Organic Compound Concentrations of Size-Segregated PM$_{10}$ during Sugarcane Burning and Growing Seasons at a Rural and an Urban Site in Florida, USA

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ABSTRACT

Florida has the most land used to grow sugarcane crops in the United States. The preharvest sugarcane leaf burning elevates ambient particle matter (PM) concentrations in rural areas with dominant sugarcane agriculture (Belle Glade) and affects the air quality of coastal urban sites (Delray Beach). In this study, ambient particles segregated by size were analyzed to identify trace organic compounds from PM sources that may cause adverse health effects. The sampling campaign was conducted simultaneously at urban and rural sites, and revealed that the organic compound concentration of each particle size varies significantly between the sugarcane burning season (SBS) in January and sugarcane growing season (SGS) in May. The results indicated that PM$_{3}$ contains at least 76% of the organic compound concentrations detected in the samples collected from both sites and during both seasons. The concentrations of trace organic compounds were higher in the SBS than in the SGS. Combustion-oriented hopanes, polycyclic aromatic hydrocarbons (PAHs), and oxygenated PAHs were mainly detected in PM$_{0.49}$. The detection of elevated levoglucosan concentrations at the urban site indicates that fine particles generated from biomass burning traveled from the rural site to the urban site. Secondary organic compounds such as dicarboxylic acids, phytol, and 6,10,14-trimethyl-2-pentadecanone exhibited similar concentration patterns in the rural and urban sites during both seasons. In the SGS, PM$_{10}$ concentrations at both sites were extremely similar; however, the organic compound levels were lower at the rural site than at the urban site in the SBS. This result should be investigated further by researchers investigating the health aspects of organic compound concentrations.

Keywords: Size segregated; Organic molecular markers; Airborne particles; Biomass burning; PM$_{10}$.

INTRODUCTION

Atmospheric particle matter (PM) is an environmental and health concern in urban (Peters and Dockery, 2005) and rural areas (Jimenez et al., 2006). Epidemiological studies have indicated that particles smaller than 10 µm have a significantly adverse effect on human health. Fine particles contain numerous trace organic species that are known to be carcinogenic and mutagenic (Pope and Dockery, 2006) and are small enough to penetrate deep into the lungs (Lin and Lee, 2004). In addition, exposure to a high concentration of fine PM for even a short period can have unwanted consequences (Rogge et al., 2011).

Ambient PM is a complex mixture of organic and inorganic constituents derived from both natural and anthropogenic sources, including fossil fuel and biomass combustion, vehicular emissions, cooking, resuspended road dust, cigarette smoke, leaf surface abrasion products, and roofing tar fumes (Rogge et al., 1996). At rural sites, fine particle sources include fugitive dust (Rogge et al., 2006), exhaust from vehicles used in the field (Hays et al., 2005), and agricultural biomass burning, such as sugarcane (Saccharum officinarum) pre-harvest burning (Le Blond et al., 2008). In addition, secondary organic aerosol is formed from the low vapor pressure products of gas-to-particle conversion reactions, which are an important additional source of fine particle matter, formed particularly under severe photochemical smog conditions (Schauer et al., 2002).

Because sources and source contributions can be substantially different in rural areas versus urban areas, the observed air quality is different in many aspects. Geographical location and meteorological conditions can cause further substantial differences in aerosol size distributions and trace compound concentrations (Qadir et al., 2014). Urban air pollution affects typically a large population. By contrast, air quality in rural areas, which are
mainly unpopulated, is expected to be much better (Ketzel et al., 2004). Rural air quality is influenced by local and surrounding sources as well as long-range particle transport (Reisen et al., 2013). For example, many agricultural activities in rural areas can substantially impact air quality, particularly preharvest sugarcane burning (Allen et al., 2004). Sugarcane burning is a major local fine particle source during harvest time in rural areas of Palm Beach County, Florida, and ultimately elevates PM concentrations throughout the region.

Selected trace organic compounds have been of interest for many years for adverse health effects and to aid source-receptor apportionment (Schauer et al., 1996). Thus, the objectives of this study were to quantify the level of selected trace organic compounds, including n-alkanes, n-alkanoic acids, n-alkenoic acids, aliphatic dicarboxylic acids, aromatic dicarboxylic acids, polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (oxy-PAHs), pentacyclic triterpanes, pesticides, steroids, saccharides, and 6,10,14-trimethyl-2-pentadecanone (HDA), by using gas chromatograph–mass spectrometry (GC–MS); to compare the results of size-segregated organic compound concentrations in each size segregate between urban and rural sites and between the sugarcane burning season (SBS) and sugarcane growing season (SGS); and to evaluate the results by employing organic trace markers that help to understand the impact of sugarcane leaf burning in rural and urban areas.

**METHODOLOGY**

**Sampling Sites**

The size-segregated PM$_{10}$ samples were collected in Delray Beach (costal urban area) and Belle Glade (agricultural rural area) in Palm Beach County (Fig. 1). The air quality of Palm Beach County is influenced by urban activities, agricultural activities, biomass burning, industrial activities, and at occasions by long-range transport, such as Saharan dust and sea spray from the Atlantic Ocean.

Delray Beach, a long narrow city located between the Atlantic Ocean and agricultural land, is a densely populated urban area on the southeast coast of Florida. In this study, the urban sampling site was located in an inner-city residential and light commercial area that is influenced by traffic and industrial emissions. The major industries in the area include construction, aircraft testing, computer and electronics manufacturing, and concrete and asphalt production. In Delray Beach, the size-segregated PM$_{10}$ sampler was located in the South County Administrative Complex (latitude, 26.455174°; longitude, –80.092155°).

The rural sampling site was located in Belle Glade, a small town situated at the southern shore of Lake Okeechobee, the second largest fresh water lake in the continental United States; Sugarcane is the most valuable agricultural product in Belle Glade. In general, the harvest season begins in mid-to-late October and is completed in mid-to-late March, spanning approximately 150 days. Preharvest sugarcane burning is conducted with the permission of the Florida Division of Forestry. Each field is individually permitted on a daily basis, and burning is typically permitted between 9 pm and one hour before sunset when climatic conditions are favorable. Wind speed and direction are primary considerations. The growing region is separated into zones, for which burning restrictions are tighter the closer to urban areas to prevent ash fallout in urban communities. Although

![Fig. 1. Sampling sites at a rural (Belle Glade) and urban area (Delray Beach).](image-url)
the same permitting procedure has been employed since 1997, more developed technological tools (e.g., the HYSPLIT model) have been adopted to more effectively manage and organize the burning. In addition, an extensive air-monitoring network, monitored by the U.S. Environmental Protection Agency and Florida Department of Environmental Protection, exists throughout the growing region. Therefore, the size-segregating PM$_{10}$ sampler was located in the Belle Glade Civic Center (latitude, 26.692699°; longitude, –80.670927°).

**Meteorological Data**

Wind speed (WS) and wind direction (WD) data were collected near the particle sampling sites, namely the University of Florida Everglades Educational and Research Center (latitude: 26.669032°; longitude: –80.631259°) in Belle Glade and the Palm Beach County Ozone Air Monitoring Site (latitude: 26.465919°; longitude: –80.074210°) in Delray Beach (Table 1). The average 24-h WS and WD data suggest that the air masses mainly moved from Belle Glade to Delray Beach or vice versa. In addition, backward trajectory analyses were conducted for both sampling sites and seasons. During the sampling period, the average ambient temperatures at Belle Glade (Delray Beach) in January and May were 18.7°C (19.1°C) and 31.4°C (25.9°C), respectively. The temperatures in January were similar at both sites. However, in May, the average temperature at the rural site exceeded that at the urban site.

Samples were collected simultaneously at both sampling sites. A 10-day backward trajectory analysis (HYSPLIT model) was conducted for both locations during the sampling days (Figs. 2 and 3). The trajectory results suggest that the wind blew from Belle Glade to Delray Beach on January 20 and 24 and on May 1 and 13 during the sampling period.

**Sampling and Measurements**

Size-segregated PM$_{10}$ was simultaneously collected at urban (Delray Beach) and rural (Belle Glade) sites during January and May of 1997, yielding five sample sets. The samples were collected for 24h each, beginning at midnight. The sampling days were determined before to the weather conditions, wind direction, and permitted burning area were known. The samples were collected using a Graseby (G1200) quartz fiber filter (28.32 × 25.40 cm, Pallflex 2500QAO-30) for each cascade, and a quartz fiber filter (SAC 230G F) for each cascade, and a quartz fiber filter (28.32 × 25.40 cm, Pallflex 2500QAO-UP) was used as a backup filter.

The sampling media were prepared in a laboratory at Florida International University. Sampling quality control was ensured using field and laboratory blanks. A batch of quartz fiber filters used in the prior ambient particle sampling was annealed at 550°C for 4 h to remove possible organic contaminants. The particle mass concentration was determined for both samplers located at the urban and rural sites by weighing filters under constant conditions (50% relative humidity, temperature 20°C). After a minimal conditioning time of 24 h, the particle mass was determined gravimetrically by weighing each filter using a Mettler Toledo semi-micro balance (Model AG 245). The samples were immediately catalogued and stored in freezers at temperatures lower than –21°C until chemical extraction.

**Sample Analysis for Organics**

Before the extraction of organic compounds from the samples collected in January and May, the filter samples were grouped according to size-fraction and calendar month for each monitoring size, forming monthly composites of five sampled filters for each particle size range. Because five filter samples of each segregate were combined for processing, the compound concentration was determined as one value. Therefore, no standard deviation was calculated. The following extraction procedure was applied. Each segregated filter sample was spiked with a measured amount of five perdeuterated standards (Cambridge Isotopes, Andover, MA), namely (1) n-decanoic–d$_{19}$ acid, (2) n-tetradecanoic–d$_{27}$ acid, (3) n-eicosane–d$_{42}$, (4) n-tetracosane–d$_{50}$, and (5) n-triacontane–d$_{62}$. The amount added was predetermined for each sample according to the estimated amount of organic carbon present in that sample and was calculated by assuming that approximately 30% of the PM collected comprised organic material and that each recovery or internal standard added should amount to 0.5% of that amount to obtain a peak size similar to that of major compounds in the sample.

The spiked filter samples were subsequently extracted for 12 h by applying the Soxhlet extraction technique and using GC-grade methylene chloride as a solvent. The filtered extract was then reduced to a volume of 3–5 mL by gentle rotary vacuum distillation and further reduced using gentle solvent evaporation with a stream of high purity N2 to a final volume of approximately 200–500 µL. Following the volume reduction, each extract was reacted with freshly produced diazomethane to convert organic acids to their methyl ester analogues and acidic hydroxyl compounds to their methoxy analogues. After derivatization, the extracts were stored at –21°C until GC–MS analysis.

**Table 1.** Average 24-h WS (km h$^{-1}$) and WD at sampling sites.

| Date       | Belle Glade | Delray Beach |
|------------|-------------|--------------|
|            | WS | WD | WS | WD |
| 7-Jan-97   | 1.1 | S  | 4.0 | S  |
| 14-Jan-97  | 9.7 | NE | 11.3 | NE |
| 20-Jan-97  | 3.2 | NW | 1.6 | NW |
| 24-Jan-97  | 1.1 | E  | 6.4 | SE |
| 30-Jan-97  | 4.8 | NE | 4.8 | NW |
| 1-May-97   | 1.6 | SW | 4.0 | SE |
| 6-May-97   | 5.3 | NE | 7.2 | NE |
| 13-May-97  | 2.1 | SW | 8.0 | SW |
| 20-May-97  | 2.1 | SE | 4.8 | SE |
| 30-May-97  | 8.0 | NE | 5.6 | NE |
Fig. 2. Backward trajectory analyses for the sampling days in January (SBS) in Belle Glade and Delray Beach.
Fig. 3. Backward trajectory analyses for the sampling days in May (SGS) in Belle Glade and Delray Beach.
Instrumental Analysis

The sample extracts were analyzed using HP5890 gas chromatography interfaced with an HP5971 mass selective detector equipped with a Grob injector that was operated in the splitless mode. The injector temperature was set to 300°C, and a 30-m DB-XLB column (J&W Scientific, Rancho Cordova, California) was used. The organic compounds were ionized through electron impact with an electron energy of 70 eV. The scanning range was set from 50 to 500 Daltons. Temperature programming of the column comprised the following steps: (1) an injection at 50°C; (2) an isothermal hold at 50°C for 1 min; and (3) a temperature increase of 6 °C min⁻¹ to a final temperature of 310°C, followed by an isothermal hold at 310°C for 20 min.

Compound Identification and Quantification

Compounds were identified and confirmed through a sequential process. First, compound identification was conducted by comparing the unknown compound mass fragmentation pattern to those in the Wiley Library, contained in the HP5971 data system. Second, the compound identification was further confirmed by comparison mass fragmentation patterns and elution times to those in the authentic standards that were injected into the GC port. Identifiable compound peaks were quantified using selective ion monitoring and the MS-data system. Relative ion counts were converted to compound mass concentrations by using the recovering of the internal recovery standards (five perdeuterated standards added to each sample before extraction), the relative response factors obtained by injecting the external standards that contained the compound of interest, and 1-phenyldodecane as a coinjection standard.

Quality Assurance

Filters were sealed in sterilized aluminum foil before and after use and were frozen between the time of collection and analysis. All filter materials (quartz fiber filter) and glass components of the extraction apparatus were annealed at 550°C, and Teflon and stainless steel parts were cleaned with solvent before use. GC Resolv grade solvents were used throughout the analysis and to prepare the standard solutions. All solvents were reanalyzed in the laboratory to ensure that any contaminants present were monitored. Procedural blanks were analyzed in conjunction with the monthly composites.

RESULTS AND DISCUSSION

Particle Size Distributions and Mass Median Aerodynamic Diameter

The monthly average size-segregated PM₁₀ concentrations in Belle Glade and Delray Beach were 34.20 ± 3.66 and 22.10 ± 3.11 µg m⁻³ in January, respectively, and 19.20 ± 7.25 and 19.25 ± 5.71 µg m⁻³ in May, respectively. The highest accumulation of n-alkanes was observed in PM₀.49. Each segregate shows individual concentration levels at both sites, especially in coarse particles. Notably,
biosynthetic n-alkanes exhibiting a strong predominance of an odd carbon number, namely nonacosane (C29), hentriacontane (C31), and tritriacontane (C33) were detected in higher concentrations in all stages at the rural site compared with at the urban site. The higher biogenic n-alkane concentrations during the SBS at Belle Glade are associated with sugarcane burning and harvesting in agricultural fields (Oros et al., 2006). The concentrations of C29, C31, and C33 at the
Table 2. Trace organic compounds associated with PM sources.

| Sugar cane Burning | Levoglucosan | PAHs             | Atrazine          |
|--------------------|--------------|------------------|-------------------|
| Pesticides         | n-Alkanes (C29, C31, C33) | n-Alkanoic Acids (C16, C18, C24, C26, C28, C30, C32, C34) | Atrazine          |
| Leaf Surface Abrasion | n-alkanes ≤ C26 | n-Alkanoic Acids ≤ C24 | PAHs              |
| Gasoline and Diesel Exhaust | Oleic Acid | Cholesterol | Hopanes          |
| Meat Cooking | PAHs | Hopanes          |
| Road Dust | PAHs | Hopanes          |

urban site during the SBS were higher than during the SGS, indicating that the air mass at the rural site influenced the urban site by carried airborne emissions. By contrast, during the SGS, the concentrations were similar at both sites and lower than those during the SBS (2.4 ng m\(^{-3}\) vs. 2.1 ng m\(^{-3}\)). The concentrations of C29, C31, and C33 in the PM\(_{0.49}\) were almost four times lower during the SGS compared with during the SBS at the rural site.

Petroleum fuel combustion-derived n-alkanes ≤ C26 revealed ambient concentration patterns in the size-segregated PM\(_{10}\) that were similar in magnitude and distribution at the two sampling sites but that differed between the sampling
n-Alkanoic Acids

The concentrations of 26 n-alkanoic acids were determined in six stages of size-segregated PM$_{10}$, which varied between the SBS and SGS and between urban and rural locations. PM$_{0.49}$ contained the highest concentrations at both sites and in both seasons (Fig. 6(b)). In addition, the n-alkanoic acid concentration patterns were similar to those of n-alkanes in all stages and at both sites. Hexadecanoic (C16), octadecanoic (C18), tetradecanoic (C24), hexacosanoic (C26), octacosanoic (C28), triacontanoic (C30), dotriacontanoic (C32) and tetracosanoic (C34) acids were the dominant compounds in n-alkanoic acid concentrations in all stages. Even-numbered alkanoic acids (≥ C24) were detected in high concentrations at the rural site for all stages in both sampling seasons, confirming that leaf abrasion particles had the highest concentrations of even-numbered alkanoic acids (Rogge et al., 1993c). In addition, fossil fuel combustion is a major source of n-alkanoic acids (≤ C24) with lower molecular weights (Rogge et al., 1993a). Analysis of the source profiles indicated that C16 and C18 were identical in the fuel and biomass combustion, road dust, and leaf surface abrasion particles that were detected with dominant carbon numbers during both sampling periods and for all stages. Although C16 and C18 concentrations were high during the SGS in all stages at the rural site, the concentrations were high only in Stages I, II, and V during the SBS at the urban site, because the urban site was mainly influenced by fuel and road dust particles whereas the rural site was mainly influenced by fuel, biomass combustion, and leaf surface abrasion particles. Therefore, the concentrations fluctuated in each stage because of the varying rates of source emissions. The concentrations of n-fatty acids (C22–C34) with a high molecular weight were consistently substantially higher at the rural site, particularly during the SBS.

Aliphatic and Aromatic Dicarboxylic Acids

Pyrolysis of plants, trees, and organic soil constituents can result in numerous organic compounds in airborne ash, including dicarboxylic acids that are formed as secondary organic aerosol in the reactive atmosphere (Rogge et al., 1993d). The formation of phthalic acids and their introduction into an urban atmosphere may involve the aging of plastic materials in an environment in which ester groups are hydrolyzed to form parent phthalic acids (Ray and McDow, 2005). Furthermore, phthalic acids and related compounds have been suggested as being produced by atmospheric chemical reactions involving directly emitted PAHs that degrade to phthalic acids upon contact with polycyclic aromatic quinones (Jang and McDow, 1997).

In the present study, aliphatic and aromatic dicarboxylic acids were mainly associated with submicron particles collected in Stages V and VI (Fig. 7(a)), except for 1,2-Benzenedicarboxylic acid, which was detected in all stages at both sampling sites and in both seasons. The detected compound concentrations were slightly higher in the SBS than in the SGS. The dicarboxylic acids were dominant at the rural site in both seasons.

Diterpene Alcohol and Isoprenoids

Biomass burning releases n-alkanes, n-alkanoic acids, n-alkan-2-ones, ketones, and monosaccharide derivatives (Simoneit, 2002a). Abas (1995) suggested that high plant epicuticular waxes are converted to ketones after direct emission by combustive processes. Phytol and 6,10,14-trimethyl-2-pentadecanone is a branched ketone that is oxidative product derived from the phytol originally attached to chlorophyll (Simoneit et al., 1988). Furthermore, Leif and Simoneit (1995) show that phytone found in aquatic sediments is the degradation product of phytol.

Phytol was detected in each segregate at the rural and urban sites in the SBS and SGS, except for in Stages I–III at the rural site (Fig. 7(b)). Sugarcane burning elevated the concentration of phytol, which was two times higher during the SBS at the rural site than the urban site. The phytol concentrations measured at the urban site were lower indicating that the rural site was affected by vegetative detritus particles and that the sugarcane burning elevated phytol levels.

6,10,14-Trimethyl-2-pentadecanone was detected in each segregate at the rural and urban sites during the SBS and SGS (Fig. 7(c)). The concentrations and distribution patterns in the all stages were similar to those of phytone. PM$_{0.49}$ contained the most compounds as mass compared to the other stages. Phytone and 6,10,14-Trimethyl-2-pentadecanone results indicate that the emission rate at the rural site exceeded that at the urban site. Although these two compound concentrations were elevated during the SBS at the rural site, no concentration elevations were detected at the urban site.

Pentacyclic Triterpanes

Hopane hydrocarbons, characteristic petroleum indicators that are usually resistant to degradation in the environment and that confirm contamination from fossil fuel residues (Abas and Simoneit, 1996), are found in lubricating and fuel oils but not in gasoline or diesel fuel (Gorka et al., 2014). Although a large set of various triterpanes exist in petroleum oil, only the major triterpanoid hopanes (22,29,30-trisnorhopane, 17a(H),21b(H)-hopane, 22R17a(H),21b(H)-homohopane) present in the ambient samples were determined.

The highest hopane concentrations, 4.3 ng m$^{-3}$ (PM$_{10}$) at the rural site and 2.2 ng m$^{-3}$ at the urban site, were measured during the SBS (Table S1). During the SGS, the hopane concentrations were 0.9 ng m$^{-3}$ at the rural site and 1.6 ng m$^{-3}$ at the urban site. The concentration patterns for the three major hopanes was similar at both sites and during both sampling periods. The highest hopane accumulation, more than 61%, was observed in PM$_{0.49}$.
In Palm Beach County, hopanes associated with airborne particulate matter could be derived from exhaust emitted from gasoline- and diesel-powered vehicles and road dust (Ke et al., 2013). The concentrations of hopanes were higher at the rural site during the SBS compared with during the SGS. The sources of hopanes in the sugarcane-harvesting process include emissions from trucks used for transferring the sugarcane foliage from the fields to facilities and from fuel used in sugarcane processing plants (Engling et al., 2006). The concentrations of hopanes at the urban site were approximately two times less than those at the rural site during the SBS. However, during the SGS, the concentrations of triterpanes at the urban site exceeded those at the rural site, a clear indication that sugarcane harvesting and processing...
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Elevated the hopane concentrations at the rural site (Fig. 8(a)). The urban site concentration patterns for each stage were similar during both seasons.

Poly cyclic Aromatic Hydrocarbons
PAHs have been investigated extensively because of their mutagenic and carcinogenic potential (Wogan et al., 2004). These compounds are the pyrolysis products from the incomplete combustion of organic matter and are mainly associated with fine particles (Rogge et al., 1993a) (Fig. 8(b)). PAH sources in ambient aerosol are vehicle exhaust, biomass combustion, and fossil fuel combustion.

During this study, 15 PAHs were quantified in the ambient samples. During the SBS, PAH concentrations in PM$_{10}$

Fig. 8. Hopane, PAH, and oxy-PAH concentrations in size-segregated PM$_{10}$ at the urban and rural sites during the SBS and SGS.
were 7.1 ng m$^{-3}$ at the rural site and 2.9 ng m$^{-3}$ at the urban site. By contrast, during the SGS, the PAH concentration measured at the rural site, 0.4 ng m$^{-3}$, was nearly 17 times lower than the concentration measured during the SBS. At the urban site, the total PAH concentration in PM$_{10}$ during the SGS was 2.4 ng m$^{-3}$, slightly lower than the concentration measured during the SBS. The concentrations are a lower estimate of the actual gas-and particle-phase PAHs. Many PAHs are semi volatile in nature. PM$_{0.49}$ contains at least 56% of all PAHs. The major source for particulate matter at the rural site was the preharvest burning of sugarcane foliage (Oros et al., 2006; Hall et al., 2012) and vehicle emissions from the field during the SBS (Cristale et al., 2012).

**Oxygenated-Polycyclic Aromatic Hydrocarbons**

Oxy-PAHs are formed through PAH degradation in the atmosphere and from the direct emissions produced at combustion sources (Marynowski et al., 2014). They are semi volatile compounds featuring higher molecular weights and lower vapor pressures than those of their parent PAHs (Liu et al., 2006) and are formed during incomplete combustion by the addition of oxygen free radicals or molecular oxygen to PAHs with subsequent rearrangements (Allen et al., 1997).

Fig. 8(c) shows the oxy-PAH concentrations associated with size-segregated PM$_{10}$. During the SBS, individual oxy-PAHs, except for 1,8-naphthalic anhydride and benz[a]anthracene-7,12-dione at the urban site, primarily accumulated at both sites in PM$_{0.49}$ and PM$_{0.95-0.49}$. The overall oxy-PAH concentration at the rural site was 2.3 ng m$^{-3}$, approximately four times higher than the concentration measured at the urban site. 9, 10-Anthracenedione, a dominant oxy-PAH observed in all stages at both sites and during both seasons, was associated with coarse particles. The individual compound concentrations were higher at the rural site than at the urban site during the SBS. The oxy-PAH concentration patterns in all stages were similar to those of the PAHs during the SBS, indicating that PAH conversion caused oxy-PAH production. The high oxy-PAH concentrations at the rural site were attributable to sugarcane burning in the fields, vehicles used for transportation, and combustion in the sugarcane-processing facilities. However, the concentrations measured during the SGS were contradictory; the concentration of oxy-PAH at the urban site exceeded that at the rural site.

**Pesticides**

Atrazine (2-chloro-4-ethylamino-6-isopropyl-amino-s-triazine) is one of the pesticides most commonly used in North America to control certain annual broadleaf and grass weeds; it is primarily used in corn crops, and is also used in sorghum and sugarcane crops, as well as in landscaping (Solomon et al., 1996). Atrazine is applied to sugarcane fields after the harvest to prevent unwanted growth on the fields before the next planting season. Consequently, the pesticide is released into the atmosphere with soil dust. Rayner (2005) reported that human exposure to atrazine is linked to several severe health problems. Substantial concentrations of atrazine were identified in the size-segregated particle samples at the rural site. The concentrations of atrazine in the size-segregated PM$_{10}$ from both sampling sites are shown in Fig. 9(a). The concentration of atrazine in PM$_{10}$ was 43 times higher and approximately 13 times higher at the rural site during the SBS and SGS, respectively, compared with that at the urban site. This result indicates that sugarcane leaf burning and processing caused the elevated atrazine concentration at the rural site. During the SBS, 28% and 51.2% of mass atrazine was accumulated in PM$_{10}$ and PM$_{0.49}$, respectively, indicating that atrazine accumulated mainly in particles smaller than 0.49 μm. Nevertheless, a considerable amount also accumulated in coarse particles because atrazine can be adsorbed onto the surface of larger particles. Atrazine was also apparent during the SGS as a dominant source indicator at the rural site. Atrazine emissions from agricultural fields can reach urban areas and are measured in size-segregated ambient samples (Cooter and Hutzel, 2002); however, a small mass was detected in this study in different stages during both seasons.

**Succharides**

Levoglucosan (1,6-anhydro-b-D-glucopyranose) can be used as a specific indicator of compounds to detect the presence of emissions from biomass burning in samples of atmospheric PM (Simoneit et al., 1999; Fabbri et al., 2009). A previous study revealed that levoglucosan can be used as a tracer for the long-range transport of biomass aerosol because it does not degrade much within 10 days (Fraser and Lakshmanan, 2000). In South Florida, the representative biomass burning is mainly that of sugarcane foliage during the SBS at the rural and urban sites (Fig. 9(b)). During the SBS, the concentrations of levoglucosan were 6.9 and 5.1 ng m$^{-3}$ in PM$_{10}$ at the rural and urban sites, respectively. Although no biomass burning occurred at the urban site, the levoglucosan concentration level was near that at the rural site in Stages IV–VI. This result, because of the strong stability of levoglucosan, indicates the long-range transportation of fine particles from the rural site to the urban site. The backward trajectory (Fig. 2) and surface wind direction (Table 1) presented that it could be effective in particle transport on January 20 from Belle Glade to Delray Beach.

**Steroids**

Cholesterol is a specific organic tracer of primary particles produced from meat cooking (Rogge et al., 1991) and by algae on the ocean surface (Simoneit, 2002b). In this study, cholesterol was below the detection limit at the rural site. At the urban site, an atmospheric concentration of cholesterol was detected only in PM$_{0.49}$ (Fig. 10(a)); the concentration varied from 0.44 during the SBS to 0.1 ng m$^{-3}$ during the SGS. The concentration was four times higher in January than in May, possibly because of elevated levels of meat cooking. Different emission rates may have also changed the ambient cholesterol concentrations.

**n-Alkenoic Acids**

Oleic acid (9-octadecenoic acid, C18:1), belonging to the n-alkenoic acid group, is a predominant compound
emitted from meat cooking (Rogge et al., 1991), vegetative detritus and surface ocean (Kawamura and Gagosian, 1987). Oleic acid is unstable and can be rapidly oxidized and degraded in the environment (Simoneit et al., 1988). Dominant concentrations of oleic acid in PM$_{7.2-3}$ and PM$_{0.95}$ were observed in both seasons and at both sites (Fig. 10(b)). During SBS the concentrations of oleic acid associated with PM$_{3}$ were higher at both sites during the SBS compared with the SGS. In contrast, during SGS, oleic acid levels where equally distributed between PM larger than 3 µm and smaller than 3 µm. Indicating, that aerosol formation through leaf surface abrasion is the major source for oleic acid at the rural site. Oleic acid and cholesterol concentration patterns at the urban site were similar in January and May.

**Mass-Normalized Compound Concentrations**

South Florida has a subtropical climate. Although the winter temperatures recorded at both sites were similar, the variations in organic compound concentrations differed considerably because of the PM emission sources at the rural site. The mass-normalized concentrations (ng µg$^{-1}$) for selected primary organic compounds originating from sugarcane burning or related sources were calculated (Table 3). A comparison of the mass-normalized concentration data from the SBS and SGS revealed that the selected organic compounds were elevated at the rural site. The ratios of concentrations at the rural site to those at the urban site exceeded one because the concentrations of organic compounds in the rural ambient air were dominant. The n-alkanes C29, C31, and C33, which represent biogenic sources (leaf surface particles), were elevated at the rural site during the SBS. Moreover, n-alkanoic acids were dominant at the rural site during both seasons, except for C16 and C18 during the SBS. However, the mass-normalized concentrations of n-alkanoic acids were higher in the SGS than in the SBS, even though PM$_{10}$ concentrations were similar at both sites. In addition, sugarcane burning emits a considerable level of PAHs, which were detected at the rural site in PM$_{10}$ during the SBS. Surprisingly, though atrazine is a pesticide used in sugarcane agriculture, it is not a compound formed after sugarcane burning. Atrazine was dominant during both sampling periods in the ambient air at the rural site. Furthermore, the low concentration of atrazine in the urban atmosphere indicates true convection.

![Fig. 9. Atrazine and levoglucosan concentrations in size-segregated PM$_{10}$ at the urban and rural sites during the SBS and SGS.](image-url)
from the rural site to the urban site. Levoglucosan is the most distinct trace organic compound derived from sugarcane burning. The normalized mass concentration data suggested that the particles produced from sugarcane burning were carried from the rural site to the urban site.

**Health Effects**

Researchers suggest that fine particles could play a major role in potential adverse health effects (Buonanno et al., 2013). National Ambient Air Quality Standards (NAAQS) are frequently applied in urban areas. Maintaining daily and annual values of PM$_{2.5}$ according to the air quality parameters in the NAAQS is essential for protecting public health. Rogge et al. (2011) determined that 3-hourly PM$_{2.5}$ concentrations can vary drastically, showing that ambient 3-hourly concentration levels can be much higher than the annual or 24-hour averaged levels. Although Belle Glade, which has a population of approximately 15,000 people, is a rural town, the size-segregated PM$_{10}$ concentration levels were the same as those measured at the urban site during the SGS, implying that the rural site was influenced by local sources and transport of particulate matter from other source regions. The populations at the rural and urban sites were exposed to the same levels of particle concentrations. However, the PAH concentrations at the rural site were substantially elevated during the sugarcane harvesting season. Although the particle concentration levels at the urban site were similar to those at the rural site, the individual organic compound concentrations differed because the source emission rates varied by season. The results indicated that the rural population was exposed to similar risks as those encountered by the urban population. Lower MMAD values indicate a greater potential for PM penetration in the respiratory system. When fine and submicron particles contain more carcinogenic compounds, lung cancer risks might increase (Pinkerton et al., 2000).

**CONCLUSIONS**

In this study, six particulate size ranges in PM$_{10}$ were
Table 3. Mass-normalized compound concentrations (ng µg⁻¹).

| Compound                        | Rural | Urban | SBS | Urban | Rural/Urban | SGS | Rural | Urban | Rural/Urban |
|---------------------------------|-------|-------|-----|-------|------------|-----|-------|-------|------------|
| n-Nonacosane (C29)              | 0.0440| 0.0461| 0.0453| 0.0396 | 0.9548     | 1.1421|       |       |            |
| n-Hentriacontane (C31)          | 0.0412| 0.0363| 0.0358| 0.0301 | 1.1337     | 1.1883|       |       |            |
| n-Tritriacontane (C33)          | 0.0243| 0.0199| 0.0171| 0.0147 | 1.2198     | 1.1598|       |       |            |
| n-Hexadecanoic acid (C16)       | 0.3166| 0.5852| 0.6407| 0.4650 | 0.5411     | 1.3760|       |       |            |
| n-Octadecanoic acid (C18)       | 0.2001| 0.3376| 0.2704| 0.2144 | 0.5926     | 1.2611|       |       |            |
| n-Tetracosanic acid (C24)       | 0.1422| 0.1413| 0.1754| 0.0652 | 1.0066     | 2.6887|       |       |            |
| n-Hexacosanic acid (C26)        | 0.1545| 0.1630| 0.2438| 0.1442 | 0.9481     | 1.6913|       |       |            |
| n-Octacosanoic acid (C28)       | 0.1954| 0.1263| 0.1399| 0.0533 | 1.5468     | 2.6257|       |       |            |
| n-Triacontanoid acid (C30)      | 0.1377| 0.0943| 0.1547| 0.0608 | 1.4605     | 2.5456|       |       |            |
| n-Dotriacontanoid acid (C32)    | 0.0541| 0.0564| 0.0936| 0.0254 | 0.9576     | 3.6790|       |       |            |
| Phenanthrene                    | 0.0308| 0.0256| 0.0350| 0.0000 | 1.2038     | NA   |       |       |            |
| Fluoranthene                    | 0.0196| 0.0148| 0.0034| 0.0230 | 1.3216     | 0.1498|       |       |            |
| Pyrene                          | 0.0198| 0.0145| 0.0031| 0.0126 | 1.3706     | 0.2454|       |       |            |
| Benzo[a]anthracene              | 0.0085| 0.0099| 0.0023| 0.0266 | 0.8623     | 0.0860|       |       |            |
| Chrysene/Triphenylene           | 0.0133| 0.0102| 0.0016| 0.0152 | 1.3064     | 0.1031|       |       |            |
| Benzo[k] & [b]fluoranthene      | 0.0281| 0.0202| 0.0048| 0.0139 | 1.3928     | 0.3433|       |       |            |
| Benzo[e]pyrene                  | 0.0226| 0.0105| 0.0025| 0.0045 | 2.1587     | 0.5521|       |       |            |
| Benzo[a]pyrene                  | 0.0065| 0.0055| 0.0003| 0.0110 | 1.1822     | 0.0269|       |       |            |
| Atrazine                        | 0.0538| 0.0019| 0.0427| 0.0032 | 27.6321    | 13.3333|       |       |            |
| Levoglucosan                    | 0.2023| 0.2302| 0.0257| 0.0000 | 0.8788     | NA   |       |       |            |

NA: Not Available.

Simultaneously sampled for an extensive chemical characterization analysis, and the emission sources at urban (Delray Beach) and rural (Belle Glade) sites during the SBS and SGS in Palm Beach County, Florida, were compared. The size-segregated PM concentrations exhibited a bimodal distribution. Organic compounds mainly accumulated in submicron particles, particularly in PM0.49, featuring a 50% or greater organic compound mass. The variations in MMAD differed because of the sizes of particles emitted from sources during both sampling periods at both sampling sites. Of the collected particle mass, 50% was smaller than 1.55 microns, a size that can more easily be inhaled. The organic compound concentrations of PM10 were approximately 80%–99% in PM0.95. The urban and rural areas of Palm Beach County are influenced by numerous sources of primary and secondary aerosols, including biogenic sources, industrial, and vehicular emissions; sugarcane burning; resuspended dust, and sea spray particles. The sugarcane burning at the rural site during SBS emits considerable amounts of particles and causes the resuspension of surface soil dust resulting from vehicle movement in the fields. However, the organic compound concentrations in size-segregated PM10 differed considerably between January (SBS) and May (SGS). Although the mean concentrations produced during the overall burning or growing season may differ from those produced during January or May, respectively, the measurements in this study were conducted in the months that were representative of these seasons. For example, levoglucosan, an indicator of biomass burning, during the SBS was evident at both sites in PM1.5–0.49. Atrazine, an herbicide, was another compound observed mainly at the rural site during both seasons and in trace amounts in the urban atmosphere. The sugarcane leaf burning and vehicle exhaust in the fields are responsible for elevated hopane, PAH, and oxy-PAH concentrations in rural areas, a topic that should be investigated in future health-related studies.

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SUPPLEMENTARY DATA

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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