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Carbonaceous aerosol characteristics over a *Pinus taeda* plantation: Results from the CELTIC experiment

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ABSTRACT

Carbonaceous particles smaller than 2.5 μm aerodynamic diameter ($PM_{2.5}$) were collected in July, 2003 over a Loblolly Pine plantation at Duke Forest, NC during the **C**hemical **E**mission, **L**oss, **T**ransformation and **I**nteractions within **C**anopies (CELTIC) field study. Organic (OC) and elemental (EC) carbon in $PM_{2.5}$ ranged from 1.4–6.3 and 0.08–0.41 μg C m^{-3}, respectively, and concentrations measured above and below the pine canopy were in good agreement. Ambient OC was lower (<3 μg C m^{-3}) during cooler periods (daytime maximum temperatures < 28 °C) and for periods following precipitation events, and was higher (>3 μg C m^{-3}) during warm humid periods. Radiocarbon analysis indicates that on average 83% (range 78–91%) of the $PM_{2.5}$ carbon was derived from contemporary (biogenic VOC and biomass burning) sources. This is higher than previous estimates from urban and suburban sites, and in good agreement with recently published data from other rural sites throughout the U.S. The estimates of contemporary $PM_{2.5}$ carbon may represent a lower limit for this site since the sampler was located above the center of a 30 meter diameter plot fumigated with 200 ppm CO_2 derived from fossil carbon sources. However, this effect is likely to be negligible. The regression relationship between OC/EC ratios and percent biogenic carbon in aerosol is very similar to those observed in recent summertime data from Tennessee and Florida. However, our values for both OC/EC and percent biogenic carbon are higher than those observed in the latter studies, likely due to the more rural character of the site. Simple box model estimates indicate that biogenic VOC (BVOC) emissions measured at the site provide sufficient reactive carbon sources to account for the observed levels of aerosol biogenic carbon. The magnitude and temporal pattern in the box model secondary organic aerosol estimates correlate well with the ambient aerosol carbon measurements. The model estimates of the relative contribution of isoprene, α-pinene, and β-caryophyllene oxidation to $PM_{2.5}$ carbon are in reasonable agreement with a study recently conducted at a nearby site where aerosol tracers of these compounds were quantitatively analyzed in ambient $PM_{2.5}$. Pinic acid concentrations in the below-canopy $PM_{2.5}$ during CELTIC (from another recently published study) similarly suggest a significant contribution of α-pinene oxidation to $PM_{2.5}$ carbon. The biomass burning tracers potassium and levoglucosan yielded fire contribution estimates to $PM_{2.5}$ consistent with their respective published emission factors. These estimates indicate that biomass burning accounted for 1 to 5% (0.015 to 0.30 μg C m^{-3}) of the $PM_{2.5}$ carbon during CELTIC.

1. Introduction

Coniferous forests in the eastern United States emit a wide range of biogenic volatile organic compounds (BVOC), many of which are thought to be precursors to secondary organic aerosol (SOA). SOA is a major component (10–70%, Turpin et al., 2000) of fine particles with an aerodynamic diameter less than 2.5 microns ($PM_{2.5}$), which is regulated as a criteria pollutant by the U.S. Environmental Protection Agency (U.S. EPA). $PM_{2.5}$ has been found to affect visibility, climate (Malm et al., 2004), ecology, and human health (Samet et al., 2000) and is a persistent air quality problem in many global regions.

Current air quality models appear to over-predict organic carbon in western U.S. aerosol, but substantially underpredict organic aerosol carbon mass in the southeastern U.S. during the summer (Mebust et al., 2003), (Yu et al., 2007). Recent isotopic analyses of ambient aerosols in urban, suburban, and rural/remote environments indicate that biogenic carbon does indeed compose a substantial fraction of the summertime ambient aerosol carbon (Lemire et al., 2002; Lewis et al., 2004, 2006, Bench et al., 2007; Gelencser et al., 2007; Schichtel et al., 2008; Geron, 2009; Szidat et al., 2004, 2009; Takahashi et al., 2007). It is important to

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characterize the sources of this biogenically derived aerosol since it may contribute significantly to ambient particle concentrations and may represent sources that are not amenable to controls in air quality improvement programs (Lewis et al., 2004). In this study, some quantitative characteristics of ambient aerosol carbon over a *Pinus taeda* plantation in North Carolina are presented. Relationships between meteorological conditions, emissions of organic precursors, and organic aerosol concentrations are presented for the CELTIC (**C**hemical **E**mission, **L**oss, **T**ransformation and **I**nteractions within **C**anopies) experiment during July of 2003. Related CELTIC studies are discussed in Bhat and Fraser (2007), Helmig et al. (2006), Sparks et al. (2008), Stroud et al. (2007) and Turnipseed et al. (2006).

2. Methodology

2.1. Site description

CELTIC was conducted at the Blackwood Division of Duke Forest C-H_2O Free Atmosphere Carbon Transfer Scheme (FACTS1) research site in Orange County, North Carolina (35.98°N, 79.09°W) during July of 2003. FACTS1 (shown in Plate 1) is located between the towns of Chapel Hill (7 km to the south-southeast), Durham (17 km to the northeast), Raleigh (40 km to the southeast) and Burlington (30 km to the northwest). The closest major highway is I-40 (2.4 km to the northeast). FACTS1 is in a Loblolly Pine (*Pinus taeda*) plantation with approximate tree heights of 18 m and tree spacing of 2.0 m × 2.4 m. The forest understory features sweetgum (*Liquidambar styraciflua*), red maple (*Acer rubrum*), yellow poplar (*Liriodendron tulipifera*), and oak (*Quercus*) species. The FACTS1 experimental design (Hendry et al., 1999, http://c-h2oecology.env.duke.edu/Duke-Face) consists of six free-air CO_2 enrichment (FACE) rings, three of which provide elevated atmospheric CO_2 concentrations, and three represent ambient control rings. $PM_{2.5}$ measurements were performed at control ring 5 at the base of the central 26 m tower, and at CO_2 enriched ring 4 at the top of the tower. The plantation is approximately 330 m × 800 m in dimension with ring 4 having a fetch of ~500 m for predominant wind directions from the southwest and ring 5 having a fetch of ~ 300 m in the same direction. The $PM_{2.5}$ carbon data collected at ring 5 are discussed by (Bhat and Fraser, 2007) and are included here for comparison as well.

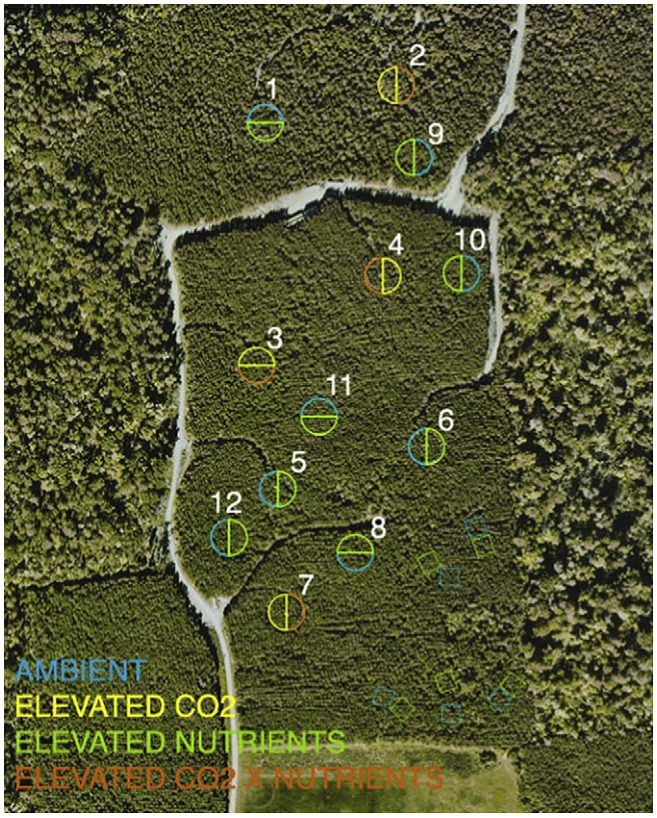

Plate 1. An aerial view of the FACTS1 site (http://face.env.duke.edu/description.cfm). The FACE rings are marked with circles. Ring 4 is in the upper third of the image. The squares indicate the location of the satellite fertilization study plots. Colors denote treatment. Note that CELTIC was performed before nutrient treatments were added to the plots.

2.2. Measurement intensive period

$PM_{2.5}$ samples were collected from July 10 to August 1, 2003. Midday conditions during the measurement intensive (10:00-14:00 EST) were typically sunny with scattered cumulus clouds. Light to moderate rainfall events occurred on four days as shown in Fig. 1. Daytime temperature and relative humidity ranges were 22.4–32 °C and 53–73%, respectively. The daytime 30-minute averaged canopy-top photosynthetic photon flux density (PPFD) ranged from 1.321–2.104 mE m^{-2} s^{-1}. Nighttime temperatures reached as low as 17 °C, and full relative humidity recharge (to 100% RH) was typically achieved for several hours nightly. Winds were predominantly from the south, southwest, and northwest, although during overcast and rainy periods winds were occasionally from the east to northeast. Measurements made with prevailing winds from the northeast to southeast can be influenced by emissions from I-40 or the Orange County landfill. On the other hand, easterly winds often bring a cleaner marine air mass to this region. Three of the 19 samples collected at ring 4 were at least partially influenced by winds from the northeast to southeast.

2.3. Measurement description

Particle sampling at rings 4 and 5 began on July 10, 2003. The ring 4 sampler operated over two consecutive 24 hr intervals and then over a 40 hour period during intermittent light rain from July 12 until the morning of July 14. In the meantime the ring 5 sampler collected $PM_{2.5}$ for 14 hours each day from approximately 5:30 a.m. until 7:30 p.m. (Eastern Daylight Time). From July 15 until July 24 the samplers at both rings sampled from approximately 5:30 a.m. until 7:30 p.m. $PM_{2.5}$ was also sampled during the nighttime periods from approximately 7:30 p.m. until 5:30 a.m. at ring 4. These measurements are summarized in Table 1.

Sample collection at ring 4 was performed with a Model 310 Universal Air Sampler (MSP, Inc., Minneapolis, MN), which sampled at 285 l min^{-1} using a virtual impactor (270/15 flow ratio) to separate the sampled aerosol into a $PM_{2.5}$ fraction (270 l min^{-1}) and a "coarse" particle fraction (15 l min^{-1}) composed mostly of particles larger than 2.5 μm aerodynamic diameter. The $PM_{2.5}$ particles deposited within an 81.0-mm diameter area on each 90-mm dia. quartz-fiber filter through use of a special filter holder adapter (MSP part no. HVI-SFH). The $PM_{2.5}$ samples were subsequently analyzed in this study. A single integrated coarse PM sample was also analyzed.

Sample collection at ring 5 was performed using a MSP Hi volume virtual impactor and an Anderson high volume sampler drawing 1100 l min^{-1} through an 8″ × 10″ quartz-fiber filter. Further details on the $PM_{2.5}$ sample collection and analysis at ring 5 are given in Bhat and Fraser (2007).

All filter handling details (preparation, transport to and from the field, and storage) were described previously (Lewis et al., 2004). Samples of 2003 growth *Pinus taeda* needles were collected from the central walkup towers in rings 4 and 5. These samples were intended to provide a consistency check of the ^{14}C content of living