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Ambient sampling was conducted in Riverside, California during the 2005 Study of Organic Aerosols in Riverside to characterize the composition and sources of organic aerosol using a variety of state-of-the-art instrumentation and source apportionment techniques. The secondary organic aerosol (SOA) mass is estimated by elemental carbon and carbon monoxide tracer methods, water soluble organic carbon content, chemical mass balance of organic molecular markers, and positive matrix factorization of high-resolution aerosol mass spectrometer data. Estimates obtained from each of these methods indicate that the organic fraction in ambient aerosol is overwhelmingly secondary in nature during a period of several weeks with moderate ozone concentrations and that SOA is the single largest component of PM2.5 aerosol in Riverside. Average SOA/OA contributions of 70-90% were observed during midday periods, whereas minimum SOA contributions of ~45% were observed during peak morning traffic periods.

These results are contrary to previous estimates of SOA throughout the Los Angeles Basin which reported that, other than during severe photochemical smog episodes, SOA was lower than primary OA. Possible reasons for these differences are discussed.

Introduction

Aerosols are of interest due to their roles in several atmospheric processes including radiative forcing, heterogeneous reactions, and regional visibility degradation, as well as their negative impact on human health. The impact of particles on these and other atmospheric processes are dependent on particle size, the majority being strongly correlated with fine particles (PM2.5 or PM10), and many also depend on chemical composition. In particular, the organic fraction ("organic aerosols"), OA, which typically constitutes a significant fraction of fine particle mass (f), is a poorly characterized aggregate of thousands of individual compounds either emitted directly in the particle phase ("primary" OA, P OA) or formed in the atmosphere from gas-to-particle conversion ("secondary" OA, SOA). Most of these compounds are not amenable to detection by currently available speciation techniques, which can identify only a small fraction of aerosol organics at the molecular level (2). The lack of molecular characterization of a large fraction of the mass is particularly important for SOA.

During the Study of Organic Aerosols in Riverside (SOAR-1), a variety of state-of-the-art instrumentation was assembled at the Air Pollution Research Center on the campus of the University of California-Riverside from July 18 through August 14, 2005 to investigate the chemical composition of ambient OA, representing, to our knowledge, the most complete set of OA field instruments at one location to date. Riverside is located ~80 km inland of the urban center of Los Angeles (LA). Due to its proximity to LA and the meteorology, topography, and intense emissions characteristic of the LA basin, Riverside and the surrounding areas are characterized by poor air quality, consistently rating as the worst in the United States for 24 h average fine particle concentrations both on short-term and annual bases (3).

Here, we estimate the fraction of SOA in fine particles using five methods including the elemental carbon (EC) and carbon monoxide (CO) tracer methods, water soluble organic carbon (WSOC) content, chemical mass balance (CMB) source apportionment of organic molecular markers (MMs), and positive matrix factorization (PMF) of high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) organic mass spectra. Results obtained from each of these methods indicate that SOA contributes the majority of organic mass during a period that cannot be described as a “photochemical episode”. Estimates obtained from each of these methods are higher than previous SOA estimates in locations throughout the LA Basin including Riverside and surrounding areas.

Experimental Section

General. All measurements were conducted in Riverside, California at the Air Pollution Research Center on the campus of the University of California-Riverside (33°58'18.40"N, 117°19'21.41"W). During SOAR-1 (July 18 through August 14, 2005), the Riverside area was characterized by moderate...
ozone concentrations (average peak daily ozone concentration in Riverside = 86 ppb; range 40–141 ppb). All times refer to Pacific Standard Time.

**Sunset Semicontinuous EC/OC Measurements.** PM$_{2.5}$ organic carbon (OC) and elemental carbon (EC) concentrations were measured hourly using both standard (4) and dual-open (5) Sunset semicontinuous carbon monitors (Sunset Laboratories, Tigard, OR).

**Filter-Based Measurements.** Filter samples were collected for source apportionment by CMIB of solvent-extractable organic MMs (2). Details regarding particle collection, filter extraction, chemical analysis, and CMIB procedures are similar to those presented in Stone et al. (6) with a few exceptions noted below.

Filter samples for CMIB were collected daily according to the following schedule: 0400–0900, 0900–1400, 1400–1900, 1900–0400. Weckday samples collected on 7/26–7/28 and 8/2–8/3 and weekend samples collected on 7/30 and 8/6/8/7 were composited based on this schedule. For this analysis, weekday and weekend CMIB source apportionment results were further composited to yield results irrespective of day of week. These samples were not disturbed. As a result, filter OC concentrations are likely inflated through adsorption of semivolatile gas-phase species. To obtain a conservative estimate of "other" OC, the results of CMIB source apportionment were used in conjunction with coinciding standard Sunset OC concentrations (i.e., "other" OC = OC$_{\text{total}}$ – primary OC (POC)). If we refer to instead use the CMIB filter OC concentrations for this estimate, other OC increases by ~7% likely as a result of these adsorption artifacts.

**Particle-Into-Liquid-Sampler (PILS) Organic Measurements.** Water soluble OC (WSOC) and total OC were measured by a PILS-WSOC and PILS-OC, respectively (7). WSOC was measured continuously every minute from 7/18–7/27 and 7/30–8/15. The PILS-OC measured total OC continuously from 7/27–7/30 at the same rate. Further details are provided elsewhere (7).

**HR-ToF-AMS Measurements.** Nonrefractory PM$_{2.5}$ aerosols were measured by an Aerodyne HR-ToF-AMS from 7/14–8/16. Details regarding the HR-ToF-AMS are provided elsewhere (8).

**Data Analysis.** Conversion of carbon mass concentrations. Measured concentrations of OC, WSOC, and water insoluble organic carbon (WIOC) were converted to organic mass (OM) concentrations prior to calculating SOA factors. PM$_{2.5}$ and WIOC were converted using a factor of 1.2 mg OM/mg DOC, whereas secondary OC (SOC) and WSOC were converted to secondary organic mass (SOM) using a factor of 1.8 mg PM/mg OC (9). In Supporting Information 2, we see the sensitivity of the calculated SOA/OC ratios to the applied SOM/SOC conversion factor using additional conversion factors of 1.6 and 2.0 mg OM/mg OC. As this table shows, SOA/OC ratios vary only a few percent when these alternate conversion factors are used.

**HR-ToF-AMS.** Unit-resolution (UMR) ToF-AMS data were analyzed using established procedures for analysis of AMS data via custom analysis software (Squirrel) (10). An AMS collection efficiency (CE) of 0.5 was used for all species, typical of aerosols measured in urban locations with similar composition (11, 12) and verified with intercomparisons with other collocated instruments. The AMS response may be slightly biased toward OA (13, 14), and these SOA/OC estimates should be considered lower limits. High-resolution (HR) ToF-AMS data were analyzed using a custom data analysis module (Pika) developed in our group (9) in Igor (Wavemetrics, Lake Oswego, OR).

**PMF Analysis.** AMS organic mass spectra were analyzed by PMF to identify the major components of PM$_{1}$ OA. PMF is a variant of factor analysis with nonnegative constraints on factor elements and has been described in detail elsewhere (15). Its application to AMS spectra has been investigated in detail recently (16, 17). HR (m/z 2–100) and UMR (m/z > 100) organic mass spectra were combined for PMF analysis. PMF2 (v4.2) was run in robust mode via a custom panel in Igor (16).

**Lack of Important Biomass Burning (BB) Impact.** Although the LA area is at times impacted by smoke from large wildfires that can increase PM$_{2.5}$ levels in the basin by 300–400% (18), fires throughout Southern California during SOAR-1 were small in size, short in duration, and not in the vicinity of the sampling location, according to the MODIS Active Fire Detections database (https://maps.geog.ucdavis.edu/maps/maps.aspx). This is supported by measurements by a collocated aerosol time-of-flight mass spectrometer that did not observe significant PM contributions from biomass burning/biofuel combustion sources (19). Moreover, m/z 60 (a BB tracer) in the AMS during the study (see SI Figure S1) as well as measured concentrations of the MM levoglucosan were low during SOAR-1 (see below).

**Results and Discussion**

**EC-Tracer Method.** This method assumes that EC results predominantly from combustion processes and can be used as a tracer for primary aerosol (20). POC is estimated by its proportionality with EC as

\[
POC = (100 \times EC) \times EC_{\text{primary}} - \text{NCPOC}
\]

where NCPOC is noncombustion POC, and SOC is determined by difference:

\[
SOC = OC - POC
\]

The simple appearance of this method is belied by significant complexities associated with determining the coefficients (OC/EC)$_{\text{primary}}$ and NCPOC/EC$_{\text{primary}}$, which are traditionally obtained by linear regression analysis of EC and OC data during periods that are deemed "not impacted by SOC." NCPOC contributions (that are not correlated with EC due to similar source locations and/or activity patterns) are small relative to errors associated with the EC-tracer method (21). Therefore, they are lumped with SOC in the following EC-tracer calculations.

For ambient sampling, the correct (OC/EC)$_{\text{primary}}$ should be $(OC/EC)$ for all primary sources. Therefore, OC and EC data used in the regression analysis must be carefully selected to limit contributions from SOC, which would incorrectly inflate both (OC/EC)$_{\text{primary}}$ and POC. For areas like the LA basin this is not trivial. Strader et al. (22) used regression analysis of data collected in California's San Joaquin Valley and found that isolating a single period that was not impacted by photochemistry was "a dangerous proposition" due to the long residence times of PM$_{1}$. Zhang et al. (23) showed that in Pittsburgh this method of estimating (OC/EC)$_{\text{primary}}$ led to an overestimation of SOA since SOA was always a significant fraction of the OA. This technique typically neglects variations in (OC/EC)$_{\text{primary}}$ throughout the day that can appear due to, e.g., variations in diesel and gasoline vehicle fractions, which may lead to some errors in the estimated diurnal profiles (24), as discussed below.

To explore the range of SOA contributions during SOAR-1, EC-tracer calculations were conducted using a range of (OC/EC)$_{\text{primary}}$ values estimated both using available emissions inventory data and from the literature. (OC/EC)$_{\text{primary}}$ was used to obtain SOA/OC estimates by the EC-tracer method, in addition to details regarding their determination, are presented in SI Table S1. (OC/EC)$_{\text{primary}}$ estimates were calculated using available vehicle emissions inventories for the South Coast Air Basin and emission factors determined in several recent tunnel studies in California. Due to the high concentration of primary emissions observed in tunnel studies which favor partitioning of semivolatile OC to the particle...