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Supplement of

Chemical climatology of the southeastern United States, 1999–2013

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Chemical Climatology of the Southeastern United States, 1999-2013

Supplemental Information

Overview

The following material supplements the manuscript, "Chemical Climatology of the Southeastern United States, 1999-2013." The tables and figures provide supporting detail to the discussion in this paper that can be used by readers in further interpreting the observations in the SEARCH region and at the CTR site.

The first part includes four tables covering (1) the basic instrumentation of the SEARCH sites, including CTR, (2) a table of a measure of apparent sulfate neutralization as ammonium salts, (3) a table comparing rural and urban aerometric observations, and (4) a survey of rural NMOC from the literature in the southeastern region.

The series of figures include: (1) a photograph of the CTR site, (2) annual emission trends of various gases and particle species, (3) a normalized seasonal plot for particle mass and composition, (4) an empirical relationship between O_3 and OH, (5) trends in $PM_{2.5}$ composition for the SEARCH network and for CTR, (6) EC and OC concentrations at CTR compared with emissions, (7) mean EC and OC concentration trends at certain SEARCH sites, (8) trends in annual fires in different states, (9) time series for optical properties of aerosols at CTR, (10) trends in annual contributions to extinction coefficient for SEARCH, and for June-July period, (11) diurnal variations in SO_2 and NO_x emissions from statewide electric power generation, (12) diurnal variations of motor vehicle emissions, (13) trend-distributions of meteorological parameters for CTR, (14) trend-distributions of gaseous constituents for CTR, (15) trend-distributions of particulate components for CTR, (16) composition reactive nitrogen balance for CTR, (17) diurnal difference between dry and wet light scattering as "water" content, (18) mean diurnal concentrations of selected NMOC groups, (19) June average isoprene and α-pinene concentrations in rural Alabama.

Table S1. Basic measurements at CTR and other SEARCH sites from 1999-2013. Sites having instrument differences are noted under "Comments." (PNS, OAK, and GFP were decommissioned at the end of 2009, 2010, and 2012, respectively).

a. Continuous meteorology at SEARCH sites (5 and 60 minute reporting intervals).

Parameter	Method	Instrument	Sampling Height (magl)	Comments
Temperature	platinum RTD	Vaisala HMT3303 Paroscientific Met 4B	2 9	2m added in 2011
Relative humidity	thin film capacitance	Vaisala HMT3303 Paroscientific Met 4B	2 9	2m added in 2011
Barometric pressure	quartz crystal resonator	Paroscientific Met 4B	9	
Surface wetness	conductivity	Decagon LSW-1	2	Added in 2011
Wind Speed/Direction	sonic anemometer	RMYoung 8100	10	
Solar Radiation (PAR)	pyranometer	Licor-200X	2	
Precipitation	gravimetry	ETI NOAH-IV	2	
Aerosol/cloud layers/mixing depth	laser ceilometer	JenOptik CHM 15k	50-15,000	GFP and OLF 2012-13 CTR and BHM 2013-14

b. Continuous trace gases at SEARCH sites (5 and 60 minute reporting intervals).

Parameter	Method	Instrument	Sampling Hgt. (magl)	Comments
O_3	UV absorption	Thermo-Scientific 49i	10	
CO	NDIR	Thermo-Scientific 48i	10	
SO_2	Pulsed UV fluorescence	Thermo-Scientific 43i	10	
NO, NOy	Mo reduction/CL	Thermo-Scientific 42i	10	
NO_2	Blue LED photolysis/CL	Thermo-Scientific 42i	10	
HNO_3	Denuder difference/Mo reduction/CL	Thermo-Scientific 42i	10	
PANS/Alkylnitrates	Thermal decomposition/Blue LED photolysis/CL	Thermo-Scientific 42i	5	CTR only, starting 6/13
NH_3	Denuder difference/Pt oxidation/Mo reduction/CL	Thermo-Scientific 42i	5	Added in 2007

CL=NO-O_3 chemiluminescence

c. Continuous PM at SEARCH sites (5 and 60 minute reporting intervals).

Parameter	Method	Instrument	Sampling Hgt. (magl)	Comments
$PM_{2.5}$ mass (dry)	Oscillating micro-balance	R&P 1400 a/b TEOM	5	
PM_{10} mass (dry)	Oscillating micro-balance	R&P 1400 a/b TEOM	5	BHM/JST only
$PM_{2.5}$ SO_4^{2-}	Reduction to SO_2 on Inconel/UV fluorescence		5	Added in 2002-3
$PM_{2.5}$ NO_3^-	Filter difference/Mo reduction/CL		5	Added in 2002-3
$PM_{2.5}$ NH_4^+	Filter difference/Pt oxidation/Mo reduction/CL		5	Added in 2002-3
$PM_{2.5}$ TC/EC	Oxidation to CO2/NDIR (TC) Optical absorption (EC)	Sunset Particulate Carbon Analyzer	5	60-min only Added in 2000-1
B_{scat} (dry)	Nephelometry @530 nm	Radiance Research M903	5	Added in 2000
B_{scat} (ambient)	Nephelometry @530 nm	Optec NGN2a	5	Added in 2013
B_{abs}	Optical absorption @880 nm and 370 nm (quartz filter)	Magee Sci. AE2x aethalometer	5	Added in 2000

d. Discrete particle and gas measurements at SEARCH sites (24-hour sampling intervals; daily or 1-in-3 sample schedule; sample height 5 magl).

Parameter	Sample Medium	Sample Device	Analytical Method	Comments
$PM_{2.5}$ mass	Teflon filter	Thermo R&P 2025 FRM	Gravimetry (w/buoyancy corr.)	
$PM_{2.5}$ anions/cations	Denuded Teflon filter	ARA PCM1	Ion chromatography	3 anions, 5 cations
$PM_{2.5}$ volatile anions	Backup nylon filter	ARA PCM1	Ion chromatography	Cl^- and NO_3^-
$PM_{2.5}$ trace elements	Teflon filter	Thermo R&P 2025 FRM	X-ray fluorescence	10 elements
$PM_{2.5}$ water-sol. trace elements	Denuded Teflon Filter	ARA PCM1	ICP-MS	12 elements
$PM_{2.5}$ EC/OC	Denuded quartz filter	ARA PCM3	Thermo-optical reflectance	7 fractions
PM2.5 Speciated OC ~125 cpds.	Quartz filter	DRI Medvol	Thermal desorption/GC-MS	BHM and JST 2006-10
PM_{coarse} mass	Teflon Filter	Andersen Inst. SA-241 dichotomous sampler	Gravimetry (w/buoyancy corr.)	
PM_{coarse} anions/cations	"	"	Ion chromatography	
PM_{coarse} trace elements	"	"	X-ray fluorescence	
PM_{coarse} water-sol. trace elements	"	"	ICP-MS	
PM_{coarse} EC/OC	Quartz filter	"	Thermo-optical reflectance	Limited sites, time periods
NH_3	Citric acid annular denuder	Shop-built pump/flow controller	Ion chromatography	Added in 2004
NMOC/OVOC	Summa canister	"	GC-MS	JST 1998-08 BHM 2006-10

Table S2. Mean ratios of SO_4-S:XRF-S (SO_4/3*XRF S) computed from 1999 – 2010 SEARCH data. The standard errors (SE) of the monthly means ranged from 0.005 to 0.03 (mean 0.01). Linear regression forced through the origin yielded slope values ranging from 0.931 $\pm$ 0.006 (December) to 1.043 $\pm$ 0.004 (August) (n=14,237 samples). Note that the filter data used for comparison derive from two different SEARCH samplers (FRM and PCM1). Since the PCM1 sampler utilizes an SO_2 denuder and the FRM sampler does not, the comparison has a sampling ambiguity that is not accounted for in the ratios.

Month	**BHM**	**CTR**	**GFP**	**JST**	**OAK**	**OLF**	**PNS**	**YRK**	**Average**
Jan	0.98	0.93	0.96	0.94	0.93	0.93	0.92	0.96	0.94
Feb	0.97	0.95	0.98	0.96	0.97	0.94	0.97	0.98	0.96
Mar	0.99	0.98	0.96	0.99	0.98	0.97	0.97	1.00	0.98
Apr	1.02	0.98	0.98	1.05	1.00	0.99	0.99	1.01	1.00
May	1.02	0.99	1.00	1.02	1.00	1.03	0.99	1.04	1.01
June	1.06	1.00	1.01	1.03	1.02	1.00	1.00	1.02	1.02
July	1.04	0.98	1.05	1.04	1.01	1.00	0.99	1.03	1.02
Aug	1.05	1.01	1.01	1.04	1.03	0.99	1.02	1.04	1.02
Sep	1.03	1.01	0.97	1.03	1.03	1.02	0.99	1.01	1.01
Oct	1.01	0.98	0.98	1.03	0.98	0.96	0.96	1.00	0.99
Nov	0.97	0.95	0.97	0.99	0.99	0.96	0.94	1.00	0.97
Dec	1.04	0.94	0.94	0.98	0.94	0.92	0.93	0.97	0.96

Table S3. Seasonal mean concentrations for a period (2004 – 2007) when all sites were operational and reported measurements of each of the tabled species: SO_2 and SO_4 as SO_2; NH_3 and NH_4 as NH_3; NO, NO_2, HNO_3, NO_3, and NO_y species as NO_2. Units are μg m^{-3}. Coastal sites are above the heavy line. For each site pair, the non-urban site is listed first. Source: Blanchard et al. (2013a).

Site	Season[a]	SO_2	SO_4	NH_3	NH_4	NO	NO_2	NO_y	HNO_3	pNO_3	EC	OM
OAK	Spring	3.5	2.3	0.4	1.0	0.2	2.6	5.2	0.7	0.2	0.5	3.5
	Summer	2.8	3.0	0.2	1.1	0.2	2.1	4.1	0.4	0.1	0.4	4.0
	Autumn	4.4	2.4	0.2	1.0	0.2	3.0	5.4	0.5	0.2	0.5	3.7
	Winter	5.2	1.5	0.2	0.8	0.4	5.3	8.2	0.7	0.4	0.8	4.7
GFP	Spring	3.0	2.3	0.7	1.1	2.3	11.1	16.1	0.2	0.3	0.6	2.9
	Summer	3.9	2.8	0.6	1.1	1.7	12.3	16.7	0.6	0.2	0.6	3.4
	Autumn	6.1	2.5	0.6	1.2	4.4	15.8	23.7	0.5	0.3	0.8	3.7
	Winter	5.9	1.4	0.5	0.8	8.7	16.3	29.1	0.3	0.5	0.7	3.1
OLF	Spring	4.2	2.3	0.5	1.1	1.0	8.1	11.3	0.5	0.3	0.6	3.3
	Summer	4.5	2.9	0.4	1.2	2.3	8.8	13.0	0.5	0.2	0.7	4.1
	Autumn	7.9	2.5	0.3	1.1	1.5	11.3	14.9	0.4	0.2	0.8	4.1
	Winter	7.0	1.4	0.3	0.7	1.8	11.8	15.5	0.2	0.4	0.6	3.1
PNS	Spring	8.4	2.3	0.8	1.2	3.7	14.4	21.1	0.8	0.4	0.6	3.3
	Summer	6.8	3.0	0.6	1.1	3.5	14.4	21.6	0.4	0.2	0.6	3.5
	Autumn	10.9	2.4	0.6	1.1	7.3	18.4	28.8	0.5	0.3	0.7	3.5
	Winter	11.4	1.5	0.6	0.8	11.8	19.7	33.7	0.1	0.4	0.8	3.8
CTR	Spring	4.2	2.3	0.3	1.1	0.3	3.3	6.3	0.9	0.2	0.6	4.9
	Summer	3.5	3.6	0.2	1.4	0.2	2.6	5.1	0.5	0.1	0.5	4.8
	Autumn	6.5	2.7	0.2	1.2	0.6	5.8	8.9	0.4	0.2	0.6	4.1
	Winter	6.9	1.5	0.3	0.8	0.8	7.5	11.1	0.6	0.4	0.6	3.5
BHM	Spring	13.8	2.8	2.4	1.5	23.4	39.5	65.1	0.9	0.6	2.1	7.3
	Summer	14.4	4.6	2.4	2.1	16.5	34.4	55.3	1.0	0.3	1.7	6.9
	Autumn	15.4	2.8	2.1	1.4	32.9	39.2	73.1	0.5	0.4	1.8	5.8
	Winter	13.3	1.7	1.4	1.1	40.2	39.8	81.2	0.4	1.0	1.7	5.4
YRK	Spring	7.4	2.7	1.7	1.5	0.5	6.0	10.8	1.5	0.5	0.6	5.0
	Summer	7.0	4.6	2.5	2.3	0.4	5.7	9.6	1.1	0.3	0.6	5.7
	Autumn	8.1	3.0	2.6	1.6	0.9	9.2	13.7	1.1	0.5	0.6	4.4
	Winter	10.9	1.5	2.0	1.1	1.6	13.0	17.7	1.0	1.0	0.6	3.5
JST	Spring	11.9	2.7	1.3	1.5	34.9	43.3	80.8	1.2	0.5	1.2	6.3
	Summer	10.9	4.7	1.2	2.2	17.0	40.1	61.5	1.2	0.3	1.4	6.1
	Autumn	12.1	3.0	1.2	1.6	49.3	44.2	96.6	0.7	0.5	1.5	5.7
	Winter	15.8	1.6	1.0	1.2	60.3	47.9	107.7	0.5	1.1	1.4	6.2

a. Winter = Dec – Feb; Spring = Mar – May; Summer = Jun – Aug; Autumn = Sep – Nov

Table S4. Comparisons of rural, summertime – midday NMOC mean concentrations from sites in the Southeast. Units are ppbC except as indicated. Intercomparison of NMOC concentrations indicates that isoprene is the major NMOC in the rural Southeast even during the period of maximum photochemical processing.

Species	West Alabama[a] (1990)	Oak Grove, MS[b] (1994)	Centreville, AL[b] (1994)	Yorkville, GA[b] (1994)	Yorkville, GA[c] (2002)	Yorkville, GA[c] (2011)	Nashville, TN (rural)[d] (1995)	Relative OH Reactivity[e]
ethane	-	1.02	1.74	0.96	1.73	3.23	nd	41
ethene	-	0.57	0.61	0.90	0.14	0.25	nd	3
acetylene	-	0.45	0.36	0.72	0.08	0.20	nd	low
propane	3.6	4.04	2.60	1.89	1.68	2.02	-	14
propene	-	0.61	0.73	1.61	0.02	0.52	-	2
i-butane	0.8	1.25	0.77	0.91	0.20	0.33	0.44	29
n-butane	1.2	1.87	1.48	1.96	0.81	0.76	0.76	17
i-pentane	1.3	5.90	2.22	5.02	1.35	0.95	0.95	10
n-pentane	0.45	16.5	1.04	2.15	0.49	0.60	0.38	23
isoprene	31(4.5[g])	11.2	21.2	9.80	6.54	9.62	4.25	1
2-methyl-pentane	0.27	2.16	3.34	3.92	0.17	0.12	0.25	25
3-methyl-pentane	0.13	0.93	0.82	1.05	0.07	0.17	0.09	34
cyclopentane	-	0.16	0.05	0.19	0.0	0.03	-	57
n-hexane	0.12	0.72	0.68	0.68	0.07	0.36	-	28
2-methyl-2-butene	-	0.10	0.06	0.19	-	-	-	5
benzene	0.60	0.69	0.61	1.22	0.21	0.22	1.26	52
toluene	0.52	3.63	1.20	4.75	0.77	0.62	0.56	10
methyl-cyclohexane	0.056	0.69	0.42	0.57	0.00	0.01	-	
m, p-xylene	0.16	0.89	0.40	1.80	0.12	0.15	0.024-0.072	4
o-xylene	0.072	0.36	0.13	0.73	0.03	0.03	0.048	19
ethyl benzene	0.08	0.45	0.20	0.95	0.04	0.08	0.14	31
α-pinene	3.0	2.71	1.60	0.11	-	-	0.07	8
β-pinene	1.7	3.04	1.36	2.06	-	-	0.06	42
acetone[f]	4.2	-	-	-	-	-	3.83	
acetaldehyde[f]	1.3	-	-	-	-	-	1.56	
methyl-ethyl-ketone[f]	0.49	-	-	-	-	-	0.30	
ethanol[f]	1.2	-	-	-	-	-	0.38	

[a]Data June-July of 1990 1:600 h CST for Kinterbish, Alabama from Goldan et al. (1995).
[b]Data summer 1994 12:00-13:00 h local standard time as part of SOS from Hagerman et al. (1997).
[c]Data from PAMS archive for YRK 2002 and 2011, 10:00-15:00 h EST.
[d]Data for summer daytime rural site 32 km SE of Nashville, Tennessee 10:00-20:00 h local standard time from Riemer et al. (1998)
[e]Ranking of k_{OH} from highest to lowest?
[f]Data in ppbv.
[g]At 04:00 h CST

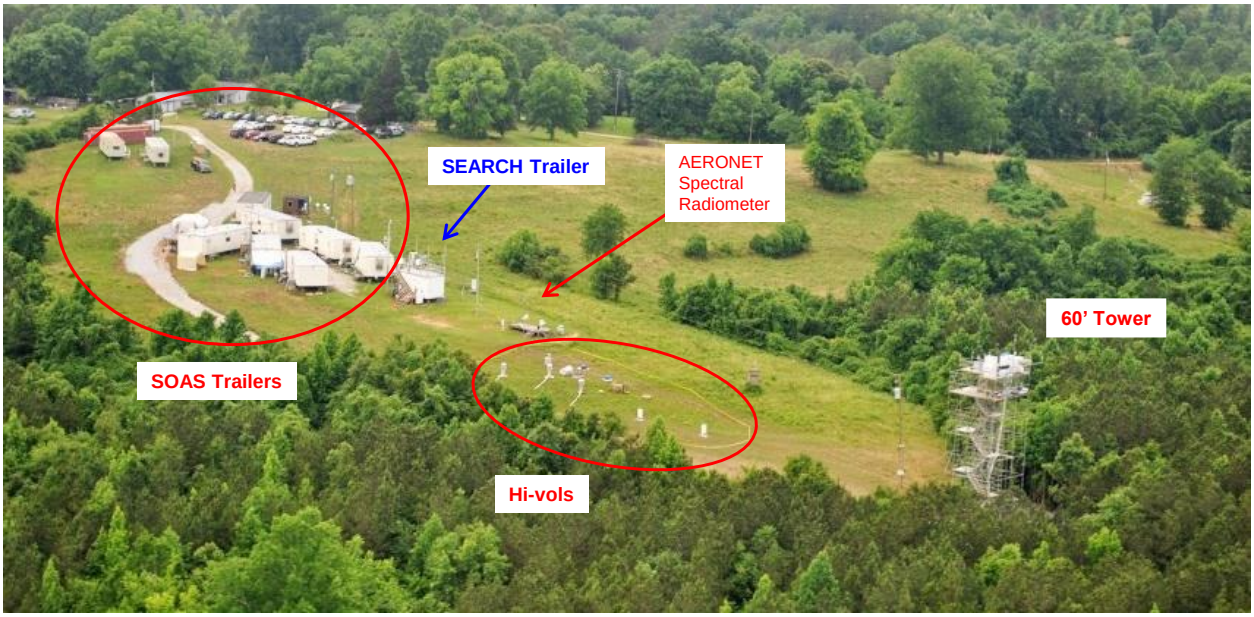


Figure S1. CTR site with instrumentation during the SOAS experiments in June-July, 2013.

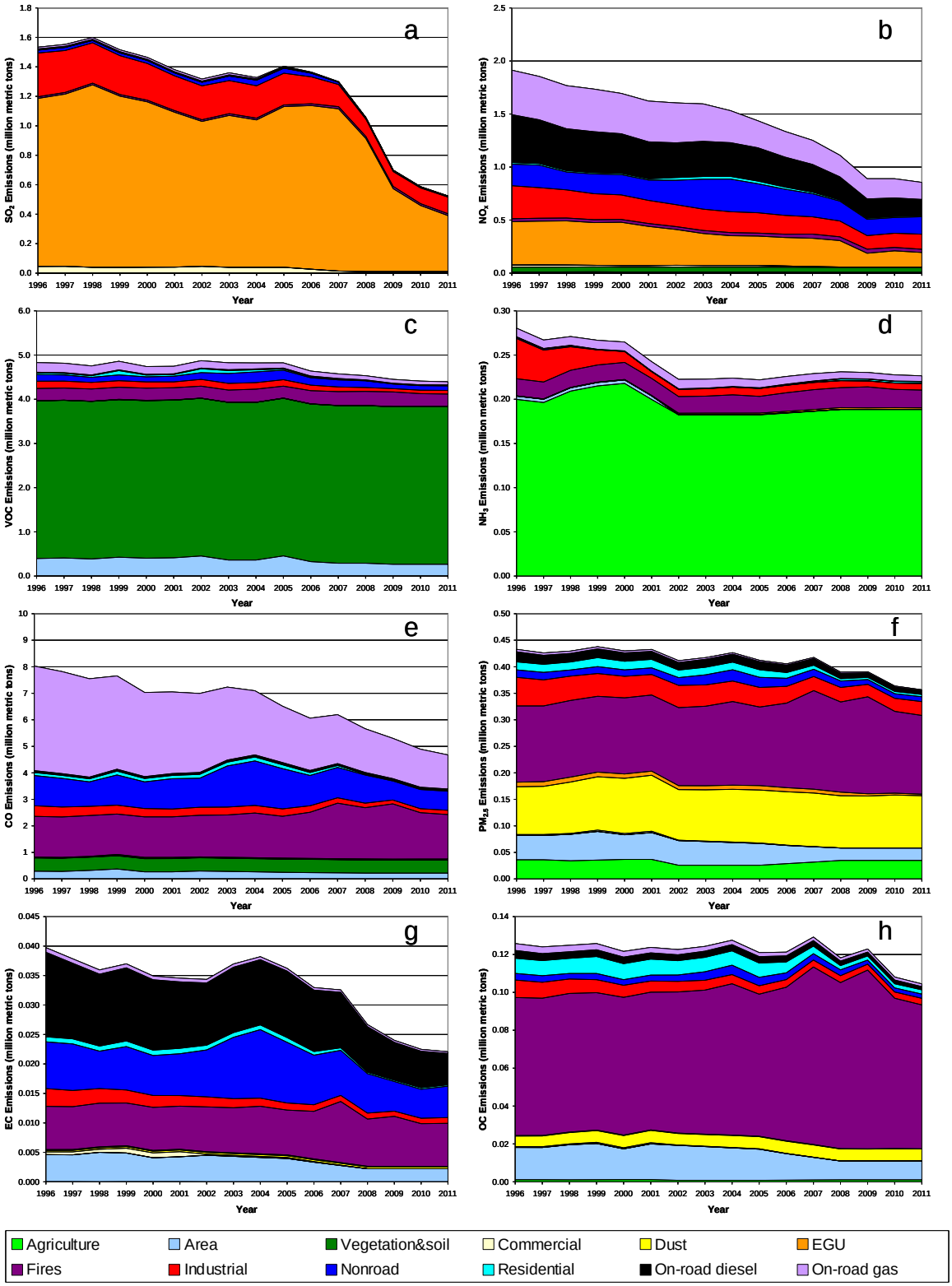


Figure S2. Emission trends in the study domain (Blanchard et al., 2013c). (a) SO_2, (b) NO_x, (c) VOC, (d) NH_3, (e) CO, (f) $PM_{2.5}$, (g) EC, (h) POC.

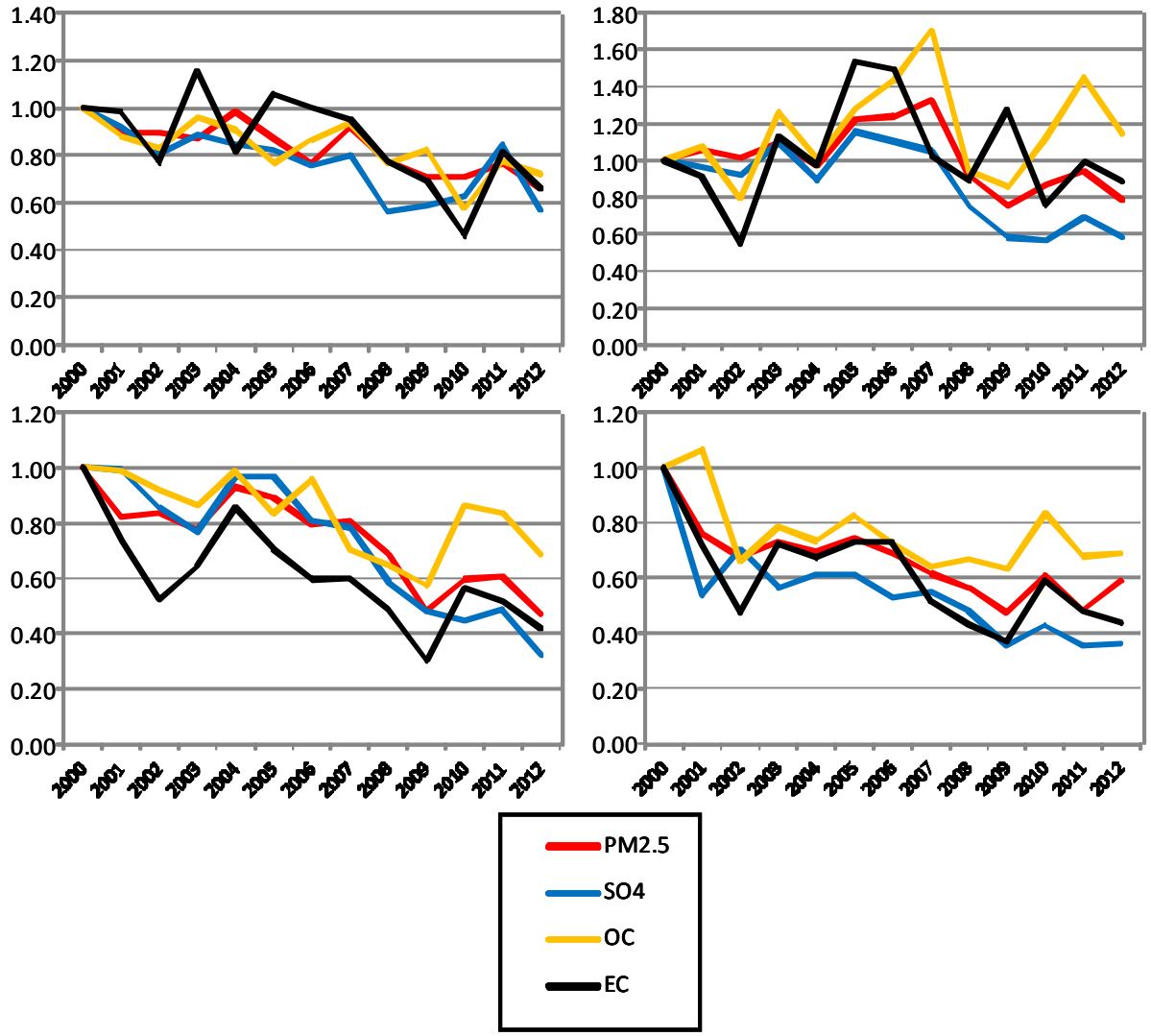


Figure S3. Normalized trends by season for $PM_{2.5}$, SO_4, OC and EC, 2000-2012. Q1 (Jan – Mar) is upper left, Q2 upper right, Q3 lower left, and Q4 lower right. All concentrations are normalized to year 2000.

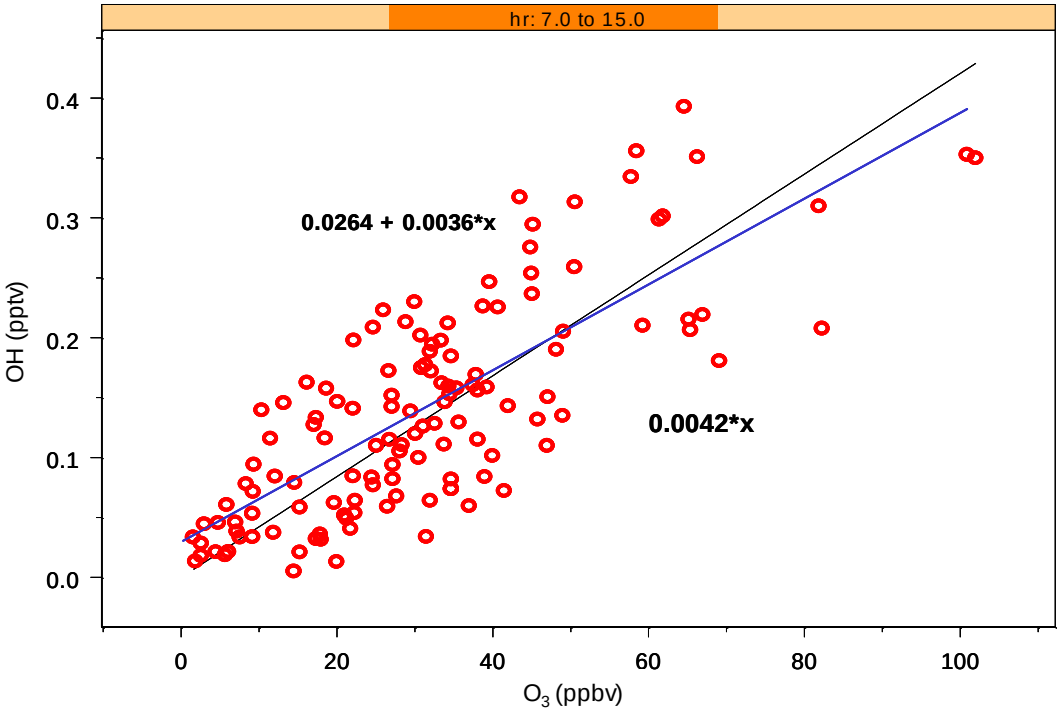


Figure S4. Daytime relation measured relationship between OH and O_3 found in New York City. Lines indicate regressions with (blue) and without (black) intercept. (From K. Demerjian, New York supersite program, summer 2001; personal communication, and including data derived from measurements of Ren et al., 2003).

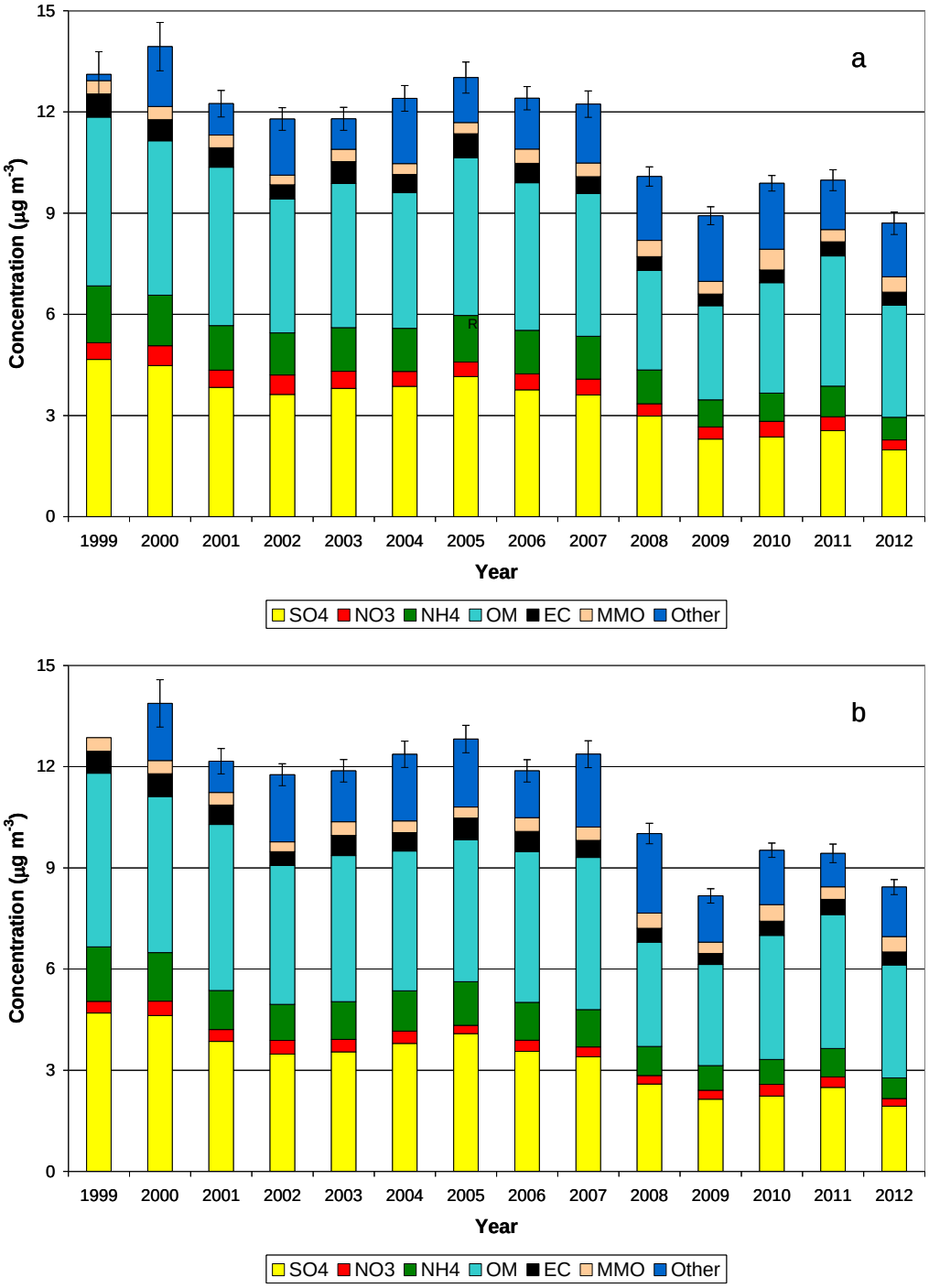


Figure S5. Trends in annual $PM_{2.5}$ mass concentration and composition at (a) rural SEARCH sites (mean) and (b) CTR. "OM" is 1.4*OC. "Other" is the difference between federal reference method (FRM) mass concentrations and the sum of measured components; it includes retained water, unmeasured species, and organic mass exceeding 1.4*OC; NO_3 is pNO_3. Uncertainties are one standard error of the intersite mean FRM mass concentrations. OM and SO_4 are the major contributors to annual $PM_{2.5}$ mass concentration over the entire period; both are declining, but the SO_4 decrease is stronger.

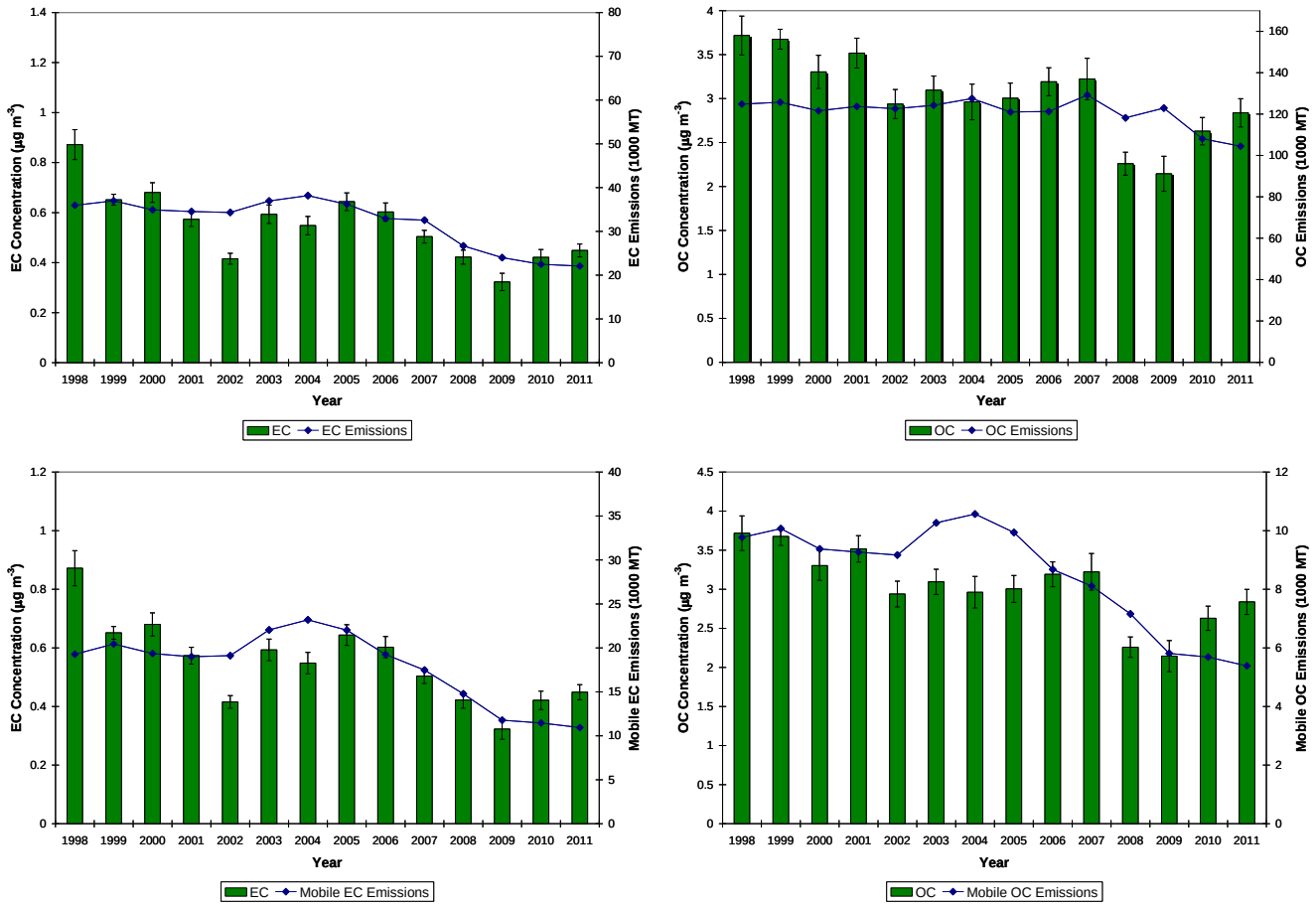


Figure S6. Mean annual EC and OC concentrations at CTR compared with emissions of EC and OC from plus non-road) sources (bottom) within Alabama, Georgia, Northwest Florida, and Mississippi. Emissions data based on the (US) National Emissions Inventory are from Blanchard et al., (2013c). EC follows closely the estimates of total and mobile emission trends, while OC corresponds less to total emissions and more to mobile emissions (see also Table 1 and discussion in text).

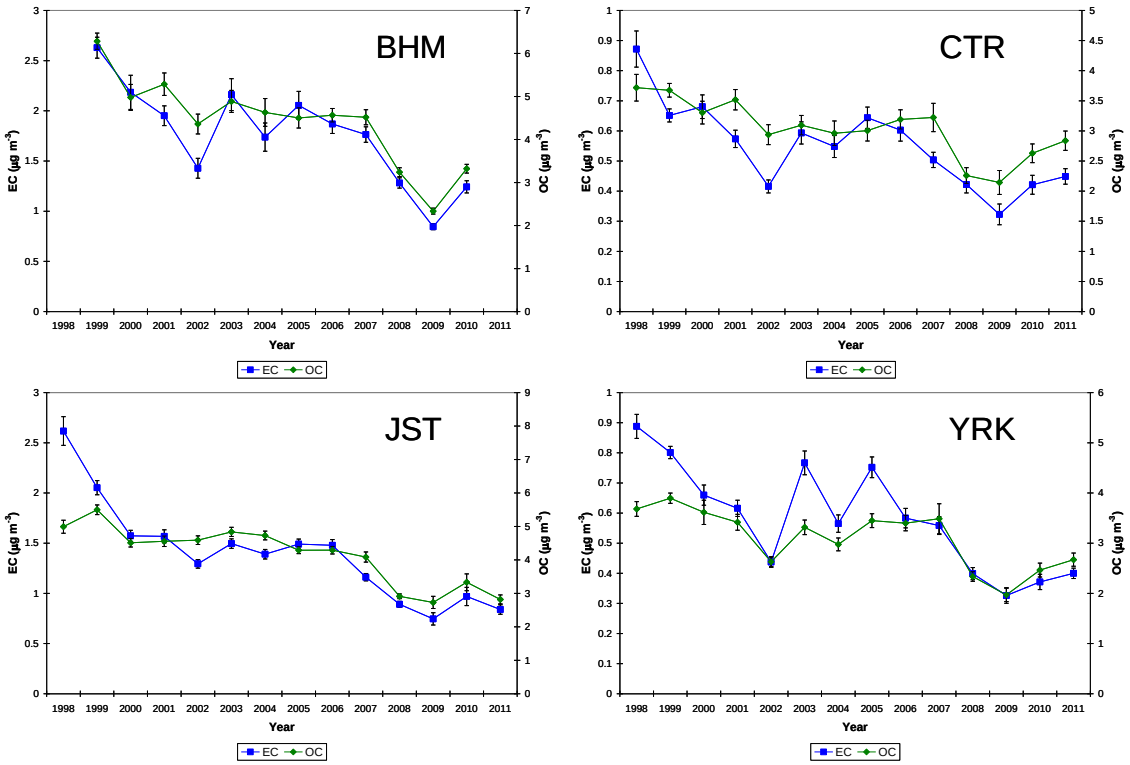


Figure S7. Mean annual concentrations of EC and OC at SEARCH sites. The parallel decrease in mean concentrations indicates common origins of the carbon components.

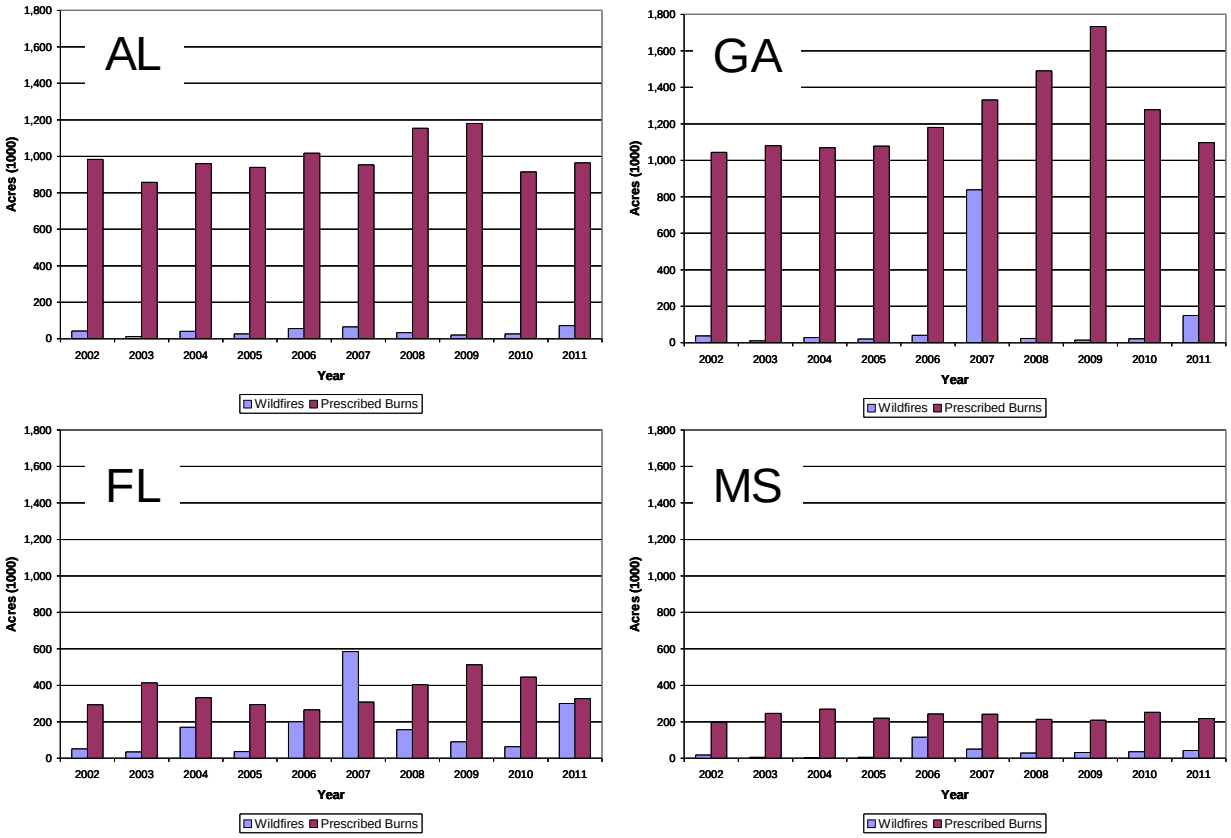


Figure S8. Annual wildfire and prescribed burn acreage by state, 2002-2011. The annual prevalence of prescribed fires is an important factor in rural ambient EC and OC concentrations. Alabama and Georgia data represent all prescribed burns and wildfire. Florida and Mississippi data represent all wildfires and prescribed burns by federal agencies. Total annual prescribed burn acreage averages approximately 2 million acres in Florida and 200,000 to 500,000 acres in Mississippi. Source: Blanchard et al. (2013c).

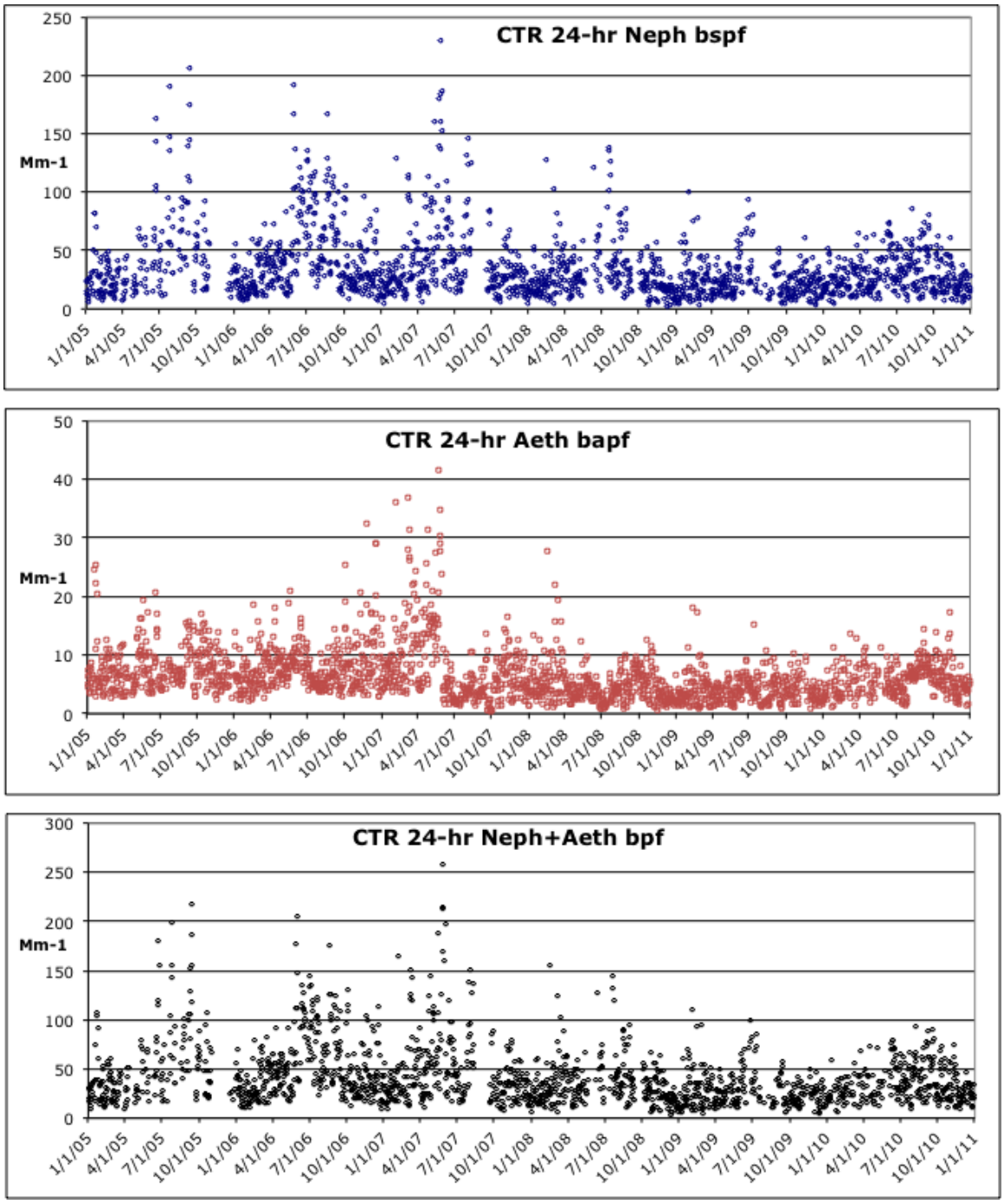


Figure S9. Timelines of 24-hr average light scattering by desiccated fine particles (top plot), light absorption by those particles (middle plot), and their sum (bottom plot) at CTR during the six years 2005-10.

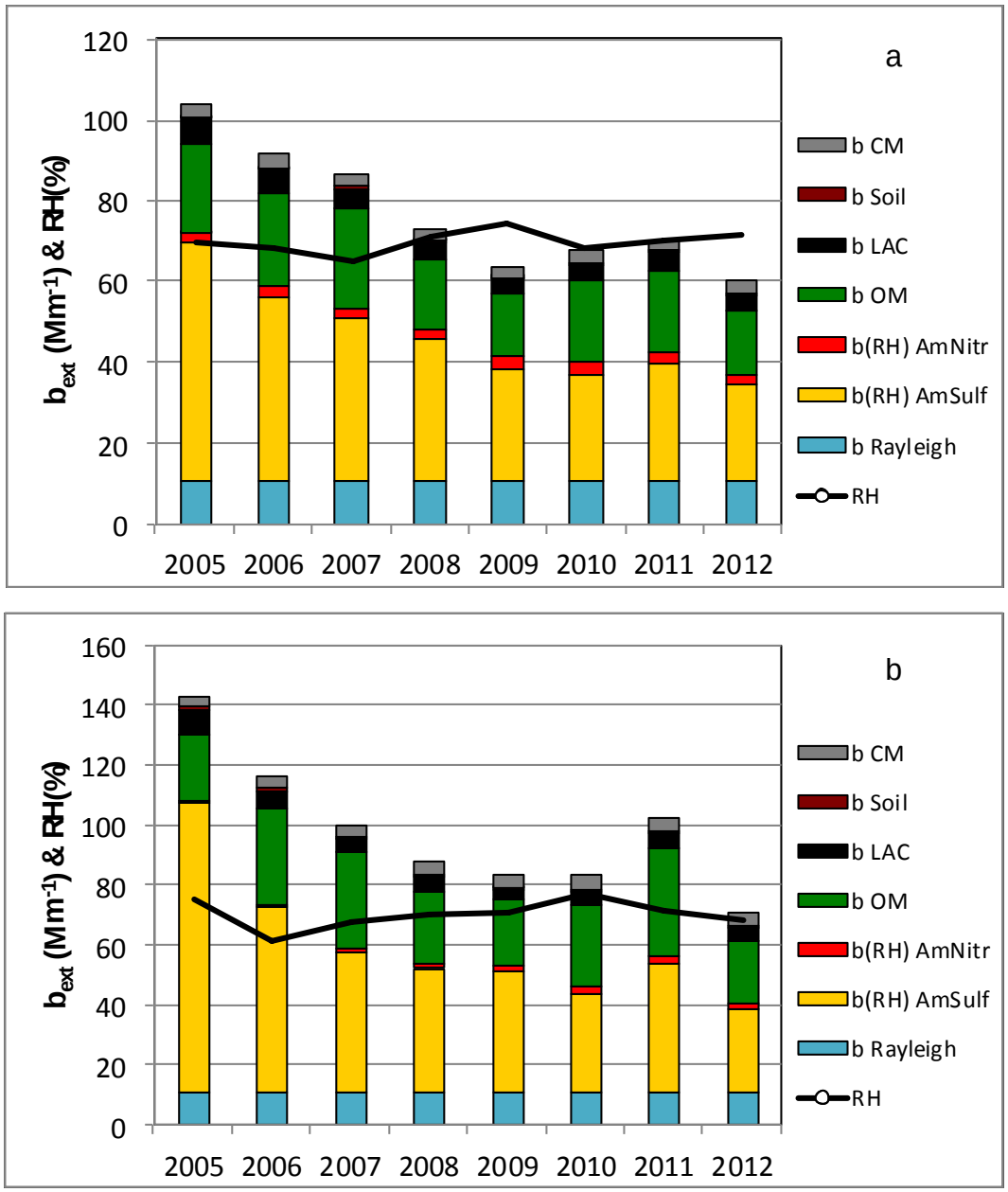
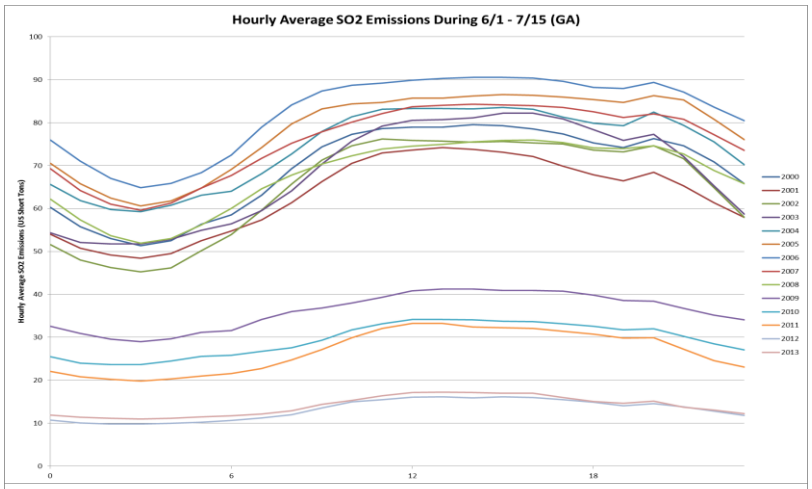
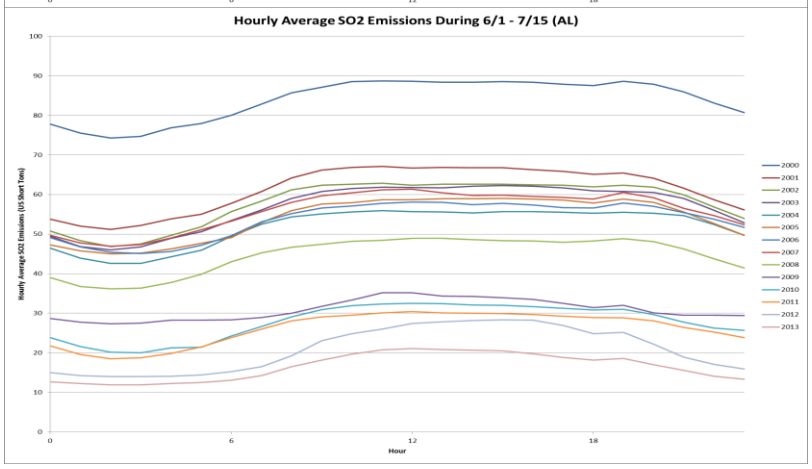


Figure S10. (a) Annual averages of light extinction by component at CTR from 2005 to 2012, as calculated using the new IMPROVE algorithm (Pitchford et al., 2007). (b) Period (June 1-July 15) averages of light extinction by component at CTR for each year. The contributions to light extinction include RH-dependent factors for ammonium sulfate and ammonium nitrate. The black line shows the average measured RH during each year.

a. GA



b. AL



c. MS

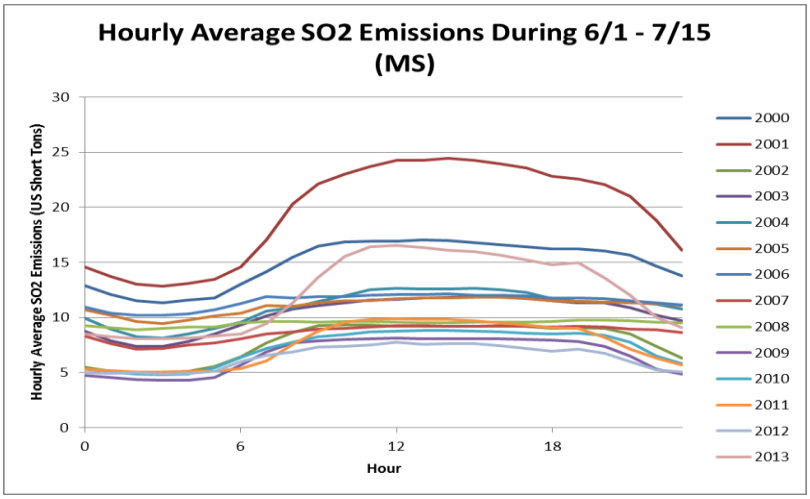
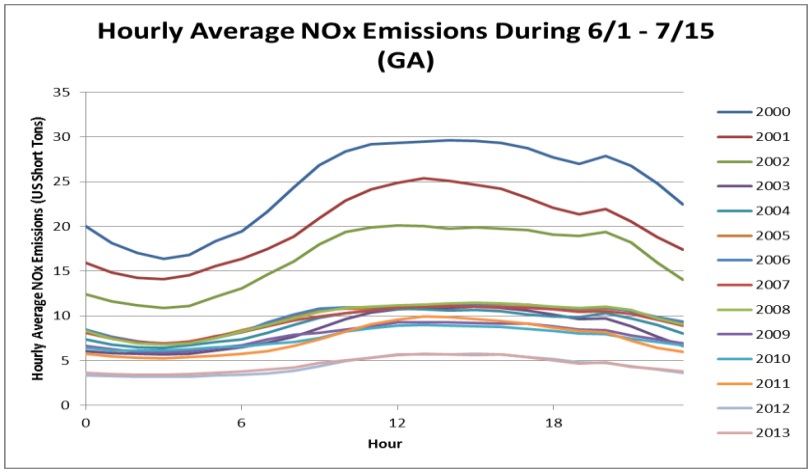
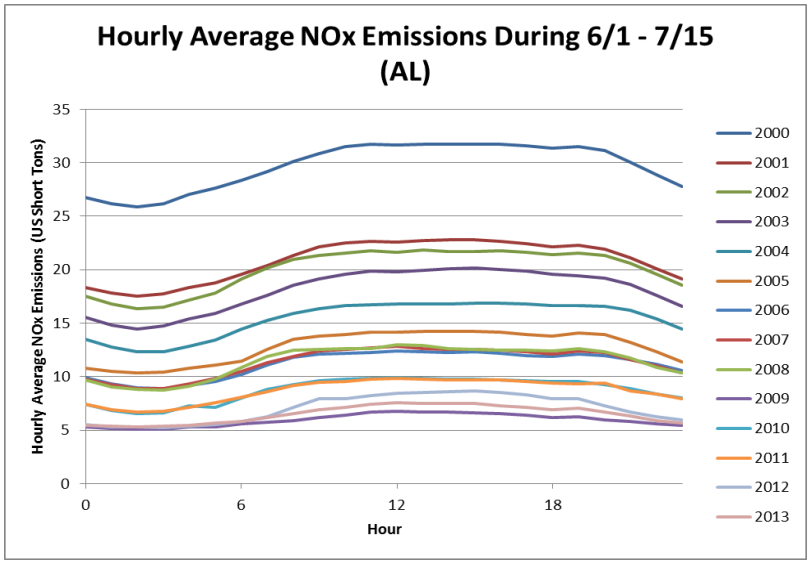


Figure S11a. Diurnal (LST) variation in SO_2 emissions from electric generating units in three states, Alabama, Georgia and Mississippi. Trends between 2000 and 2012 from the Air Markets Program Data (AMPD) (http://ampd.epa.gov/ampd).

a. GA



b. AL



c. MS

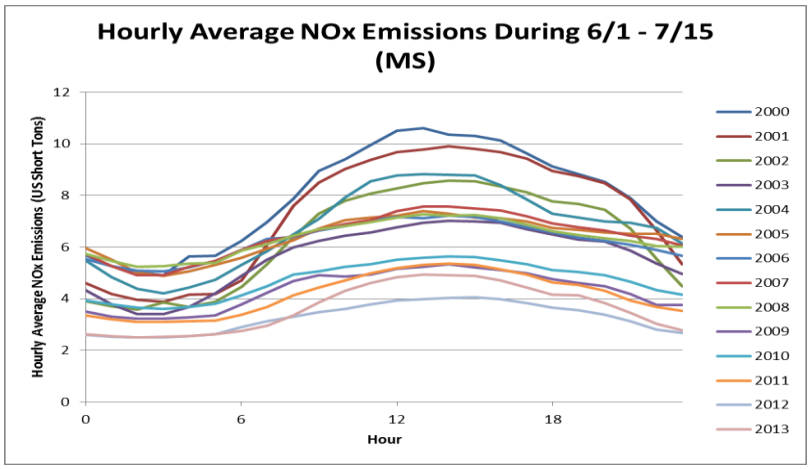


Figure S11b. Diurnal (LST) variation in NO_x emissions from electric generating units in three states, Alabama, Georgia and Mississippi. Trends between 2000 and 2012 from the Air Markets Program Data (AMPD) (http://ampd.epa.gov/ampd).

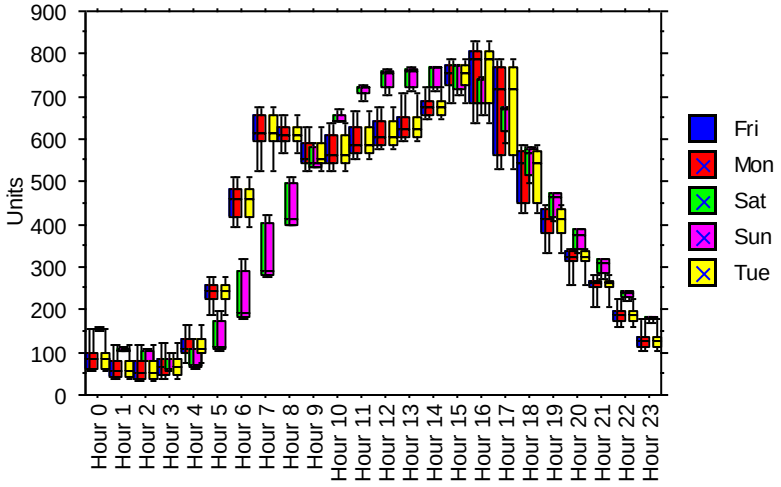


Figure S12. Statistical LST distributions of national-average hourly allocations of mobile-source emissions across 48 vehicle categories showing differences among days of the week. The "Tuesday" profile applies also to Wednesdays and Thursdays. Each box-and-whiskers indicates the 5th, 25th, 50th, 75th, and 95th percentiles of the 48 vehicle categories for a given day and hour. Units are arbitrary and sum to approximately 10,000 across 24 hours. Source: U.S. EPA, ftp://ftp.epa.gov/EmisInventory/2011v6/v1platform/reports/temporal_profiles/, http://www.cmascenter.org/smoke/documentation/3.5/html/ch08s03.html (accessed February 28, 2014).

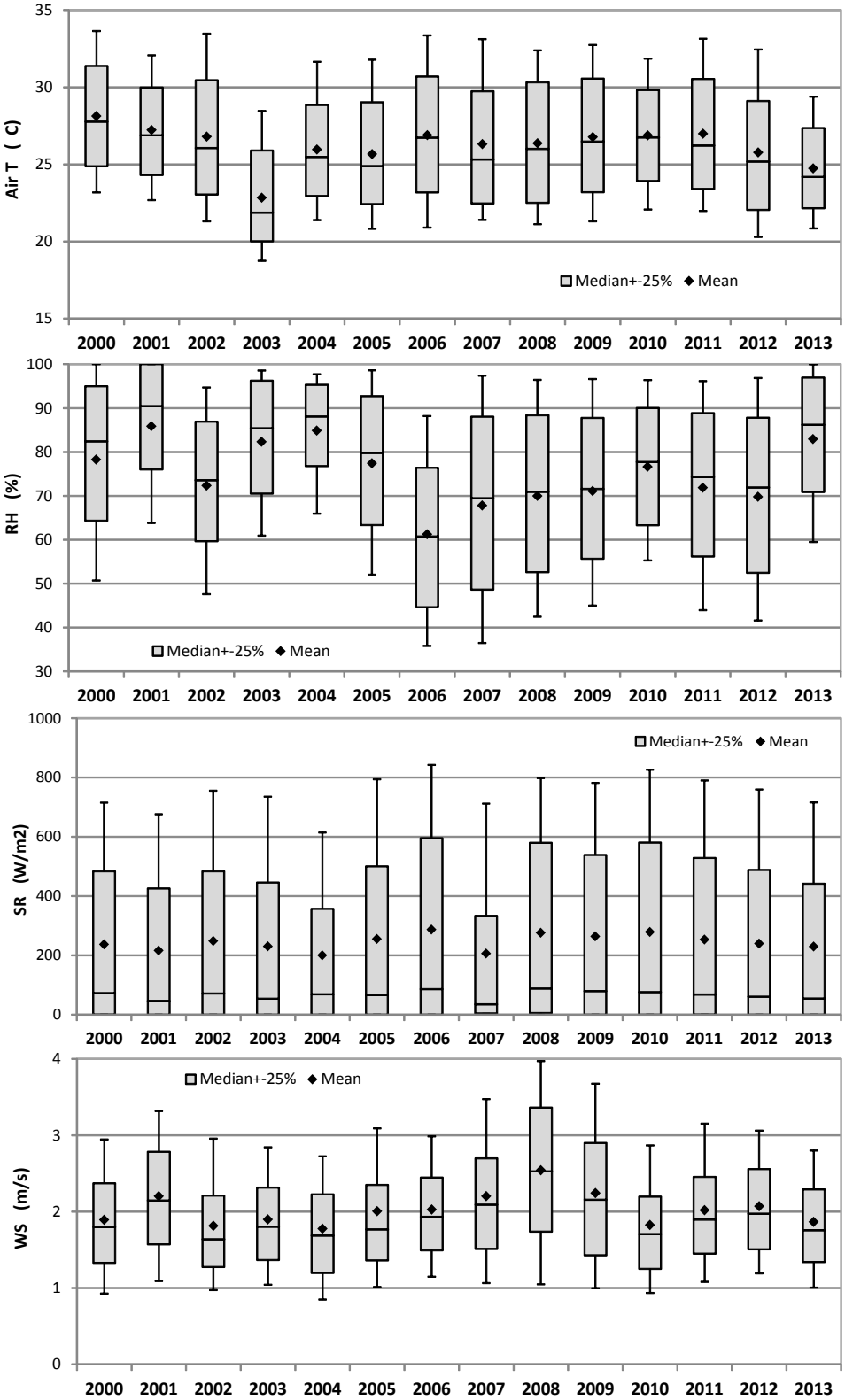


Figure S13. Statistical distributions of hourly temperature (T), relative humidity (RH), solar radiation (SR), and wind speed (WS) at CTR from June 1 through July 15 each year. The plots indicate the median (horizontal line), mean (diamonds), 25th and 75th%tiles (boxes), and the 10th and 90th percentiles (vertical lines).

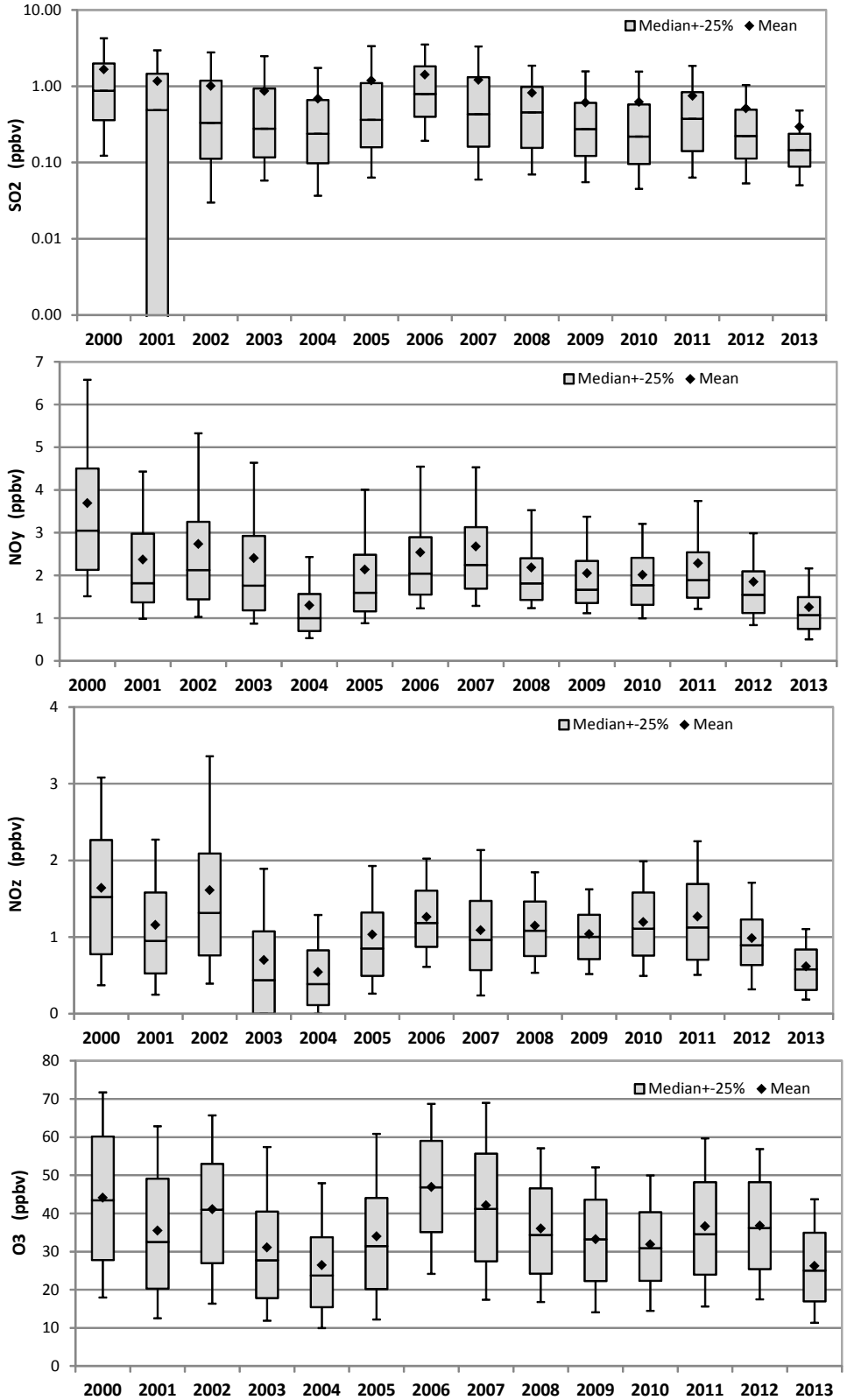


Figure S14. Statistical distributions of trace gases SO_2, NO_y, NO_z, and O_3 at CTR from June 1 through July 15 each year. The plots indicate the median (horizontal line), mean (diamonds), 25th and 75th%tiles (boxes), and the 10th- 90th percentiles (vertical lines).

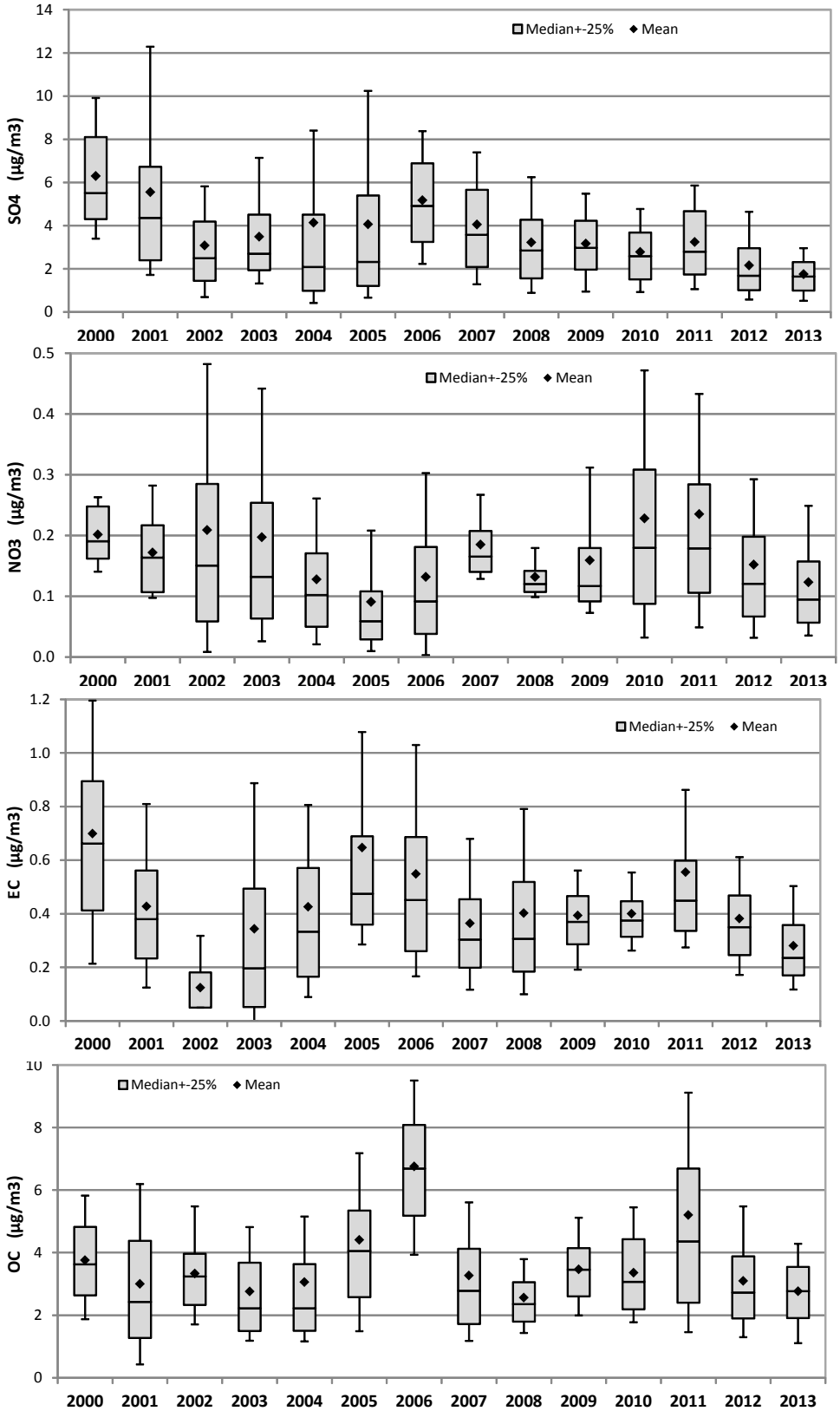


Figure S15. Statistical distributions of $PM_{2.5}$ SO_4, NO_3, EC, and OC at CTR from June 1 through July 15 each year. The plots indicate the median (horizontal line), mean (diamonds), 25th and 75th%tiles (boxes), and the 10th- 90th percentiles (vertical lines).

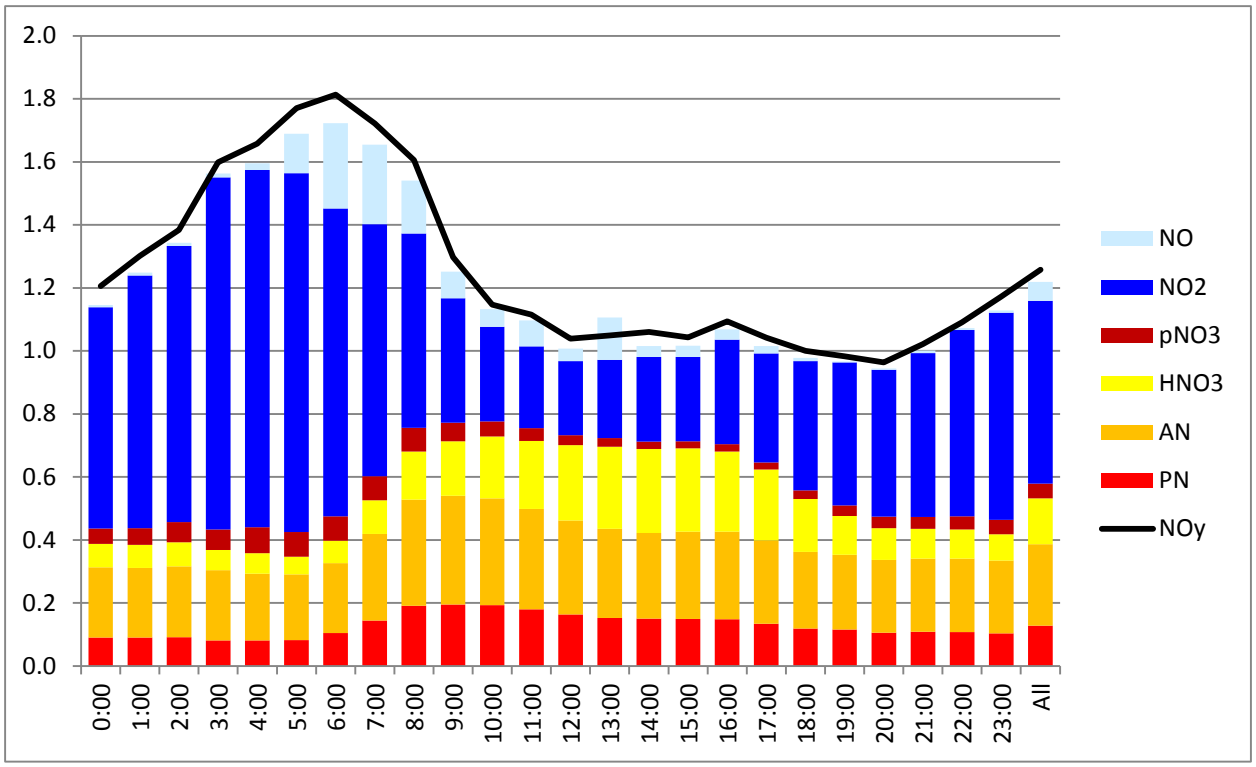


Figure S16. Composite ambient odd-nitrogen balance for CTR June-July, 2013, showing mean hourly (local time) concentrations of NO, NO_2, $PM_{2.5}$ NO_3 (pNO_3), HNO_3, alkyl nitrates (AN), and peroxyalkylnitrates (PN) in relation to measured concentrations of NO_y. Alkyl nitrates (AN) and peroxyalkyl nitrates (PN) determined from thermophotolytic conversion to NO measurement.

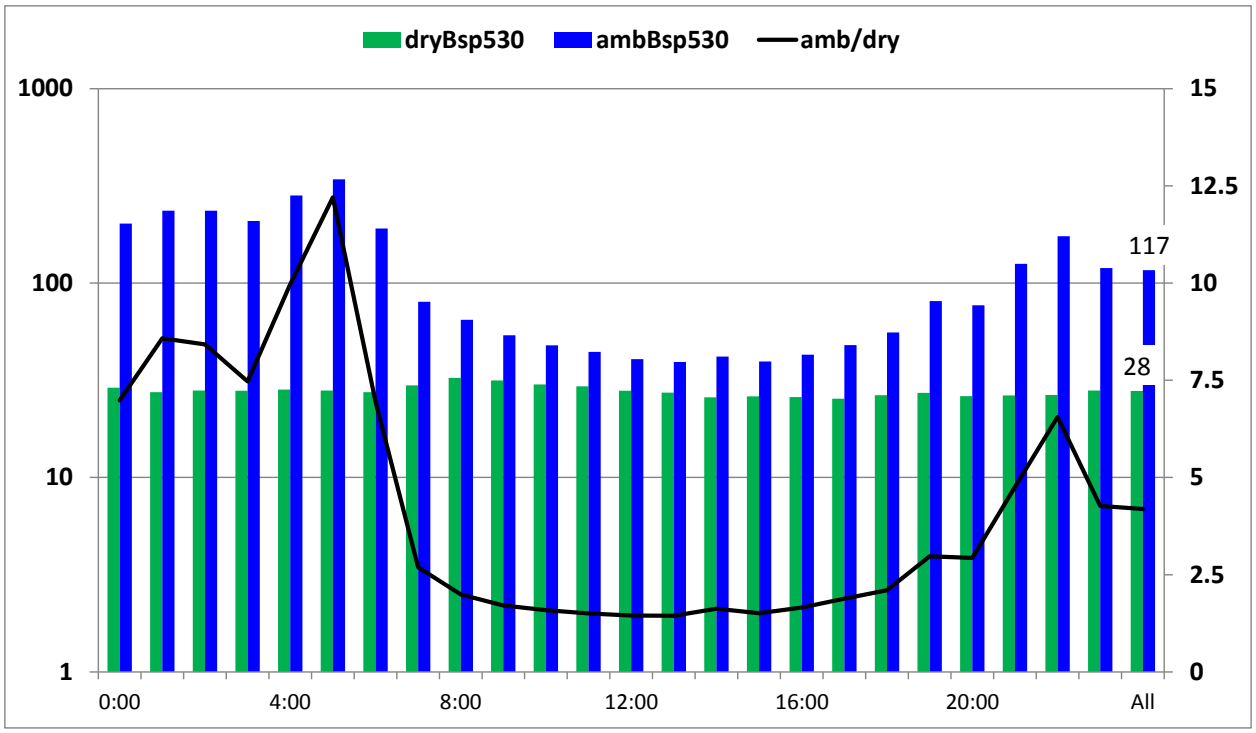


Figure S17. Mean hourly light scattering coefficient (b_{sp}) for ambient and dried aerosol (left axis, Mm^{-1}) versus hour local time during June 1 – July 15, 2013. Ambient and dry period means (117, 28 Mm^{-1}, respectively) are shown as rightmost bar. The ratio of ambient to dry light scattering (line, right axis) indicates response, with equilibration, of particles at CTR to RH.

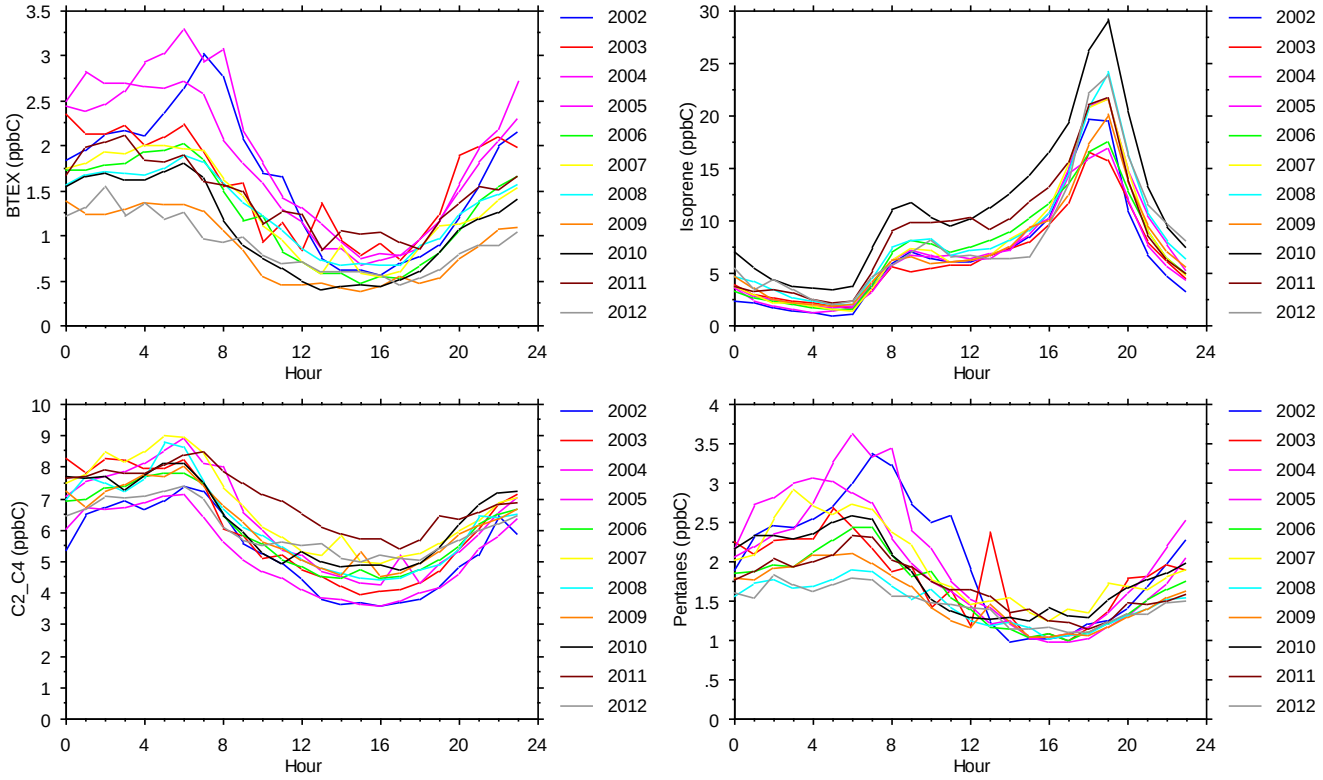


Figure S18. Mean diurnal LST concentrations of BTEX compounds, isoprene, C_2-C_4 alkanes, and pentanes, at YRK, showing differences between variations of biogenic isoprene anthropogenic species concentrations. Measurements were made by the PAMS network from June 1 through August 31 of each year. The NMOC concentrations show strong differences between the anthropogenic species and naturally occurring isoprene (Data described in EPA, 1999).

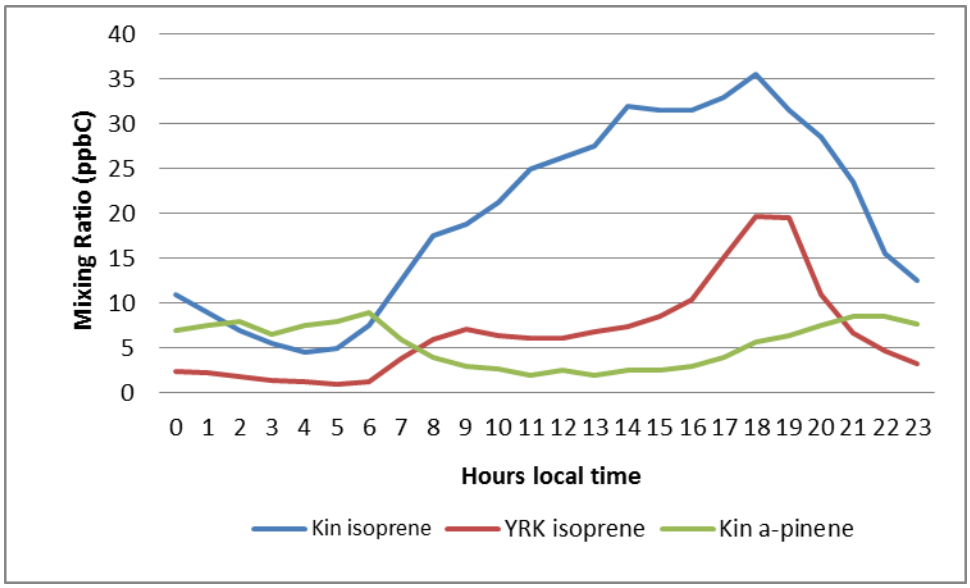


Figure S19. Average isoprene and α-pinene concentrations in ppbC from rural Kinterbish State Park, (western) Alabama taken in June-July 1990 (Goldan et al., 1995) compared with YRK PAMS data in summer 2002. The diurnal (LST) variation in isoprene indicates an early morning increase in concentration with increased emissions and mixing with inversion breakup, followed by dilution and photochemical oxidation at midday, ending with a maximum before decline to nighttime levels. This occurs in both the Kinterbish data and at YRK; the YRK late afternoon maximum is lower than shown at Kinterbish. The YRK pattern also is seen at the other PAMS sites (Conyers and S. DeKalb) around Atlanta. The daytime α-pinene concentrations (ppbv) are found to be low relative to isoprene, with a morning maximum, mixing during inversion break up, and increased emissions with temperature rise. The α-pinene concentrations then decrease through the midday, later rising to a maximum in early evening.