

**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

**The 2005 Study of Organic Aerosols at  
Riverside (SOAR-1): instrumental  
intercomparisons and fine particle  
composition**

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Received: 2 November 2010 – Accepted: 29 December 2010 – Published: 23 February 2011

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

## Abstract

Multiple state-of-the-art instruments sampled ambient aerosol in Riverside, California during the 2005 Study of Organic Aerosols at Riverside (SOAR) to investigate sources and chemical composition of fine particles ( $PM_f$ ) in the inland region of Southern California. This paper briefly summarizes the spatial, meteorological and gas-phase conditions during SOAR-1 (15 July–15 August) and provides detailed intercomparisons of complementary measurements and average  $PM_f$  composition during this period. Daily meteorology and gas-phase species concentrations were highly repetitive with meteorological and gas-phase species concentrations displaying clear diurnal cycles and weekday/weekend contrast, with organic aerosol (OA) being the single largest component contributing approximately one-third of  $PM_f$  mass. In contrast with historical characterizations of OA in the region, several independent source apportionment efforts attributed the vast majority ( $\sim 80\%$ ) of OA mass during SOAR-1 to secondary organic aerosol (SOA). Given the collocation of complementary aerosol measurements combined with a dominance of SOA during SOAR-1, this paper presents new results on intercomparisons among several complementary measurements and on  $PM_f$  composition during this period. Total non-refractory submicron ( $NR-PM_1$ ) measurements from a high-resolution aerosol mass spectrometer (HR-AMS) are compared with measurements by tapered element oscillating microbalances (TEOM) including a filter dynamics measurement system ( $TEOM_{FDMS}$ ).  $NR-PM_1$  is highly correlated with  $PM_{2.5}$   $TEOM_{FDMS}$  measurements and accounts for the bulk of  $PM_{2.5}$  mass with the remainder contributed primarily by refractory material. In contrast, measurements from a heated TEOM show substantial losses of semi-volatile material, including ammonium nitrate and semi-volatile organic material. Speciated HR-AMS measurements are also consistent and highly correlated with several complementary measurements, including those of a collocated compact AMS (C-AMS). Finally, elemental analysis (EA) of HR-AMS OA spectra allows direct comparison of HR-AMS organic carbon (OC) with measurements from two collocated Sunset thermal-optical semi-continuous monitors,

ACPD

11, 6301–6362, 2011

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and investigation of the elemental composition of OA in Riverside. While HR-AMS and base OC measurements from both Sunset instruments are similar within the combined uncertainties, a correction intended to account for the loss of semivolatile OC from the Sunset yields OC measurements ~30% higher than either HR-AMS or base Sunset measurements. Oxygen is the main heteroatom of ambient OA during SOAR-1 with a minimum atomic O/C of 0.28 during the morning rush hour and maximum of 0.42 during the afternoon. H/C is broadly anti-correlated with O/C, while N/C and S/C (excluding organonitrate (ON) and organosulfate (OS) functionalities) are far lower than O/C at about 0.015 and ~0.001, respectively. O/C, N/C, and S/C increase by 21%, a factor of 2, and a factor of 30, respectively, while H/C changes little when ON and OS estimates are included. This implies that ON account for ~1/2 of the organic nitrogen while OS dominate organic sulfur at this location. Accounting for the estimated ON and OS also improves the agreement between anions and cations measured by HR-AMS by ~8%, while amines have a very small impact (1%) on this balance.

## 1 Introduction

Aerosols are of interest due to their widespread impact on atmospheric processes including radiative forcing, heterogeneous reactions, visibility reduction on both local and regional scales, and their role in increased human morbidity and mortality. The role of aerosols in each of these processes is influenced both by particle size and chemical composition with many of the effects being strongly correlated with fine particles ( $PM_f$ , typically defined as particles having aerodynamic diameters,  $d_a$ ,  $<2.5\ \mu m$  ( $PM_{2.5}$ ) or  $<1\ \mu m$  ( $PM_1$ )). The effect of chemical composition on these processes is not well understood due to both the complexity of  $PM_f$  and its rapid variation in space and time. Generally,  $PM_f$  is comprised of mixtures of organic species (collectively “organic aerosols”, OA), “black” or “elemental” carbon (BC or EC), and inorganic species (both soluble ionic and crustal). Due to the small number of species involved and relatively simple chemistry, the inorganic fraction of ambient aerosols is reasonably well

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



characterized. The composition of OA, however, remains poorly characterized despite the fact that OA contributes about half of  $PM_f$  mass on a global basis (Zhang et al., 2007a).

OA is comprised of thousands of individual compounds either emitted directly into the atmosphere (“primary” OA, POA) or formed in the atmosphere as a result of gas-to-particle conversion (“secondary” OA, SOA). The distinction between POA and SOA and the apportionment of each to various sources has profound implications for regulatory and control strategies that seek to mitigate the negative consequences of  $PM_f$  (de Gouw and Jimenez, 2009). A variety of analytical techniques have been used to characterize the composition of bulk ambient OA samples including recent advancements in OA instrumentation that have enabled new approaches to its characterization (Hallquist et al., 2009). Historically, these efforts have largely relied on speciated measurement techniques such as gas chromatography/mass spectrometry (GC/MS). Although a distinct set of organic molecular marker (OMM) species have been identified from GC/MS analyses which have been used to apportion POA among various sources in a bottom-up chemical mass balance (CMB-OMM) approach (e.g., Schauer et al., 1996; Schauer et al., 2002), OMM representing SOA have only very recently been isolated and applied in CMB-OMM models (Kleindienst et al., 2007; Stone et al., 2009b) due to difficulties inherent in their identification and measurement. Measurements from an in-situ thermal desorption aerosol gas chromatograph (TAG), first deployed during SOAR, also show promise for further characterizing OA composition (Williams et al., 2010a).

Complementing speciated analysis techniques, instruments such as the aerosol mass spectrometer (AMS) (Jayne et al., 2000; Canagaratna et al., 2007) have been developed to monitor the bulk chemical composition of OA in real time. The AMS reports non-refractory submicron ( $NR-PM_1$ ) particle mass in good agreement with collocated instruments at a variety of locations (Canagaratna et al., 2007 and references therein). Factor analysis of AMS OA spectra has allowed for the quantification of several characteristic OA components (Zhang et al., 2005a; Lanz et al., 2007; Ulbrich et al., 2009) most of which are consistent at many locations throughout the world (Zhang

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



et al., 2007a; Jimenez et al., 2009; Ng et al., 2010). Despite recent advancements in aerosol instrumentation, however, large uncertainties remain regarding the various sources, formation mechanisms, and composition of ambient PM<sub>f</sub> and especially OA.

## 2 Overview of the Study of Organic Aerosols at Riverside (SOAR)

Riverside is located 82 km east of the urban center of Los Angeles at the eastern end of the South Coast Air Basin (SoCAB), which is bordered on the north and east by tall mountains ranging in height from 1 to <3 km that inhibit the movement of air masses out of the basin. Additionally, during the summer the region is characterized by a persistent on-shore (westerly) air flow at the surface that transports air masses inland from the coast and strong temperature inversions that limit vertical dilution of pollutants. Due to the topography and meteorological conditions of the SoCAB, Riverside and the surrounding communities routinely experience very high PM<sub>f</sub> concentrations, which consistently rank among the highest in the United States on both short-term and annual bases (American Lung Association, 2010).

The majority of non-OA PM<sub>f</sub> mass in the SoCAB is contributed by ammonium, nitrate, and sulfate. Among inorganic anions, particulate nitrate concentrations are particularly enhanced in the vicinity of Riverside (Chow et al., 1994; Kim and Hopke, 2007) by high concentrations of ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>). The enhancement of particulate nitrate is largely driven by gas-to-particle conversion of nitric acid, which is in turn driven by the availability of gaseous ammonia (NH<sub>3</sub>) in interior regions of the basin (Neuman et al., 2003). Although sources of NH<sub>3</sub> in the SoCAB include agricultural activities and emissions from light-duty vehicles and households, the largest emissions sources are dairy operations. Although a substantial number of dairy operations have been relocated out of the basin, NH<sub>3</sub> emissions remain high and were estimated to be nearly 18 t/day in 2004 (Lester and Woods, 2004). Inorganic sulfate concentrations in contrast are driven primarily by the influx of marine background aerosol and primary emissions of SO<sub>2</sub> from an array of stationary and mobile sources. Among the most significant

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



mobile sources are commercial shipping operations centered around the ports of Los Angeles and Long Beach which contribute >50% of total basin-wide SO<sub>2</sub> emissions (Eckerle et al., 2007; Huang et al., 2010) and are projected to have a substantially increased impact on future air quality within the basin (Vutukuru and Dabdub, 2008).

5 Unlike nitrate, sulfate concentrations are more uniform across most locations throughout the SoCAB (Chow et al., 1994; Kim and Hopke, 2007).

OA contributes the remainder, and often the majority, of PM<sub>f</sub> mass in the inland regions of the SoCAB including Riverside (Chow et al., 1994; Kim et al., 2000; Christoforou et al., 2000). Despite its importance, the sources and composition of OA in the  
10 SoCAB are not fully characterized primarily due to instrumental limitations in chemically speciating those compounds that contribute the bulk of OA mass. However, several methods have been used historically to apportion OA among various regional sources in the SoCAB including the use of selective solvent-extraction-carbon analysis and high resolution mass spectrometry (Appel et al., 1979), regional modeling (Pandis et al., 1992), EC-tracer analysis (Gray et al., 1986; Hildemann et al., 1993), and CMB-  
15 OMM (Schauer et al., 1996). These earlier investigations consistently concluded that outside of short-term photochemical smog episodes, characterized by sustained, very elevated ozone concentrations (Turpin and Huntzicker, 1995; Schauer et al., 2002), the majority of OA is directly emitted POA.

20 Based on characteristically high particle concentrations in the region, SOAR was organized to advance our understanding of both the sources and composition of PM<sub>f</sub> and OA by deploying in the field for the first time several new instruments and source apportionment techniques together with more established measurements and apportionment methods. SOAR-1 (15 July–15 August) represents one of the most comprehensive efforts to date to characterize ambient OA composition and sources (Docherty and Jimenez, 2005). Table S1 presents a list of participating groups and instrumentation deployed during SOAR and resulting publications to date. Many of the instruments that sampled during SOAR-1 are now widely used in aerosol research and air quality  
25 monitoring applications and their respective measurements are commonly used in

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## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



source apportionment efforts.

For multiple instruments, including the Aerodyne high-resolution aerosol mass spectrometer (HR-AMS), SOAR-1 was the first field deployment. As described in DeCarlo et al. (2006), the HR-AMS enhances the performance and information content of previous AMS versions and has been adopted very rapidly by many research groups for the characterization of aerosol chemical composition. Of the many benefits of the HR-AMS are an enhanced mass resolution ( $\Delta m/m \sim 4000\text{--}5000$ ), which allows for elemental analysis (EA, Aiken et al., 2008) of OA spectra, as well as a high time resolution (Kimmel et al., 2010). In addition to the HR-AMS, other novel instruments field-deployed for the first time during SOAR-1 included the TAG (Williams et al., 2006), the aircraft aerosol time-of-flight mass spectrometer (A-ATOFMS) (Pratt et al., 2009a), a dual oven Sunset monitor (Grover et al., 2009), a particle-into-liquid sampler for total organic carbon (PILS-OC) (Peltier et al., 2007), and a water-based nano-particle counter (Iida et al., 2008). SOAR-1 was also the first use of the fast-stepping thermodesorber (TD) (Huffman et al., 2008) which was interfaced to both the HR-AMS (Huffman et al., 2009) and the A-ATOFMS (Denkenberger et al., 2007) to investigate chemically-resolved volatility of ambient aerosols.

Following the study, various source apportionment methods were applied to SOAR-1 measurements in a number of independent analyses the results of which contrasted sharply with earlier studies in that each consistently indicated that the vast majority of OA mass during SOAR-1 was secondary in nature. For example, Eatough et al. (2008) applied positive matrix factorization (PMF) to aggregate 1-h semi-continuous measurements from a suite of instruments both with and without data from the HR-AMS and A-ATOFMS. The more definitive analysis was done using both the speciated measurements and the HR-AMS and A-ATOFMS data where a total of 16 factors were identified. This latter analysis attributed over three-quarters of total  $PM_f$  to secondary processes, with about equal amounts due to local production vs. downwind transport from Los Angeles while 62% of OA was attributed to SOA. Similarly, PMF analysis of HR-AMS OA mass spectra during SOAR-1 (Docherty et al., 2008b, 2010; Huffman et

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





al., 2009), similarly found that the composition of OA in Riverside is dominated by SOA with smaller contributions from POA and a number of locally emitted components including an amine-containing component (Docherty et al., 2010). Williams et al. (2010a) also applied PMF to hourly TAG measurements obtained during SOAR. Four SOA components were identified from this analysis that were largely attributed to the oxidation of anthropogenic precursor gases and, when combined, contributed the bulk (88%) of OA mass consistent with the dominance of SOA during this period. The most comprehensive source apportionment analysis was performed by Docherty et al. (2008b) who applied several independent source apportionment techniques (EC-tracer, CO-tracer, CMB-OMM, water soluble organic carbon (WSOC), and PMF of AMS OA spectra) to SOAR-1 OA measurements. The five different methods consistently indicated that, on average, the bulk of OA mass (average 78%) was secondary in nature despite the absence of “photochemical smog episode” conditions.

Other results of SOAR-1 sampling, when compared with similar sampling in other regions of the country, suggest that the origins and predominance of SOA in the inland areas of the SoCAB may be unique to the region. Stone et al. (2009b) applied CMB-OMM to filter samples collected in Riverside during SOAR-1 and a number of locations in the midwestern United States using both traditional POA tracers as well as a number of SOA tracers identified from chamber photooxidation of isoprene,  $\alpha$ -pinene,  $\beta$ -caryophyllene, and toluene. In Riverside, only one-quarter of OA mass could be attributed to POA sources while a similar amount could be attributed to *known* secondary sources. The remaining 50% of the measured OA (significantly higher than the unattributed fraction from Midwest locations) could neither be attributed to primary nor secondary sources. Although this fraction was expected to be secondary in nature based on its chemical characteristics, it suggests the presence of yet unknown sources and mechanisms of SOA formation in the SoCAB.

Although a fraction of SOA is non water-soluble (Weber et al., 2007), SOA generally dominates WSOC in the absence of biomass burning events, as was the case during SOAR-1 (Docherty et al., 2008b), due to its higher degree of oxidation and in-

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



creased polarity. Consistent with a dominance of SOA, the particle-into-liquid water soluble organic carbon (PILS-WSOC) measurements of Peltier et al. (2007) indicated that the majority ( $0.56 \pm 0.05$ ) of total OC sampled during SOAR-1 was water soluble. The composition of the water soluble fraction of SOAR-1 OA was investigated by Reemtsma et al. (2006) using offline electrospray ionization ultrahigh resolution mass spectrometry and by Stone et al. (2009a) using liquid chromatography tandem mass spectrometry. Results of these analyses indicate the presence of unique compounds attributed to SOA production. For example, Reemtsma et al. observed and reported for the first time several classes of compounds including fulvic acids and high molecular weight sulfur-, nitrogen-, and sulfur-and-nitrogen-containing compounds, all with a high degree of structural similarity. Such analogues have not previously been identified from terrestrial humic-like substances (HULIS) and were attributed to SOA formation. Although previous investigations have identified organosulfates (OS) from chamber reactions (Surratt et al., 2007) their detection in ambient OA has been limited to rural areas (Surratt et al., 2008; Lukacs et al., 2009) and their contribution to urban OA is largely unknown. Stone et al. (2009a) also investigated the contribution of functional groups to the water soluble fraction of OA in a variety of locations including Riverside to better understand the formation of HULIS in atmospheric aerosols. While results of this analysis suggest that motor vehicles, biomass burning, and SOA, each may make significant contributions to the HULIS formation, OS in the range  $m/z$  200–600 had a non-negligible contribution (0.6–3.2% of total measured carbon) in Riverside indicating a potential role for oligomers in the formation and growth of OA within the SoCAB.

Although oligomers have previously been identified from OA formed in chamber reactions (Tolocka et al., 2004), they have not been widely identified in ambient aerosols. Denkenberger et al. (2007), however, observed signature oligomeric spectra during SOAR-1 using the A-ATOFMS. Oligomer concentrations were observed to be highest in small particles ( $d_{va} = 140\text{--}200\text{ nm}$ ) and occurred coincident with oxidized OA, amines, nitrate, and sulfate ion markers pointing to the role of atmospheric aging in their formation. Although oligomer signatures were found in both unheated and heated

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



aerosols when the A-ATOFMS was interfaced with the TD, the relative intensity of oligomeric spectra increased at high TD temperatures ( $>150^{\circ}\text{C}$ ) suggesting that either the oligomeric fraction of ambient OA has a relatively low volatility, or that oligomer formation is accelerated in the TD at high temperatures due to the removal of semi-volatile species and the increase of acidity (Denkenberger et al., 2007). Oligomeric spectra were not directly observed by the TD-AMS. However, the measurements of Huffman et al. (2009) are consistent with their possible presence in aerosol sampled during SOAR-1. In general, the volatility of the main NR-PM<sub>1</sub> species measured in Riverside (and also in Mexico City) follows the general trend (highest to lowest): chloride>nitrate>ammonium>bulk OA>sulfate. Although AMS sulfate (mostly as ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ ) has a lower average volatility than bulk OA, OA was nevertheless found to dominate the mass remaining at the highest TD temperatures indicating the presence of a residual OA fraction potentially having a lower volatility than  $(\text{NH}_4)_2\text{SO}_4$ . This residual OA is consistent with a low-volatility fraction of SOA which may be formed or enhanced due to TD heating.

The advent of advanced source apportionment techniques along with the use of measurements from various instruments therein highlights the need to ensure the consistency of measurements employed in apportionment efforts. This need is even greater in the case of SOAR-1 due to the overwhelming contribution of SOA and the unique composition of OA existing at that time. Although a number of SOAR-1 publications have previously compared complementary measurements from different instruments and found them to be consistent, these comparisons were limited in scope with respect to either of the number of corresponding measurements included in the comparison or its duration, particularly with respect to organics measurements. Grover et al. (2008) for example evaluated PM<sub>2.5</sub> mass closure using two TEOM instruments, a dual-channel Sunset OC/EC instrument and a particle concentrator-based organic sampling system (PC-BOSS) and found that corresponding PM<sub>f</sub> measurements among the various instruments were consistent and highly correlated. Although poor correlation was observed among the various sulfate measurements, total PM<sub>f</sub> mass measured

by the TEOM<sub>F<sub>DMS</sub></sub> and the sum of measured PM<sub>2.5</sub> components showed good agreement. With respect to the comparison of organics measurements, Grover et al. (2008) compared only a limited number (30) of 1-hour averaged *total* carbon measurements from the dual-channel Sunset and the PC-BOSS.

Likewise, both Grover et al. (2009) and Snyder and Schauer (2007) compared EC measurements from the dual-channel and standard Sunset instruments, respectively, with BC measured by collocated instruments. Although EC measurements from the various instruments were consistent and highly correlated, similar comparisons of OC measurements between different monitors were not conducted. The most comprehensive of such comparisons is that of Peltier et al. (2007) who compared OC measured by the PILS OC instrument with those of a standard Sunset instrument. Although PILS OC and Sunset measurements were highly correlated, an intercept of  $-1.69$  indicated either a positive offset on the part of the Sunset instrument or an inability of the PILS-OC instrument to analyze larger insoluble particles. While the results in this case clearly demonstrate the intrinsic value of comparing complementary measurements in order to understand the limitations of both novel and widely accepted measurement techniques, the comparison was also limited in duration comparing measurements over a period of only three days. As a result, rigorous, long-term comparisons among the larger set of OC measurements present during SOAR-1 have not been presented.

In order to capitalize on the collocation of many state-of-the-art aerosol instruments and expand instrumental comparisons to this larger set of measurements under conditions where SOA dominated the composition of OA, below we provide additional detailed comparisons among measurements obtained by the HR-AMS and an ensemble of PM<sub>2.5</sub> instruments that are routinely employed in the characterization of ambient aerosol composition. Additionally, to establish a unified framework for SOAR publications and other studies in the LA area (such as CalNex-2010) we report the results of OA elemental analysis as well as the average composition of PM<sub>f</sub> during SOAR-1 based on separate PM<sub>2.5</sub> and NR-PM<sub>1</sub> measurements.

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3 Experimental

#### 3.1 General considerations

5 Sampling during SOAR-1 was conducted at the Air Pollution Research Center on the University of California-Riverside (UC-Riverside) campus (33°58'18.40" N, 117°19'21.41" W, ~700 ft elevation). All times herein refer to Pacific Standard Time (PST, i.e.: local time – 1 h.) and all concentrations are reported at ambient temperature and pressure. Unless otherwise stated, all linear regressions were performed in Igor Pro (Wavemetrics, Lake Oswego, OR, USA) using an orthogonal distance regression technique which is appropriate for fitting data when there are measurement errors in  
10 both variables.

#### 3.2 PM<sub>2.5</sub> measurements

Two Rupprecht and Patashnick (R & P, Thermo Fisher Scientific, Waltham, MA, USA) tapered element oscillating microbalances (TEOM), one operating at 50 °C (TEOM<sub>50C</sub>) and the other operated at ambient temperature after a R & P Filter Dynamics Measurement System (TEOM<sub>FDMs</sub>) (Grover et al., 2005), provided hourly measurements of PM<sub>2.5</sub> mass concentration. The TEOM<sub>50C</sub> filter is operated at an elevated temperature to remove particle-bound water and water adsorbed to the filter which can cause high measurement noise. However, this results in collateral loss of semi-volatile material (SVM) including ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and semi-volatile organic material (SVOM) (Eatough et al., 2003). As a result, the TEOM<sub>50C</sub> measurement is considered  
15 a measure of less-volatile PM<sub>2.5</sub> mass. In contrast, the TEOM<sub>FDMs</sub> uses intermittent sampling through a HEPA filter to account for the mass of SVM lost due to volatilization and is considered a comprehensive measurement of both non-volatile and semi-volatile PM<sub>2.5</sub> mass (Grover et al., 2008). PM<sub>2.5</sub> inorganic nitrate (IC-nitrate) and sulfate (IC-sulfate) concentrations were also measured hourly by ion chromatography (Grover et  
20  
25

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



al., 2008).

Hourly organic carbon (OC) and elemental carbon (EC) were measured using both a standard (Sunset 1) and a dual-oven (Sunset 2) semi-continuous carbon monitor (Sunset Laboratories, Tigard, OR, USA) using the NIOSH 5040 method (Bae et al., 2004).

Details regarding sample collection and analysis for Sunset 1 (Snyder and Schauer, 2007) and Sunset 2 (Grover et al., 2008, 2009) are presented elsewhere. EC concentrations measured by Sunset 1 compared well with BC from two absorption measurements (Snyder and Schauer, 2007). Additionally, Sunset 1 EC concentrations were compared with integrated filter EC concentrations. While Sunset 1 concentrations were slightly higher (~11%) than comparable filter measurements, they were highly correlated.

### 3.3 NR-PM<sub>1</sub> measurements

Total and speciated non-refractory submicron (NR-PM<sub>1</sub>) aerosol measurements were made by a pair of Aerodyne time-of-flight aerosol mass spectrometers (ToF-AMS generally): a high-resolution ToF-AMS (HR-AMS, sampling period: 14 July–13 August 2005) and a compact (unit mass resolution) ToF-AMS (C-AMS, sampling period: 3 August–13 August 2005). Detailed descriptions of these instruments are provided elsewhere (DeCarlo et al., 2006; Drewnick et al., 2005). Ambient air was sampled by both instruments from a height of ~6 m above ground level through a PM<sub>2.5</sub> cyclone (URG Corp., Chapel Hill, NC, USA) at a rate of ~12 L min<sup>-1</sup>. The sampled air was drawn through copper tubing with total transit times of 10-15 seconds from the inlet to the ToF-AMS instruments. Unless otherwise stated, ToF-AMS ensemble mass spectra (MS) and concentrations of major NR-PM<sub>1</sub> components ammonium (NH<sub>4</sub>), chloride (Cl), nitrate (NO<sub>3</sub>), OA, and sulfate (SO<sub>4</sub>) were averaged every five min. Note that we do not use the ion charges in the discussion below when referring to nominally inorganic species (e.g., we use SO<sub>4</sub> instead of SO<sub>4</sub><sup>2-</sup>) because the ToF-AMS data are known to contain organic contributions, e.g. an organosulfate contribution to the SO<sub>4</sub> signal, as discussed below. Ambient sampling was interrupted only for instrument calibrations or

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



maintenance or to sample from an indoor environmental smog chamber (Aiken et al., 2008; Mohr et al., 2009).

Unique to SOAR-1 is the fact that both of these instruments were operated using specialized sampling protocols including an in-line heated thermal denuder (TD) (Huffman et al., 2008) and vaporizer temperature cycling (VTC) (Docherty et al., 2008a). The VTC protocol uses computer control to systematically vary the ToF-AMS vaporizer temperature ( $T_{\text{vap}}$ ) in order to investigate the impact of vaporizer temperature on ambient OA MS. From 23 July–10 August 2005, the HR-AMS was intermittently interfaced with the TD while the C-AMS operated with the VTC protocol from 3 August–10 August 2005. From 10 August–13 August 2005, the sampling protocols were switched between the ToF-AMS instruments. Details regarding TD operation are provided elsewhere (Huffman et al., 2009). Under VTC operation, the ToF-AMS samples at  $T_{\text{vap}} = 600^\circ\text{C}$  for a period of 10 min after which time  $T_{\text{vap}}$  was stepped through three preset temperatures ( $T_{\text{vap}} = 200, 350, \text{ and } 450^\circ\text{C}$ ) for a period of 10, 5, and 5 min, respectively, before returning to  $600^\circ\text{C}$ . For the current analyses, data collected during non-standard sampling intervals (i.e., TD or  $T_{\text{vap}} < 600$ ) have been removed from both HR-AMS and C-AMS datasets to compare data that were acquired only during routine ambient sampling periods.

Analysis of unit mass resolution (UMR) ToF-AMS data was conducted using the custom-developed “Squirrel” software package (Sueper, 2008) which implements the analysis algorithms described previously by Jimenez et al. (2003), Allan et al. (2003, 2004), and DeCarlo et al. (2006). A collection efficiency of 0.5 was used for all species in both instruments, typical of aerosols measured in urban locations with similar compositions (e.g., Canagaratna et al. (2007) and references therein) and verified with inter-comparisons with collocated instruments (see discussion below). A potentially higher collection efficiency due to high nitrate fraction (Nemitz et al., 2010) was evaluated and found to increase concentrations by only a few percent. Since this impact is much lower than the uncertainty of AMS measurements, it has not been implemented here. High-resolution (HR) spectra from the HR-AMS were analyzed using a custom data analysis

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





module (“Pika”) developed by our group (DeCarlo et al., 2006) in Igor Pro. Elemental analysis (EA) of HR OA spectra was conducted according to the procedures of Aiken et al. (2008). Spikes present in the OA time series during a limited number of overnight periods were selectively removed during data analysis. These spikes were observed only during a few nights when wind speeds were low and direction was variable, spikes were very short in duration (5–10 min), and typically OA mass concentrations more than doubled. Additionally, mass spectra during these spikes were similar to that of reduced hydrocarbons such as lubricating oil. As a result of these characteristics, these spikes were attributed to emissions from an air compressor that was located at ground level about 8 m from the ToF-AMS common inlet and operated only at night during the first two weeks of SOAR-1 after which time it was turned off. Spikes were not observed after the use of the compressor was discontinued.

## 4 Results and discussion

### 4.1 Representativeness of the sampling site

The sampling site was located near potential local emission sources including the I-215 highway, the campus water cooling towers, and a number of greenhouses used for agricultural studies. The most potentially significant of these sources is I-215, a major interstate highway that carries ~170 000 automobiles per day in the vicinity of UC-Riverside (State of California, 2010) located ~0.5 km due west of the site. During the day, the prevailing winds typically arrive to the site from the west, placing the site downwind of I-215 and the greenhouses. Since the goal of this study is to characterize the composition of  $PM_f$  in the Eastern LA basin, we compare on- and off-site  $PM_{2.5}$  measurements in order to evaluate to what extent, these local sources contributed to  $PM_f$  at the site. Off-site measurements were obtained from a beta-attenuation monitor (BAM) operated at the California South Coast Air Quality Management District Rubidoux monitoring site which is located ~7 km west of UC-Riverside. Under prevailing wind conditions, the

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Rubidoux site is upwind of I-215 and other major interstates throughout the daytime hours when traffic is heaviest. We compare on-site TEOM<sub>FDMS</sub> PM<sub>2.5</sub> concentrations with those of the Rubidoux BAM as they are equivalent PM<sub>2.5</sub> measurements (Schwab et al., 2006; Grover et al., 2006).

TEOM<sub>FDMS</sub> and Rubidoux BAM measurements during SOAR-1 are compared in Fig. 1. Overall, the instruments track each other closely and the average PM<sub>2.5</sub> concentrations from the TEOM<sub>FDMS</sub> (average = 28.6  $\mu\text{g m}^{-3}$ ; range = 9–68  $\mu\text{g m}^{-3}$ ) are similar to those from Rubidoux (31.0  $\mu\text{g m}^{-3}$ ; 6–76  $\mu\text{g m}^{-3}$ ). Measurements at both locations are strongly correlated ( $r^2 = 0.62$ ) despite the geographical separation. The Rubidoux measurements are consistently higher throughout overnight and morning hours possibly due to an increased influence of motor vehicles near Rubidoux. Linear regression yields a slope of 0.87 with a recovery slope (i.e., when a fixed intercept of zero is used) of 0.91. Similar mass concentrations and the strong correlation observed here highlight the spatial consistency of PM<sub>f</sub> mass in inland regions of the SoCAB and suggest that contribution of PM<sub>f</sub> mass from very local sources is minor. This is consistent with the smooth variations in the time series of most species described below and in previous publications. Although their mass contributions are minor, these sources, particularly traffic along I-215, emit large numbers of low-mass particles which significantly impact number concentrations at the site (Cubison et al., 2008).

## 4.2 Meteorology and gas-phase pollutants during SOAR-1

Meteorological conditions during SOAR-1 were typical of those routinely experienced in the SoCAB inland valleys during the summer and exhibited little variation on a day-to-day basis. Time series and diurnal profiles of meteorological variables and gas-phase species during SOAR-1 are shown in Fig. 2. A similar plot showing conditions during SOAR-2 (15 October–15 November) are provided in Fig. S1 for reference. Only conditions during SOAR-1 are discussed here, as this is the main focus of this manuscript. During SOAR-1, relative humidity (RH) and temperature are generally anti-correlated

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



with an average RH maximum ( $\sim 80\%$ ) coinciding with average minimum temperatures ( $\sim 20^\circ\text{C}$ ) during the early morning hours while average minimum RH ( $\sim 30\%$ ) coincides with average maximum temperature ( $\sim 35^\circ\text{C}$ ) during mid-day. Absolute humidity (shown as the dewpoint in Fig. 1) showed little variation during most of SOAR-1.

5 Wind speed and direction were highly repetitive displaying little day-to-day variation. Wind speed was low ( $\sim 0.2\text{ m s}^{-1}$ ) and its direction variable during the late evening and overnight periods. On average, air masses arrived to the site from the south during the night, while maximum wind speeds ( $\sim 2\text{ m s}^{-1}$ ) were associated with westerly winds during the warmest part of the day.

10 Average ozone ( $\text{O}_3$ ) and odd oxygen ( $\text{O}_x$ ) concentrations (Fig. 2d) were lowest during overnight periods with maximum average concentrations of  $\sim 90$  and  $\sim 100$  ppbv, respectively, observed just after noon. Primary combustion emission markers including carbon monoxide ( $\text{CO}$ ), oxides of nitrogen ( $\text{NO}_x$ ), and elemental carbon ( $\text{EC}$ ) (Fig. 2e) displayed the opposite trend with elevated concentrations throughout the overnight period and maximum average concentrations of  $\sim 600$  ppb,  $\sim 60$  ppb, and  $2\ \mu\text{g m}^{-3}$ , respectively, during the early morning coincident with morning rush hour traffic. The concentration of these primary species rapidly declined to their minima during the afternoon and early evening periods, likely due to the combined effects of decreased emissions, increased vertical dilution from the growing boundary layer, and perhaps also horizontal advection.

20 Although the SoCAB is often severely impacted by wildfires that can significantly increase particle concentrations (e.g., Phuleria et al., 2005), the contribution of biomass burning OA (BBOA) during SOAR-1 was minimal according to many different metrics (Docherty et al., 2008b) including the MODIS Active Fire Detections database (<http://maps.geog.umd.edu/firms/>) which confirmed the low incidence of wildfires in and around the SoCAB during SOAR-1. Additionally, the ratio of  $m/z$  60 to OA signal in the HR-AMS ( $f_{60}$ ), which is a marker for BBOA (Aiken et al., 2009; Aiken et al., 2010; Lee et al., 2010), was at background levels, while measurements of the BBOA molecular marker levoglucosan also indicated a very small contribution from biomass

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



burning (Docherty et al., 2008b).

### 4.3 Total PM<sub>f</sub> intercomparisons

Multiple instruments including the TEOM<sub>50C</sub>, TEOM<sub>FDMS</sub>, and ToF-AMS instruments measured PM<sub>f</sub> mass during SOAR-1. The TEOM and ToF-AMS differ both in size cut and the measurement of refractory and semi-volatile material (SVM). Both TEOM instruments measure PM<sub>2.5</sub> and refractory material. In terms of AMS sampling, “refractory” materials do not volatilize sufficiently fast at the ToF-AMS vaporizer temperature and high vacuum conditions to be detected, and it includes dust, sea salt, and black carbon (Canagaratna et al., 2007). Among the TEOM instruments, only the TEOM<sub>FDMS</sub> is considered a comprehensive measure of PM<sub>2.5</sub> mass. As previously stated, the TEOM<sub>50C</sub> suffers from evaporation of semi-volatile species including ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and semi-volatile organic material (SVOM) (Eatough et al., 2003). As a result, the TEOM<sub>50C</sub> is considered a measure of only less-volatile PM<sub>2.5</sub> mass and the difference between the TEOM<sub>FDMS</sub> and TEOM<sub>50C</sub> has been used to estimate SVM (Grover et al., 2008). In contrast, the ToF-AMS measures total non-refractory submicron (NR-PM<sub>1</sub>) mass (e.g., Canagaratna et al., 2007 and references therein). Thus higher TEOM<sub>FDMS</sub> measurements than obtained from the ToF-AMS can be due to (1) non-refractory material between PM<sub>2.5</sub> and PM<sub>1</sub> (NR-PM<sub>2.5-1</sub>) and (2) PM<sub>2.5</sub> refractory material. Because of SVM volatilization, ToF-AMS measurements can either be greater (high SVM) or less than (low SVM) those of the TEOM<sub>50C</sub>. NR-PM<sub>1</sub> must also be supplemented by the sum of refractory PM<sub>2.5</sub> (e.g., EC and non-EC refractory material such as dust, sea salt, and metals) and NR-PM<sub>2.5-1</sub> in order to be comparable with the TEOM<sub>FDMS</sub>. However, because among these only EC was measured quantitatively during SOAR-1, we compare the sum of HR-AMS NR-PM<sub>1</sub> and Sunset 1 EC (AMS+EC) with TEOM measurements.

Although non-EC refractory material was not measured during SOAR-1, an estimate is available from ATOFMS measurements of PM<sub>2.5</sub> aged sea salt and dust. The concentration of refractory material estimated using ATOFMS measurements was

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4.7  $\mu\text{g m}^{-3}$  ( $\sim 16\%$  of  $\text{PM}_{2.5}$ ) (Qin et al., 2011), which is consistent with previous measurements in the vicinity of Riverside. Measurements by Christoforou et al. (2000) in Rubidoux in 1982, 1986, and 1993 consistently indicated that  $\text{PM}_{2.5}$  non-EC refractory material contributes 3-4  $\mu\text{g m}^{-3}$  throughout the year. Similarly, Chow et al. (1994) obtained an estimate of 1.6  $\mu\text{g m}^{-3}$  in Rubidoux. This latter estimate did not consider contributions from metals or sea salt and is, therefore, likely be a lower bound estimate of non-EC refractory material. More recently, Kim and Hopke (2007) reported a non-EC refractory material estimate of  $\sim 3.6 \mu\text{g m}^{-3}$ .

$\text{TEOM}_{\text{FDMS}}$ ,  $\text{TEOM}_{50\text{C}}$ , and AMS+EC time series are shown in Fig. 3, respectively, together with the diurnal profile of each measurement. AMS+EC tracks  $\text{TEOM}_{\text{FDMS}}$  measurements closely throughout the entire sampling period. As expected, average AMS+EC concentrations throughout SOAR-1 (average = 19.9  $\mu\text{g m}^{-3}$ ; range = 4.2–62.9  $\mu\text{g m}^{-3}$ ) are lower than those of the  $\text{TEOM}_{\text{FDMS}}$  (28.6  $\mu\text{g m}^{-3}$ ; 9–68  $\mu\text{g m}^{-3}$ ) due to contributions from non-EC refractory and NR- $\text{PM}_{2.5-1}$  mass. Diurnal profiles of each measurement are also similar with prominent maxima at  $\sim 0800$ , concurrent with morning rush-hour traffic, and a second smaller maximum in the early afternoon. Daily minimum concentrations, however, are slightly different among the three measurements. While  $\text{TEOM}_{\text{FDMS}}$  and AMS+EC concentrations reach a minimum during the early evening,  $\text{TEOM}_{50\text{C}}$  concentrations are at a minimum overnight. As expected based on their similar diurnal profiles, the absolute difference between AMS+EC and  $\text{TEOM}_{\text{FDMS}}$  measurements is nearly constant throughout the day. A scatter plot is shown in Fig. 3d. AMS+EC and  $\text{TEOM}_{\text{FDMS}}$  are highly correlated ( $r^2 = 0.77$ ). A slope of 0.73 was obtained by linear regression with a small intercept value (0.8% of average  $\text{TEOM}_{\text{FDMS}}$ ) with a recovery slope of 0.76.

24-h average  $\text{TEOM}_{50\text{C}}$  measurements (15.0  $\mu\text{g m}^{-3}$ ; -4.9–39.7  $\mu\text{g m}^{-3}$ ) are lower than those of the  $\text{TEOM}_{\text{FDMS}}$  and AMS + EC due to the loss of SVM. Significant contributions of SVM to  $\text{PM}_{2.5}$  have previously been reported in Riverside (Grover et al., 2005, 2008) and other locations (Cheng et al., 2009; Eatough et al., 2003; Wilson et

**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



al., 2006; Grover et al., 2009). The contribution of SVM, however, appears to vary both throughout the day as well as over extended periods during SOAR-1. On a daily basis, the diurnal profile of TEOM<sub>50C</sub> measurements displays many of the same features as the other measurements including maximum concentrations during the morning. As detailed in Table S2, TEOM<sub>FDMS</sub> and TEOM<sub>50C</sub> measurements are more similar during the first half of SOAR-1 ( $P_1$ : 7/18–8/1) whereas these measurements exhibit a larger deviation during the latter half ( $P_2$ : 8/2–8/14) thereby suggesting a larger contribution of SVM, or a variation in instrument performance. The correlation between TEOM<sub>50C</sub> and AMS+EC measurements ( $r^2=0.46$ ) is significantly lower than that obtained from comparison of TEOM<sub>FDMS</sub> and AMS + EC measurements.

As shown in Fig. S2, the agreement between TEOM<sub>50C</sub> and TEOM<sub>FDMS</sub> measurements improves substantially during both  $P_1$  (18 July–1 August 2005) and  $P_2$  (8/2–8/13/2005) when TEOM<sub>50C</sub> measurements are supplemented with NH<sub>4</sub>NO<sub>3</sub> concentrations (TEOM<sub>50C</sub> + NH<sub>4</sub>NO<sub>3</sub>). NH<sub>4</sub>NO<sub>3</sub> concentrations were calculated using IC-nitrate measurements and assuming its full neutralization by NH<sub>4</sub>, consistent with the HR-AMS ion balance as discussed below in Sect. 4.9. Linear regression of TEOM<sub>50C</sub> against TEOM<sub>FDMS</sub> during  $P_1$  results in a slope of 0.61 while the same during  $P_2$  results in a slope of 0.42. Similar regressions of TEOM<sub>50C</sub> + NH<sub>4</sub>NO<sub>3</sub> against TEOM<sub>FDMS</sub> measurements yield similar slopes during both  $P_1$  (0.78) and  $P_2$  (0.74) in addition to much higher correlation thereby indicating both the large contribution of volatile NH<sub>4</sub>NO<sub>3</sub> during both periods, particularly during  $P_2$ , as well as the importance of NH<sub>4</sub>NO<sub>3</sub> volatilization in TEOM<sub>50C</sub> measurements. By extension, if we assume that the remaining difference between TEOM<sub>50C</sub> + NH<sub>4</sub>NO<sub>3</sub> and TEOM<sub>FDMS</sub> is due to volatilization of SVOM, this comparison suggests that SVOM consistently contributes approximately 24% (+2%) of total PM<sub>2.5</sub> mass during SOAR-1, consistent with the findings of Grover et al. (2008).

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



#### 4.4 Intercomparison of ToF-AMS measurements

Previous intercomparisons between two quadrupole AMS (Q-AMS) instruments (Salcedo et al., 2005) and between a Q-AMS and C-AMS (Hings et al., 2007) have shown that collocated AMS instruments generally provide consistent and highly correlated measurements. The collocated operation of the HR-AMS and C-AMS during a period of SOAR-1 (3 August–13 August 2005) provides an opportunity to make, to our knowledge, the first published intercomparison of two ToF-AMSs. HR-AMS and C-AMS measurements are plotted in Fig. 4. Total NR-PM<sub>1</sub> from both ToF-AMS instruments are shown in Fig. 4a along with TEOM<sub>FDMS</sub> PM<sub>2.5</sub> for comparison. Overall, ToF-AMS total NR-PM<sub>1</sub> measurements track each other and TEOM<sub>FDMS</sub> PM<sub>2.5</sub> closely throughout this period. HR-AMS total is also plotted against C-AMS total in Fig. 4b while speciated HR-AMS measurements are plotted against those of the C-AMS in Fig. 4c–g along with the results of linear regression in each case. Linear regression was performed using a fixed-zero intercept since the zero of both ToF-AMS instruments was checked regularly by sampling through a HEPA filter. Linear regression of total NR-PM<sub>1</sub> results in a slope of 1.06 with high correlation ( $r^2 = 0.83$ ). Similar results are obtained from the comparison of speciated measurements including OA (slope = 1.11;  $r^2 = 0.81$ ), NO<sub>3</sub> (0.98; 0.89), and NH<sub>4</sub> (0.97; 0.79), SO<sub>4</sub> (1.06; 0.77), and Cl (1.13; 0.77). In all cases the differences are smaller than the estimated AMS uncertainty of  $\pm 25\%$ . Thus both ToF-AMS instruments provided consistent and highly correlated total and speciated mass concentrations throughout the SOAR-1 comparison period. Results obtained here are similar to or, in some cases, slightly better than those obtained from the comparisons of Salcedo et al. (2005) and Hings et al. (2007) despite the fact that these previous studies compared 30 min average measurements while five minute averages were compared here. Specifically with regard to the comparison of Salcedo et al. (2005) in Mexico City where, even though they sampled at the same site, the Q-AMS instruments were vertically separated by about 30 m and used different inlets, increased consistency and correlation of ToF-AMS measurements during SOAR-

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



1 are relatively higher likely due to the immediate proximity of the instruments and their use of a common inlet.

#### 4.5 Comparison of NR-PM<sub>1</sub> vs. PM<sub>2.5</sub> inorganics

5 HR-AMS NO<sub>3</sub> and SO<sub>4</sub> concentrations are compared with corresponding IC-nitrate and IC-sulfate measurements, respectively, in Fig. S3. Similar comparisons of Cl and NH<sub>4</sub> are not possible because PM<sub>2.5</sub> concentrations were not measured during SOAR-1. HR-AMS NO<sub>3</sub> is plotted against corresponding IC-nitrate measurements in Fig. S3a along with the results of linear regression. As this plot shows, NO<sub>3</sub> measurements from both instruments were very highly correlated. Both the standard and recovery slope  
10 obtained from linear regression are also very similar and near unity indicating that the measurements were highly consistent despite the different size cut between the two instruments, and that the vast majority of PM<sub>2.5</sub> NO<sub>3</sub> is contained within PM<sub>1</sub>. Diurnal plots of both NO<sub>3</sub> measurements are shown in Fig. S3b. As expected, the diurnal profile using each technique is similar exhibiting broad, bi-modal maxima during the morning and early afternoon with minimum concentrations observed during the late  
15 afternoon and early evening.

HR-AMS SO<sub>4</sub> is plotted against corresponding IC-sulfate measurements in Fig. S3c while diurnal profiles of each are provided in Fig. S3d. In sharp contrast to the consistency and high correlation of ToF-AMS SO<sub>4</sub> measurements, a much larger deviation and smaller correlation results from comparison of HR-AMS and IC-sulfate concentrations. Due to the amount of scatter, the choice of intercept has a large influence on regression results. For example, standard linear regression provides a slope of 0.51 with an intercept value of 1.44 while the recovery slope is 0.82. The recovery slope  
20 obtained in this case is likely more accurate considering both the amount of scatter associated between the two measurements and the fact that SO<sub>4</sub> concentrations rarely decrease below 2 μg m<sup>-3</sup> during SOAR-1, as well as the fact that the zero values of the HR-AMS was regularly checked with a HEPA filter. The differences between hourly average SO<sub>4</sub> measurements also suggest that IC-sulfate is ~20% higher than HR-AMS  
25

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



measurements, suggesting the presence of a fraction of SO<sub>4</sub> mass in supermicron particles.

#### 4.6 OC Comparison between the HR-AMS and Sunset instruments

In order to directly compare HR-AMS OA and Sunset OC measurements, one must be converted using an organic mass/organic carbon (OM/OC) ratio, which can be highly variable depending on OA composition (Turpin and Lim, 2001). Previous comparisons have converted AMS OA to OC using either a single estimated OM/OC ratio (Takegawa et al., 2005) or using different OM/OC ratios for different components identified by factor analysis (Zhang et al., 2005c). Here, we apply time-dependent OM/OC ratios determined from OA elemental analysis (EA) (ref. Sect. 4.7) to directly calculate OC from the HR-AMS data, and the measurements are compared in Fig. 5. Two different measurements are shown for the Sunset2 instrument in light of its separate measurement of SVOC (Grover et al., 2008, 2009). Here, “Sunset 2” corresponds to direct Sunset 2 measurements (i.e., in the absence of SVOC correction) while “Sunset 2 + SVOC” corresponds to the Sunset 2 OC values that have been supplemented by measured SVOC. Note that, given the similar setup of both Sunset instruments during SOAR-1 (e.g., the use of charcoal-impregnated denuders upstream of both Sunset instruments to remove volatile organics), Sunset 1 and Sunset 2 measurements are similar in principle although differences still exist such as different sampling lines, etc. Sunset 1 values are used here with no adjustment for SVOC.

HR-AMS OC is plotted against Sunset 1 measurements in Fig. 5a. Since there was always a significant OC background in Riverside during SOAR-1 which almost never went below 2.5 μgC m<sup>-3</sup>, the results of regressions calculated with both a free and fixed-zero intercept are shown. When comparing HR-AMS vs. Sunset 1 OC, both regressions provide similar results, with slopes of 1.10–1.08 (fixed zero intercept), and  $r^2 = 0.53$ . Average OC concentrations during different diurnal periods (Fig. 5b) are also quite similar. The results of this comparison are somewhat different than previous comparisons between PILS-OC with Sunset 1 OC values during SOAR-1 as reported

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



by Peltier et al. (2007). In that case, linear regression provided a slope near unity with an intercept of  $-1.69 \pm 0.22$  that was attributed to either a positive bias in the Sunset 1 OC measurement, or the inability of the PILS-OC to measure large insoluble particles. The intercept is poorly determined in our regression due to the lack of measurements below  $2.5 \mu\text{g m}^{-3}$ , so we are unable to shed light on the possible reasons for that discrepancy.

HR-AMS and Sunset2 OC are compared in Fig. 5c. In this case the regression results are highly dependent on the choice of zero vs. fitted intercept. Linear regression with a fitted intercept provides a slope of 0.67 with a large positive intercept while the recovery slope is near unity. The standard regression is likely influenced by the lack of points below  $\sim 2.5 \mu\text{g C m}^{-3}$ , together with the scatter between the measurements. However, as was the case for Sunset 1 measurements, average HR-AMS and Sunset 2 OC are quite similar for the different diurnal periods as shown in Fig. 5d. HR-AMS and Sunset2+SVOC are compared in Fig. 5E. Although these measurements are associated with a slightly higher correlation relative to Sunset 2 ( $r^2 = 0.45$  vs. 0.36), Sunset 2 + SVOC concentrations are consistently higher than both HR-AMS and Sunset 1. The linear regression results are relatively insensitive to the choice of intercept with similar fitted-intercept regression ( $m = 0.72$ ) and recovery ( $m = 0.71$ ) slopes. Sunset 2+SVOC values are also consistently larger throughout the day (Fig. 5f).

Unlike the high degree of correlation between HR-AMS and C-AMS OA measurements (Fig. 4c,  $r^2 = 0.81$ ), measurements from the collocated Sunset instruments are associated with a lower degree of correlation. This is also unlike previous comparisons of Sunset EC (Park et al., 2006; Snyder and Schauer, 2007) and OC (Bae et al., 2004; Schauer et al., 2003) which found measurements from different instruments to be highly correlated. EC, OC, and TC measured by Sunset 1 are plotted against corresponding Sunset 2 measurements in Fig. S4. Among these measurements, EC is the most highly correlated with  $r^2 = 0.77$ . Even in this case, however, both instruments are not equivalent as demonstrated by the consistent slope of 0.63–0.64 using linear regression in the presence and absence of a fixed-zero intercept. Unlike EC, the result

**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of linear regression between Sunset 1 and Sunset2 OC measurements is highly sensitive to the choice of intercept, as was the case when HR-AMS and Sunset 2 OC were compared. Standard linear regression yields a slope of 0.47 and an intercept of 2.43 while the recovery slope is 0.90. Sunset OC concentrations are also associated with a much lower degree of correlation ( $r^2 = 0.42$ ) than was found between corresponding EC measurements or between HR-AMS and C-AMS OA measurements. Figure S4d compares Sunset 1 and Sunset2+SVOC OC. In this case, although the correlation increases to  $r^2 = 0.52$  and the fitted-intercept and recovery slopes are more consistent, both slopes indicate that Sunset2 + SVOC is at least 37% higher than Sunset 1 OC. Comparison of TC measurements from the different Sunset instruments resembles those of OC due to its dominance during SOAR-1.

Differences among the three OC measurements throughout the day are further explored in Fig. 6 which shows both average diurnal profiles of OC from HR-AMS, Sunset 1, Sunset 2, and Sunset 2+SVOC (Fig. 6a) as well as diurnal profiles of the absolute difference between HR-AMS and each Sunset measurement (Fig. 6b). The diurnal profiles are similar with some differences, e.g. HR-AMS OC measurements exhibit two maxima, while the Sunset measurements instead exhibit a single broad maximum. As shown in Fig. 6b, the largest difference between HR-AMS and Sunset OC occurs during overnight and early morning hours, which corresponds to periods with elevated contributions of HOA (Docherty et al., 2008b). It should be noted however, that even during these times, the difference between HR-AMS and the Sunset OC measurements are mostly within  $\pm 15$  and otherwise within  $\pm 25\%$  of the HR-AMS OC, which is within the uncertainties of both measurements. The diurnal profile of Sunset 2 + SVOC measurements is similar to Sunset measurements and exhibits a single maximum throughout the majority of the day. However, average Sunset 2 + SVOC concentrations are  $\sim 30\%$  higher than either HR-AMS or Sunset measurements. In summary, the differences between the base Sunset and Sunset +SVOC measurements are as large as those observed between the HR-AMS and either base measurement. Table S3 provides a summary of statistical comparisons between all OC measurements. Interestingly the

**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



OC measurements of the HR-AMS have an equal or greater degree of correlation to the Sunset measurements than they have between themselves.

The difference between Sunset and HR-AMS measurements could be due, among other reasons, to either a positive bias on the part of the HR-AMS due to potentially higher relative ionization efficiency (RIE) or CE for HOA (Jimenez et al., 2003; Zhang et al., 2005b; Aiken et al., 2009). If the difference were due entirely to such a bias, the difference between HR-AMS and Sunset OC suggests that the HR-AMS response could be ~10–20% higher when sampling OA in which HOA and OOA contribute equally. This difference should be considered an upper limit, as other effects such as biases in AMS elemental analysis, small differences in size cuts, variations in OC artifacts in the Sunset filter, or a small variation of the AMS CE due to nitrate could also contribute to the observed time dependence. We recommend that similar comparisons are carried out in other studies to evaluate whether this variation is consistent across locations.

#### 4.7 Elemental analysis of OA

Elemental analysis (EA) of HR-AMS OA mass spectra (Aiken et al., 2008) has been used previously to characterize ambient OA (Aiken et al., 2008; Dunlea et al., 2009) as well as OA generated in smog chamber experiments (Shilling et al., 2009; Chhabra et al., 2010). EA results for SOAR-1 are presented in Fig. 7. Most elemental ratios show little day-to-day variability indicating a consistent OA composition during SOAR-1. Diurnal profiles are shown in Fig. 7b–c and show the trends more clearly. Diurnal profiles of OM/OC and O/C ratios are broadly anti-correlated with H/C. OM/OC and O/C exhibit minima at 0700 and maxima at 1200. Following the mid-day maximum, average OM/OC and O/C values steadily decrease throughout the late afternoon while average H/C values increase from their minimum values. Several characteristics of the EA ratios are similar to those observed by Aiken et al. (2008) in Mexico City. For example, the high similarity of OM/OC and O/C is consistent as oxygen is the dominant heteroatom at both locations. Average (range) of O/C and OM/OC values for the above time period are 0.35 (0.19–0.53) and 1.62 (1.42–1.85), respectively. The average OM/OC value

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



obtained from SOAR-1 ( $1.6 \pm 0.2 \mu\text{g}/\mu\text{g C}$ ) is similar to the recommended value of Turpin and Lim (2001) for urban areas, although SOAR-1 O/C and OM/OC are slightly lower than those measured by Aiken et al. (2008) in Mexico City (0.42 and 1.72, respectively). The lower latitude and intense photochemistry of Mexico City, as well as the presence of BBOA (O/C = 0.31) in MILAGRO (Aiken et al., 2009) but not SOAR-1 may explain these differences. The relative changes of O/C and H/C follow a slope of  $-1$  as recently reported by Heald et al. (2010).

Results from Mexico City have indicated that the ratio of unit resolution  $m/z$  44 to total OA signal ( $f_{44}$ ) is correlated to O/C obtained from EA and, thereby,  $f_{44}$  can be used to provide a rapid estimate of O/C using unit resolution data and while in the field (Aiken et al., 2008). As shown in Fig. S5,  $f_{44}$  and O/C ratios of bulk OA measured during SOAR-1 are also consistent and follow a similar trend as was observed by Aiken et al. Linear regression results for SOAR-1 are similar although slightly lower ( $\sim 8\% \pm 9\%$ ) for the range of O/C observed during this campaign. The intercept is substantially lower than observed in Mexico City, but its value is poorly constrained as no measurements were observed at very low average O/C due to the continuous dominance of SOA during SOAR-1.

A variety of N- and S-containing compounds can contribute to the N/C and S/C ratios of ambient aerosol. For instance, characteristic mass spectral fragments have been observed to indicate the presence of amines in particles sampled in a number of locations (Murphy et al., 2007; Angelino et al., 2001). Additionally, N-containing products formed from amines (e.g., Murphy et al., 2007) have been observed in SOA from chamber reactions. Organic nitrates (ON) have been suggested to contribute to the N content of ambient OA based on smog chamber results (Matsunaga et al., 2009; Fry et al., 2009), however they may be destroyed in the atmosphere due to hydrolysis reactions (Day et al., 2010). In any case, the N from ON is not included in the OA elemental analysis as carried out here, since most of the N therein is contained in  $\text{NO}_x^+$  ions which are assigned here to “nitrate” and not OA when using the standard AMS field data analysis procedures (Farmer et al., 2010). Similarly S from species such as

**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





sulfonic acids will be captured by our analysis, but S arising from organosulfates (OS) is lumped with “sulfate” and is not separately quantified in standard AMS field analysis (Farmer et al., 2010).

As shown in Fig. 7a, the contribution of N and S (excluding ON and OS) to OA mass in Riverside is far smaller than that of O with N/C and S/C ratios being between one and two orders of magnitude lower than O/C ratios, respectively. S/C was calculated using a calibration factor of 1.0 and obtained ratios should be considered a lower bound, since S is an electronegative element and similar to O, it may have a somewhat reduced tendency to retain the charge during the ion fragmentation process (Aiken et al., 2007), although this effect should be far smaller than an order of magnitude. Average N/C and S/C ratios of 0.016 and 0.001, respectively were obtained by EA. Diurnal profiles of N/C and S/C are shown in Fig. 7c. Both ratios show highest values during overnight hours when the site experienced low speed, variable winds.

Not including the contributions of ON and OS to  $\text{NO}_x^+$  and  $\text{SO}_x^+$  ions can have a large impact on calculated elemental ratios, particularly in the case of S/C. To evaluate this impact we recalculate these ratios using the estimates of Farmer et al. (2010), i.e., assuming that ON contributes  $\sim 10\%$  of  $\text{NO}_3$  and OS contributes  $\sim 12\%$  of  $\text{SO}_4$  during SOAR-1. Using these values we estimate average N/C and S/C ratios of 0.032 and 0.024, respectively. Both ratios are still an order-of-magnitude below O/C. The N/C ratio doubles and the S/C ratios increases by a factor of  $\sim 24$  when including the estimated ON and OS, respectively. H/C also increases only minimally ( $< 1\%$ ) and O/C increases by 21% when ON and OS estimates are taken into account. Note that according to Farmer et al. (2010), the oxygen which is bonded to a carbon in ON and OS is detected by the AMS as part of “organic” (C-containing) fragments and is thus included in the O/C of OA in the standard EA analysis procedures, while only the  $-\text{NO}_2$  part of  $-\text{ONO}_2$  and the  $-\text{SO}_3$  part of  $-\text{OSO}_3$  are not included in standard EA since they are not bound to a carbon when detected by the AMS. In summary, these estimates suggest that neglecting ON and OS in the standard EA method results in minor difference in H/C, substantial increases in O/C and N/C, and an order-of-magnitude increase in S/C in

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





urban areas. We recommend that these conclusions are evaluated at other locations, especially as direct ON and OS measurements become available.

#### 4.8 Average NR-PM<sub>1</sub> + EC composition during SOAR-1

The time series and fractions of NR-PM<sub>1</sub> components and Sunset 1 EC are shown in Fig. 8, with diurnal profiles in Fig. 9. The average values for each component are also reported in Table S4. Overall, OA is the largest single component contributing nearly half of AMS+EC mass on average. The majority of EC in the SoCAB during SOAR-1 should be due to diesel vehicles (~89%) based on the reported emissions factors of Kirchstetter et al. (1999) and CARB fuel usage data (California Air Resources Board, 2009). EC accounts for a few percent of the mass, with maximum concentrations in the early morning during rush hour as a result of both increased emissions and shallow mixing layer heights. EC concentrations decline after ~0800. EC displays minimum concentrations in the mid afternoon while OA increases again during the mid afternoon to another maximum at ~1300. OA concentrations are similar in the morning (avg. of 11.9 μg m<sup>-3</sup>) and mid afternoon (11.4 μg m<sup>-3</sup>). However, the relative contribution of OA increases in the afternoon, as OA contributes ~43% of PM<sub>f</sub> mass during morning rush hour and increases to ~55% during the late afternoon, mostly due to the decrease in NH<sub>4</sub>NO<sub>3</sub>. The disparity between the diurnal cycles of EC and OA and PM<sub>f</sub> is similar to that observed in Mexico City (Paredes-Miranda et al., 2009), and it is thought to be due mostly to dilution in the growing boundary layer and SOA formation (Paredes-Miranda et al., 2009; Docherty et al., 2008b). Source apportionment of OA during SOAR-1 is beyond the scope of the current manuscript and so is not discussed here but is the subject of an upcoming manuscript (Docherty et al., 2010).

Inorganics contribute the remainder of AMS+EC mass with chloride contributing the smallest amount of mass (0.44%) on average. Semi-volatile NH<sub>4</sub>Cl is thought to be responsible for at least some of the AMS chloride, since NaCl is thought to be poorly detected (Salcedo et al., 2006). The presence of semi-volatile chloride species is consistent with the diurnal profile during SOAR-1 which shows highest and lowest

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



concentrations during overnight and morning periods and during the mid afternoon, respectively.  $\text{SO}_4$  and  $\text{NO}_3$  contribute nearly equally to AMS + EC mass throughout the duration of sampling. The diurnal profiles of both their mass concentrations and relative contributions display distinctly different behaviors consistent with these ions having different volatilities and sources. Average  $\text{SO}_4$  concentrations show little diurnal variation. This is consistent with its non-volatile nature and also reflects the ubiquity of particulate  $\text{SO}_4$  in inland regions of the SoCAB, consistent with a larger fraction from non-local production through regional secondary processes (Zhang et al., 2005b; DeCarlo et al., 2010; Huang et al., 2010).

Unlike  $\text{SO}_4$ ,  $\text{NO}_3$  concentrations are significantly elevated in inland regions of the SoCAB relative to locations closer to the coast (Neuman et al., 2003). The bulk of particulate  $\text{NO}_3$  in the vicinity of Riverside is due to secondary formation of  $\text{NH}_4\text{NO}_3$ . As mentioned above,  $\text{NH}_4\text{NO}_3$  was determined to be among the most volatile aerosol components during SOAR-1. Due in large part to its relatively high volatility,  $\text{NO}_3$  has a strong diurnal profile that is very different from that of  $\text{SO}_4$ . The diurnal profile of  $\text{NR-PM}_{10}$   $\text{NO}_3$  exhibits two maxima. The first maximum occurs in the morning concurrent with rush hour while the second occurs during the early afternoon. This is similar to several previous studies in the Riverside area that also reported two maxima in the diurnal profile of  $\text{NO}_3$  concentrations (Stolzenburg and Hering, 2000; Fine et al., 2003). Stolzenburg and Hering observed a morning maximum following the increase in gas-phase nitric oxide during the morning rush hour but before an increase in  $\text{O}_3$  concentrations while the afternoon increase coincided with the increase in  $\text{O}_3$  with the maximum occurring near the time of maximum daily temperature. Diurnal profiles of  $\text{NR-PM}_{10}$   $\text{NO}_3$ , nitric oxide,  $\text{O}_3$ , and ambient temperature during SOAR-1 are presented in Fig. 10. Similar to the observations of Stolzenberg and Hering, average morning maximum  $\text{NO}_3$  concentrations during SOAR-1 occur at or just after maximum  $\text{NO}$  concentrations while the second maximum occurred just prior to maximum daily temperature and  $\text{O}_3$  measurements. Consistent with the semi-volatile nature of  $\text{NH}_4\text{NO}_3$ , minimum  $\text{NO}_3$  concentrations were observed during the late afternoon concurrent with

**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



maximum average daily temperatures.

#### 4.9 Anion/cation balance in NR-PM<sub>1</sub> during SOAR-1

Due to high ammonia emissions upwind and concentrations in the area of Riverside, NR-PM<sub>1</sub> anionic species (NO<sub>3</sub>, SO<sub>4</sub>, Cl) and bulk aerosols should be largely neutralized. This is quantitatively evaluated in Fig. 11 in which measured NH<sub>4</sub> concentrations are compared against concentrations predicted for full neutralization of measured NR-PM<sub>1</sub> cations, ignoring ON and OS (Zhang et al., 2007b) and using inorganic species concentrations determined from high-resolution data. This comparison also assumes that mineral and sea salt cations (e.g. Ca<sup>2+</sup>, Na<sup>+</sup>) are low although some interference from dust is possible for SOAR-1. Overall, measured and predicted NH<sub>4</sub> are highly correlated with  $r^2 = 0.99$ . Linear regression results in a slope of 0.86 while the ratio of average values is 0.91 indicating that essentially all of the NO<sub>3</sub> and SO<sub>4</sub> are present as ionic species and are neutralized by NH<sub>4</sub> during SOAR-1 within the experimental uncertainty of this determination. The predicted NH<sub>4</sub> concentrations are slightly larger than measured. The inset in Fig. 11 shows the range of concentrations (<3 μg m<sup>-3</sup>) where (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> represents nearly the entire contribution of NR-PM<sub>1</sub> NH<sub>4</sub>. Linear regression of measured and predicted NH<sub>4</sub> concentrations within this range results in a slightly larger slope (0.92) and smaller intercept (0.01) again suggesting that NR-PM<sub>1</sub> SO<sub>4</sub> was nearly completely neutralized. Additionally, this suggests that the deviation between measured and predicted NH<sub>4</sub> is driven by slightly larger differences at higher NH<sub>4</sub> concentrations (i.e., >3 μg m<sup>-3</sup>) where the majority of NH<sub>4</sub> is associated with NO<sub>3</sub>.

The presence of ON and OS as well as the unaccounted presence of other particulate cations may also contribute to the observed difference between measured and predicted NH<sub>4</sub>. Figure 11b investigates the impact of particulate OS, ON, and amines on the NH<sub>4</sub> balance. To explore their impact on HR-AMS ion balance, ON and OS have been assumed to contribute on the order of 10% and 12% of measured NO<sub>3</sub> and SO<sub>4</sub> mass and that OS is partially (here we assume 50%) neutralized by NH<sub>4</sub> (Farmer et

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



al., 2010). The influence of amines on the HR-AMS ion balance is unknown. Amines may contribute to fragments nominally assigned to  $\text{NH}_4$  (e.g.,  $m/z$  16, 17, and 18) in which case they would artificially increase both measured “ammonium” and apparent particle basicity. However, amines can compete with  $\text{NH}_4$  for particulate anions such as inorganic  $\text{SO}_4$  and  $\text{NO}_3$  forming salts (Murphy et al., 2007; Lloyd et al., 2009), thereby increasing the anion concentrations. If amine salts produced  $\text{NH}_x^+$  ions with similar molar efficiency as  $\text{NH}_4$ , the ammonium balance calculation would only be minimally affected by their presence, as they would contribute equal amounts of nominal anions and cations to the balance. In order to estimate an upper bound as to the impact of amines on the ion balance, we assume here that the detected amines do not contribute appreciable signal to fragments nominally assigned to  $\text{NH}_4$ . An amine-containing OA component contributes 4% of AMS OA during SOAR-1 (Docherty et al., 2011), and we estimate that 17% of the mass of that component (i.e. 0.7% of the OA mass) is accounted by amine functional groups. We also assume that amines were present as salts which were more strongly associated with  $\text{NO}_3$  and  $\text{SO}_4$  during SOAR-1 as indicated by Pratt et al. (2009a). OS and ON have the largest impact on the HR-AMS ion balance with the regression slope increasing from 0.86 to 0.94 when the estimates of OS and ON are used in the charge balance calculation. In contrast, amines have only a  $\sim 1\%$  impact increasing the slope only marginally from 0.94 to 0.95 when included in the ion balance calculation.

#### 4.10 Average $\text{PM}_{2.5}$ composition during SOAR-1

HR-AMS  $\text{NR-PM}_1$  measurements and those from an ensemble of  $\text{PM}_{2.5}$  instruments were used to separately reconstruct the average  $\text{PM}_{2.5}$  composition during SOAR-1, as shown in Fig. 12. TEOM<sub>FDMS</sub>, IC-nitrate, IC-sulfate, as well as OC and EC from Sunset 1 were used to construct the composition from  $\text{PM}_{2.5}$  instruments. OC mass was converted to OA mass using hourly OM/OC values obtained from elemental analysis of HR-AMS OA spectra. Particulate  $\text{NH}_4$  and non-EC refractory material were calculated using available data due to these components not being measured.  $\text{NH}_4$

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



was calculated using  $\text{PM}_{2.5}$   $\text{NO}_3$  and  $\text{SO}_4$  measurements from the IC-nitrate and IC-sulfate, respectively, assuming full neutralization of these species. Similarly,  $\text{PM}_{2.5}$  non-EC refractory material was calculated as the difference between the  $\text{TEOM}_{\text{FDMS}}$  mass and the sum of  $\text{PM}_{2.5}$  species.  $\text{PM}_{2.5}$  chloride was also not measured during SOAR-1. As discussed above, ToF-AMS measurements indicate that NR- $\text{PM}_1$  chloride concentrations are minor and it is therefore likely that the concentration of NR chloride in  $\text{PM}_{2.5-1}$  is also very small. Refractory chloride, mostly due to sea salt, can be significantly larger and is absorbed here into non-EC refractory material.

Similarly, mass concentrations of  $\text{PM}_{2.5}$  non-EC refractory material and NR- $\text{PM}_{2.5-1}$  are needed to create the HR-AMS-based ensemble composition. Non-EC refractory material concentrations were determined as above, while NR- $\text{PM}_{2.5-1}$  was estimated as the difference between measured  $\text{TEOM}_{\text{FDMS}}$  concentrations and the sum of the individual NR- $\text{PM}_1$  components, Sunset 1 EC, and non-EC refractory material. Overall, there is high similarity between both ensemble compositions. Each indicates that OA is the largest single component of  $\text{PM}_{2.5}$  mass. Both the concentration and contribution of OA to  $\text{PM}_{2.5}$  is similar in both reconstructions. In contrast, those of the major inorganic components  $\text{NO}_3$ ,  $\text{SO}_4$ , and  $\text{NH}_4$  are slightly higher in the ensemble composition, which may be due to inorganic contributions in supermicron particles or other differences in the  $\text{SO}_4$  or calculated  $\text{NH}_4$  concentrations as discussed above. Results from the CalNex study, conducted in the summer of 2010 in Pasadena, also suggest that OA is largely confined to the submicron mode in the LA basin while the inorganic anions have a supermicron fraction (R. Weber, Georgia Tech, personal communication, 2010), which is consistent with our results. If the estimates of ON and OS discussed above are correct, this would cause a difference between the NR- $\text{PM}_1$  and  $\text{PM}_{2.5}$   $\text{NO}_3$ ,  $\text{SO}_4$  (and the calculated  $\text{NH}_4$ ) of about 10%, since the former would include the signal from ON and OS while the latter would not. This would in turn suggest that the fraction of  $\text{SO}_4$  and  $\text{NO}_3$  in  $\text{PM}_{2.5-1}$  is slightly larger than in the default estimate in Fig. 12a.

**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 5 Conclusions

Multiple state-of-the-art instruments sampled ambient aerosols during SOAR-1 in order to investigate the sources and composition of fine particles in the inland LA basin. NR-PM<sub>1</sub> measurements from the HR-AMS were consistent with and (for most species) highly correlated to complementary measurements from a suite of PM<sub>2.5</sub> instruments. As a result, separate reconstructions of average PM<sub>2.5</sub> composition during SOAR-1 were remarkably similar. NR-PM<sub>1</sub> + EC accounted for the majority (~75%) of PM<sub>2.5</sub> mass, nearly a third of which was contributed by OA, the single largest component of ambient particles in Riverside. HR-AMS OC is consistent with complementary measurements by available Sunset semi-continuous instruments. However, substantial scatter is observed between the AMS and both Sunsets, and also between Sunset instruments, which is larger than observed between two AMSs. The use of a correction designed to account for the presence of SVOC resulted in OC concentrations about 30% higher than obtained from either the regular Sunset or AMS measurements. Results of elemental analysis of AMS OA are similar although slightly less oxidized than previous results from Mexico City. Oxygen is the dominant heteroatom in OA, while organic N and S are present in at least an-order-of-magnitude lower concentrations. When accounting for the estimated ON and OS concentrations, H/C does not change substantially, O/C increases by 21%, N/C increases by a factor of 2, and S/C increases a factor of 24.

The remainder of fine particle mass in Riverside was contributed by inorganics, primarily NO<sub>3</sub> and SO<sub>4</sub> as their ammonium salts. Diurnal characteristics of each of these components reflect both their different source regions throughout the SoCAB as well as differences in volatility. SO<sub>4</sub> concentrations were relatively stable throughout the day reflecting the consistent presence of SO<sub>4</sub> in particles irrespective of changes in the age and origin of air masses thereby highlighting the regional nature of SO<sub>4</sub>. SO<sub>4</sub> intercomparisons from different instruments had a low degree of correlation for unclear reasons. In contrast, particulate NO<sub>3</sub> measurements among various instruments were

### 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



highly correlated and exhibit diurnal profiles different from that of SO<sub>4</sub>. NO<sub>3</sub> concentrations display two maxima during morning and early afternoon periods and also a profound minimum during the late afternoon concurrent with maximum average daily temperature and minimum humidity. The anions were neutralized by ammonium during SOAR-1 within the uncertainty of this determination. Accounting for the estimated ON and OS improved the quantitative agreement of anions and cations by ~8%, while amines made a very minor impact.

**Supplementary material related to this article is available online at:**  
[http://www.atmos-chem-phys-discuss.net/11/6301/2011/  
acpd-11-6301-2011-supplement.pdf](http://www.atmos-chem-phys-discuss.net/11/6301/2011/acpd-11-6301-2011-supplement.pdf).

*Acknowledgements.* The research described here was partially supported by EPA STAR grants R831080 and RD-83216101-0, NSF CAREER grant ATM 0449815, NSF/UCAR contract S05-39607, by NOAA grant NA08OAR4310565, and by a CARB CalNex grant. ACA, JAH, and IMU acknowledge NASA Earth Science Graduate Fellowships, and PFD acknowledges an EPA STAR Graduate Fellowship. We thank the University of California-Riverside for hosting the site and much logistical support. We would additionally like to thank J. R. Kimmel, M. J. Cubison, E. J. Dunlea, A. Trimborn, and M. Northway for assistance with ToF-AMS operation during SOAR and J. J. Schauer for Sunset 1 data.

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## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**2005 Study of  
Organic Aerosols at  
Riverside**

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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K. S. Docherty et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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ACPD

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## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

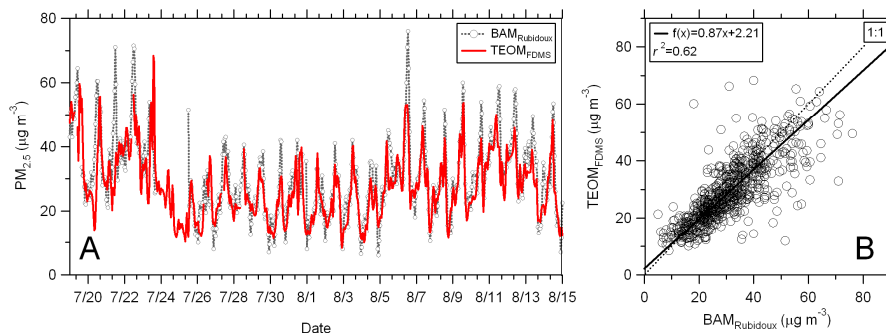
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[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



2005 Study of  
Organic Aerosols at  
Riverside

K. S. Docherty et al.



**Fig. 1.** Comparison of on- and off-site  $\text{PM}_{2.5}$  mass concentrations: **(A)** time series and **(B)** scatter plot. On-site measurements were obtained from the  $\text{TEOM}_{\text{FDMS}}$  while off-site measurements were obtained by the BAM at Rubidoux. See text for details.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

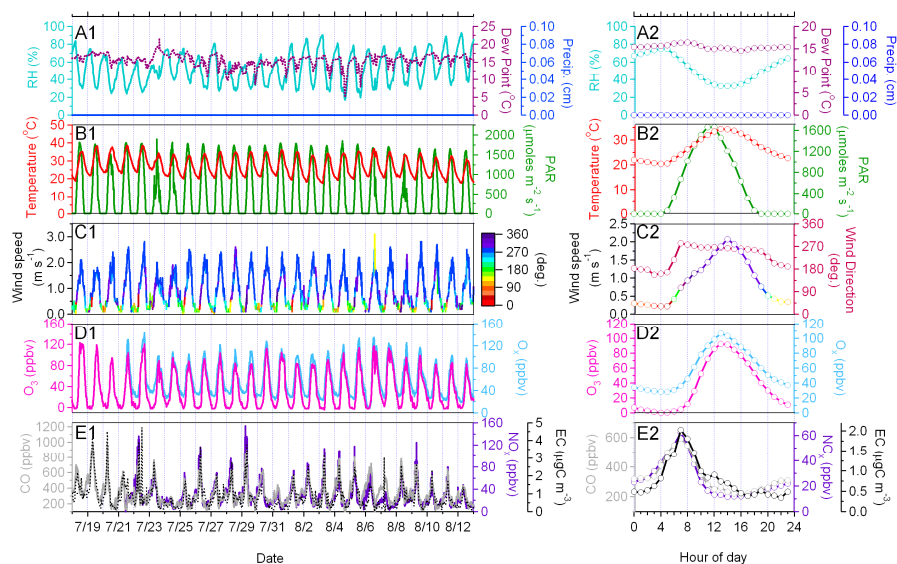
Printer-friendly Version

Interactive Discussion



## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.



**Fig. 2.** Time series (left) and diurnal profiles (right) of meteorological conditions (RH, temperature, wind speed and direction), gas-phase species (O<sub>3</sub>, O<sub>x</sub>, CO, and NO<sub>x</sub>), and elemental carbon during SOAR-1. Note that CO concentrations (in panels E1 and E2) have been offset vertically to account for a CO background of 100 ppbv.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

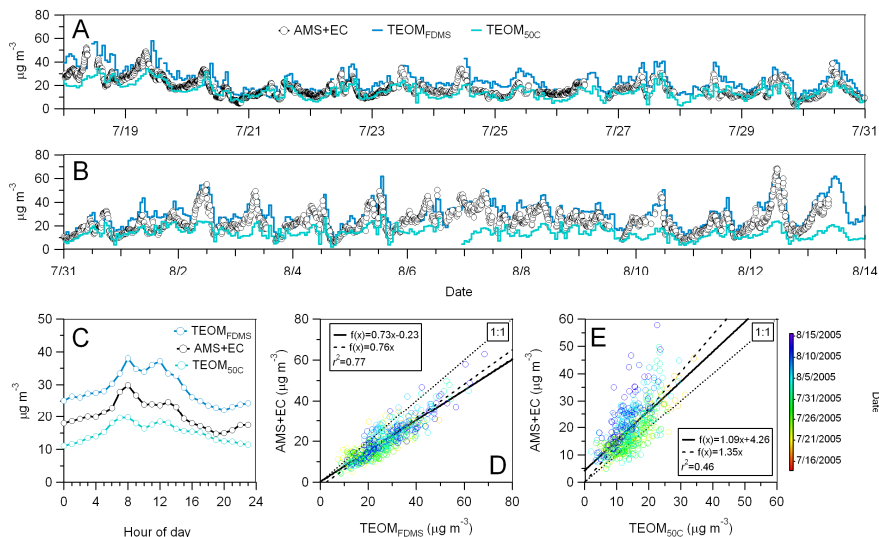
Printer-friendly Version

Interactive Discussion



## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

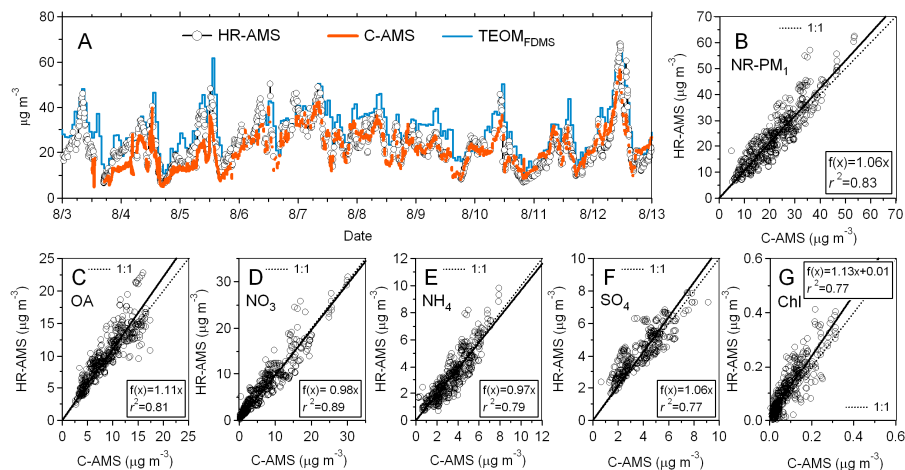


**Fig. 3.** Comparison of AMS + EC, TEOM<sub>FDMS</sub>, and TEOM<sub>50C</sub>. Time series of each measurement are shown in panels (A) and (B) over the periods 17 July–31 July and 1 August–13 August, respectively, while panel (C) shows average diurnal profiles of AMS+EC, TEOM<sub>FDMS</sub>, and TEOM<sub>50C</sub> throughout the duration of SOAR-1. AMS + EC concentrations are plotted against TEOM<sub>FDMS</sub> and the TEOM<sub>50C</sub> concentrations in panels (D) and (E), along with the results of linear regression, with and without a fixed-zero intercept, and coefficients of correlation ( $r^2$ ).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.



**Fig. 4.** Time series of NR-PM<sub>1</sub> concentrations measured by each ToF-AMS over the period 3 August–13 August 2005 are shown in panel (A). TEOM<sub>FDMS</sub> concentrations are also provided for visual reference. Scatter plots of total and speciated NR-PM<sub>1</sub> are shown in panels (B)–(G) with the results of linear regression and correlation ( $r^2$ ) values also provided in each plot.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

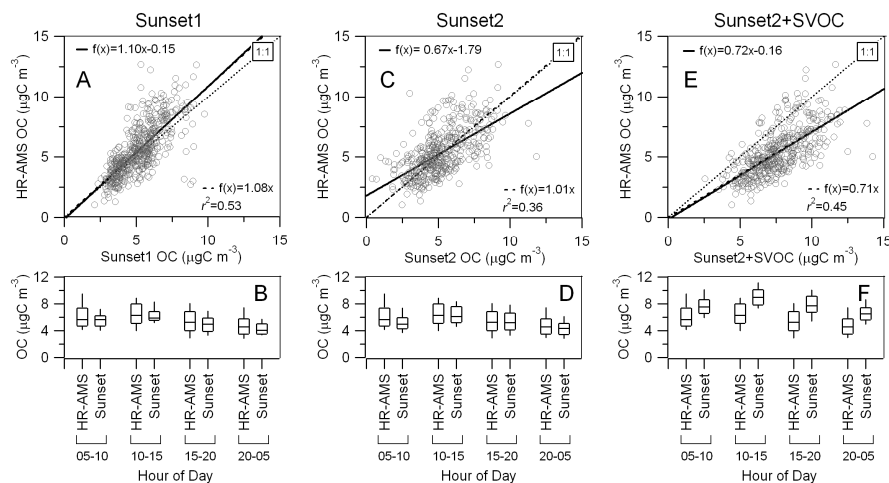
Printer-friendly Version

Interactive Discussion



## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

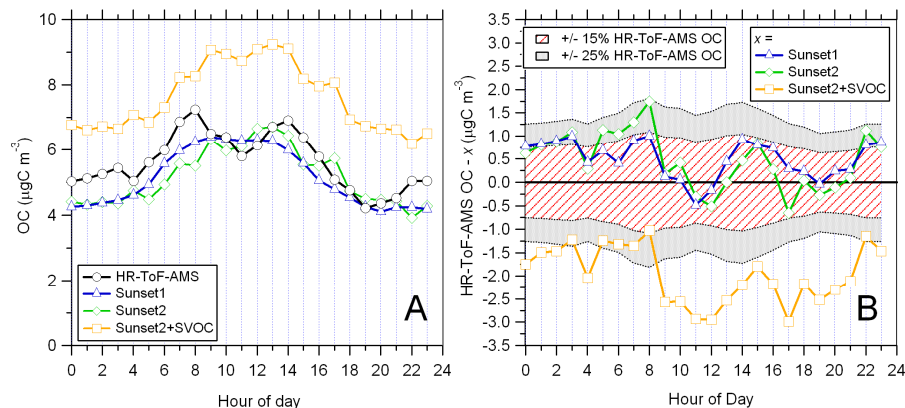


**Fig. 5.** Comparison of HR-AMS and Sunset measured OC concentrations. HR-AMS OC concentrations are plotted against Sunset 1, Sunset2, and Sunset2 + SVOC along with results of linear regression and correlation values ( $r^2$ ) in panels (A), (C), and (E), respectively. HR-AMS OM was converted to OC using the diurnal profile of OM/OC values obtained from elemental analysis. Box and whisker plots located below each scatter plot compare the various percentiles of HR-AMS and Sunset OC measurements throughout SOAR-1 for different time periods (0500–1000, 1000–1500, 1500–2000, and 2000–0500). Boxes correspond to 25-th and 75-th percentiles while whiskers correspond to 10-th and 90-th percentiles.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


2005 Study of  
Organic Aerosols at  
Riverside

K. S. Docherty et al.



**Fig. 6.** Diurnal profiles of HR-AMS and Sunset OC measurements. Diurnal averages are shown in panel (A) while profiles of difference between HR-AMS and Sunset measurements (i.e., HR-AMS OC – Sunset OC) are shown in panel (B), along with bands that represent  $\pm 15\%$  and  $\pm 25\%$  of the HR-AMS OC measurement.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

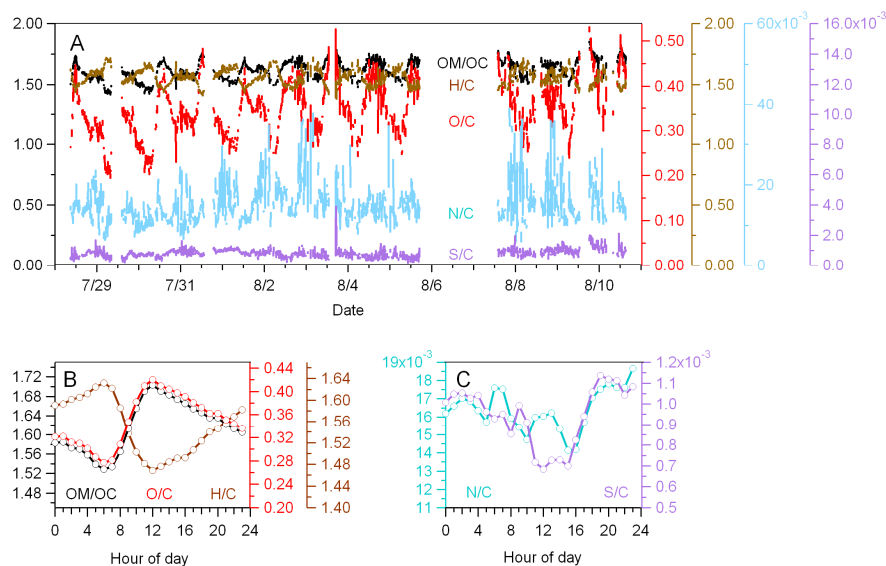
Printer-friendly Version

Interactive Discussion



## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.



**Fig. 7.** Results of elemental analysis of bulk OA during SOAR-1. Time series and diurnal profiles of elemental ratios and organic mass to organic carbon (OM/OC) ratio are shown in panel (A). Panel (B) shows diurnal profiles of OM/OC, O/C, and H/C while panel (C) shows diurnal profiles of N/C and S/C ratios.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

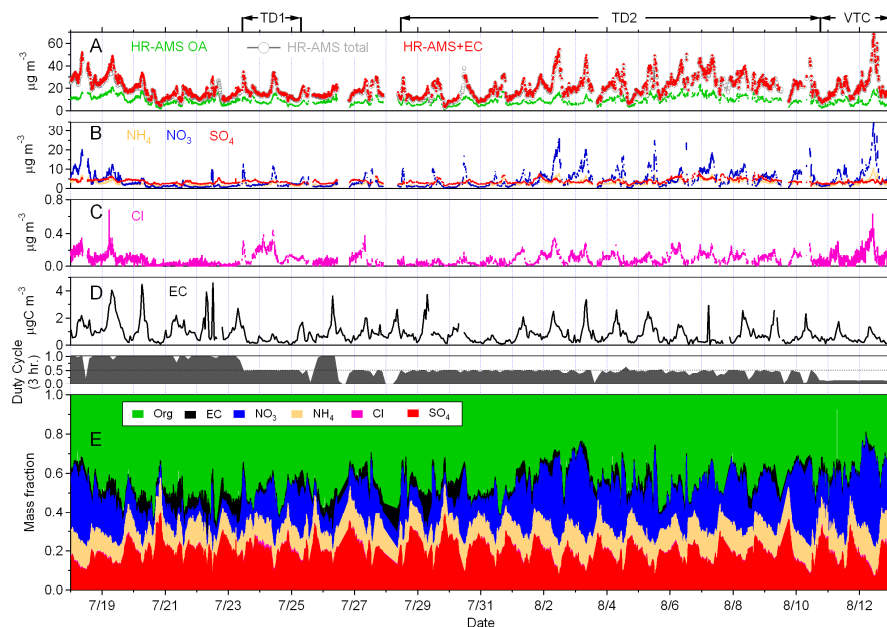
Interactive Discussion





## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.



**Fig. 8.** Time series of HR-AMS NR-PM<sub>1</sub> total and speciated measurements during SOAR-1. Time series of total, OA, and AMS + EC are shown in panel (A), inorganics (NH<sub>4</sub>, NO<sub>3</sub>, and SO<sub>4</sub>) are shown in panel (B), chloride in panel (C), and Sunset 1 EC in panel (D). The stack plot in panel (E) shows the relative contribution of each major NR-PM<sub>1</sub> component to AMS+EC. The plot between panels D and E shows the ambient sampling duty cycle of the HR-AMS (i.e., the fraction of time sampling under standard conditions) averaged over a period of 3 h. Periods when duty cycles are <1 result from the use of the thermal denuder (TD1, TD2) and vaporizer temperature cycling (VTC) protocols during which the duty cycle of the AMS was 50% and ~13%, respectively.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

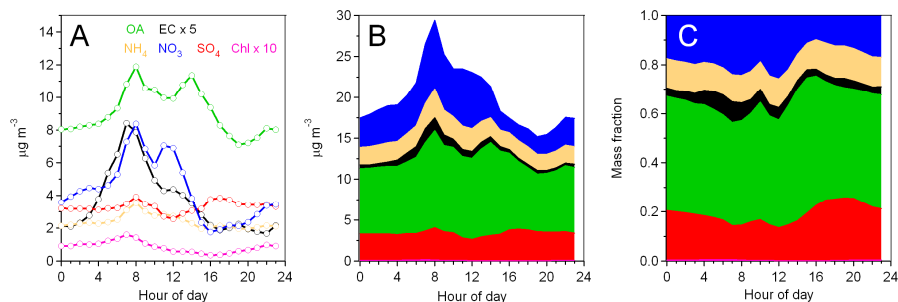
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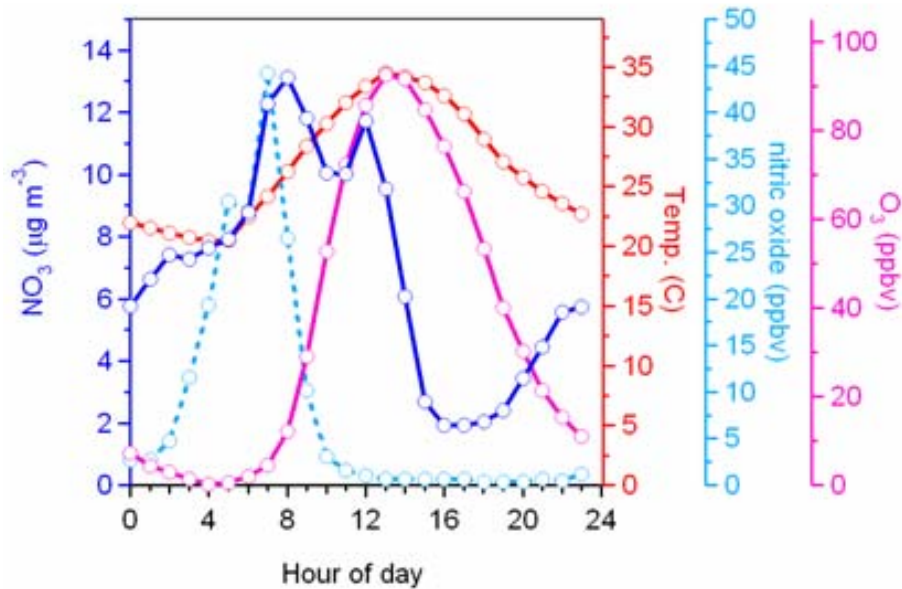
2005 Study of  
Organic Aerosols at  
Riverside

K. S. Docherty et al.



**Fig. 9.** Diurnal profiles of major NR-PM<sub>1</sub> components and EC. Standard profiles are shown in panel (A). Note that the absolute concentration of chloride has been multiplied by a factor of 10 (in panel (A) only) for clarity. The same diurnal profiles are shown in panels (B) and (C), but in a different format to show both the composition of AMS + EC and the relative contribution of each component.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



**Fig. 10.** Diurnal profiles of HR-AMS NO<sub>3</sub> along with those of gas-phase NO, O<sub>3</sub>, and ambient temperature during SOAR-1.

**2005 Study of Organic Aerosols at Riverside**

K. S. Docherty et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

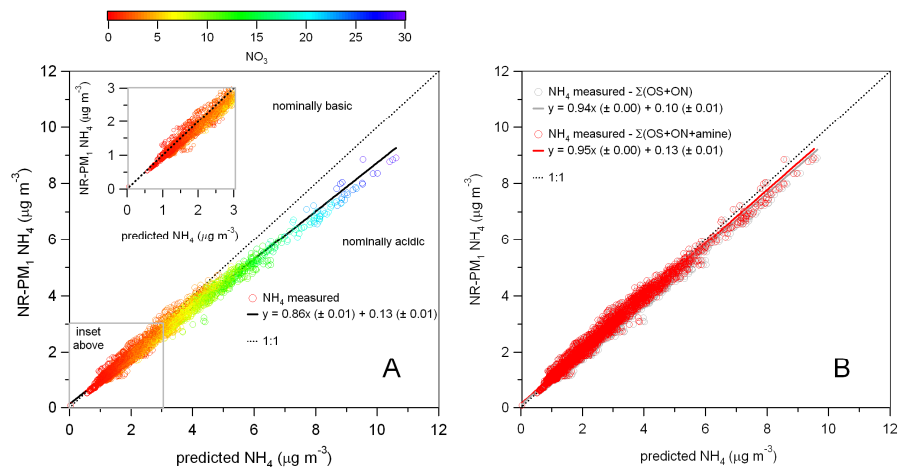
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Interactive Discussion



## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.

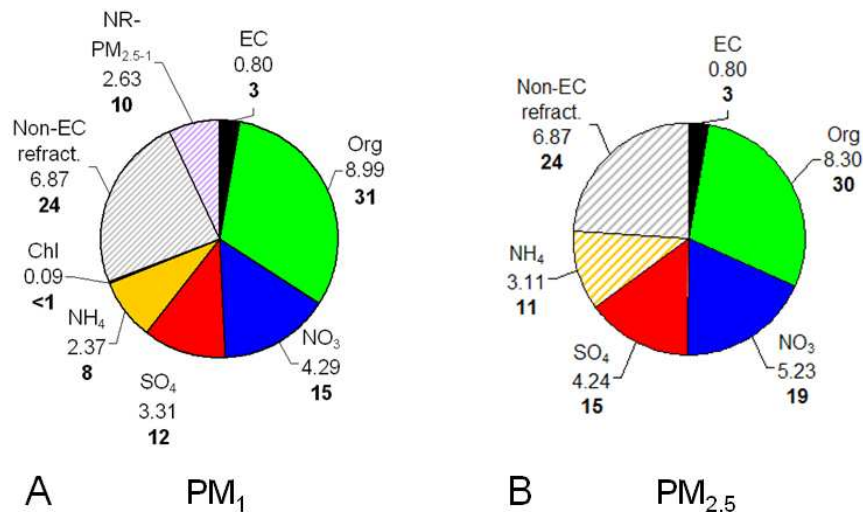


**Fig. 11.** Anion/cation balance of SOAR-1 particles based on HR-AMS measurements. In **(A)**, measured  $\text{NH}_4$  is plotted against predicted  $\text{NH}_4$  assuming full neutralization of  $\text{NO}_3$ ,  $\text{SO}_4$ , and  $\text{Cl}$ . In **(B)**, predicted  $\text{NH}_4$  has been adjusted to include the contribution of organonitrates, organosulfates, and amine contributions (see text for details). Results of linear regression are also shown in each plot.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


## 2005 Study of Organic Aerosols at Riverside

K. S. Docherty et al.



**Fig. 12.** Average composition of PM<sub>2.5</sub> throughout the duration of SOAR-1. The composition shown in **(A)** was calculated using NR-PM<sub>1</sub> HR-AMS measurements while that shown in **(B)** was calculated using measurements from the full complement of PM<sub>2.5</sub> instruments (i.e., TEOM<sub>FDMS</sub>, OC and EC from Sunset 1, IC-NO<sub>3</sub>, and IC-SO<sub>4</sub>). Filled segments in each pie chart correspond to actual measurements while hashed segments (e.g., non-EC refractory material) were calculated using available measurements (see text for details).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)