CRC Report No. A-60

Organic Aerosol Spatial/Temporal Patterns: Perspectives of Measurements and Model

Final Report

January 2008

COORDINATING RESEARCH COUNCIL, INC.
3650 MANSELL ROAD·SUITE 140·ALPHARETTA, GA 30022

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Foreword

Based on research conducted from December 1, 2006 to January 31, 2008 under CRC Project A-60 **"Conceptual Model of Organic PM Formation,"** Betty K. Pun and Christian Seigneur, Atmospheric & Environmental Research, Inc. San Ramon, CA, produced a journal manuscript detailing their research results. The title of the manuscript is "Organic Aerosol Spatial/Temporal Patterns: Perspectives of Measurements and Model"; it is currently under review for publication in Environmental Science and Technology. Full citation and ordering information will be provided as it becomes available.

An Abstract of the work conducted is included in this document along with an executive summary and additional supporting data and information not presented in the journal article.

Organic Aerosol Spatial/Temporal Patterns: Perspectives of Measurements and Model

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ABSTRACT.

Ambient measurements from SEARCH and model results from CMAQ-MADRID are analyzed side by side in the southeastern United States to understand the strengths and weaknesses of an air quality model in reproducing key spatial and temporal patterns related to organic aerosol (OA), with inferences regarding secondary organic aerosol (SOA). The model predicts a larger difference between an urban and a rural site but stronger correlation in OA concentrations than indicated by measurements. On average, urban OA emissions may be understated, while production of SOA is likely to be less concentrated near urban areas and more sustained on the regional scale than represented in the model. Modeled diurnal fluctuations for OA are stronger than measured, due partially to overestimations of the temperature dependence parameters (ΔH_{vap}) for SOA in the model. Inferred urban-rural differences in the composition of SOA are not properly captured by the model, which does not represent multiple generations of SOA or varied reaction pathways as a function of chemical regimes. Model results are hampered by day-of-the-week and diurnal allocation issues related to EC and OA emissions. Observed top quintile (20%) afternoon OA concentrations occur in both warm and cold seasons at the urban site. The frequency of high OA in the cold season is overstated in the model relative to the warm season. The model predicts the warm vs. cold season frequency of elevated OA episodes better at YRK than at JST, suggesting that regional emissions, chemistry and transport are better simulated than the urban processes.

EXECUTIVE SUMMARY.

Organic aerosol (OA) represents a weak link in the air quality community's understanding of particulate matter (PM). Unlike other major PM components, such as sulfate and nitrate, OA is a complex mixture of primary and secondary compounds of anthropogenic and biogenic origins. Processes leading to the formation and accumulation of OA are not fully understood, and their representation in models tend to be rudimentary and insufficient to reproduce observed spatial and temporal patterns. In this study, ambient measurements from SEARCH and model results from CMAQ-MADRID are analyzed side by side in the southeastern United States to understand the strengths and weaknesses of an air quality model in reproducing key spatial and temporal patterns related to OA. Inferences are made regarding weaknesses in primary organic aerosol (POA) emissions and model formulation for secondary organic aerosol (SOA).

Ambient OA is calculated from measurements of organic carbon (OC). The OC tracer method is used to determine the fraction of OC that is primary versus secondary, and appropriate conversion factors (1.2 for primary and 1.4-2.1 for secondary) are used to convert OC to OA. Observations show similar levels of OA on an annual average basis at an urban site (Atlanta) and a rural site (Yorkville). The model predicts a larger difference between the urban and rural sites, with the rural concentrations being underpredicted. Rural underprediction of OA may be attributed to underestimation of SOA in Yorkville on an annual average basis. Because the model predicts SOA to account for the majority of OA in both Atlanta and Yorkville, it predicts a stronger correlation in OA concentrations between Atlanta and Yorkville than indicated by the measurements. Urban OA emissions may be understated, while production of SOA is likely to be less concentrated near urban areas and more sustained on the regional scale than represented in the model.

Modeled diurnal fluctuations for OA and SOA are stronger than measured, as shown in Figure ES-1 for Yorkville. Assuming that the accumulation of SOA, and hence OA, in the early evening is due to the partition of additional condensable material into the PM phase from the gas phase due to changes in the equilibrium partitioning as temperature falls, the temperature dependence parameter (ΔH_{vap}) can be estimated from the median diurnal profiles. The ΔH_{vap} derived from CMAQ profiles is 81 kJ/mol, which is consistent with parameters used in the model. The ΔH_{vap} derived from observations is 24 kJ/mol. Therefore, the larger range of modeled diurnal fluctuations is due partially to overestimations of the temperature dependence parameters used in the SOA model.

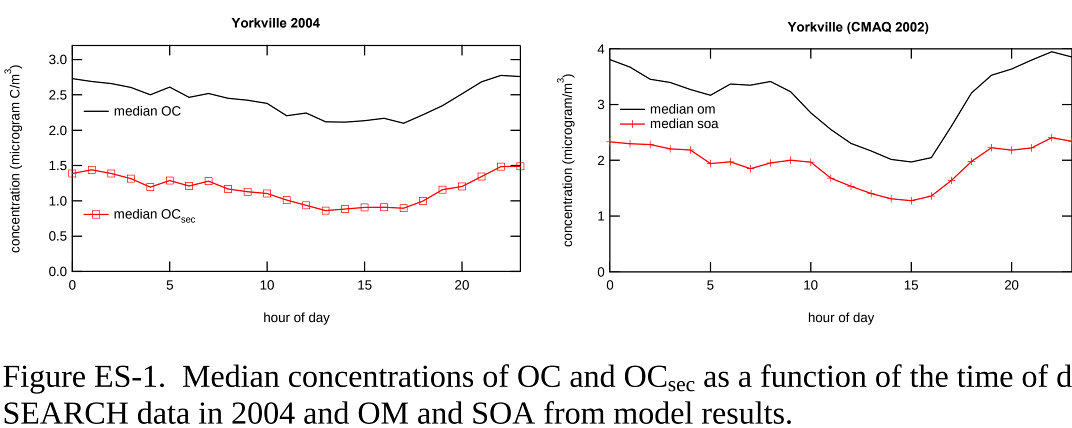


Figure ES-1. Median concentrations of OC and OC_{sec} as a function of the time of day from SEARCH data in 2004 and OM and SOA from model results.

For Atlanta, the measurement-derived ΔH_{vap} is 67 kJ/mol, which is a factor of 2.5 higher than the value at Yorkville, reflecting a much different, probably aged SOA mixture at the rural site compared to a fresher SOA mixture at the urban site. The model-derived value is 106 kJ/mol in Atlanta, which is a factor of 1.3 higher than the corresponding value in Yorkville, reflecting a somewhat more similar mixture. Urban-rural differences in the composition of SOA inferred from measurements are not properly captured by the model, which does not represent multiple generations of SOA or varied reaction pathways as a function of chemical regimes.

Day-of-the-week specific diurnal profiles of OC, EC, and OC/EC ratios are shown in Figure ES-2 for Atlanta. In Atlanta, EC profiles are lower on weekends compared to weekdays, but OC profiles do not show a statistically significant difference between weekends and weekdays. The elevated OC/EC ratios reflect changes in the source mixture (e.g., heavy duty vs. light duty vehicles) on weekends especially in the early morning. The measurements are consistent with a small increase or no change in the POA, rather than an increase in SOA on weekends. Model results show a less significant decrease in EC on weekends. For model emissions, the increase in the OC/EC ratios on weekends is less than inferred in the ambient OC/EC ratios. POA, SOA and EC decrease on weekends in the model. There is also an erroneous evening peak for modeled EC and OC. Model results are hampered by day-of-the-week and diurnal allocation issues related to EC and OA emissions.

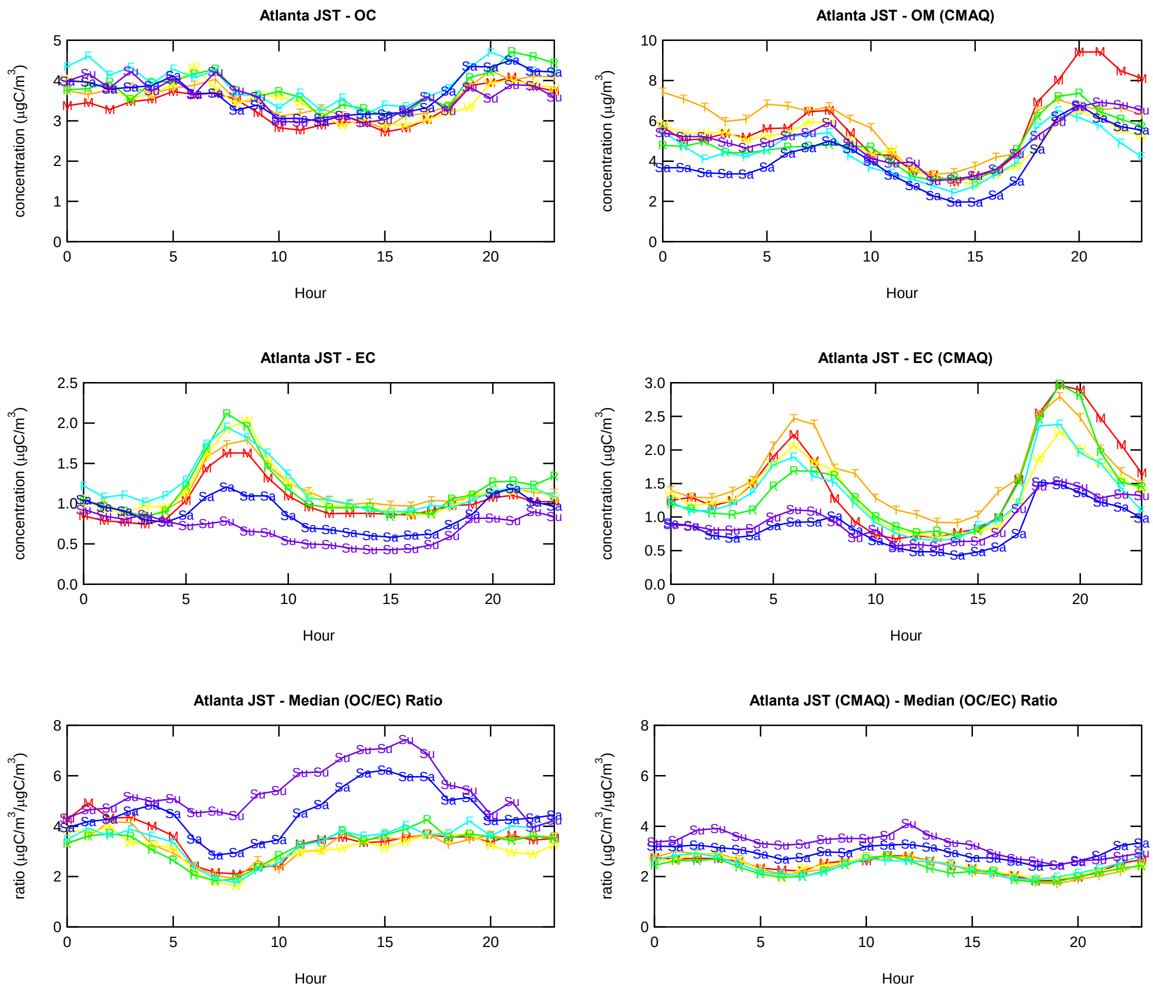


Figure ES-2. Diurnal profile for each day of the week at JST for (a) SEARCH OC or modeled OM, (b) SEARCH or modeled EC, and (c) SEARCH or modeled OC/EC. (Key: M = Monday, T = Tuesday, W = Wednesday, R = Thursday, F = Friday, Sa = Saturday, Su = Sunday.)

Observed top quintile (20%) afternoon OA concentrations occur in both warm and cold seasons at the urban site. The conditional probability of a high OA day in the warm season is 0.23, whereas only 17% of the periods during the cold season are associated with high OA. The frequency of high OA in the cold season is overstated in the model relative to the warm season. High OA concentrations in the cold season are driven by primary emissions, because high SOA concentrations tend to be associated with warm weather. Therefore, the model may be missing a process that generates SOA under relatively polluted conditions at high temperature and oxidant levels. In Yorkville, the model predicts the warm vs. cold season frequency of elevated OA episodes better than in Atlanta, suggesting that regional emissions, chemistry and transport are better simulated than the urban processes.

SUPPORTING DOCUMENTS.

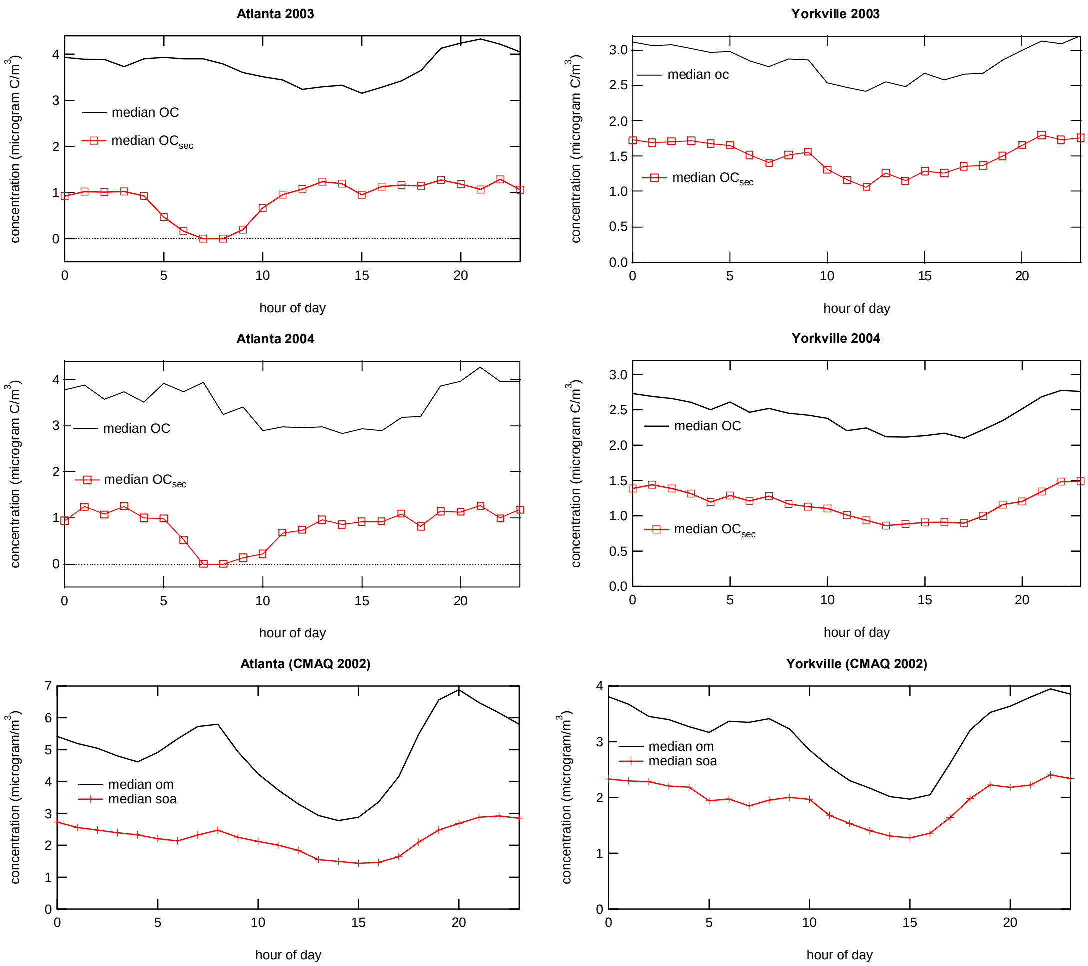


Figure S1a. Median concentrations of OC and OC_{sec} from SEARCH data in 2003 and 2004 and OM and SOA from model results for Atlanta and Yorkville.

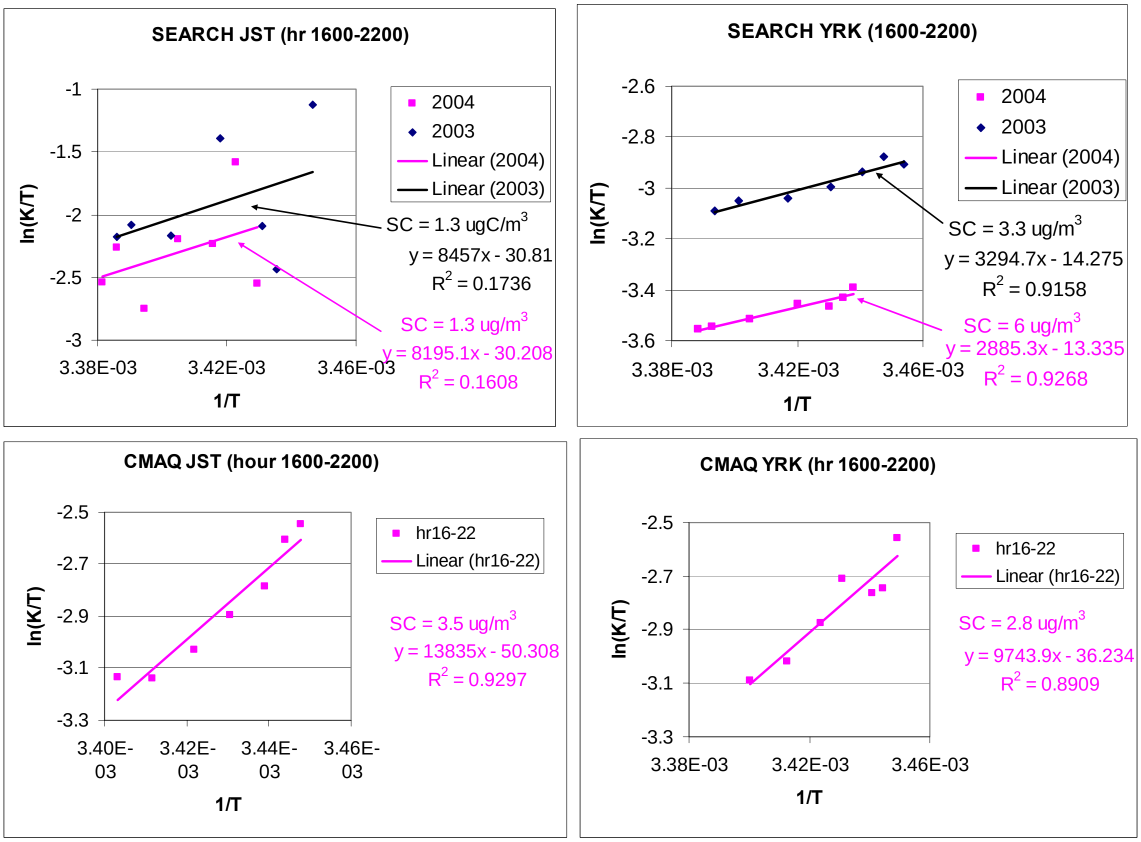
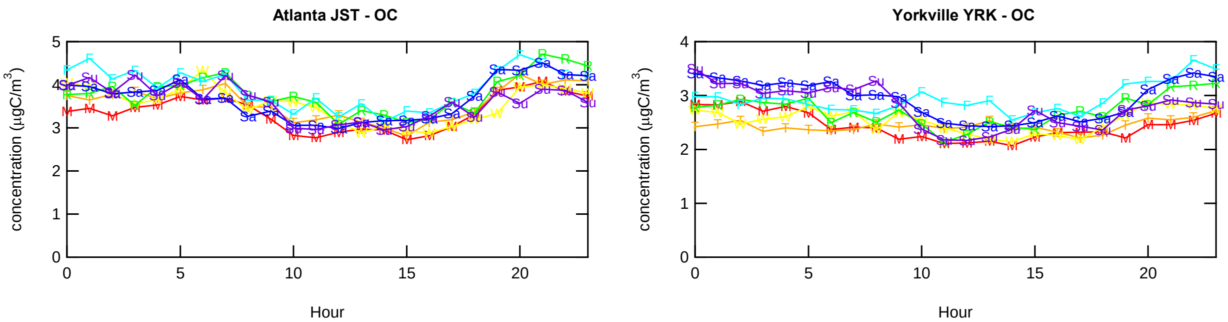
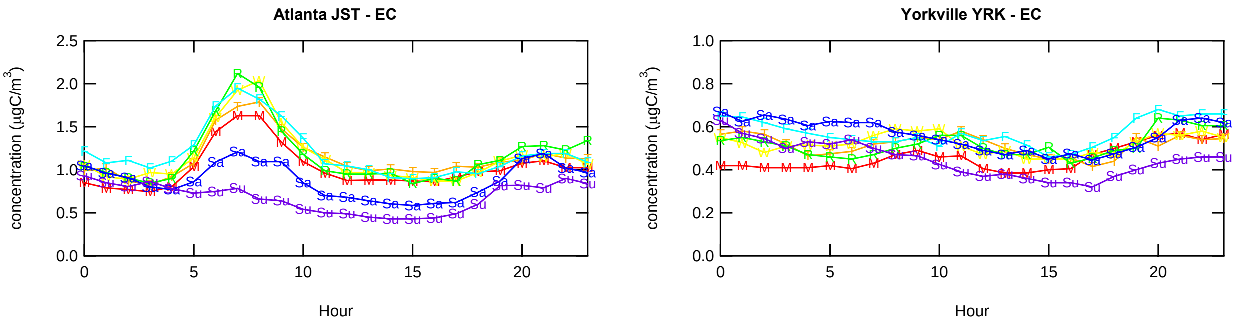


Figure S1b. ln(K/T) vs. 1/T during hours 16:00-22:00 for JST (left) and YRK (right). (top) measurements. (bottom) model data

(a)



(b)



(c)

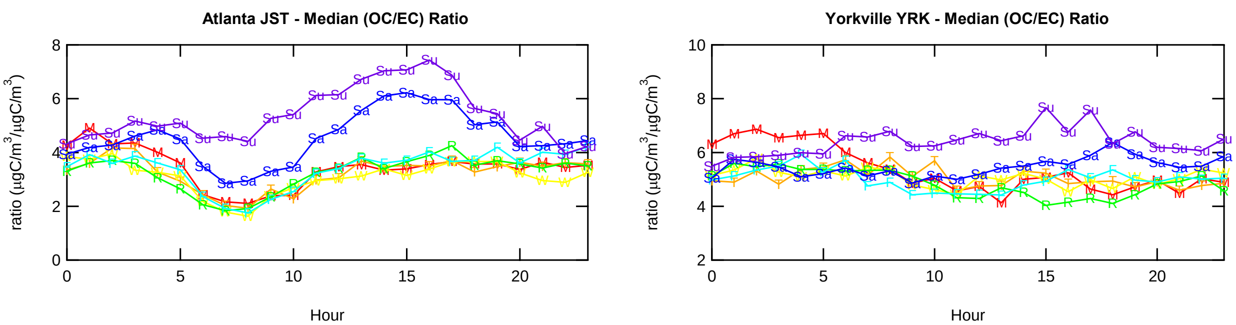


Figure S2a. Diurnal profile based on SEARCH data for each day of the week at JST and YRK for (a) OC, (b) EC, and (c) OC/EC. (Key: M = Monday, T = Tuesday, W = Wednesday, R = Thursday, F = Friday, Sa = Saturday, Su = Sunday.)

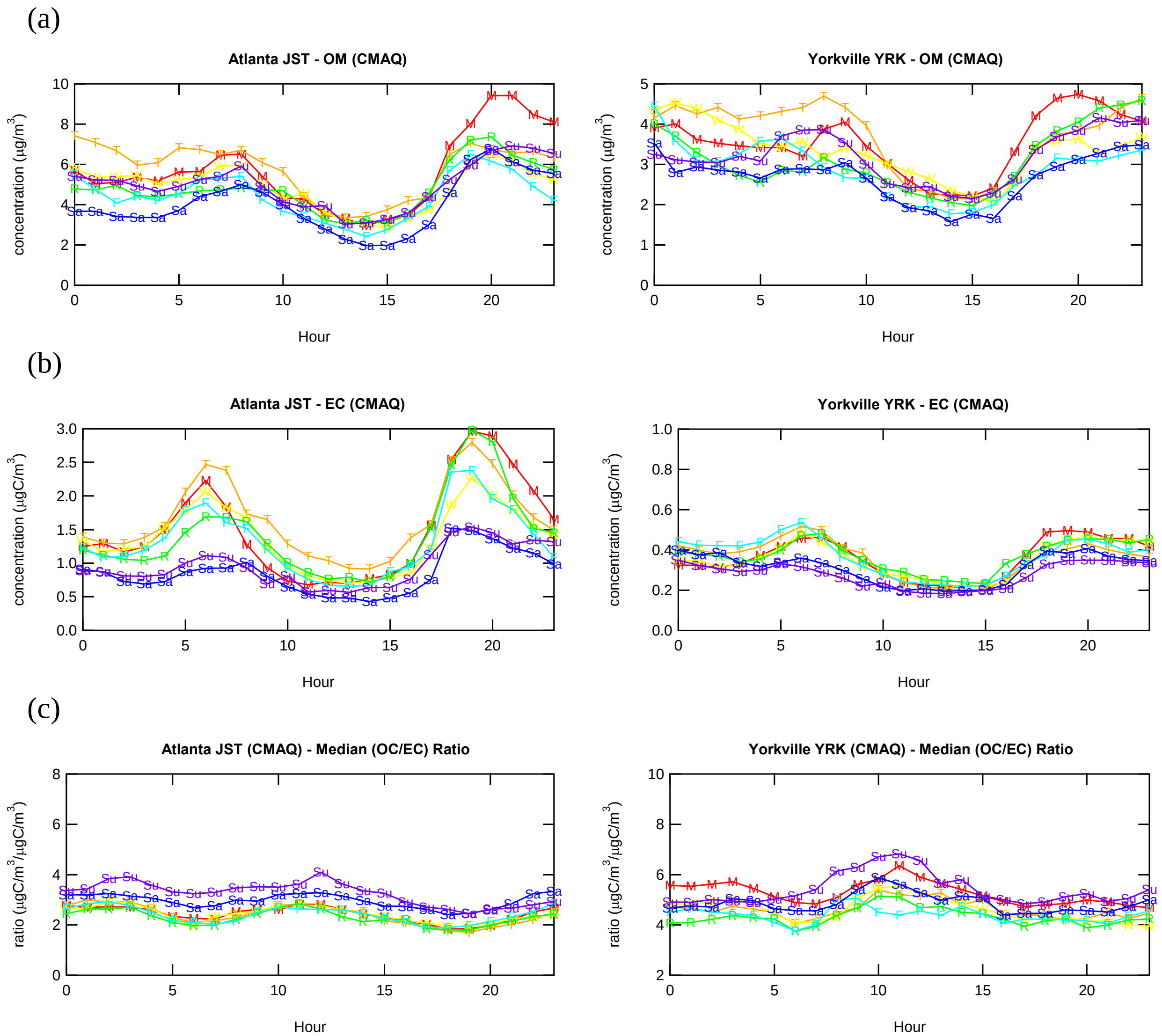


Figure s2b. Diurnal profile based on model results for each day of the week at JST and YRK for (a) OM, (b) EC, and (c) OC/EC. (Key: M = Monday, T = Tuesday, W = Wednesday, R = Thursday, F = Friday, Sa = Saturday, Su = Sunday.)

Table S1. Conditions at JST when measurement-derived OC concentrations are high (OC > 4.73 μgC/m^3) or modeled OM concentrations are high (OM > 6.26 μg/m^3) relative to the respective measured (2004) or modeled average conditions in the warm season (May – October), and the cold season (January – April; November – December).

When OC or OM are top quintile	Warm season		Cold season	
	measured	modeled	measured	modeled
Variables that are higher	$PM_{2.5}$ mass [a]	$PM_{2.5}$ mass	$PM_{2.5}$ mass [a]	$PM_{2.5}$ mass
	nitrate	nitrate	nitrate	nitrate
	ammonium	ammonium	ammonium	ammonium
	Sulfate	sulfate	Sulfate	sulfate
	EC	EC	EC	EC
	--	SOA	--	SOA
	TC	TC	TC	TC
	anion [c]	anion	anion [c]	anion
	enc [d]			
	temperature		temperature	temperature
		RH	RH (insig.)	RH
	pressure	pressure	pressure	
	O_3		O_3	
	CO	CO	CO	CO
	SO_2 (insig. [b])	SO_2		SO_2
		NO	NO	NO
	NO_2 (insig.)	NO_2	NO_2	NO_2
	HNO_3	HNO_3	HNO_3	
	NO_y	NO_y	NO_y	NO_y
	nitrate+ HNO_3	nitrate+ HNO_3	nitrate+ HNO_3	nitrate+ HNO_3
Variables that are lower		enc	enc	enc
	enc/SO4	enc/SO4	enc/SO4	enc/SO4
	wind speed (wdr [e] more frequent from 67.5-90)	wind speed (no change in wdr)	wind speed (wdr more frequent from 135 -157.5)	wind speed (wdr more frequent from 90 -180)
		temperature		
	RH			
				pressure
	solar rad (insig.)	solar rad.	solar rad. (insig.)	solar rad.
		O_3		O_3
			SO_2 (insig.)	
	NO			
				HNO_3

(a) $PM_{2.5}$ mass from "das_teom" measurements. (b) insig = statistically insignificant. Statistical significance tested using bootstrap sampling. If N_{top} samples are selected randomly from all data, the mean of the subset is significantly different when less than 5 % of bootstrap samples (random samples from population with replacement) that have a mean as different as or more different than the subset's mean value. (c) anion = SO4 * 2 / 96 + NO3/62; (d) enc = excess negative charge = anion – NH4/18 (can be negative); (e) wdr = wind direction, most frequent compass direction.

Table S2. Conditions at YRK when measurement-derived OC_{sec} concentrations are high ($OC > 3.59$ μgC/m^3) or modeled OM concentrations are high ($OM > 3.71$ μg/m^3) relative to the respective measured or modeled average conditions in the warm season (May – October) 2004, and the cold season (January – April; November – December) 2004

When OC or OM are top quintile	Warm season		Cold season	
	measured	modeled	measured	modeled
Variables that are higher	$PM_{2.5}$ mass [a]	$PM_{2.5}$ mass	$PM_{2.5}$ mass [a]	$PM_{2.5}$ mass
	nitrate	nitrate	nitrate	nitrate
	ammonium	ammonium	ammonium	ammonium
	sulfate	sulfate	sulfate	sulfate
	EC	EC	EC	EC
	--	SOA	--	SOA
	TC	--	TC	--
	anion [c]	anion [c]	anion [c]	anion
		enc [d]	enc [d]	
		enc/SO4	enc/SO4 (insig.)	
	temperature		temperature	temperature
		RH	RH (insig.)	RH
	pressure	pressure	pressure (insig.)	
			solar rad. (insig.)	
	O_3	O_3	O_3	
	CO (insig.)	CO	CO	CO
		SO_2	SO_2 (insig.)	SO_2
		NO		NO
		NO_2	NO_2	NO_2
	HNO_3	HNO_3	HNO_3	HNO_3
	NO_y (insig.)	NO_y	NO_y	NO_y
	nitrate+HNO_3	Nitrate+HNO_3	nitrate+HNO_3	nitrate+HNO_3
Variables that are lower	enc			enc
	enc/SO4 (insig)			enc/SO4
	wind speed (wdr [e] more variable)	wind speed (no change in wdr)	wind speed (insig.; wdr more frequent from 135 -157.5)	wind speed (wdr more frequent from 112.5 - 135)
		temperature		
	RH (insig.)			
				pressure
	solar rad. (insig.)	solar radiation		solar radiation
				O_3
	SO_2 (insig)			
	NO	NO	NO (insig.)	
	NO_2 (insig.)			

(a) $PM_{2.5}$ mass from "das_teom" measurements. (b) insig = statistically insignificant. Statistical significance tested using bootstrap sampling. If N_{top} samples are selected randomly from all data, the mean of the subset is significantly different when less than 5 % of bootstrap samples (random samples from population with replacement) that have a mean as different as or more different than the subset's mean value. (c) anion = SO4 * 2 / 96 + NO3/62; (d) enc = excess negative charge = anion – NH4/18 (can be negative); (e) wdr = wind direction, most frequent compass direction.

Table S1a Average conditions at JST when measured OC concentrations are high (OC > 4.73 microgramC/m ^{3})

Observations	when OC high in warm season [(a)]	$N_{high,warm}$	all warm season	N_{warm}	when OC high in cold season [(a)]	$N_{hign,cold}$	all cold season	N_{cold}
OC (μgC/m^3)	6.47	214	3.55	928	6.05	168	2.99	976
$PM_{2.5}$ mass (μg/m^3)	22.1	190	15.42	1020	14.00	154	8.30	1003
nitrate (μg/m^3)	0.31	202	0.26	921	1.31	133	0.959	987
ammonium (μg/m^3)	3.01	211	2.06	1062	1.57	152	1.00	998
sulfate (μg/m^3)	10.7	196	7.19	974	3.64	152	2.62	1017
BC (μgC/m^3)	1.27	214	0.979	1024	1.21	168	0.763	1064
TC (μgC/m^3)	7.75	214	4.57	992	7.26	168	3.82	1000
anion (μmol/m^3) [(b)]	0.2280	187	0.15	840	0.1030	124	0.0713	933
excess negative charge (enc) (μmol/m^3) [(c)]	0.0576	187	0.03581	837	0.0127	121	0.0164	919
enc/SO4	-0.000735	198	0.001974	837	0.003060	121	0.006778	919
wsp (m/s)	1.91	192	2.17	1019	2.28	150	2.74	935
wdr (º) [(d)]	67.5-90, 225-315	191	270-292.5, 225-247.5	1017	135-157.5	151	292.5-337.5	956
temp (ºC)	27.3	209	26.4	1081	17.7	166	13.8	1076
rh (%)	62.6	210	64	1084	54	166	51	1079
bp (mb)	983.8	214	982.6	1091	984.8	167	983.5	1083
sr (W/m^2)	400.4	214	417.3	1087	291.0	166	302.4	1081
o3 (ppb)	60.3	194	50	972	31.8	144	29.4	959
co (ppb)	286.1	203	260.3	1031	405.6	131	325.0	964
so2 (ppb)	4.61	204	4.25	1002	3.46	155	4.85	1020
no (ppb)	2.32	203	2.44	1046	11.40	159	8.28	1057
no2 (ppb)	9.65	188	9.15	963	19.2	144	15.6	1044
hno3 (ppb)	1.34	201	1.08	1020	0.72	148	0.55	991
noy (ppb)	15.8	204	14	1041	34.0	156	25.5	1015
nitrate+hno3 (μg/m^3)	3.68	190	2.92	866	3.24	114	2.36	919

(a) warm season = May - October; cold season = January - April + November - December
(b) anion = SO4*2 / 96 + NO3 / 62
(c) enc = excess negative charge = anion - NH4 / 18 (can be negative)
(d) wdr = most frequent wind direction

Table S1b Average conditions at JST when modeled OM concentrations are high (OM > 6.26 microgram/m ^{3})

Observations	when OM high in warm season [(a)]	$N_{high,warm}$	all warm season	N_{warm}	when OM high in cold season [(a)]	$N_{hign,cold}$	all cold season	N_{cold}
OM (μg/m^3)	8.21	117	3.59	1104	10.20	321	4.90	1086
SOA (μgC/m^3)	5.81	117	2.46	1104	2.18	321	1.45	1086
$PM_{2.5}$ mass (μg/m^3)	33.7	117	16.12	1104	39.6	321	20.19	1086
nitrate (μg/m^3)	0.58	117	0.19	1104	3.66	321	1.71	1086
ammonium (μg/m^3)	4.78	117	2.33	1104	4.89	321	2.62	1086
sulfate (μg/m^3)	10.5	117	6.56	1104	4.95	321	3.23	1086
BC (μgC/m^3)	2.54	117	0.92	1104	4.67	321	2.06	1086
TC (μgC/m^3)	N/A		N/A	N/A	N/A		N/A	
anion (μmol/m^3) [(b)]	0.23	117	0.1397	1104	0.16	321	0.0948	1086
excess negative charge (enc) (μmol/m^3) [(c)]	-0.038	117	0.0103	1104	-0.109	321	-0.0510	1086
enc/SO4	-0.0100	117	-0.003352	1104	-0.0236	321	-0.018446	1086
wsp (m/s)	1.95	117	2.88	1104	2.01	321	3.08	1086
wdr (º) [(d)]	67.5-112.5	117	67.5-112.5	1104	90-180; 292.5-315	321	292.5-337.5	1086
temp (ºC)	25.1	117	26.9	1104	13.3	321	13.0	1086
rh (%)	71	117	56	1104	72	321	64	1086
bp (mb)	983.2	117	983.1	1104	986.6	321	986.0	1086
sr (W/m^2)	323.5	117	512.3	1104	220.8	321	338.7	1086
o3 (ppb)	31	117	50	1104	8.7	321	22.2	1086
co (ppb)	1039	117	481.9	1104	1720	321	918.9	1086
so2 (ppb)	8.12	117	4.7	1104	14.6	321	8.86	1086
no (ppb)	18.3	117	5.22	1104	65.7	321	27.21	1086
no2 (ppb)	34.0	117	15.9	1104	43.7	321	26.7	1086
hno3 (ppb)	1.95	117	1.74	1104	0.665	321	0.79	1086
noy (ppb)	56.6	117	24.7	1104	111	321	55.3	1086
nitrate+hno3 (μg/m^3)	5.51	117	4.55	1104	5.40	321	3.78	1086

(a) warm season = May - October; cold season = January - April + November - December
(b) anion = SO4*2 / 96 + NO3 / 62
(c) enc = excess negative charge = anion - NH4 / 18 (can be negative)
(d) wdr = most frequent wind direction

Table S2a Average conditions at YRK when measured OC concentrations are high (OC > 3.59 microgramC/m^3)

Observations	when OC high in warm season [(a)]	$N_{high,warm}$	all warm season	N_{warm}	when OC high in cold season [(a)]	$N_{hign,cold}$	all cold season	N_{cold}
OC (μgC/m^3)	5.74	153	3.04	579	5.54	143	2.34	906
$PM_{2.5}$ mass (μg/m^3)	25.3	146	17.18	999	14.6	131	8.01	929
nitrate (μg/m^3)	0.3	153	0.221	1088	1.02	97	0.67	849
ammonium (μg/m^3)	3.37	153	2.05	1071	1.41	136	0.91	1010
sulfate (μg/m^3)	9.23	135	6.54	992	4.05	130	2.53	944
BC (μgC/m^3)	0.763	153	0.508	1091	0.928	143	0.467	1052
TC (μgC/m^3)	6.50	153	3.55	579	6.47	143	2.79	943
anion (μmol/m^3) [(b)]	0.197	135	0.1398	989	0.099	92	0.0614	769
excess negative charge (enc) (μmol/m^3) [(c)]	0.0077	135	0.0258	972	0.0200	91	0.0116	764
enc/SO4	-0.00356	135	-0.001477	972	0.00326	91	0.001268	764
wsp (m/s)	2.51	141	2.87	1043	3.62	141	3.76	925
wdr (º) [(d)]	247.5-315	154	292.5 - 337.5	1104	135-157.5	143	292.5 - 337.5	1092
temp (ºC)	27.5	153	25.6	1103	17.3	143	13.7	1061
rh (%)	65.7	153	67	1103	57	143	56.0	1061
bp (mb)	971.4	153	970.3	1104	973.7	143	973.2	1073
sr (W/m^2)	409.5	153	425.3	1104	314.8	143	313.8	1073
o3 (ppb)	61.0	153	50.4	1054	45.3	143	39.0	1042
co (ppb)	169.3	149	147.9	982	204.8	127	169.6	963
so2 (ppb)	2.15	135	2.29	935	4.08	134	3.43	959
no (ppb)	0.103	153	0.17	1059	1.07	141	1.14	1021
no2 (ppb)	1.12	145	1.31	994	6.32	139	4.64	1003
hno3 (ppb)	1.38	134	1.05	972	0.89	141	0.68	1024
noy (ppb)	3.71	134	3.51	990	9.39	141	7.30	1026
nitrate+hno3 (μg/m^3)	3.65	134	2.86	962	2.97	97	2.30	825

(a) warm season = May - October; cold season = January - April + November - December
(b) anion = SO4*2 / 96 + NO3 / 62
(c) enc = excess negative charge = anion - NH4 / 18 (can be negative)
(d) wdr = most frequent wind direction

Table S2b Average conditions at YRK when modeled OM concentrations are high (OM > 3.71 microgram/m^3)

Observations	when OM high in warm season [(a)]	$N_{high,warm}$	all warm season	N_{warm}	when OM high in cold season [(a)]	$N_{hign,cold}$	all cold season	N_{cold}
OM (μg/m^3)	5.58	288	2.94	1104	5.15	150	2.19	1086
SOA (μg/m^3)	4.68	288	2.39	1104	2.85	150	1.11	1086
$PM_{2.5}$ mass (μg/m^3)	21.82	288	13.08	1104	15.96	150	8.61	1086
nitrate (μg/m^3)	0.17	288	0.06	1104	0.93	150	0.52	1086
ammonium (μg/m^3)	2.77	288	1.72	1104	1.76	150	1.12	1086
sulfate (μg/m^3)	10.11	288	6.45	1104	3.63	150	2.32	1086
BC (μgC/m^3)	0.416	288	0.25	1104	0.770	150	0.340	1086
TC (μgC/m^3)	N/A		N/A		N/A		N/A	
anion (μmol/m^3) [(b)]	0.213	288	0.1353	1104	0.091	150	0.0569	1086
excess negative charge (enc) (μmol/m^3) [(c)]	0.0593	288	0.0396	1104	-0.0074	150	-0.0055	1086
enc/SO4	-0.00170	288	-0.002358	1104	-0.00538	150	-0.013476	1086
wsp (m/s)	2.38	288	2.91	1104	3.01	150	3.71	1086
wdr (°) [(d)]	90-112.5	288	90-112.5	1104	112.5-135	150	270-360	1086
temp (°C)	26.2	288	26.5	1104	15.9	150	13.3	1086
rh* (%)	64	288	58	1104	58	150	56	1086
bp (mb)	983.4	288	983.2	1104	985.8	150	986.1	1086
sr (W/m^2)	444.1	288	520.2	1104	233.6	150	332.9	1086
o3 (ppb)	56.7	288	53.6	1104	35.4	150	37.3	1086
co (ppb)	262	288	194.8	1104	334	150	244.2	1086
so2 (ppb)	3.85	288	2.56	1104	3.16	150	2.68	1086
no (ppb)	0.28	288	0.3	1104	1.37	150	0.90	1086
no2 (ppb)	3.98	288	2.57	1104	8.80	150	5.31	1086
hno3 (ppb)	1.60	288	1.12	1104	1.15	150	0.91	1086
noy (ppb)	8.33	288	5.66	1104	12.2	150	7.63	1086
nitrate+hno3 (μg/m^3)	4.2	288	2.9	1104	3.95	150	2.92	1086

(a) warm season = May - October; cold season = January - April + November - December
(b) anion = SO4*2 / 96 + NO3 / 62
(c) enc = excess negative charge = anion - NH4 / 18 (can be negative)
(d) wdr = most frequent wind direction