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Sources of primary and secondary organic aerosol and their diurnal variations

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HIGHLIGHTS

- Primary species exhibited significant urban–rural difference.
- Spatial distribution of secondary components was more homogeneous.
- Cholesterol should be used with caution as meat cooking tracer in rural areas.

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ABSTRACT

$PM_{2.5}$, as one of the criteria pollutants regulated in the U.S. and other countries due to its adverse health impacts, contains more than hundreds of organic pollutants with different sources and formation mechanisms. Daytime and nighttime $PM_{2.5}$ samples from the August Mini-Intensive Gas and Aerosol Campaign (AMIGAS) in the southeastern U.S. were collected during summer 2008 at one urban site and one rural site, and were analyzed for organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC), and various individual organic compounds including some important tracers for carbonaceous aerosol sources by gas chromatography–mass spectrometry. Most samples exhibited higher daytime OC concentration, while higher nighttime OC was found in a few events at the urban site. Sources, formation mechanisms and composition of organic aerosol are complicated and results of this study showed that it exhibited distinct diurnal variations. With detailed organic tracer information, sources contributing to particulate OC were identified: higher nighttime OC concentration occurring in several occasions was mainly contributed by the increasing primary emissions at night, especially diesel exhaust and biomass burning; whereas sources responsible for higher daytime OC concentration included secondary organic aerosol (SOA) formation (e.g., *cis*-pinonic acid and non-biomass burning WSOC) together with traffic emissions especially gasoline engine exhaust. Primary tracers from combustion related sources such as EC, polycyclic aromatic hydrocarbons, and hopanes and steranes were significantly higher at the urban site with an urban to rural ratio between 5 and 8. However, this urban–rural difference for secondary components was less significant, indicating a relatively homogeneous distribution of SOA spatially. We found cholesterol concentrations, a typical tracer for meat cooking, were consistently higher at the rural site especially during the daytime, suggesting the likely additional sources for this tracer at rural site and that it should be used with caution as meat cooking tracer in rural areas in the future.

1. Introduction

Increased mortality and morbidity in communities with elevated fine particulate matter ($PM_{2.5}$) concentrations in the atmosphere have been reported by a variety of epidemiological studies [1,2]. The exposure to fine particles is associated with premature death from heart or lung disease and linked to various effects such as respiratory symptom, cardiovascular symptom

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and heart attacks. After evaluating hundreds of health studies and conducting an extensive peer review process, the United States Environmental Protection Agency (US EPA) promulgated a new National Ambient Air Quality Standards (NAAQS) for ground-level $PM_{2.5}$ at concentrations of 15 $\mu g/m^3$ (annual average) and 65 $\mu g/m^3$ (daily average) in 1997. In 2006, US EPA strengthened the 24-h fine particle standard to 35 $\mu g/m^3$ to protect public health, welfare and visibility and established a considerable size of the national $PM_{2.5}$ monitoring network.

Unlike single-component air pollutants such as ozone, particulate matter, though regulated by its mass concentration, is composed of hundreds or even thousands of compounds. It is important to obtain a clear understanding of the composition of atmospheric particulate matter as some compounds or species such benzo(a)pyrene pose health threats. Some species can be used as powerful tracers for sources. Such information is particularly important for $PM_{2.5}$ source apportionment in order to lower $PM_{2.5}$ concentration in ambient air and protect human health.

Organic aerosol (OA) or organic matter (OM), often estimated by OC multiplied by a factor of 1.4 or higher, is not only a major component of $PM_{2.5}$, but also contains multiple organic pollutants such as polycyclic aromatic hydrocarbons (PAHs). OM is a major component of $PM_{2.5}$ in the southeastern U.S. constituting up to approximately 70% of the $PM_{2.5}$ mass in individual samples and 20–30% for annual averages across the southeastern U.S. [3,4]. Gas chromatography–mass spectrometry (GC–MS) is useful for organic aerosol speciation [5,6], in which hundreds of particle-phase individual species were identified and quantified. Though only between 10% and 20% of the total particulate organic carbon mass could be identified [4], some of these compounds are unique tracers. Among these tracers include levoglucosan for biomass burning, hopanes and steranes for gasoline engine exhaust, 2-methyltetrols, pinic acid and *cis*-pinonic acid for secondary organic aerosol [6,7].

Carbonaceous aerosol exhibits diurnal variations. EC concentration was usually elevated at night [8,9] and early morning [10–12], primarily due to enhanced emissions from combustion sources, such as fossil fuel and biomass as well as shallower boundary layer. However, diurnal pattern of OC seems more variable. For example, comparable OC during daytime and nighttime has been reported by Lin et al. [9] and Stone et al. [5], while it was found higher during nighttime [13] or daytime [11,12], suggesting the complexity of OC sources and compositions. Most previous studies focused on the diurnal variations of $PM_{2.5}$ and EC, while the information of diurnal variation of organic species/pollutants is still scarce. The knowledge of these species is particularly helpful for assessing exposure and health impacts of air pollutants and some of them are important indicators of $PM_{2.5}$ sources, including those from primary emissions and secondarily formed in the atmosphere such as SOA.

There are a few studies about diurnal variation of aerosols in the southeastern U.S., e.g., diurnal variation of $PM_{2.5}$ mass concentration by Butler et al. [14] and of EC and OC by Lim and Turpin [11]. However, there is no study aiming to understand diurnal variations of organic species, which have the power of indicating specific emission sources and explaining the underlying reasons of diurnal variation of organic aerosol. Atlanta is a typical urban environment, but strongly influenced by biogenic sources [15]. Despite the need to investigate diurnal variations of air pollutants and their sources especially some carcinogenic and mutagenic species such as PAHs, such study provides valuable data when to estimate human exposures and potential health impacts. Increased time resolution (8-h vs. a monthly-composite $PM_{2.5}$ sample) in organic aerosol measurement would provide valuable information for other research areas such as three-dimensional air quality modeling. In our previous collaborative study, results from the Community Multi scale Air Quality model had to be compared to data from the monthly composite $PM_{2.5}$ samples due to the lack of enough material for analysis using a low volume sampler [16]. In addition, the investigation of individual organic tracers in daytime and nighttime $PM_{2.5}$ can help to better understand its formation mechanisms. This information cannot be obtained with a daily or monthly sampling protocol.

The Southeastern Aerosol Research and Characterization program (SEARCH), initiated in 1998, is a timely response to the need for better and advanced knowledge for fine particles. Although continuous gaseous and particulate measurements are available in the SEARCH program, detailed speciation of organic aerosol still relies on 24-h discrete sampling methods [17] or monthly composite samples [6] to collect sufficient mass for organic speciation analysis. This study, for the first time, deployed an 8-h sampling protocol in the southeastern U.S. to allow the investigation of diurnal variation of organic aerosol and $PM_{2.5}$.

The present study is part of the AMIGAS campaign, in which 8-h high volume $PM_{2.5}$ samples were collected during August 2008 at a pair of urban–rural sites, two of eight SEARCH sites in the southeastern U.S. Several research groups participated in the AMIGAS campaign with various instrumentation and objectives. For example, the influence of acidity on SOA formation was investigated with liquid chromatography mass spectrometers and electrospray ionization time-of-flight mass spectrometers by Chan et al. [18]. Isoprene-derived epoxydiols and other isoprene SOA tracers (i.e., 2-methyltetrols)were identified and quantified by California Institute of Technology [19]. Sulfur compounds in $PM_{2.5}$ such as organosulfates were analyzed using the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) by the group of University of California, San Diego [20]. Physical properties related to particle formation and growth (such as mixing state and compositional effects on cloud condensation nuclei (CCN) activity) was investigated by a group at Georgia Institute of Technology [21]. As part of this campaign, our group focuses on composition and sources of organic aerosol. Therefore, our primary goal is to study primary and secondary organic tracer compounds using GC/MS and then identify daytime–nighttime difference for characteristics and sources of fine particulate matter.

2. Experiment

2.1. Sampling

AMIGAS program aims to study biogenic and anthropogenic emissions and their impact on secondary organic aerosol formation, and August is the period when SOA is more abundant. Several research groups participated in and focused on different air quality measurements at two sites in Georgia. Detailed information about sampling sites was given by Hansen et al. [3]. Briefly, sampling was conducted at one urban site at Atlanta, GA (Jefferson Street (JST)), and one rural site at Yorkville, GA (YRK). JST is about 4.2 km northwest of downtown Atlanta, surrounded by warehouses, storage buildings, parking lots, city streets, bus maintenance facilities (250 m south), and residential neighborhoods. YRK is located in a rural–agricultural area, ~55 km west northwest of downtown Atlanta (Fig. 1). $PM_{2.5}$ was sampled on quartz fiber filter (8 × 10 in, Whatman) using a high-volume sampler from August 1st through September 10th, 2008 during daytime and nighttime (10:00–18:00 and 22:00–06:00 Eastern standard time (EST), respectively). After each sampling period, the quartz filters were stored at −20 °C until laboratory analysis. 22 samples from JST and 12 from YRK along with 2 field blanks were obtained and chemically characterized in the present study. All daytime samples collected during August 24–26 were combined due to much lower concentration under raining weather condition, and so did the nighttime samples. The FRM sampler (Rupprecht & Patashnick model 2025 sequential sampler) was equipped at each site to measure $PM_{2.5}$ mass with the 47 mm Teflon filter by the gravimetric method.