



Effects of emission reductions on organic aerosol in the southeastern United States

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Effects of emission reductions on organic aerosol in the southeastern United States

C. L. Blanchard¹, G. M. Hidy², S. Shaw³, K. Baumann⁴, and E. S. Edgerton⁴

¹Envair, Albany, CA, USA

²Envair/Aerochem, Placitas, NM, USA

³Environmental Sector, Electric Power Research Institute, Palo Alto, CA, USA

⁴Atmospheric Research and Analysis, Cary, NC, USA

Received: 26 May 2015 – Accepted: 04 June 2015 – Published: 22 June 2015

Correspondence to: C. L. Blanchard (cbenvair@pacbell.net)

Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Long-term (1999 to 2013) data from the Southeastern Aerosol Research and Characterization (SEARCH) network are used to characterize the effects of anthropogenic emission reductions on fine particle organic aerosol (OA) concentrations in the southeastern US. On average, 45 % (range 25 to 63 %) of the 1999 to 2013 mean organic carbon (OC) concentrations are attributed to combustion processes, including fossil-fuel use and biomass burning, through associations of measured OC with combustion products such as elemental carbon (EC), carbon monoxide (CO), and nitrogen oxides (NO_x). The 2013 mean combustion-derived OC concentrations were 0.5 to 1.4 $\mu\text{g m}^{-3}$ at the five sites operating in that year. Mean annual combustion-derived OC concentrations declined from $3.8 \pm 0.2 \mu\text{g m}^{-3}$ (68 % of total OC) to $1.4 \pm 0.1 \mu\text{g m}^{-3}$ (60 % of total OC) between 1999 and 2013 at the urban Atlanta, Georgia, site (JST) and from $2.9 \pm 0.4 \mu\text{g m}^{-3}$ (39 % of total OC) to $0.7 \pm 0.1 \mu\text{g m}^{-3}$ (30 % of total OC) between 2001 and 2013 at the urban Birmingham, Alabama, site (BHM). The urban OC declines coincide with reductions of motor-vehicle emissions between 2006 and 2010, which may have decreased mean OC concentrations at the urban SEARCH sites by $> 2 \mu\text{g m}^{-3}$. BHM additionally exhibits a decline in OC associated with SO_2 from $0.4 \pm 0.04 \mu\text{g m}^{-3}$ in 2001 to $0.2 \pm 0.03 \mu\text{g m}^{-3}$ in 2013, interpreted as the result of reduced emissions from industrial sources within the city. Analyses using non-soil potassium as a biomass-burning tracer indicate that biomass-burning OC occurs throughout the year at all sites. All eight SEARCH sites show an association of OC with sulfate (SO_4) ranging from 0.3 to 1.0 $\mu\text{g m}^{-3}$ on average, representing ~ 25 % of the 1999 to 2013 mean OC concentrations. Because the mass of OC associated with SO_4 averages 20 to 30 % of the SO_4 concentrations, the mean SO_4 -associated OC declined by ~ 0.5 to 1 $\mu\text{g m}^{-3}$ as SO_4 decreased throughout the SEARCH region. The 2013 mean SO_4 concentrations of 1.7 to 2.0 $\mu\text{g m}^{-3}$ imply that future decreases in mean SO_4 -associated OC concentrations would not exceed ~ 0.3 to 0.5 $\mu\text{g m}^{-3}$. Seasonal OC concentrations, largely associated with ozone (O_3), vary from 0.3 to 1.4 $\mu\text{g m}^{-3}$ (~ 20 % of the total OC concentrations).

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1 Introduction

In much of North America, organic aerosol (OA) represents ~ half of average PM_{2.5} mass concentrations in ambient air (Kanakidou et al., 2005). OA composition in the southeastern US provides indications of emission source origins, but results have not been consistent across studies. The ambiguities in accounting for OA sources and the chemistry of secondary organic aerosols (SOAs) helped motivate a major suite of field experiments during the summer of 2013, the Southern Oxidant and Aerosol Study (SOAS) (SOAS, 2013) and associated campaigns that comprised the Southeast Atmosphere Study (SAS) (SAS, 2014). Ground-level measurements were located at rural sites, with many studies situated at a Southeastern Aerosol Research and Characterization (SEARCH) network monitoring location outside Brent, near Centreville, Alabama (CTR), a regionally representative site (Hidy et al., 2014).

CTR and other SEARCH sites offer a long-term record of trace-gas and particle observations (Hidy et al., 2014) that provide insight into the effects of anthropogenic emission reductions on organic aerosol trends in the southeastern U.S. The SEARCH record complements the six-week-long SAS and SOAS investigations of key atmospheric processes and chemical reactions. Specific questions relevant to SOAS and SAS goals that can be addressed using the SEARCH data include:

1. What fraction of measured organic carbon (OC) was emitted by combustion processes, such as motor vehicle exhaust and biomass burning? How has this fraction responded to emission reductions?
2. Over a long period of record, can the fractions of OA directly emitted in the condensed phase (primary organic aerosol, POA) and of SOA formed in the atmosphere via reactions of gaseous or condensed-phase precursors be quantified or constrained based on diurnal, seasonal, and annual variations of OC, elemental (or black) carbon (EC), ozone (O₃), sulfate (SO₄), and other aerometric measurements? How have inferred SOA concentrations responded to emission reductions?

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3. Do the long-term gas and particle measurements indicate how much biogenic SOA is present on daily, seasonal, or annual time scales? How has SOA of biogenic origins been affected by anthropogenic emission reductions?

This paper describes analyses of aerometric data from CTR and the seven other SEARCH sites that address these questions. We apply five complementary data analysis methods that provide insight into the sources of aerosol carbon in the Southeast. Because uncertainties and differences among previous studies have been challenging to resolve due to inconsistent or ambiguous definitions and terminology used to describe carbon measurements, an appendix defines terminology and identifies unresolved questions.

2 Methods

The data for this study of aerosol carbon derive primarily from long-term SEARCH measurements obtained from up to eight operating sites, comprising four urban-rural or urban-suburban pairs, between 1999 and 2013 (e.g., Hansen et al., 2003; ARA, 2014; Hidy et al., 2014). The dataset includes particle mass concentrations and composition, gases, and meteorological parameters (Atmospheric Research and Analysis, 2014) as previously described in Hansen et al. (2003) and Edgerton et al. (2005, 2006). Special data from ancillary experiments in the SEARCH network supplement the long-term data. We also use emission data derived from the EPA National Emission Inventory (NEI), augmented as described in Blanchard et al. (2013) and Hidy et al. (2014).

Multiple empirical methods are employed to understand OA sources and SOA formation in the southeastern US, utilizing the SEARCH data to obtain a multi-year and multi-season interpretation. The methods are: (1) comparison and correlation of measured OC with EC concentrations and use of the OC / EC ratios as indicators of combustion-related emissions and SOA formation, (2) computation of organic mass (OM) / OC ratios utilizing PM_{2.5} mass and sums of species concentrations as evidence for the presence of oxidized OA, (3) estimation of biomass-burning contributions to measured EC

and OC using biomass burning tracers, (4) application of receptor modeling (principal component analysis, PCA, supplemented with comparisons to positive matrix factorization, PMF) to identify and quantify atmospheric processes affecting OA concentrations, and (5) comparison of observations with augmented NEI emission estimates (Hidy et al., 2014). Computational details are described within the results and discussion section and in the supplemental information.

3 Results and discussion

3.1 Ambient EC and OC concentrations and trends

Trends and spatial variations are evident for mean annual and seasonal EC and OC concentrations (Table 1 and Fig. 1). Mean EC concentrations were 2.0 to 3.5 times greater at Jefferson Street (JST), in Atlanta, Georgia, than at CTR, thereby indicating two- to three-fold greater influence of combustion sources within Atlanta compared to rural CTR because EC is a tracer of combustion (Appendix). The ratio of JST EC to CTR EC declined from 2.8 : 1 to 2.1 : 1 between the first and third five-year periods. Mean OC concentrations were 1.0 to 1.8 times greater at JST than at CTR, indicating urban sources of OC possibly superimposed on a relatively high regional baseline. The JST OC to CTR OC ratio decreased from 1.5 : 1 to 1.2 : 1 between the first and third five-year periods, possibly declining along with declining urban OC emissions. Both EC and OC exhibit decreasing trends at all SEARCH sites (Hidy et al., 2014), particularly after 2007 but with a possible rise between 2009 and 2011 (Fig. 1). The relation of these ambient trends to emission trends is discussed in a later section.

No season consistently exhibits the highest mean EC and OC concentrations but the CTR mean OC concentrations and OC / EC ratios are highest during summer, interpreted as the influence of aging and SOA formation during warmer months. In contrast, JST mean OC and EC concentrations tend to be higher during autumn and winter (Table 1). The differences between JST and CTR mean summer OC concen-

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trations decline from $1.1 \mu\text{g m}^{-3}$ in 1999–2003 to less than $0.1 \mu\text{g m}^{-3}$ in 2009–2013, interpreted as reductions of urban OC concentrations toward a regional baseline level (Table 1).

Mean OC / EC ratios are higher at CTR than at JST, again consistent with regional-scale aging of ambient aerosol and a relatively greater influence of SOA at CTR. The period mean OC / EC ratios at JST range from 2.3 : 1 to 4.0 : 1, suggesting variable contributions from multiple sources. For comparison, typical OC / EC ratios are ~ 1 in freshly emitted motor vehicle emissions (Chow et al., 2004), $\sim 5 : 1$ – $20 : 1$ in near-source biomass burning plumes (Andreae et al., 1996; Andreae and Merlet, 2001; Hobbs et al., 1996; Lee et al., 2005), and potentially much greater than unity as oxidation and SOA formation proceed (Robinson et al., 2007).

Temporal trends in ambient EC and OC correlated within individual sites and across the SEARCH domain (e.g., CTR and JST, Fig. 1), indicating regional coherence of trends and seasonal variations for both EC and OC. The strong correlation of EC and OC at all SEARCH sites, averaging times (annual, seasonal, monthly, daily), and seasons indicates that combustion processes are a major source of OC (Table S1; Fig. S2). However, significant correlations of SO_4 with both EC and OC during summer suggest the influence of SO_4 on SOA formation in summer, consistent with results from SOAS (Xu et al., 2015; Budisulistiorini et al., 2015). In summary, the EC and OC measurements indicate influence of multiple emission sources or atmospheric processes affecting all SEARCH sites, though differently at urban and rural locations.

3.2 OM / OC ratios

More oxygenated OA has higher ratios of OM / OC, so OM / OC potentially serves as an indicator of atmospheric aging. A low value (e.g., OM / OC ~ 1.4 to 1.6) suggests little aging (i.e., POA is a large fraction of OA), whereas a high value (e.g., > 2) suggests more aging (SOA is a large fraction of OA). For comparison, OM / OC ratios are 1.2 for pentane (and higher molecular weight alkanes), 1.1 for isoprene, and 2.0 for isoprene

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epoxydiol (IEPOX) (a gas-phase intermediate of isoprene oxidation, yielding SOA). The average motor-vehicle OM / OC ratio is ~ 1.2 to 1.4 (Landis et al., 2007) while biomass burning OM / OC averages ~ 1.4 to 1.8 (Reid et al., 2005).

We estimate the OM / OC ratio for the urban and rural SEARCH sites using a mass balance computation based on particle composition. The sum of species concentrations, including estimated particle-bound water (PBW) at laboratory temperature and relative humidity (RH), is:

$$\text{Sum of species} = f_1 \cdot \text{SO}_4 + f_2 \cdot \text{NO}_3 + f_3 \cdot \text{NH}_4 + \text{EC} + \text{OC} + \text{MMO} + \text{Na} + \text{Cl} \quad (1)$$

(inorganic species concentrations are from ion measurements). PBW at laboratory RH of 38% is represented by the coefficients f_1 (1.28), f_2 (1.15), and f_3 (1.25) (Tombach, 2004, as derived from Tang et al., 1996). The coefficient f_1 is an average of the coefficients for NH_4HSO_4 (1.27) and $(\text{NH}_4)_2\text{SO}_4$ (1.29), f_2 is the coefficient for NH_4NO_3 , and f_3 is a weighted average reflecting higher SO_4 than NO_3 concentrations. MMO is the sum of the concentrations of six crustal elements (Al, Ca, Fe, Mg, Si, Ti) (XRF measurements), expressed as oxides (Hansen et al., 2003). This estimate of crustal mass is likely conservative, since it does not include Mn and the assumed Ca mass (as CaO) would be less than the mass of CaCO_3 (if present). The difference between $\text{PM}_{2.5}$ mass and the sum of species concentrations is denoted as “non-measured” (NM) mass:

$$\text{NM mass} = \text{PM}_{2.5}\text{mass} - \text{Sum of species} \quad (2)$$

An upper bound for OM is calculated as $\text{OM}^* = \text{OC} + \text{NM mass}$, which assumes that all NM mass is associated with OA. Any mass that is missing from the computed sum of species would bias NM mass high, thereby also causing OM^* to be higher than the true OM. Similarly, underestimation of PBW would bias NM mass and OM^* high.

At all SEARCH sites, NM mass concentrations averaged 1.5 to $1.9 \mu\text{g m}^{-3}$ (interquartile range ~ 0.5 to $\sim 2.5 \mu\text{g m}^{-3}$ at all except YRK) during the most recent five-year period (2009 to 2013; Na and Cl ions were not measured prior to 2008) (Fig. S3).

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Daily NM mass correlated with daily OC to varying degrees: r^2 was 0.2–0.3 at Birmingham, Alabama (BHM), Gulfport, Mississippi (GFP), (rural) Oak Grove, Mississippi (OAK), and 0.4–0.5 at CTR, JST, (rural) Yorkville, Georgia (YRK), (suburban) Outlying Landing Field, Pensacola, Florida (OLF), and Pensacola, Florida (PNS). The average $\Delta\text{OM}^* / \Delta\text{OC}$ varied by site from 1.5 (BHM) to 2.0 (YRK) (1.6 to 1.9 without intercept terms) (Fig. 2), which suggests a regionally characteristic but spatially and temporally variable mix of less-oxidized and more-oxidized OA. The consistency of the slope ratios, and their relatively low values in the range of 1.6 to 1.9, indicate that POA is a major portion of OA at both urban and rural sites with modest variations in the degree of oxidation or SOA mass. However, higher OM^* / OC and OM^* / EC occur in the warmest months (Fig. S4), consistent with seasonal SOA formation and the seasonal variations discussed above. Method 2 (OM^* / OC) agrees with Method 1 (OC / EC analysis) in indicating a substantial contribution of relatively fresh combustion-derived POA, and suggests that urban-rural differences in OC / EC ratios derive in part from differences in nearby emission source influence (e.g., more mobile-source and domestic heating influence in urban areas; more biomass burning and biogenic influence in rural locales).

3.3 Biomass-burning tracers

Emission inventories indicate that biomass burning, including prescribed burns, wildfires, agricultural burns, and domestic heating, is the largest source of $\text{PM}_{2.5}$ OC emissions in the Southeast on an annual-average basis (Hidy et al., 2014). Prescribed burns are the largest source of biomass-burning OC emissions, again on an annual basis (Hidy et al., 2014). In the Southeast, prescribed burns are employed to manage roughly 4 million hectares (ha) (~ 10 million acres) of land every year, primarily between January and April; wildfires may occur year-round but are more frequent in warmer months (Wade et al., 2000; Haines et al., 2001). Nearby (e.g., ~ 10 km) biomass-burning plumes are sometimes evident in CTR hourly data and substantially affect observed concentrations of EC, OA, CO, NO_y , NH_3 , and O_3 (Fig. S5). However,

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the cumulative effect of widespread and potentially wide-ranging biomass burning on long-term ambient OA concentrations is more difficult to determine. The available data record does not include organic biomass-burning tracers, such as levoglucosan, except during special studies such as the six-week SOAS campaign. However, non-soil potassium (K) has been used as an indicator of biomass combustion in previous studies (Calloway et al., 1989; Lewis et al., 1988; Lewis, 1996; Pachon et al., 2010, 2013) and can be determined from K measurements reported in the long-term SEARCH data. Using a single tracer species to identify and quantify biomass-burning contributions to ambient OA is subject to important uncertainties, so the results of this analysis are considered in relation to those of the other methods.

Non-soil K (nsK) is estimated from coarse PM (PM_{coarse} or PM_{crs} , PM between 2.5 and 10 μm) and $PM_{2.5}$ XRF measurements of K and Si following the K tracer approach of Pachon et al. (2013). Briefly, the method regresses measured K against species X concentrations: $K = \alpha + \beta * X$ (where X derives primarily from crustal material). Si measurements are used to represent the crustal species, X , because Si concentrations are routinely well above the limits of detection and tight correlations of Si with Al and other known crustal elements indicate few or no interfering sources of Si. The correlations of PM_{coarse} XRF K and Si are very strong, with consistent values of the slope $\beta = \Delta K / \Delta Si$ of 0.10 to 0.13 and $r^2 \sim 0.8$ at all sites (Figs. S6–S8). These slopes therefore define the expected ratio of K/Si in crustal material in the region. The ratios are lower than, but consistent with, a value of 0.15 ± 0.01 reported for data from Phoenix, AZ (Lewis et al., 2003). In contrast to PM_{crs} , $PM_{2.5}$ measurements exhibit large excesses of K over the expected K/Si ratios, indicating the presence of one or more non-crustal sources of $PM_{2.5}$ K (Figs. S6 to S8). We apply the slopes β to compute $nsK = K - \beta * Si$ from $PM_{2.5}$ data (Fig. S6). The agreement between computed nsK and measured water-soluble K (K ion, KI; measured beginning 2008) supports the interpretation of non-soil K as an indicator of biomass-burning K (K_{bb}) (which is water-soluble) at rural inland sites such as CTR (Fig. S6). Possibly, both K ion and computed nsK could also have a marine origin at some coastal sites (e.g., OLF) or an industrial process origin at some urban

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sites (e.g., BHM). Detailed review of computed nsK indicated that all nsK > 0.4 $\mu\text{g m}^{-3}$ occurred on or one day after the 4 July and 1 January, and only at urban sites (Fig. S8). This result appears to indicate fireworks as a source of nsK on such occasions. Other than samples from 1 and 2 January and from 4 and 5 July, we identify nsK as biomass-burning K (Kbb), recognizing some uncertainty in this identification for BHM and coastal sites. Since nsK can be computed from the XRF measurements of K and Si for the full SEARCH record (1999 to 2013), whereas K ion measurements commenced in 2008, we use nsK as our biomass-burning tracer.

The ratio of total carbon (TC = EC + OC) to Kbb (TCbb / Kbb) in biomass burning is known to vary widely among fire types (e.g., wildfires differ from prescribed burns) and among fire stages (e.g., flaming vs. smoldering). The variability of emissions among and within fires implies that biomass-burning tracers are more useful for estimating statistical average impacts than for quantifying burn contributions during individual events. We use a single average scaling factor based on consideration of emissions information (Hidy et al., 2014) and the correlation of modern C with non-soil K (Fig. S9). Inventory annual average TCbb/Kbb is in the range 28 : 1–36 : 1 (Blanchard et al., 2013). Our assumed scaling factor of 32 for TCbb/Kbb is similar to carbon isotope data from CTR winter samples (Fig. S9, CTR regression slope $\Delta\text{TC}_{\text{modern}} / \Delta\text{Kbb} = 43$), when prescribed burns are more common and SOA formation rates are lower. The higher slope of 71 : 1 at JST could reflect a different type of biomass burning (e.g., residential wood combustion), while the lesser correlation of modern TC with non-soil K (assumed to represent Kbb) at BHM and higher slope at PNS potentially reflect the confounding influence of industrial (BHM) or marine (PNS) sources of non-soil K. A higher scaling ratio (e.g., $\Delta\text{TCbb} / \Delta\text{Kbb} = 70$ rather than 32) would yield higher computed TCbb and therefore higher OCbb. Based on $\Delta\text{OC} / \Delta\text{EC}$ in actual biomass-burning events observed at SEARCH sites, we compute $\text{OCbb} = 0.9 \cdot \text{TCbb}$ for all days having measurements of both EC and OC (the ratio OCbb / TCbb could be higher in some burn events).

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CTR monthly-average concentrations indicate a downward trend in OC but not in computed OC_{bb}, so that OC_{bb} has become a larger fraction of OC at CTR since 2007 (Fig. 3). The absence of trend in computed OC_{bb} reflects the absence of trend in measured K and computed non-soil K. OC_{bb} tends to be higher in winter months, when prescribed burns are more common and residential heating needs are greatest, but OC_{bb} is present during all seasons (Fig. 3) and at all SEARCH sites (Fig. S10). Retene, a tracer of coniferous wood combustion, is evident at the sites where it was measured (urban BHM and JST) with a pronounced seasonal cycle (Fig. S11). Retene emissions from prescribed burning in the Southeast are highly variable and depend largely on the amount of softwood present in the fuel. Since historical fire suppression has led to the accumulation of significant amounts of hardwood in a thick midstory of pine-dominated forests (e.g. Provencher et al., 2001; Varner et al., 2005), retene no longer can be assumed to be a unique indicator for prescribed burning emissions in the Southeast.

The analysis of K measurements from the SEARCH data reinforces the conclusion that biomass burning is an important component of combustion-related OA in the SEARCH domain, at all sites and in all seasons. The contribution is especially important for regional-scale OA, as suggested by the CTR data. Uncertainties in the estimation procedure and scaling factors imply that the computed CTR mean OC_{bb} ($1.6 \mu\text{g m}^{-3}$, 1999–2013 average) could be either over- or under-estimated.

3.4 Principal component analysis

Important insight into the origins of ambient aerosol can be obtained with multivariate statistical methods, such as principal component analysis (PCA), which is a well-established method for PM source apportionment (Dattner and Hopke, 1982). PCA generates mathematically independent groupings of measurements based on the correlations among the measured variables (classically, the groups are geometrically orthogonal to one another). The number of groups reproduces as large a fraction of the total variance of a data set as possible subject to optimization criteria, typically explain-

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ing ~ 75 to 80 % of the variance of, e.g., ~ 20 to 25 air pollutant species concentrations with ~ 5 to 10 groups, also known as factors or components. Although PCA factors may be identifiable with emission sources in some applications, factors fundamentally represent correlations among species and potentially reflect a variety of aerometric processes (e.g., secondary species formation, meteorological effects). In our application, we interpret PCA factors as associations among species that are indicative of variations in the chemical environment, and refer to such species associations as components for brevity. A related methodology, positive matrix factorization (PMF) (U.S. EPA, 2014), differs in part from PCA in that PMF constrains factors to positive values. This constraint is physically realistic if PCA factors are interpreted as unique emission source contributions. Nevertheless, the negative values permitted by PCA are in fact meaningful and informative if, in addition to emissions, factors represent a larger suite of physical and chemical processes (e.g., deposition; chemical loss processes; contrasts between inland versus marine air mass transport). The sensitivity of our results to the choice of statistical method is examined through comparison of PCA with PMF in the supplementary information.

We report two main versions of PCA, with additional versions used for sensitivity tests and auxiliary information. *PCA1* is applied to measurements made at SEARCH sites from 2008 through 2013. The 23 gas and $PM_{2.5}$ measurements comprise daily-average concentrations of $PM_{2.5}$ EC and OC (thermal-optical reflectance, TOR), daily averages of gases NH_3 (measured continuously or at 24-hour resolution) and continuous NO_x and NO_z , secondary species (daily peak 8-hour O_3 , plus $PM_{2.5}$ SO_4 , NH_4 , and NO_3), and $PM_{2.5}$ crustal elements (XRF measurements of Al, Si, and Fe), species associated with salts ($PM_{2.5}$ Na, Cl, Mg, and Ca ions), and trace metals ($PM_{2.5}$ Zn, Cu). Both daily averages and daily 1-hour-maxima of gases (CO and SO_2) are included to match the temporal resolution of the other daily data while also potentially capturing shorter-duration plumes. Water-soluble $PM_{2.5}$ K (K ion) is included as a potential indicator of biomass combustion. Because some species used in *PCA1* were not measured throughout the 15-year SEARCH program, *PCA2* is carried out to inter-

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pret long-term OC trends from 1999 through 2013. PCA2 excludes measurements that commenced in 2008 (water-soluble Ca, Mg, K, Na, and Cl). XRF Ca and non-soil K are used instead of water-soluble Ca and K, respectively. Without Na and Cl in PCA2, salts are not detectable, as will be discussed. NH_3 is excluded from PCA2, since those measurements began in 2004. Daily-average O_3 is included in PCA2 to complement daily peak 8-hour O_3 .

PCA1 and PCA2 each reveal 6–8 components at each SEARCH site (Table 2). A consistent set of components is evident across sites, and is similar for PCA1 and PCA2. Component characteristics are discussed below. For clarity, we designate the components as: (1) combustion, (2) crustal, (3) seasonal, (4) SO_2 , (5) SO_4 , (6) metals, (7) salt, and (8) other. The full orthogonal solutions are shown in the Supplement (Tables S2 to S9). The values in Tables S2 to S9 are the coefficients of the linear combinations of standardized species concentrations (daily concentration less mean divided by standard deviation); each tabled value is also the correlation (r) between a given species and a particular component. High (~ 1) or low (~ -1) values indicate high correlation or anti-correlation, respectively; both are meaningful. A value near zero indicates little or no correlation, so values in the range of ~ -0.5 to 0.5 represent associations ranging from moderate anti-correlation (-0.5) to zero correlation to moderate correlation (0.5).

All sites exhibit a suite of species associated with combustion processes (EC, OC, CO, NO_x or NO_z). The variations in combustion associations among sites suggest different source mixes, differences in air mass ages (e.g., fresh emissions at urban sites, more aged emissions at rural sites), or differing transport of polluted air masses. For example, NO_z is more strongly associated than NO_x with the combustion component at the two most rural sites, CTR and OAK.

A crustal component is present at all sites, associated with Al, Si, Fe, and, to varying degrees, Ca. At BHM, Fe associates more prominently with a metals component, consistent with previous studies indicating the impact of industrial facilities (including metals fabrication) on $\text{PM}_{2.5}$ at BHM (Baumann et al., 2008; Blanchard et al., 2014a).

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A seasonal component is present at all sites, but in two forms: positive O_3 and NH_3 (if measured), along with negative NO_3 , at BHM PCA2, CTR, GFP, JST PCA1, OAK, OLF, PNS, and YRK, or with reverse signs (e.g., relatively weak negative O_3) at BHM PCA1 and JST PCA2. As noted, sign reversals simply represent a change in coordinate directions and need not have physical significance; however, the association of OC with the seasonal component may differ depending on sign (discussed below). We denote this component “seasonal” rather than “photochemical”. While this factor has photochemical properties, it is comprised of species with seasonality variations that result from multiple processes: emissions (NH_3), photochemistry (O_3), and temperature- and RH-sensitive thermodynamic equilibrium (NO_3). The seasonal component evidently represents seasonal variations not otherwise described by the seasonal variations of the crustal, SO_4 , and “other” components.

The SO_2 component, also present at all sites, identifies influences of relatively fresh plumes, whether from electric generating units (EGUs) or industrial sources. At CTR, NO_x is more strongly associated with the SO_2 component than with the combustion component, consistent with relatively less aged point-source plumes and more aged general combustion influences.

SO_4 and NH_4 are always associated and usually represented by a single component, denoted “ SO_4 .” However, SO_4 and NH_4 are part of the seasonal component for PNS and YRK PCA2, suggesting that differentiation of the SO_4 and seasonal components is subject to uncertainty. Otherwise, O_3 is associated with both seasonal and SO_4 components (correlations up to $r = 0.4$ to 0.6 with the SO_4 component; $|r| = 0.6$ to 0.9 with the seasonal component).

Cu and Zn appear on a metals component at six sites (BHM, CTR, GFP [PCA2], JST [PCA2], OAK, and OLF [PCA2]); otherwise, Cu and Zn are associated with combustion or are split between the metals and “other” components. The Cu and Zn correlations range from $r = 0.1$ to 0.3 in the full 1999 to 2013 data set, which does not suggest a simple or tight association between these two species.

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A salt component (of marine or other origins) is evidenced by Na, Cl, and Mg in PCA1. Na appears as a separate “other” component for JST PCA1, suggesting multiple urban sources of one or more of these species. These species are not necessarily unique marine tracers; various combustion processes generate Cl emissions, for example.

A component designated as “other” is present for BHM PCA1, GFP PCA1, JST PCA1, PNS PCA2, and YRK PCA1 and PCA2, indicating variability at urban and near-urban (YRK) sites not otherwise represented by the major components (Table 2).

Additional PCA applications are carried out using special data or to test the sensitivity of results to the choice of measurements or measurement periods. NMOC measurements made every day at JST from 1999 through 2008 are incorporated to generate PCA3 as a modification of PCA2 (no ions and only XRF elements, and shorter time period, see Table S10). For PCA3, the sum of alkanes, sum of aromatics, and α -pinene are associated with the combustion component, whereas isoprene is associated predominantly with the SO₄ component. The measured alkane and aromatic species are known constituents of motor vehicle exhaust (Blanchard et al., 2010), consistent with a mobile-source contribution to the JST combustion component. Correlations between α -pinene and CO, EC, and NO_x range from $r = 0.5$ to 0.6 , mathematically associating these species, but the physical processes underlying the correlation are ambiguous (e.g., seasonal or meteorological versus common source emissions). Isoprene and pinenes can be factors in O₃ formation, and the association of isoprene with SO₄ could arise from a common seasonality or from atmospheric chemical processes generating SOA from isoprene (Surratt et al., 2007; Xu et al., 2015).

Alternate versions of PCA2 are carried out for 2004–2013 CTR data to see if factor loadings are robust and relatively insensitive to seasonal indicators (PCA4 and PCA5, Table S11). PCA4 and PCA5 yield consistent results when NH₃ or daily-average O₃ are either included or excluded from the analysis.

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PCA1 and PCA2 each indicate that OC is associated with multiple components at all sites. Except at YRK and OLF (PCA2 only), the overall OC associations are strongest for the combustion component (Tables S2 to S9).

OC contributions during particular days, seasons, or time periods could vary substantially from the overall averages, so daily OC concentrations at each site are apportioned using the daily PCA factor scores. The OC apportionment is carried out with multiple regression of daily OC concentrations against daily factor scores. Since the PCA components are orthogonal, the regression coefficients are more stable than would be the case for multiple regression against various tracer species, which are typically intercorrelated.

The OC apportionments indicate statistically-significant relationships between OC and four to seven PCA components (Tables S12 and S13). Differences between urban and rural sites are evident; for example, OC at CTR and YRK is not significantly related to the SO₂ factors, but OC is related to the SO₂ factors at urban sites. This difference indicates the influence of SO₂ emission sources within urban areas, consistent with visual observations made at BHM and measurements made near emission sources in Birmingham (Blanchard et al., 2014a).

The factor scores and regression coefficients are used to compute the contributions of each statistically-significant component to daily OC at each site using both PCA1 and PCA2. Mean contributions are summarized in Table 3; these contributions are expressed as percentages of total OC in Table S12.

Mean combustion OC ranges from 0.7 to 1.6 μg m⁻³ for PCA1 (2008–2013) and from 1.5 to 2.6 μg m⁻³ for PCA2 (1999–2013), except at YRK (Table 3). Daily PCA1 and PCA2 combustion OC concentrations are correlated at all sites (Fig. S12). Mean absolute differences between PCA1 and PCA2 computed combustion OC, interpreted here as a representation of methodological uncertainty, range from 0.1 to 0.7 μg m⁻³ (not tabled). The differences between the daily PCA1 and PCA2 combustion OC apportionments are methodological (Tables S13 and S14). However, the mean PCA1 and PCA2 combustion OC apportionments are averaged over different time periods, so the

differences in their averages are also due to declining EC, CO, and NO_x concentrations (Table 1). Trends in OC components are discussed further below. Mean PCA2 combustion OC ranged from 25 to 63% of mean OC concentrations (Table 3).

Various combustion processes influence individual SEARCH sites differently. At BHM, multiple regression of OC against NO and non-polar OC compounds (including PAHs and iso/anteisoalkanes, or hopanes and steranes) measured on a daily basis from 2006 to 2010 (Blanchard et al., 2014b) correlates with PCA1 combustion OC (Fig. S13). In the urban environment surrounding BHM, NO and non-polar OC compounds likely have a mobile-source origin (Blanchard et al., 2014b). In contrast, the CTR PCA1 combustion-associated OC closely tracks OC_{bb} during summer 2013 (Fig. S13 and previous section), suggesting that the combustion component at CTR is more significantly associated with biomass burning than with motor-vehicle exhaust. Computed CTR OC_{bb} during this period is about equal to the sum of PCA1 combustion and crustal OC, but the reason is unclear. There are two episodes with high crustal OC at CTR during June 2013.

The mean crustal-associated OC concentrations vary from 0.1 to 0.3 μg m⁻³ at inland sites (Table 3). Coastal sites exhibit non-significant, minor, or inverse associations of OC with crustal elements (-0.1 to 0.1 μg m⁻³, Table 3). PCA1 and PCA2 crustal OC concentrations correlate (Fig. S14). Their mean absolute differences range from 0.1–0.2 μg m⁻³ (not tabled; see also Table 3); these differences are large in relative terms but not on a concentration basis. Crustal OC correlates with Si (Fig. S15). The small differences between coastal and inland sites suggest that crustal-associated OC does not derive from a single phenomenon (e.g., transport of Saharan dust), but may stem from ubiquitous and widely distributed activities that suspend crustal material. Potential sources could include soil-derived OC (e.g., agricultural activities, construction, or road dust), or biomass burning that lofts crustal material (e.g., through plowing material into debris piles). Road dust is known to include OC among its constituents (e.g., McDonald et al., 2013).

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The mean PCA1 seasonal-component OC (OC associated with higher O_3 , higher NH_3 , lower NO_x , or lower $PM_{2.5}$ NO_3) ranges from 0.4 to 0.6 $\mu g m^{-3}$ at all sites (e.g., 23 % of OC at CTR, 13 % at BHM and JST, 28 % at OLF), except at YRK where the average is 1.0 $\mu g m^{-3}$. The positive association with O_3 suggests that this OC component represents SOA formation from either or both anthropogenic and biogenic precursors. PCA2 seasonal OC correlates with PCA1 seasonal OC, except at JST. The JST PCA2 seasonal OC shows an inverse correlation (Fig. S16), indicating that the seasonal component represents higher winter (lower O_3 , higher NO_3) OC concentrations, possibly pointing to an influence from domestic wood combustion for heating. The positive association of OC with O_3 is quantified within the JST PCA2 SO_4 component. The mean absolute differences between PCA1 and PCA2 seasonal-component OC concentrations range from 0.2 to 0.5 $\mu g m^{-3}$.

All SEARCH sites show an association of OC with SO_4 ranging from 0.3 to 0.6 $\mu g m^{-3}$ on average for PCA1 and from 0.5 to 1.0 $\mu g m^{-3}$ on average for PCA2 (Table 3), with PCA2 SO_4 OC representing 15 to 44 % of the 1999-to-2013 mean OC concentrations (15 % at BHM; 22–25 % at CTR, GFP, JST, and OAK; 44 % at OLF). Mean PCA1 associations of OC with SO_4 were 14 % of OC at CTR, 15 % at BHM, 18 % at OLF, 10 % at JST, and 11 % at YRK. PCA1 and PCA2 SO_4 OC concentrations are correlated (Fig. S17) with mean absolute differences in PCA1 and PCA2 SO_4 -associated OC concentrations of 0.2 to 0.5 $\mu g m^{-3}$; PCA2 did not separate the seasonal and SO_4 components at PNS and YRK (Tables S8 and S9). The mass of OC associated with SO_4 averages 20 to 30 % of the SO_4 concentrations (Fig. S18), so that SO_4 -associated OC concentrations decline over time along with decreasing SO_4 concentrations. The presence and relative importance of SO_4 -associated OC is consistent with research indicating the role of SO_4 in transferring isoprene gas-phase reaction products to the condensed phase (e.g., Surratt et al., 2007; Xu et al., 2015). Seasonal variations, discussed below, also support biogenic origins of SO_4 -OC.

OC associated with SO_2 , indicative of fresh emissions, accounted for 0.07 to 0.37 $\mu g m^{-3}$ on average (12 % of OC at BHM, 2 % at JST, 7 % at GFP, 20 % at OAK,

and 10 % at OLF, none at other sites using PCA1) (Tables 3 and S12). PCA1 and PCA2 SO₂ OC concentrations are correlated (Fig. S19).

Coastal sites show an inverse association of OC with Na and Cl (sea salt) (Table S13) and a negative mean OC contribution from salt (Table 3). We interpret this result as evidence that baseline OC concentrations are lower at coastal sites when marine salt species concentrations are higher (i.e., anti-correlated), indicating that marine air masses are not an important source of OC. In contrast, mean salt-associated OC ranges from 0.14 to 0.15 $\mu\text{g m}^{-3}$ (BHM and YRK) to 0.64 $\mu\text{g m}^{-3}$ (JST); however, the species associations for the BHM and JST salt and “other” components suggest urban influences precluding identification of the salt component with marine air masses. Regardless of interpretation, OC associated with salt is a minor component of total OC concentrations.

Temporal variations of the 1999-to-2013 PCA2 results are described here primarily for CTR and JST, representing (as in Table 1) one rural and one urban location having extensive SEARCH data records. At JST, day-of-week variations are evident for the combustion-derived OC and for the OC associated with crustal species (Fig. S20), consistent with the occurrence of weekly activity cycles for driving, construction, and other anthropogenic emission sources. Day-of-week variations are not apparent for other OC associations at JST or for any OC factors at CTR. Seasonal and SO₄-associated OC exhibit pronounced monthly variations at both CTR and JST, with higher values of SO₄-associated OC and of CTR seasonal OC occurring during warmer months (Figs. S21 and S22). The patterns for CTR SO₄-associated OC (highest in July and August) and seasonal OC (higher in spring and autumn than in July) are not entirely independent.

Mean annual combustion-derived OC concentrations decline from 3.8 ± 0.2 to $1.4 \pm 0.1 \mu\text{g m}^{-3}$ between 1999 and 2013 at JST (Figs. 4, S23) and from 2.9 ± 0.4 to $0.7 \pm 0.1 \mu\text{g m}^{-3}$ between 2001 and 2013 at BHM (not shown). Declining combustion OC concentrations at the urban JST and BHM sites coincide with reductions of motor-vehicle emissions during this time period (discussed below), though these urban sites may also be affected by industrial emissions. BHM additionally benefits from a decline

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in OC associated with SO₂ from $0.4 \pm 0.04 \mu\text{g m}^{-3}$ in 2001 to $0.2 \pm 0.03 \mu\text{g m}^{-3}$ in 2013, probably as a reflection of declining emissions from industrial sources within Birmingham. In contrast, combustion-derived OC at CTR does not exhibit a statistically significant decline, equaling $1.5 \times 0.1 \mu\text{g m}^{-3}$ in 1999 and $1.3 \times 0.1 \mu\text{g m}^{-3}$ in 2013 (Figs. 4, S24). At CTR, downward OC trends are evident only for SO₄ and seasonal OC (mean decreases of $0.6 \mu\text{g m}^{-3}$ and $0.7 \mu\text{g m}^{-3}$, respectively) (Fig. S24). The OC associated with SO₄ at CTR exhibits declines during all seasons, with the weakest such change in winter (Fig. S25).

The trend results are consistent with the combined effects of (1) regional-scale reductions of ambient SO₄ and O₃ concentrations, (2) reductions of urban OC due to declining mobile-source OC and VOC emissions, and (3) likely predominance of biomass burning OC at CTR (Hidy et al., 2014). Carbon-isotope measurements from 2004 show that fossil carbon represented ~20% of CTR TC that year (Blanchard et al., 2011), indicating that mobile-source or other fossil-fuel emissions affect CTR to some extent. Enhanced hourly concentrations of EC, OC, and CO at CTR are associated with winds from the directions of Birmingham, Tuscaloosa, and Montgomery (Hidy et al., 2014). EC declined by $\sim 0.3 \mu\text{g m}^{-3}$ at CTR between 1999 and 2013 (Fig. 1), suggesting an influence of mobile-source emission reductions that is possibly too modest to detect using our PCA methods or is masked by annual variability in biomass-burning emissions. For comparison, mean EC concentrations at JST decrease by $\sim 1.4 \mu\text{g m}^{-3}$ (Fig. 1), and the overall mean EC at JST ($1.35 \mu\text{g m}^{-3}$) is ~4 times the overall mean EC at CTR ($0.35 \mu\text{g m}^{-3}$).

The trends in mean annual OC from each identified species association indicate that anthropogenic emission reductions directly decreased mean annual urban OC concentrations by $2.4 \mu\text{g m}^{-3}$ at JST and at BHM (and, by inference, other metropolitan areas in the Southeast), and indirectly decreased SO₄ and seasonal OC by ~ 1.1 to $1.3 \mu\text{g m}^{-3}$ throughout the southeastern US between 1999 and 2013 (Fig. 4). As of 2013, the overall mean annual combustion-derived OC is 1.3 to $1.4 \mu\text{g m}^{-3}$ at CTR and

JST, whereas the sum of the mean annual SO_4 and seasonal component OC is 0.4 to $0.8 \mu\text{g m}^{-3}$ at CTR and JST (Fig. 4).

The EPA PMF model (version 5; US EPA, 2014) was utilized to study the sensitivity of results to the choice of statistical method. PMF was applied to the same CTR and JST measurements used in PCA2. PMF requires estimates of measurement uncertainty, which may be species-specific or even sample-specific. Two sets of uncertainty estimates were employed: uniform (10 % of species concentrations), and species-specific (incorporating detection limits and species uncertainties of 5 to 25 % of measured concentrations). The PMF source profiles varied depending on the choice of uncertainty inputs, but yielded average apportionments that were qualitatively comparable to PCA2 (Fig. S26). The day-specific apportionments of crustal OC and SO_4 -associated OC were comparable among methods (Fig. S27). However, PMF and PCA split the seasonal and combustion components differently, in part because the PCA seasonal component generally comprised contrasts (e.g., positive O_3 , negative NO_3) whereas PMF forced positive solutions. PMF source profiles combined CO and O_3 , whereas PCA tended to separate O_3 from CO, leading to day-specific differences in the apportionment of OC to combustion and seasonal components (Fig. S27). In these applications, PCA predicted high OC concentrations better than PMF did (Fig. S28).

3.5 Emission sources and trends

In the southeastern US, anthropogenic emissions of EC, CO, and VOCs declined by 30 to 40 %, while emissions of NO_x and SO_2 decreased by ~ 60 and 75 %, respectively, between 1999 and 2013 (Hidy et al., 2014). Ambient concentrations of EC, NO_y , SO_2 , and SO_4 at SEARCH sites decreased in nearly 1 : 1 proportion to emission reductions, as did NMOC at JST (Hidy et al., 2014). SEARCH measurements show statistically-significant linear relations of ambient SO_2 and SO_4 concentrations with regional SO_2 emissions; the trend analyses show no SO_2 intercept but a statistically-significant SO_4 intercept of $\sim 1 \mu\text{g m}^{-3}$ interpreted as indicative of eastern North American background

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SO₄ (Hidy et al., 2014). Reductions in ambient NO_y and CO levels track the regional NO_x and CO emission reductions between 1999 and 2013 (Hidy et al., 2014). Current mobile-source CO emissions represent ~ 50 % of total CO emissions in the Southeast, and the 1999 to 2013 downward trend in total CO emissions is largely attributable to mobile-source emission reductions (Blanchard et al., 2013; Hidy et al., 2014). In contrast, NO_x emissions derive from multiple source types, including on-road and non-road mobile sources, electric generating units, and industrial sources, with downward trends in NO_x emissions stemming from multiple types of emission reductions. Observed ambient EC decreases at SEARCH sites track EC emissions, especially coinciding with an EC emission decline occurring between 2005 and 2013 that results from new EPA standards for diesel engines and fuels (effective in 2007 for on-road vehicles, in mid-2010 for non-road mobile sources, and in mid-2012 for rail and marine sources) (Hidy et al., 2014). Because mobile-sources account for over 50 % of EC emissions in the Southeast (Blanchard et al., 2013), ambient EC concentrations are expected to decrease with declining mobile-source EC emissions. In contrast, mobile-source OC emissions represent less than 10 % of OC emissions in the Southeast, with biomass burning accounting for ~ 75 % of OC emissions in emission inventories (Blanchard et al., 2013; Hidy et al., 2014), so mobile-source emission controls should not strongly affect ambient OC concentrations outside urban areas with dense vehicular traffic. The ambient concentrations of non-polar PM_{2.5} OC species, such as hopanes and steranes, decline substantially (> 50 %) at BHM and JST between 2006 and 2010, linking mobile-source emission reductions during those years with observed decreases in urban OC concentrations (Blanchard et al., 2014b). Our contrasting urban and rural PCA results are consistent with trends from the emission inventory and with differences between urban and rural emission densities.

4 Conclusions

Fifteen years of measurements of an extensive suite of gas and particle species at eight SEARCH sites offer important insights into the sources of OA and the effects of anthropogenic emission reductions on OA concentrations in the southeastern U.S. Five analytical methods indicate that a major component (~ 45 % on average, 1999 to 2013, all sites; intersite range 25 % to 63 %) of OA derives from combustion sources, including motor-vehicles and biomass burning, at all urban and rural sites and throughout the year. Reductions of emissions from combustion sources directly decreased overall mean annual OC concentrations by $2.4 \mu\text{g m}^{-3}$ at JST and BHM (and, by inference, throughout the Atlanta and Birmingham metropolitan areas) between 1999 and 2013. OA is identified partly with an SO_4 -OA relationship (~ 25 % of OC, on average), which is consistent with hypothesized isoprene oxidation pathways. OA is also partly identified with other seasonal atmospheric processes, including photochemical atmospheric reactions (~ 20 % of OC, on average). Reductions of anthropogenic emissions of SO_2 , NO_x , and VOC decreased SO_4 -associated OC and seasonal-component OC concentrations by ~ 1.1 – $1.3 \mu\text{g m}^{-3}$ between 1999 and 2013 throughout the SEARCH region, thereby indicating that reductions of anthropogenic emissions reduced SOA concentrations.

As of 2013, the SEARCH mean annual combustion-derived OC concentrations are 1.3 to $1.4 \mu\text{g m}^{-3}$ at CTR and JST (~ 60 % of total OC), while the mean annual OC concentrations associated with the SO_4 and seasonal components are 0.4 to $0.8 \mu\text{g m}^{-3}$ at CTR and JST (~ 35 % and ~ 22 %, respectively). Additional attention to OC from combustion emissions could yield further reductions of $\text{PM}_{2.5}$ OC concentrations, now averaging ~ $2.5 \mu\text{g m}^{-3}$ in the southeastern US. Since biomass burning is a major source of OC emissions in the southeastern US, minimizing the extent of these emissions could help improve regional air quality.

Additional work could improve quantitative assessments of source contributions. Carbon-isotope measurements of archived SEARCH samples are in process, and will

provide further insight into the observed OA trends. Future research could also help define the sensitivity of the SO₄-associated OC and seasonal OC to ongoing reductions of anthropogenic SO₂, NO_x, and VOC emissions. Current research by many investigators is better defining the role of naturally occurring VOCs, including isoprene. The SOAS and SAS campaigns of June – July 2013 help resolve uncertainties and ambiguities in OA chemistry specific to that time period. Extrapolation of the short-term results to seasonal and interannual time periods can be achieved through analyses of long-term EC and OC monitoring data.

Appendix A: Measurement conventions and issues

Carbonaceous aerosol is conventionally divided into EC and OC, operationally defined by measurement protocol, either by thermal differentiation or by light absorption (for clarity, protocols based on light absorption typically report data as light-absorbing carbon [LAC] or black carbon [BC], rather than as EC). EC is comprised of extended aromatic rings, and is characteristically refractory, insoluble, chemically inert, and light absorbing (Cappa, 2011). EC derives from combustion and is believed to be exclusively from primary emission sources, including motor vehicles, other transportation sources, industrial processes, and vegetation burning (Chow et al., 2010; Watson et al., 2011). OC is the carbonaceous component of OA and refers here to specific measurements, such as filter-based measurements made by thermal-optical reflectance (TOR) (Chow et al., 2005, 2007a, b). Combustion sources that emit EC also emit OC.

Organic compounds that are directly emitted in the condensed phase are typically identified as POA, whereas SOA commonly refers to organic material transferring from gases to the condensed phase through chemical transformation (Kanakidou et al., 2005). Gases of varying degrees of volatility may be oxidized and incorporated into the condensed phase (Robinson et al., 2007; Huffman et al., 2009). Atmospheric chemical reactions involving VOCs (Hallquist et al., 2009), especially including compounds of intermediate volatility (de Gouw et al., 2011), are known to generate oxygenated reaction

products on time scales of minutes to days. Secondary organic species may be associated with other secondary species, such as O₃ or SO₄, either through a common driver of photochemical oxidation processes or due to direct chemical relationships; this is an active area of research.

The initial aging of fresh, concentrated emissions begins with turbulent dilution seconds after hot exhaust effluent enters into the cooler atmosphere. Fine particle evolution then takes place more slowly over ~5–7 day lifetimes as particles are mixed and transported, and lost by deposition. These processes are often referred to as “aging” of a freshly emitted aerosol. The aging processes can be chemical in nature, or may involve physical processes as well, including absorption in clouds or precipitation followed by hydrometeor evaporation.

The exceptions to the definition of SOA as material transferring from gas to condensed phases through chemical transformation include: (1) volatile or semi-volatile material that condenses into aerosol without undergoing chemical transformation (Kanakidou et al., 2005), (2) gases absorbed into hydrometeors, leaving residual aerosol on evaporation, which might be understood as either POA or SOA depending on absence or occurrence of chemical transformation (Kanakidou et al., 2005), and (3) material emitted in the condensed phase that undergoes chemical transformation, possibly shifting multiple times between gas and aerosol, and that appears as oxidized compounds on analysis of aerosol samples (Donahue et al., 2009). The last exception is especially ambiguous: such material may be classified as POA in an emission inventory, but be identified as SOA according to measurements designated as “more oxygenated aerosol (OOA)” by aerosol mass spectrometry (AMS).

Dilution sampling is routinely used to characterize exhaust emissions because it yields estimates of EC and OC at temperatures characteristic of the ambient atmosphere, but further phase exchange of POA may be expected in the real world with ongoing dilution. Photochemical chamber studies demonstrate that organic aerosol from hot exhaust emissions (e.g., diesel engine exhaust) shifts from POA to SOA dominance typically within one or more hours of photo-oxidation (Presto et al., 2014). The com-

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parability of POA measurements from such studies to emission inventory estimates of mobile-source PM is poorly characterized. For modeling, a volatility basis set (VBS) provides more realistic diluted emission estimates by recognizing that POA spans a range of volatilities, and cannot be treated as entirely nonvolatile (Robinson et al., 2007; Donahue et al., 2009, 2012).

The mass concentrations of EC are approximately conserved from emission sources to receptor sites, whereas losses due to volatilization of certain PM_{2.5} organic compounds readily occur. OA concentrations may increase as SOA forms not only from POA vaporization, subsequent reactions and condensation, but also, perhaps predominantly, from atmospheric reactions of gas-phase precursors. Organic mass (OM), which includes not only carbon but also other atoms (e.g., oxygen and hydrogen) that are components of OA, is not conserved. There is no accepted measure of aging in atmospheric aerosols, but some workers have adopted OM / OC as an indicator. As POA ages, the ratio of oxygen-to-carbon typically increases, increasing the mass of OM. Aerosol aging can, therefore, increase both the OM / EC ratio and the OC / EC ratio (by definition, EC concentrations are not expected to increase with the formation of species during aging). A graphical depiction of various categorizations of OA is shown in the supplement (Fig. S1).

Linking ambient OA measurements to their emission sources is complicated by post-emission volatilization and chemical reactions involving exchanges of material between the gas and condensed phases on various time scales. Receptor-modeling methods have identified POA source types using measurements of conservative organic tracer species (Schauer et al., 1996), indicating that motor vehicles contribute ~2 to 4 μg m⁻³ to annual-average OC concentrations in Atlanta (e.g., Zheng et al. 2002, 2006). SEARCH thermal desorption-gas chromatograph mass spectrometer (TD-GC/MS) measurements suggest that 30 to 50 % of the observed 2006 to 2010 OC trend in Atlanta, Georgia and Birmingham, Alabama could be due to changes in mobile-source emissions (Blanchard et al., 2014). These trends need not be entirely from changes in POA emissions; diesel SOA, for example, is an important component

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of mobile-source OA (Presto et al., 2014), and is linked to EC and POA emissions. Aside from motor vehicle exhaust, biomass burning is a major source of EC and the largest source of OC emissions in the southeastern U.S. according to emission inventories, with little evidence for substantial trend between 1999 and 2013 (Hidy et al., 2014). Carbon-isotope (^{14}C) measurements at SEARCH sites indicate that on average 2 to $4\ \mu\text{g m}^{-3}$ of OC is modern in origin (rural and urban sites), with $\sim 40\%$ fossil in Atlanta and $\sim 60\%$ fossil in Birmingham during 2004 and 2005 (Blanchard et al., 2011). Together, the measurements suggest the presence of a large modern-carbon contribution added to downward-trending mobile-source contributions (Hidy et al., 2014).

Significant emissions of VOC from vegetation, including isoprene and terpenes, occur in the southeastern US and represent a major, and possibly a dominant, source of SOA (Goldstein et al., 2009). Although incompletely quantified, SOA derived from anthropogenic and biogenic VOCs has been estimated to be ~ 20 to 60% of the OA observed in the southeastern US, varying among samples and especially by season (Lim and Turpin, 2002; Zheng et al., 2006; Saylor et al., 2006; Blanchard et al., 2008). Field and laboratory work over the years has refined the chemical pathways, with evidence for both aqueous and gas-phase chemistry. Ground-level filter samples from southeastern sites have yielded expected tracers of SOA-formation chemistry from biogenic precursors (Gao et al., 2006; Surratt et al., 2007; Chan et al., 2010; Hatch et al., 2011a, b). The presence of naturally occurring VOCs, modulated by temperature and solar radiation, is expected to be roughly constant over a period of years, suggesting a near constant level of biogenic SOA. However, isoprene concentrations appear to have increased at Atlanta-area sites between 2002 and 2012 (Hidy et al., 2014); the reason for, and significance of, this trend for SOA trends in the Southeast is unclear. Interaction of biogenic and anthropogenic emissions potentially affect SOA formation (Weber et al., 2007; Shilling et al., 2012; Xu et al., 2015), so biogenic SOA trends could result from anthropogenic emission reductions.

**The Supplement related to this article is available online at
doi:10.5194/acpd-15-17051-2015-supplement.**

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Author contributions. C. L. Blanchard, G. M. Hidy, S. Shaw, K. Baumann, and E. S. Edgerton designed the study. E. S. Edgerton and K. Baumann operated the measurement program and prepared the data sets. C. L. Blanchard carried out the statistical analyses. C. L. Blanchard and G. M. Hidy wrote the manuscript with contributions from all co-authors.

- 5 *Acknowledgements.* The authors thank J. Jansen, E. Knipping, and the ARA staff for their contributions to this work. Funding for the SEARCH network has come from Southern Company and the Electric Power Research Institute. We are indebted to these sponsors for supporting this unique long-term measurement program.

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Table 1. Five-year seasonal mean EC and OC concentrations at CTR and JST with mean OC/EC^a.

Period ^b	CTR EC	CTR OC	CTR		JST EC	JST OC	JST OC/EC
			OC/EC				
1999–03W	0.490 × 0.025	2.615 × 0.154	5.34	1.725 × 0.068	4.801 × 0.153	2.78	
1999–03Sp	0.607 × 0.030	3.411 × 0.154	5.62	1.410 × 0.037	4.465 × 0.096	3.17	
1999–03Su	0.537 × 0.020	3.541 × 0.100	6.59	1.439 × 0.035	4.664 × 0.090	3.24	
1999–03A	0.684 × 0.026	3.814 × 0.145	5.58	1.808 × 0.060	5.264 × 0.150	2.91	
2004–08W	0.538 × 0.036	2.348 × 0.167	4.37	1.319 × 0.050	4.099 × 0.125	3.11	
2004–08Sp	0.556 × 0.029	3.269 × 0.199	5.88	1.173 × 0.034	4.283 × 0.135	3.65	
2004–08Su	0.528 × 0.030	3.267 × 0.151	6.19	1.292 × 0.032	4.114 × 0.077	3.19	
2004–08A	0.551 × 0.024	2.850 × 0.120	5.17	1.375 × 0.049	3.852 × 0.093	2.30	
2009–13W	0.402 × 0.027	2.066 × 0.136	5.14	0.859 × 0.060	2.828 × 0.155	3.29	
2009–13Sp	0.354 × 0.018	2.243 × 0.117	6.34	0.699 × 0.039	2.774 × 0.128	3.97	
2009–13Su	0.357 × 0.017	2.818 × 0.112	7.89	0.723 × 0.024	2.870 × 0.095	3.97	
2009–13A	0.437 × 0.024	2.579 × 0.105	6.31	0.926 × 0.042	2.934 × 0.110	3.05	

^a Uncertainties are one standard error of the means. OC/EC is computed as ratios of means. Propagation of errors yields one standard error of OC/EC ranging from 0.30 to 0.49 for CTR (mean 0.41) and 0.10 to 0.29 for JST (mean 0.16). ^b W = Dec, Jan, Feb; Sp = Mar, Apr, May; Su = Jun, Jul, Aug; A = Sep, Oct, Nov.

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Table 2. Species associated with each PCA factor (component). Component names are keyed to the species. Three species are listed in decreasing order of association for associations of 0.6 or greater (or -0.6 or smaller). Negative values indicate anti-correlation. CO^x and SO₂^x are 1-hour daily maximum CO and SO₂, respectively. O₃^x is 8-hour daily maximum O₃. PCA1, 2008 – 2013; PCA2, 1999 – 2013. N = number of days.

PCA	Site	N	Combustion	Crustal	Seasonal	SO ₂	SO ₄	Metals	Salt	Other
1	BHM	364	CO, NO _x , OC	Al, Si	NO ₃	SO ₂ ^x , SO ₂	NH ₄ , SO ₄	Zn, Cu, Fe	K	NO ₂
1	CTR	383	EC, OC, CO	Si, Fe, Al	NH ₃	SO ₂ , SO ₂ ^x	SO ₄ , NH ₄	Cu, Zn	Na, Cl, Mg	
1	GFP	100	CO, CO ^x , NO _x	Si, Fe, Al	O ₃ ^x , NH ₃	SO ₂ , SO ₂	NH ₄ , SO ₄		Cl, Na, Mg	Ca
1	JST	516	CO, NO _x , EC	Si, Al, Fe	O ₃ ^x , NH ₃ , -NO ₃	SO ₂ ^x , SO ₂	NH ₄ , SO ₄		K, Cl, Mg	Na
1	OAK	100	CO ^x , CO	Fe, Al, Si	NH ₃ , O ₃ ^x	SO ₂ ^x , SO ₂	SO ₄ , NH ₄	NO _x , Cu, NO ₂ , Zn	Na, Cl, Mg	
1	OLF	327	NO _x , CO, EC	Si, Al, Fe	NH ₃ , O ₃ ^x	SO ₂ , SO ₂ ^x	SO ₄ , NH ₄	Cu	Na, Mg, Cl	
1	PNS	44	CO, NO _x , EC	Si, Al, Fe	O ₃ ^x	SO ₂ , SO ₂ ^x	NH ₄ , SO ₄		Na, Mg, Cl	
1	YRK	426	NO _x , NO ₃ , CO	Si, Fe, Al	O ₃ ^x , OC, EC	SO ₂ ^x , SO ₂	SO ₄ , NH ₄	Cu	Na, Cl, Mg	Zn
2	BHM	1513	CO, CO ^x , NO _x	Al, Si	O ₃ , O ₃ ^x , -NO ₃	SO ₂ ^x , SO ₂	NH ₄ , SO ₄	Zn, Cu, Fe		
2	CTR	1258	OC, EC, CO ^x	Si, Fe, Al	O ₃ ^x , O ₃	SO ₂ , NO _x	SO ₄ , NH ₄	Cu		
2	GFP	376	CO ^x , CO, NO _x	Si, Fe, Al	O ₃ , O ₃ ^x	SO ₂ ^x , SO ₂	NH ₄ , SO ₄	Cu, Zn		
2	JST	2593	CO, CO ^x , NO _x	Si, Al, Fe	NO ₃ , -O ₃ ^x , -O ₃	SO ₂ ^x , SO ₂	NH ₄ , SO ₄ , O ₃	Cu		
2	OAK	707	CO ^x , CO, EC	Si, Fe, Al	O ₃ , O ₃ ^x	SO ₂ ^x , SO ₂	SO ₄ , NH ₄	Cu, Zn		
2	OLF	948	CO ^x , CO, NO _x	Si, Fe, Al	O ₃ , O ₃ ^x	SO ₂ ^x , SO ₂	NH ₄ , SO ₄ , NO ₂	Zn, Cu		
2	PNS	445	EC, CO, NO _x	Si, Al, Fe	O ₃ ^x , O ₃	SO ₂ ^x , SO ₂	SO ₄ , NH ₄	Cu		NO ₂
2	YRK	1435	CO ^x , NO _x , NO ₃	Si, Fe, Al	O ₃ ^x , SO ₄	SO ₂ ^x , SO ₂	SO ₄ , NH ₄ , O ₃ , NH ₄	Cu		Zn



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Table 3. Mean OC concentrations associated with components identified by PCA1 (2008–2013) and PCA2 (1999–2013). NS = not statistically significant, NA = not applicable (component not present in PCA). Units are μgm^{-3} . Standard errors of the means ranged from 0.003 to 0.09 μgm^{-3} (up to 0.25 μgm^{-3} for PNS PCA1).

PCA	Site	N	Combustion	Crustal	Seasonal	SO ₂	SO ₄	Metals	Salt	Other
1	BHM	364	1.36	0.09	0.40	0.35	0.45	0.15	0.14	0.10
1	CTR	383	1.28	0.26	0.56	NS	0.33	NS	NS	NA
1	GFP	100	0.95	NS	0.45	0.15	0.25	NS	-0.41	0.62
1	JST	516	1.09	0.16	0.49	0.07	0.27	NA	0.64	0.11
1	OAK	100	0.40	NS	0.50	0.37	0.53	0.32	-0.27	NA
1	OLF	327	0.74	-0.08 ^a	0.52	0.16	0.27	NS	-0.09 ^a	NA
1	PNS	44	1.95	NS	0.33	NS	0.56	NA	-0.63	NA
1	YRK	426	0.14	0.14	1.09	NS	0.26	0.16	0.15	0.47
2	BHM	1513	1.60	0.19	0.47	0.38	0.57	0.48	NA	NA
2	CTR	1258	1.50	0.12	0.69	NS	0.66	NS	NA	NA
2	GFP	376	0.72	0.14	0.37	0.21	0.50	0.25	NA	NA
2	JST	2593	2.58	0.32	0.06 ^b	NS	1.01 ^b	0.13	NA	NA
2	OAK	707	1.50	NS	0.47	NS	0.59	NS	NA	NA
2	OLF	948	0.81	-0.06 ^a	0.25	0.09	1.02	0.20	NA	NA
2	PNS	445	1.55	NS	0.45 ^c	0.17	NA	NS	NA	0.36
2	YRK	1435	0.76	0.20	1.40 ^c	0.05	NA	0.39	NA	0.29

^a OLF PCA1 and PCA2 crustal and PCA1 salt OC mean concentrations are negative due to inverse associations of OC with crustal and salt components at OLF (Tables S7 and S12). ^b JST PCA2 seasonal OC is associated with NO₃; JST PCA2 SO₄ component includes OC associated with O₃ (Table 2). ^c PNS and YRK PCA2 seasonal components include OC associated with SO₄ (Table 2).

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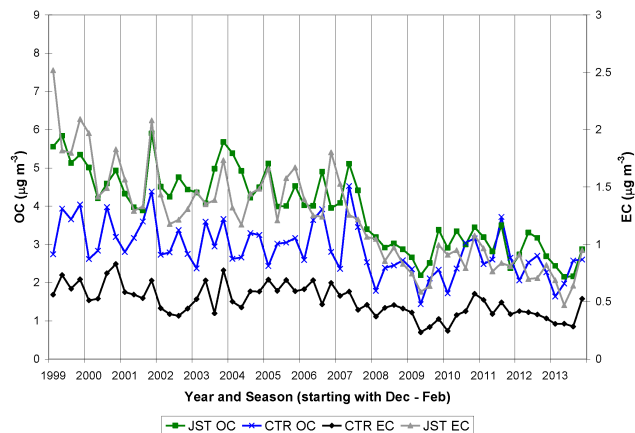


Figure 1. Seasonal mean EC and OC concentrations at CTR and JST. All correlations among the four time series are statistically significant ($p < 0.05$): CTR EC and OC, $r = 0.68$ (95 % CI 0.52–0.80); JST EC and OC, $r = 0.87$ (95 % CI 0.79–0.92); CTR EC and JST EC, $r = 0.76$ (95 % CI 0.62–0.85); CTR OC and JST OC, $r = 0.68$ (95 % CI 0.51–0.79).

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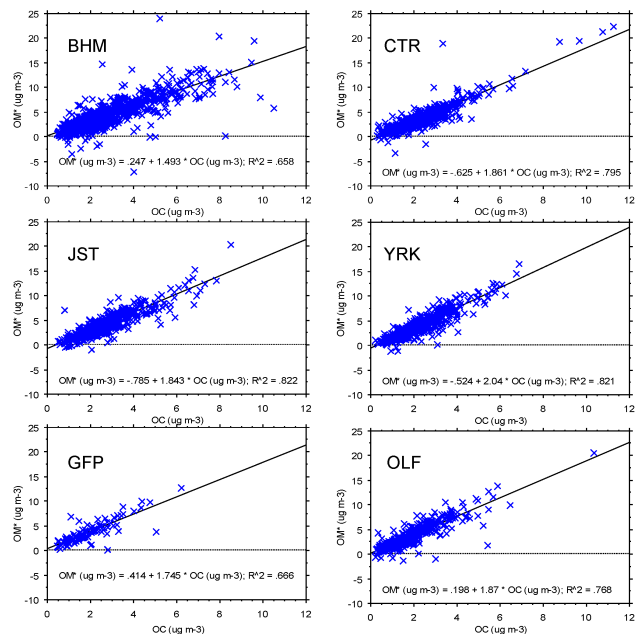


Figure 2. OM* vs. OC at SEARCH sites, 2009–2013. OM* is the sum of measured OC and the computed difference of PM_{2.5} mass minus the sum of measured species concentrations. OM* is an upper bound for OM (see text).

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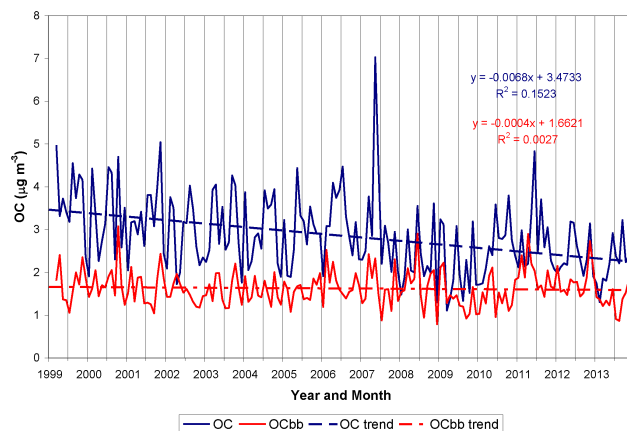


Figure 3. Monthly-average measured OC and computed biomass-burning OCbb at CTR.

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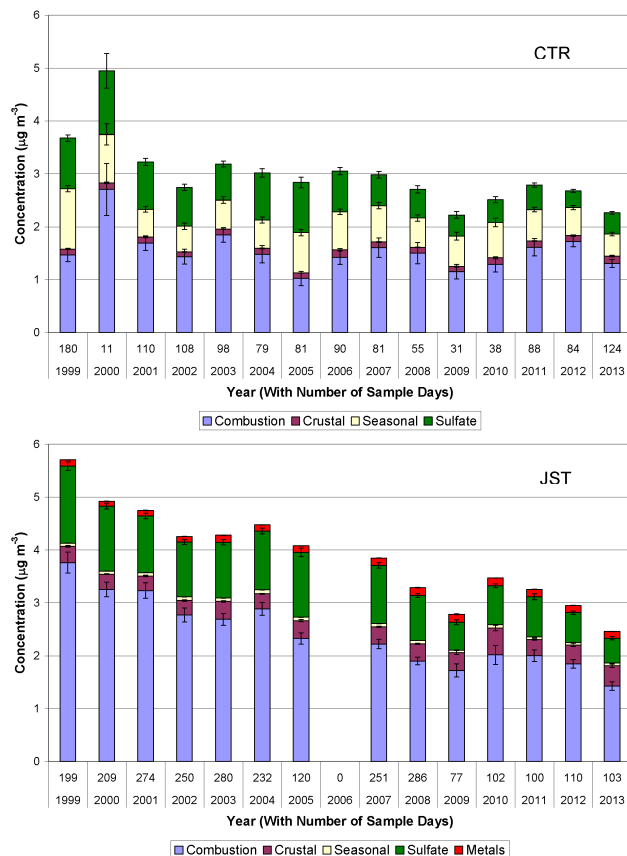


Figure 4. Trends in source contributions to OC at CTR and JST determined from PCA2.

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