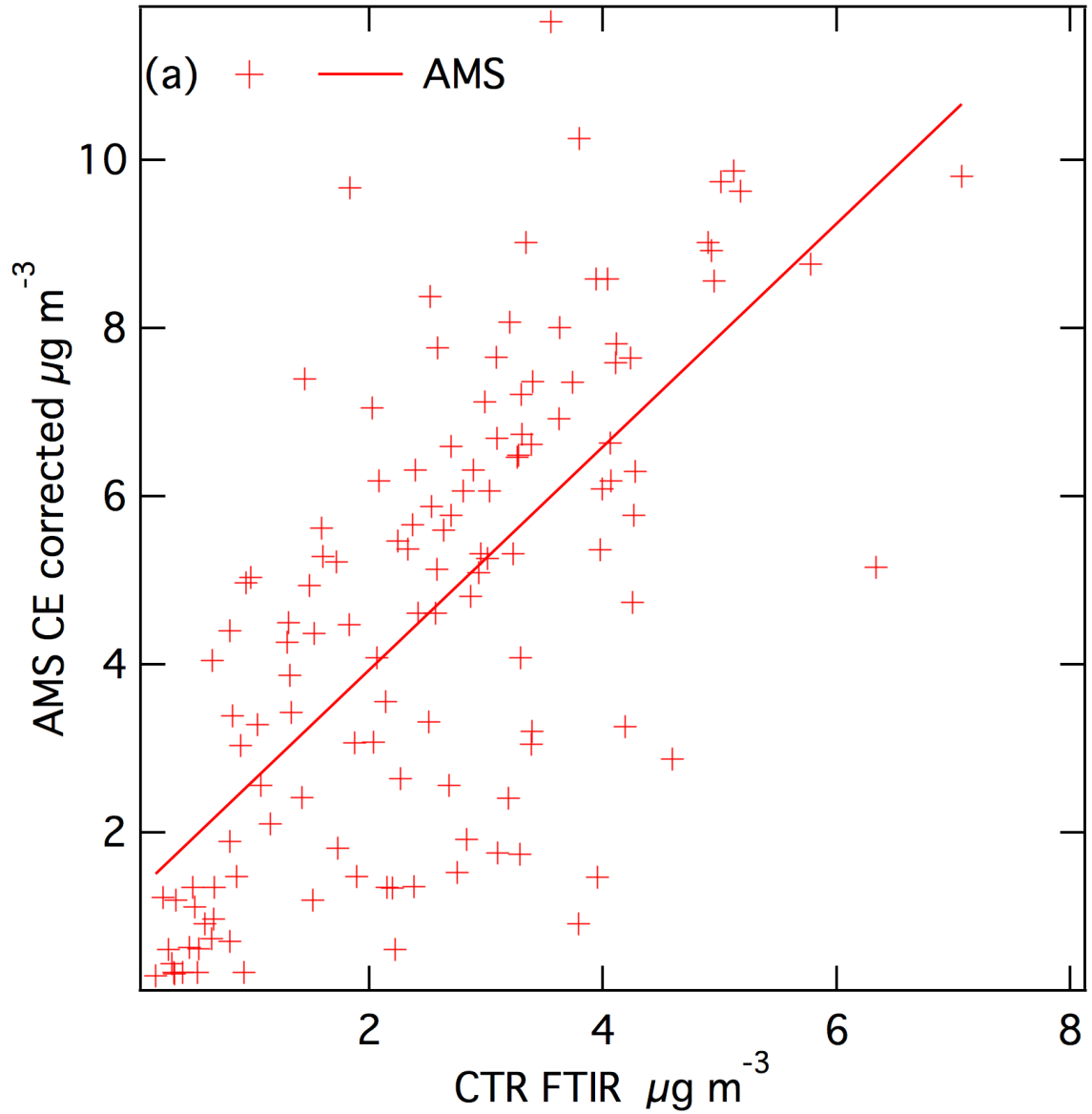

(a)
(b)
FTIR
Hydroxyl
Carbonyl
Amine
Alkane
Carboxylic acid
AMS
OM
Time of Precipitation
Look Rock μg m-3
Centreville μg m-3
PM1 AMS OM and Functional Group Mass
0
2
4
6
8
10
12
14
6/1/13
6/11/13
6/21/13
7/1/13
7/11/13
Local Time

Figure S2.


(a)
AMS
AMS CE corrected μg m-3
CTR FTIR μg m-3
2
4
6
8
10

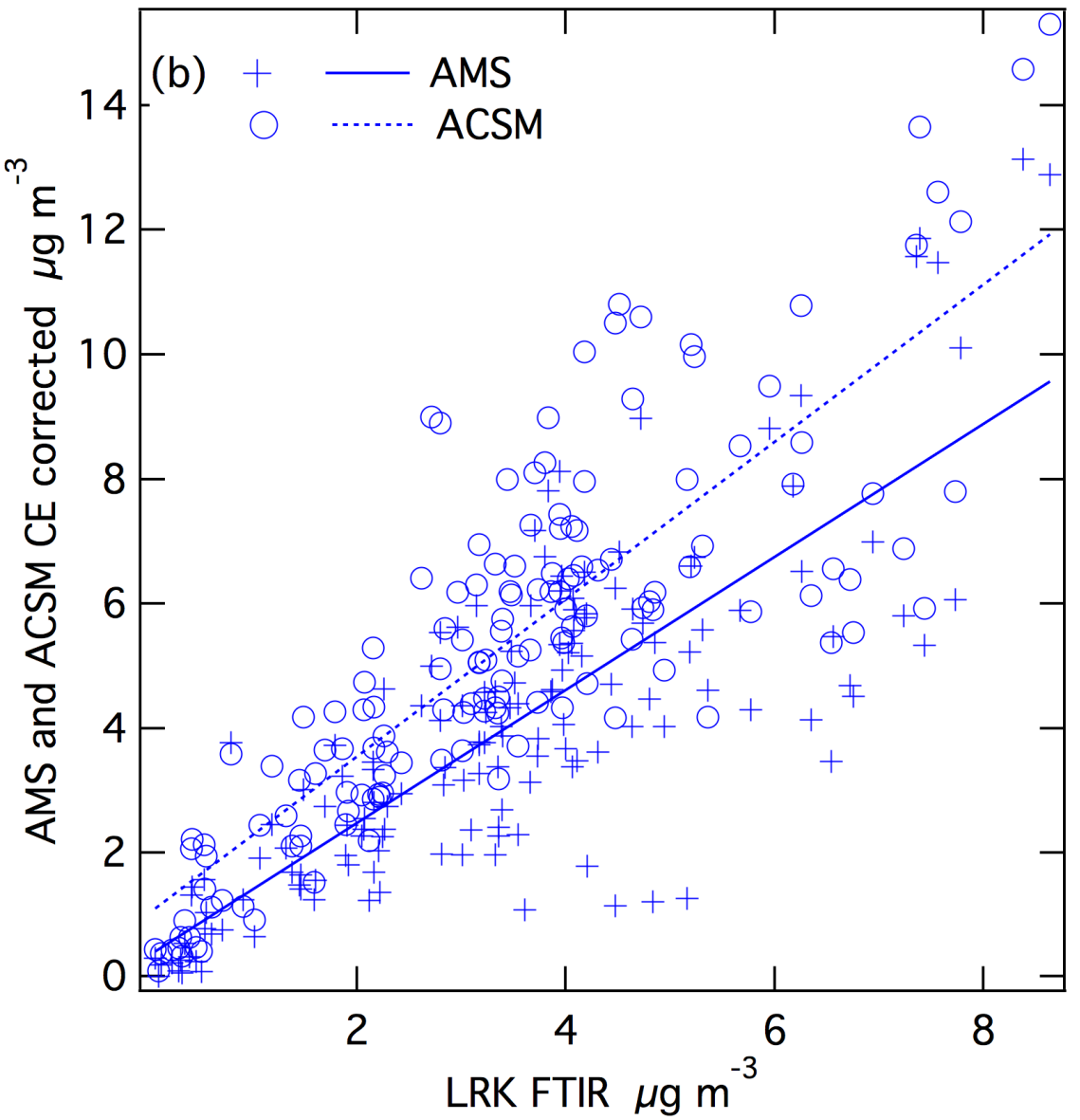

(b)
AMS
ACSM
AMS and ACSM CE corrected μg m-3
LRK FTIR μg m-3
0
2
4
6
8
10
12
14

Figure S3.

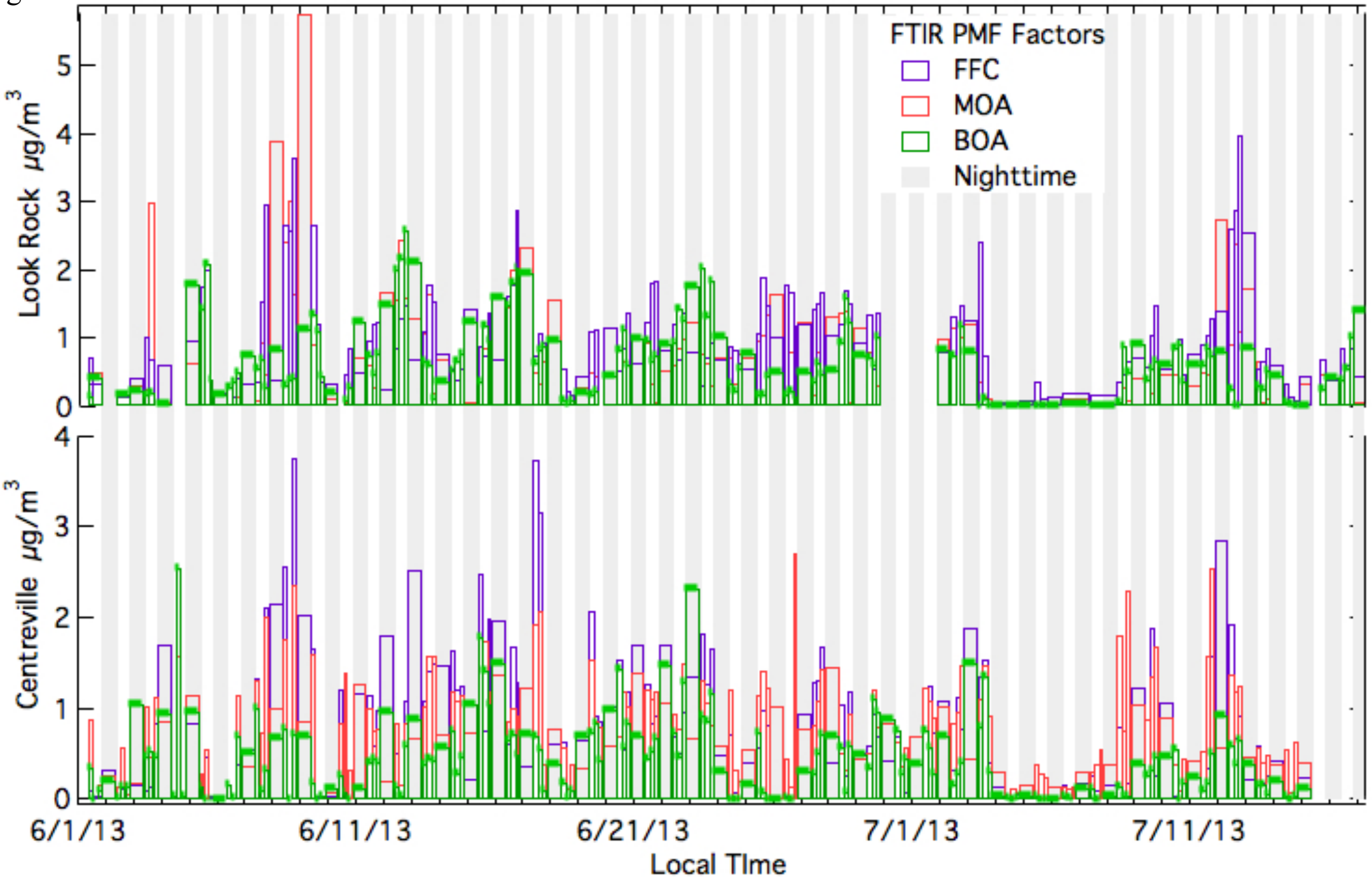

FTIR PMF Factors
FFC
MOA
BOA
Nighttime
Look Rock μg/m3
Centreville μg/m3
6/1/13
6/11/13
6/21/13
7/1/13
7/11/13
Local TIme

Figure S4.

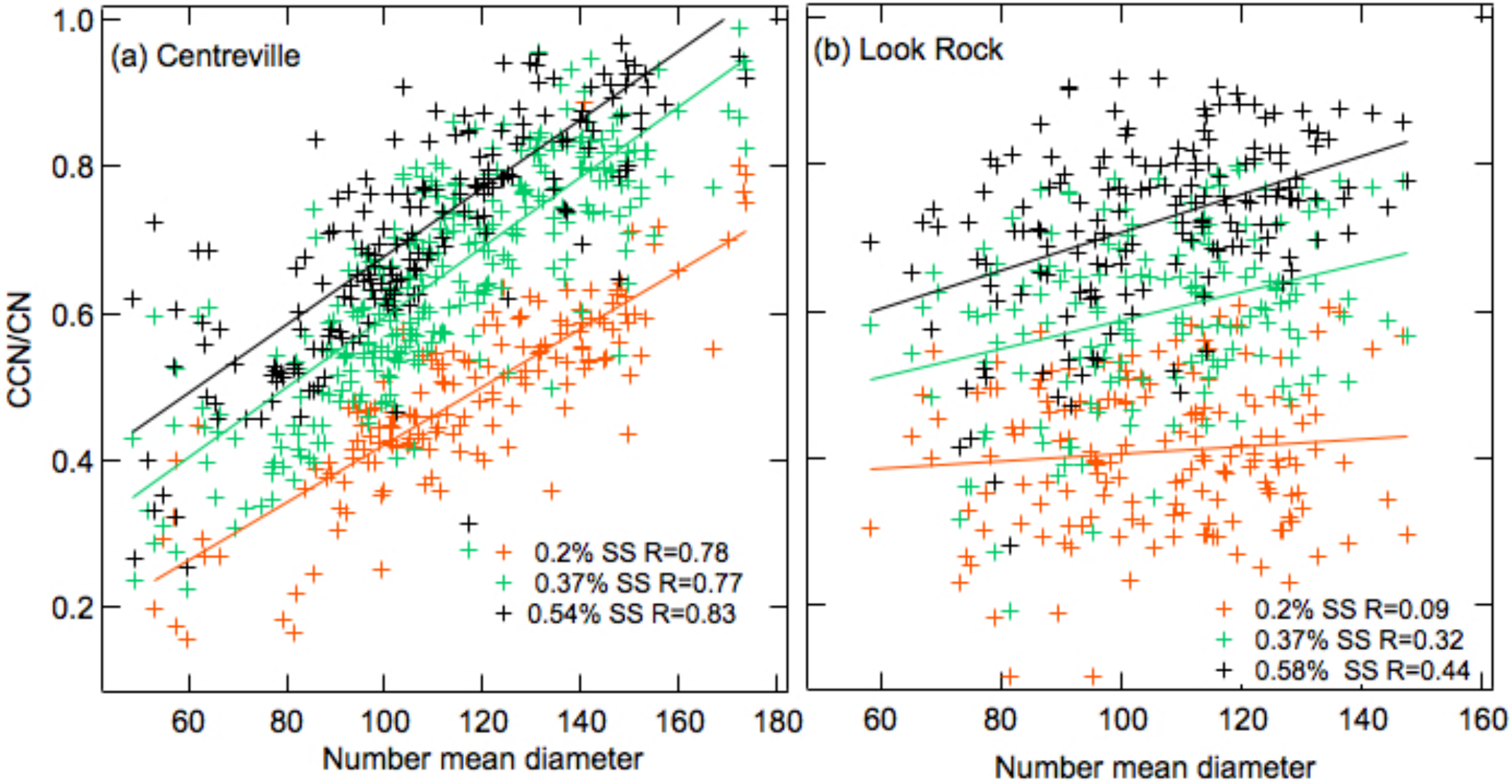

(a) Centreville
(b) Look Rock
CCN/CN
Number mean diameter
Number mean diameter
0.2% SS R=0.78
0.37% SS R=0.77
0.54% SS R=0.83
0.2% SS R=0.09
0.37% SS R=0.32
0.58% SS R=0.44
1.0
0.8
0.6
0.4
0.2
60
80
100
120
140
160
180

Figure S5.

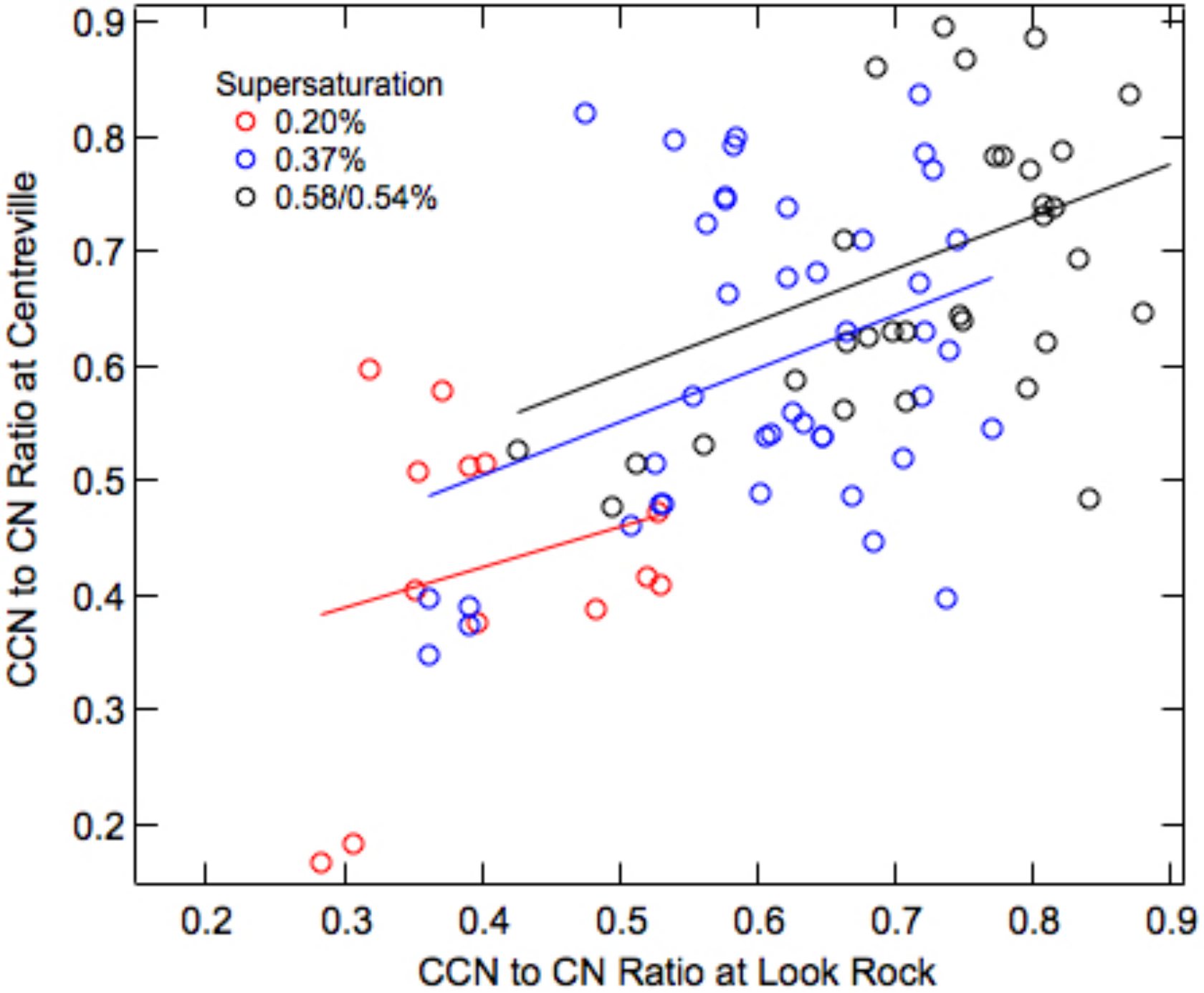

Supersaturation
0.20%
0.37%
0.58/0.54%
CCN to CN Ratio at Centreville
CCN to CN Ratio at Look Rock
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

Figure S6.

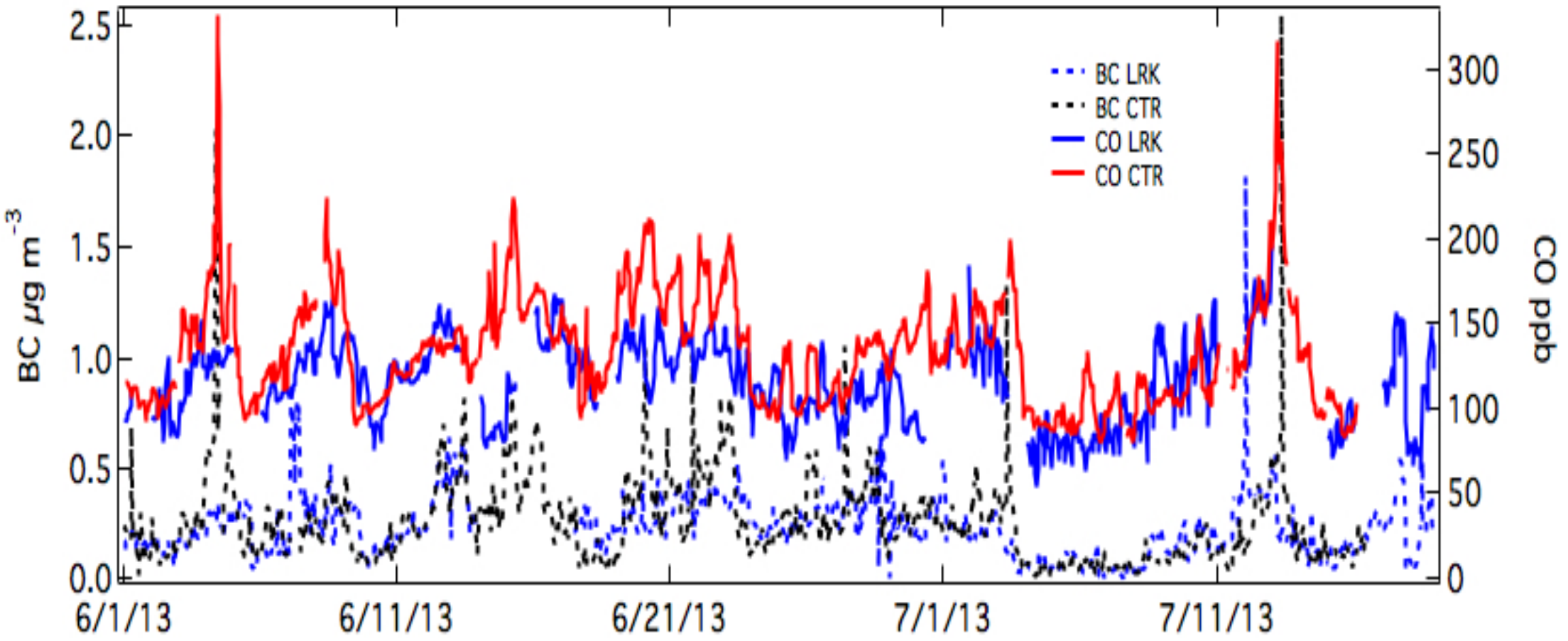
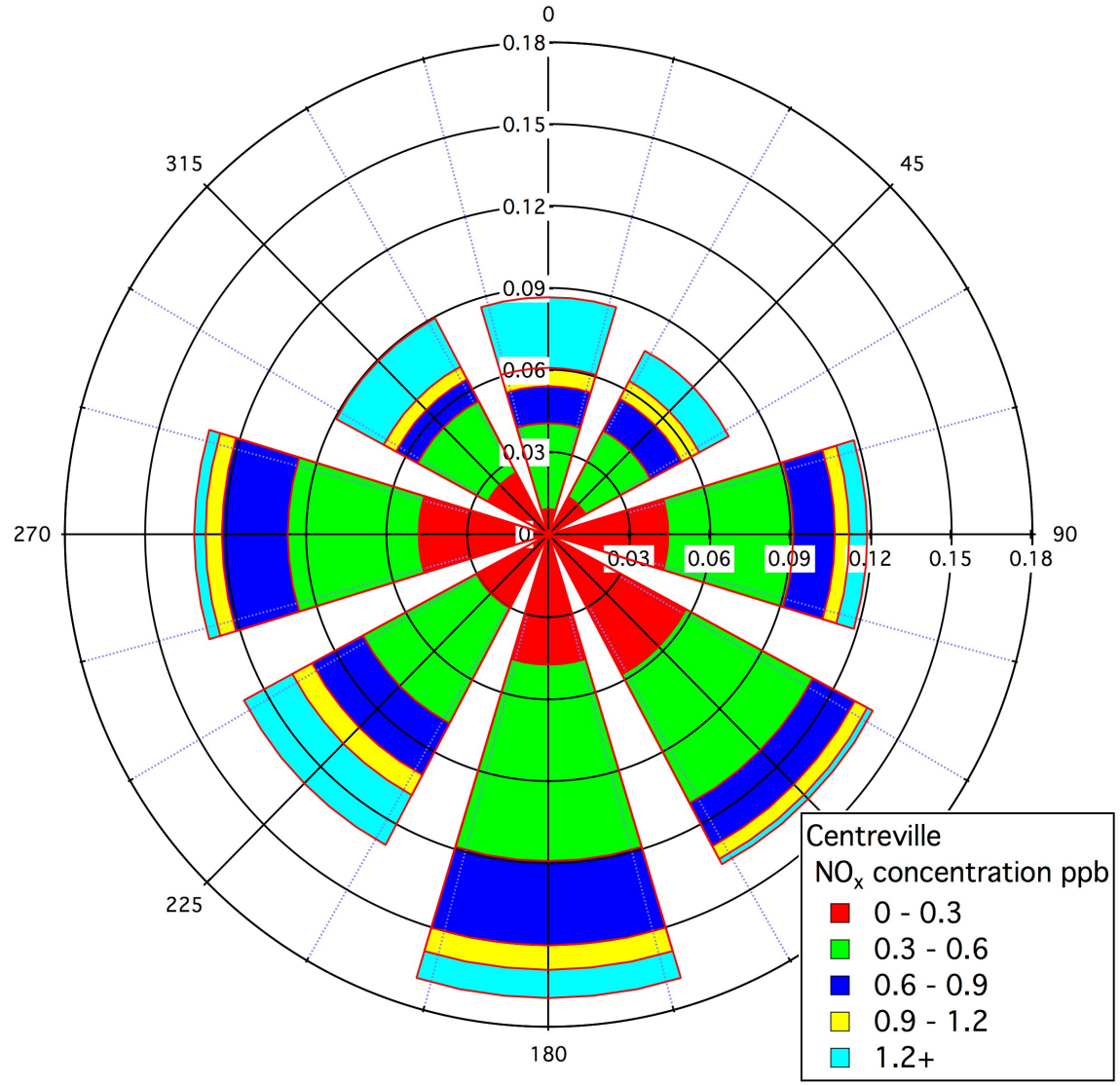

BC LRK
BC CTR
CO LRK
CO CTR
BC μg m-3
CO ppb
2.5
2.0
1.5
1.0
0.5
0.0
300
250
200
150
100
50
0
6/1/13
6/11/13
6/21/13
7/1/13
7/11/13

Figure S7.


0
0.18
0.15
0.12
0.09
0.06
0.03
315
45
270
90
225
180
0.03
0.06
0.09
0.12
0.15
0.18
Centreville
NOx concentration ppb
0 - 0.3
0.3 - 0.6
0.6 - 0.9
0.9 - 1.2
1.2+

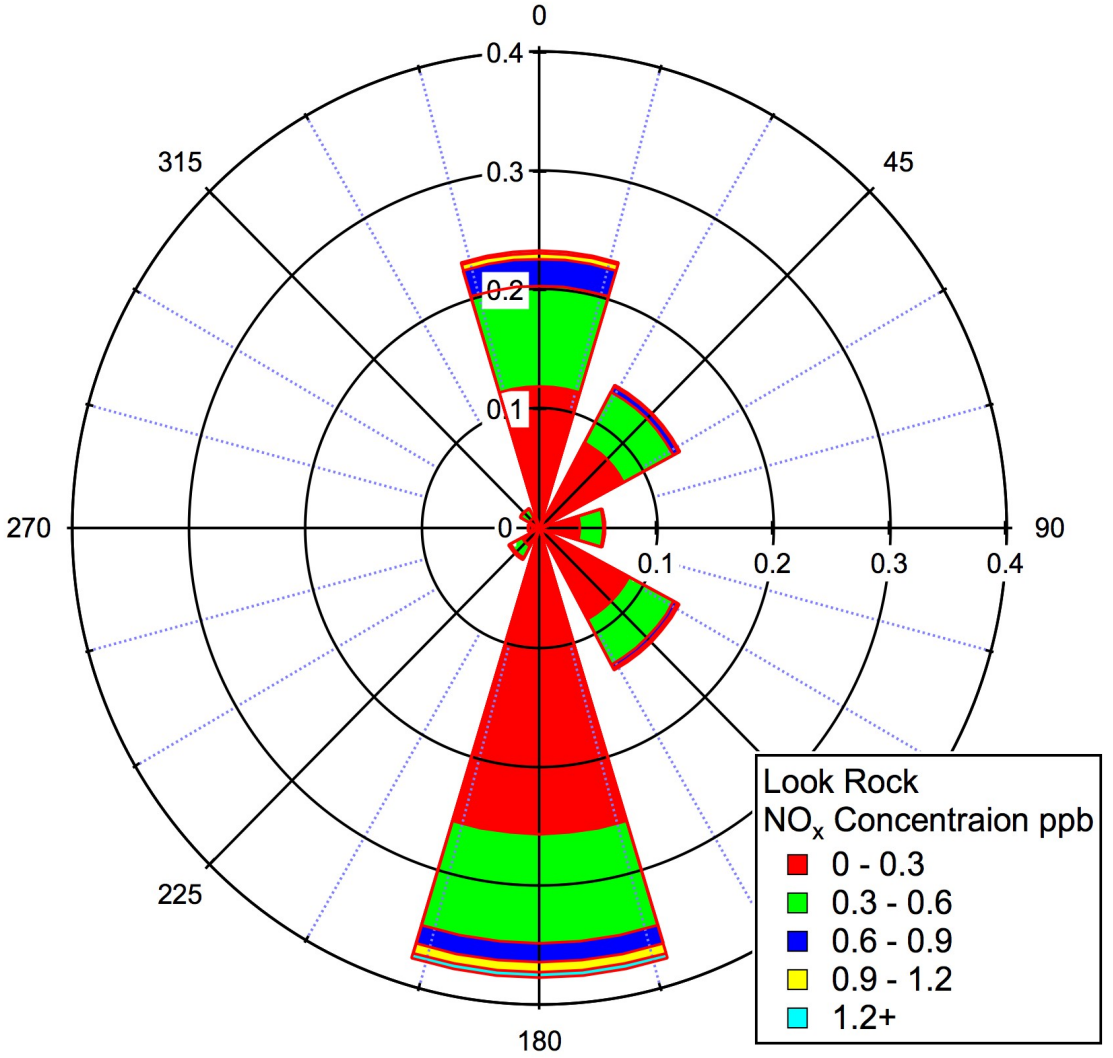

0
0.4
0.3
0.2
0.1
315
45
270
90
225
180
0.1
0.2
0.3
0.4
Look Rock
NOx Concentraion ppb
0 - 0.3
0.3 - 0.6
0.6 - 0.9
0.9 - 1.2
1.2+

Figure S8.

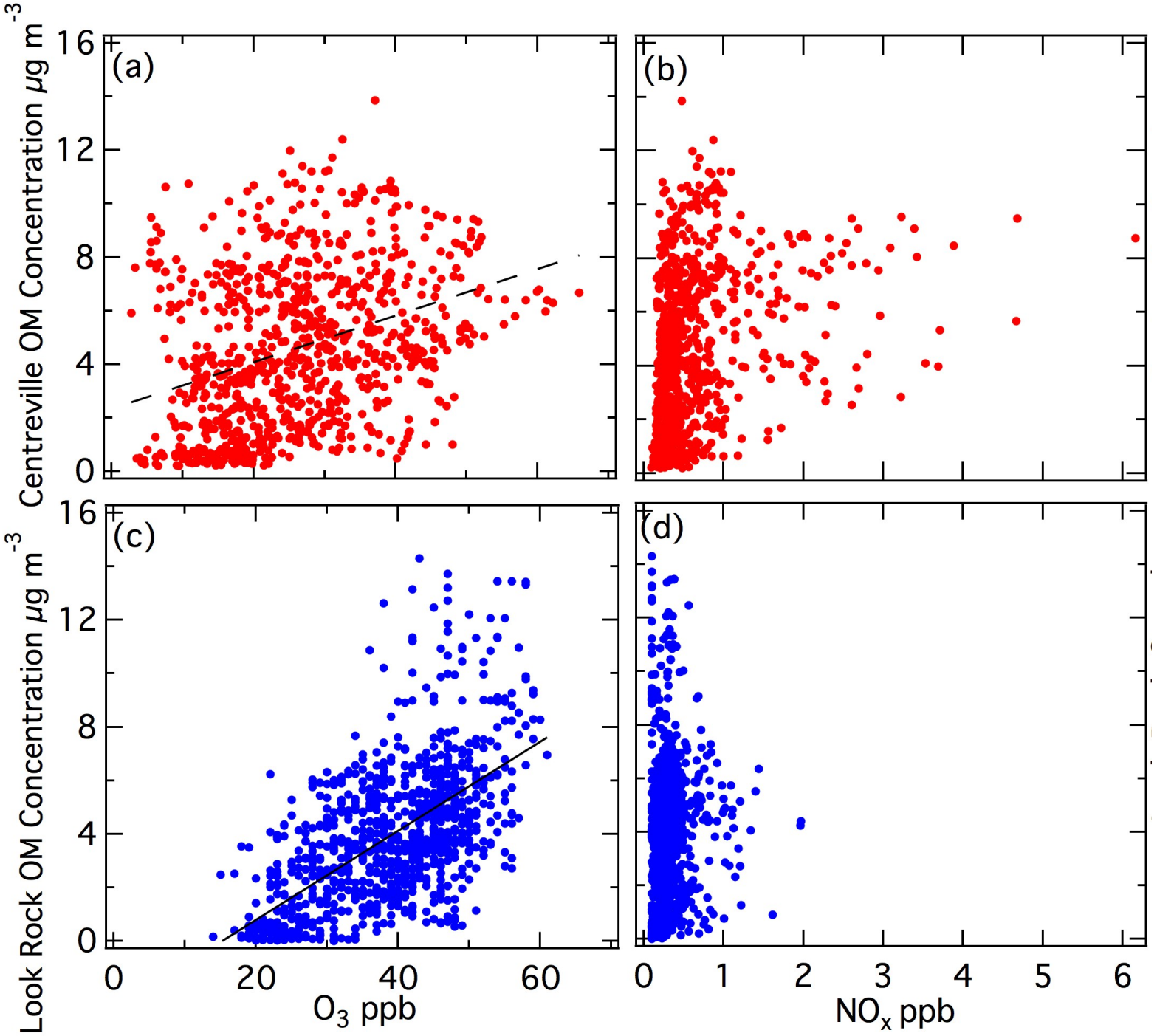

(a)
(b)
(c)
(d)
Centreville OM Concentration μg m-3
Look Rock OM Concentration μg m-3
0
4
8
12
16
0
20
40
60
O3 ppb
0
1
2
3
4
5
6
NOx ppb

Figure S9.

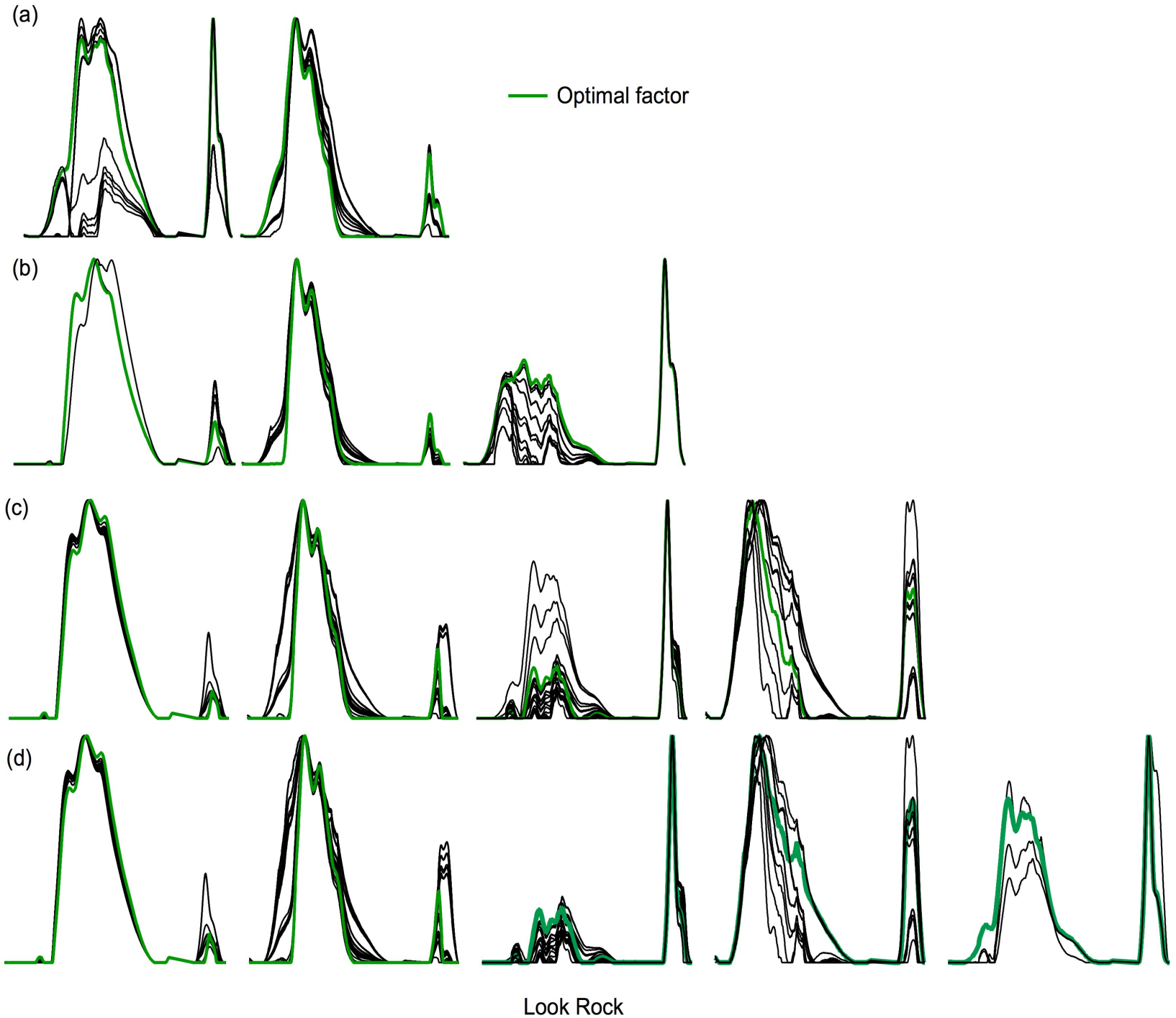
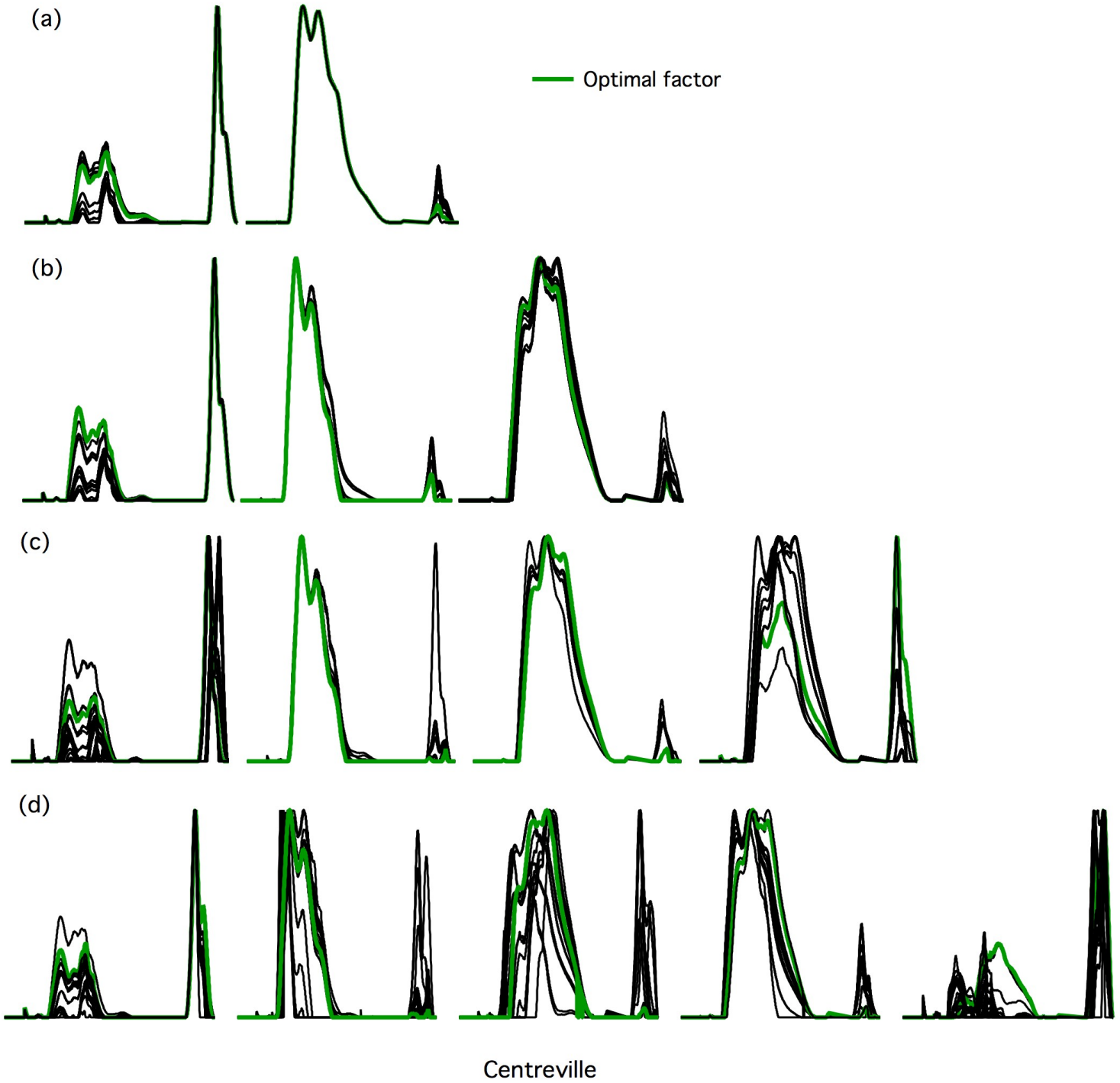


Figure S10.



Tables

Table S1.

Cosine Similarity	LRK-Factor82	LRK-Factor44	LRK-Factor91
CTR-Isoprene-OA	**0.99**	0.78	0.65
CTR-MO-OOA	0.81	**0.98**	0.35
CTR-LO-OOA	0.95	0.84	0.66
CTR-BBOA	0.95	0.87	0.55
ACSM LRK-IEPOXOA	**0.80**	0.82	0.36
ACSM LRK-LVOOA	0.67	**0.84**	0.49
ACSM LRK-91fac	0.82	0.80	0.66
Correlation of Time Series	LRK-Factor82	LRK-Factor44	LRK-Factor91
ACSM LRK-IEPOXOA	**0.93**	0.43	0.51
ACSM LRK-LVOOA	0.59	**0.87**	0.71
ACSM LRK-91fac	0.51	0.74	**0.87**

Table S2.

Correlation Coefficient (R)	LRK			CTR		
	FFC	BOA	MOA	FFC	BOA	MOA
SO_2	0.15	0.12	-0.01	0.26	0.01	0.11
NOx	0.1	-0.02	0.07	0.1	**0.41**	0.12
NO_y	**0.4**	0.34	0.28	0.23	**0.54**	0.25
CO	**0.53**	0.45	0.46	0.28	**0.71**	0.38
O_3	0.32	**0.51**	0.36	0.27	0.22	0.19
BC	**0.51**	**0.55**	0.43	0.23	**0.62**	0.28
Ca	**0.64**	0.31	0.06	0.31	0.06	0.28
Fe	0.32	0	-0.25	0.32	0.01	0.28
Mn	0.37	0.09	-0.37	**0.41**	0.16	0.31
MVK/MACR	0.28	**0.66**	0.36	-	-	-
SO_4	**0.64**	0.45	**0.65**	0.31	0.28	0.38
NO_3	0.25	0.44	0.37	0.09	**0.51**	0.29
NH_4	**0.59**	0.44	**0.62**	0.35	0.34	0.43
CTR-Isoprene-OA/ LRK-Factor82	0.43	0.56	**0.58**	0.41	0.34	**0.47**
CTR-MO-OOA/LRK-Factor44	0.47	**0.76**	0.45	0.33	**0.51**	0.25
LRK-Factor91 /CTR-LO-OOA	0.25 -	**0.73** -	0.28 -	- 0.04	- **0.61**	- 0.16

$p<0.05$ when $R>0.35$.

Table S3.

Cosine Similarity	Experiment Conditions	Ambient BOA Factors+				
		Hyytiala/ Whistler	CTR pm_1	CTR $pm_{2.5}$	LRK pm_1	LRK $pm_{2.5}$
α- Pinene + NO_3 seeded*	RH=50%; UV light off	0.38/0.48	0.38	0.44	0.61	0.57
α - Pinene + O_3 unseeded	RH=0; UV light off	0.8/0.85	0.83	0.86	0.91	0.9
α - Pinene + OH and NO_x unseeded	RH=50%; UV light: 30 min at 50%	0.84/0.87	0.85	0.85	0.88	0.88
Isoprene + OH and NO_x unseeded	RH=0; UV light: 40 min at 100%	0.88/0.9	0.89	0.89	0.87	0.88
Isoprene + OH and NO_x seeded*	RH=50%; UV light: 30 min at 50%	0.52/0.61	0.53	0.58	0.74	0.70

*Seeded with neutral $(NH_4)_2SO_4$ and ammonium removed from spectra
+Ammonium removed from spectra.

Table S4.

Correlation Coefficient	Low NOx (<0.5 ppb)	High NOx (>1 ppb)
CTR-LO-OOA/CTR-BOA	0.18/0.13	0.36/0.69
LRK-Factor91/LRK-BOA	0.16/0.15	0.83/NA*
CTR-MO-OOA/CTR-FFC	-0.22/0.00	-0.26/0.37
LRK-Factor44/LRK-FFC	0.23/0.01	0.45/NA*
CTR-Isoprene-OA/CTR-MOA	-0.11/0.04	0.25/0.23
LRK-Factor82/ LRK-MOA	0.10/0.09	0.12/NA*
CTR-AMS OM/CTR-FTIR OM	0.03/0.06	0.14/0.58
LRK-AMS OM/LRK-FTIR OM	0.00/0.08	-0.36/NA*

*NA indicates that there were too few measurements for a comparison, namely less than 6 AMS or 2 FTIR measurements.

Table S5.

Threshold		0.7	0.8	0.9	1	1.1	1.2	1.3
AMS LOOOA	Normailized SD	0.51	0.48	0.48	0.49	0.49	0.49	0.49
	Slope	0.53	0.45	0.48	0.53	0.52	0.50	0.46
	R	0.36	0.32	0.35	0.36	0.36	0.33	0.30
FTIR BOA	Normailized SD	0.81	0.78	0.78	0.76	0.69	0.66	0.65
	Slope	0.37	0.42	0.88	0.98	1.06	1.01	1.03
	R	0.27	0.30	0.61	0.69	0.58	0.54	0.52

Table S6

Number Criteria \ Factor	2	3	4	5	6
Q/Q_{exp}	2.35/1.33	0.95/0.57	0.62/0.42	0.54/0.36	0.48/0.34
Absolute residual	20.6/18.3%	14.7/13.0%	13.9/11.7%	13.4/10.9%	12.9%/10.1%
Temporal correlation factor strength (r>0.8)	None/None	None/None	None/None	None/None	1 pair/None
Similarity of factor spectra (r>0.8)	None/None	None/None	2 /1 pair(s)	4/2 pairs	4/3 pairs
Factors with less than 6% OM	None/None	None/None	None/None	1/1	1/2

* Values at LRK/ CTR

Table S7

Category				Average Concentration (CTR/LRK) μg m^{-3}	CMAQ model species
bSOA	NOx related	Monoterpene		0.3/0.1	AMTNO3
		Isoprene		<0.1/<0.1	AISOPNN
	Not related to NOx	Isoprene	Dry	0.5/0.5	AISO1+AISO2+ AOLGB*(AISO1+AISO2)/(ATRP1+ATRP2+ASQT+AISO1J+AISO2)
			IEPOX	0.6/0.7	AIETET+AIEOS+AIDIM
			MAE, HMML	<0.1/<0.1	AIMGA+AIMOS
		Monoterpene		0.4/0.2	ATRP1+ATRP2+ AOLGB*(ATRP1+ATRP2)/(ATRP1+ATRP2+ASQT+AISO1J+AISO2)
Anthropogenic OA	Anthropogenic			1.1/1.3	Benzene OA+ toluene OA+ xylene OA + PCSOA+POA+OPOA.