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Qualitative and quantitative assessment of unresolved complex mixture in $PM_{2.5}$ of Bakersfield, CA

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HIGHLIGHTS

- Physicochemical properties of two separate UCM peaks for Bakersfield, CA.
- Daily trends for the two UCM peaks during the Jun 2010 CalNex-Bakersfield campaign.
- Physicochemical properties of UCM from NIST urban dust SRM 1649b

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ABSTRACT

The 2010 CalNex (California Nexus) field experiment offered an opportunity for detailed characterization of atmospheric particulate carbon composition and sources in Bakersfield, CA. In the current study, the authors describe and employ a new protocol for reporting unresolved complex mixture (UCM) in over 30 daily samples. The Bakersfield, CA site has significant contribution from UCM, 2.9 ± 2.2% of the daily OC, which makes it an ideal first application. The new protocol reports two UCM peaks for Bakersfield with unique mean vapor pressure, retention time, mass spectra and daily ambient concentration trends. The first UCM peak, UCM-A, was comprised of semi-volatile compounds including alkanes, alkenes, and alkynes, with a mean vapor pressure of 2E-04 Torr and medium to heavy-duty diesel exhaust as a likely source. The second UCM peak, UCM-B, was comprised of linear, branched, and cyclic alkanes, with a mean vapor pressure of 1E-08 Torr. UCM-B had strong similarities to UCM in the NIST Standard Reference Material 1649b (urban dust) and to previously reported, detailed UCM for a representative Bakersfield sample, with possible sources including: motor vehicle exhaust, agricultural activities, and construction activities.

1. Introduction

In 2010, the CalNex field experiment was conducted with two main ground sites to investigate the intersection of climate and air quality in Southern and Central California (California Nexus, http://www.arb.ca.gov/research/calnex2010/calnex2010.htm). Bakersfield, CA was chosen to improve understanding of the sources and atmospheric chemistry in the Central Valley with a focus on particulate matter (PM). Located at the southern end of the Central Valley, Bakersfield is bordered by coastal ranges in the west and by the Sierra Nevada Mountains in the east. These topographic features can combine with shallow boundary layers to trap and accumulate pollutants in the valley (Chow et al., 2006; Ahlm et al., 2012). $PM_{2.5}$ (PM ≤ 2.5 μm in aerodynamic diameter) concentrations in this region can reach 50 $\mu g\ m^{-3}$ in the winter (well above the annual NAAQS standard of 12 $\mu g\ m^{-3}$ and the 24-h standard of 35 $\mu g\ m^{-3}$) of which ammonium nitrate and organic mass are the dominant components (Chow et al., 2006). The Bakersfield–Delano metropolitan area has ~800,000 inhabitants and, in terms of known emission sources, it is surrounded by extensive highway systems, agriculture, and industrial areas including crude oil extraction and

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refinement which could contribute to the ambient $PM_{2.5}$ concentrations (Chan et al., 2013; Guzman-Morales et al., 2014). These sources can impact both primary and secondary organic aerosol (SOA) concentrations. For a more detailed site description, see Liu et al. (2012), who indicated that motor vehicle exhaust, wood combustion, and meat cooking comprise a significant fraction of the local PM (Liu et al., 2012). In addition to local anthropogenic sources, the prevailing wind direction during the CalNex campaign was from the Northwest (Ahlm et al., 2012), which could potentially transport biogenic hydrocarbons to the site (Liu et al., 2012). Thus, CalNex 2010 is ideally located to investigate PM composition at the urban-rural boundary.

Recent research has targeted semi-volatile organic compounds (SVOC) for their potential importance in the production of SOA (Robinson et al., 2007; Presto et al., 2010; Tkacik et al., 2012). Gasoline and diesel-powered motor vehicle exhaust emit characteristic SVOCs and thereby contribute to SOA formation, which include individual compounds and groups of unresolved organic mass. Both composition and vapor pressure are relevant for modeling SOA formation. Using one-dimensional gas chromatography mass spectrometry (GCMS), the majority of the SVOC mass cannot be speciated and is reported as an unresolved complex mixture (UCM) (Schauer et al., 1999, 2002). Usually the term UCM refers to a raised hump in the total ion count (TIC) of a chromatogram, which comprises hundreds of unresolved peaks (Gough and Rowland, 1991; Fraser et al., 1997; Wang et al., 2012; White et al., 2013). The presence of UCM was described in earlier studies (Blumer et al., 1970), but Farrington and Quinn were the first to use the term UCM in their paper describing sediments from Narragansett Bay (Rhode Island, USA) (Farrington and Quinn, 1973; White et al., 2013). Though first measured in sediments, UCM has been measured in atmospheric semi-volatile and particulate organic carbon as well (Fraser et al., 1997). Very recent advances in UCM analysis, for example GCxGCMS, have been applied to characterize atmospheric particulate organic carbon collected at CalNex sites on select days in Bakersfield and Pasadena, CA. This GCxGCMS technique offers improved resolution of the individual constituents which compose the UCM (Chan et al., 2013).

Conventional motor oil (lubricating oil), which consists of mineral base oil and other polymers, has been particularly challenging to resolve using 1-D GCMS techniques. The mineral base oil in this blend consists of petroleum hydrocarbons in the C_{20} to $>C_{40}$ range, and appears as a UCM hump in a chromatogram (Frysinger et al., 2003; Wang et al., 2004). Lubricating oils are known to be a major source of environmental hydrocarbon contamination (Gough and Rowland, 1990, 1991). In environmental samples, the presence of UCM is considered to be an indicator for petroleum pollution (White et al., 2013); other than crude oil and petroleum products, recently photosynthesized carbon or naturally derived lipids may also contribute to UCM in aerosols and sediments (Venkatesan and Kaplan, 1982; Laureillard et al., 1997; Silva et al., 2012). In earlier studies, a ratio of the UCM to resolved components (U:R) in atmospheric organic aerosols, observed during GCMS analysis, has been used as a qualitative indicator for the degree of anthropogenic contribution to atmospheric organic carbon (Cox et al., 1982; Simoneit and Mazurek, 1982; Mazurek et al., 1989; Hildemann et al., 1991). Aerosol samples dominated by vegetation derived organics showed U:R ratios less than 2.0; whereas urban aerosol samples had U:R ratios of 2.6–25 (Mazurek et al., 1989; Hildemann et al., 1991). Characterization of UCM in ambient $PM_{2.5}$ is relevant for understanding potential SOA formation and emission impacts on organic aerosol concentrations. Because of the potential variability in UCM methods, it is also vital to present physicochemical properties and method validation using standard reference materials.

To understand the daily trends in UCM composition and concentrations observed at Bakersfield, CA during the CalNex 2010 campaign, a new method was developed for deconvolution and quantification of multiple UCM peaks. This method was applied to the full CalNex Bakersfield campaign (May 19–June 26, 2010) and will be compared with the UCM previously characterized by Chan et al. (2013) which used GCxGCMS for the June 23, 2010 Bakersfield sample.

2. Materials and methods

2.1. Field sampling

The CalNex Bakersfield sampling campaign ran from May 19 to June 26, 2010 (Liu et al., 2012; Chan et al., 2013). The sampling site was located in Kern County, near Bakersfield in the San Joaquin Valley, 35.35°N, 118.97°W (Liu et al., 2012). During that time 38 samples were collected on a midnight to 11 pm schedule local time (23 h, PDT). $PM_{2.5}$ samples were collected on 86 cm^2 quartz fiber filters (Pall Life Sciences, NY, USA), with a medium-volume sampler (Tisch, OH, USA; flow rate of 226 L min^{-1}). The filters used for sampling were preconditioned by baking at 550 °C for 6 h to remove any potential organic contaminants. Field blanks were collected approximately every 10 days by placing a preconditioned filter on the sampler for ~15 min. The field blanks were handled and stored in the same manner as the sampled filters. During the sampling period, the temperature and relative humidity were consistent with averages of 24 ± 7 °C and $38 \pm 17\%$, respectively (Liu et al., 2012).

2.2. Chemicals

Phosphate-free biodegradable detergent (Liqui-Nox by Alconox, NY, USA) was used for washing the glassware and extraction cells (34 ml). The cleaned and baked glassware and extraction cells were rinsed with methanol followed by dichloromethane (DCM; ≥99.8% purity, J.T. Baker, NJ, USA) immediately prior to usage. The samples were spiked with a known quantity of an isotopically-labeled internal standard, IS#6 (Wisconsin State Laboratory of Hygiene, WI, USA) before extraction. The IS#6 standard includes: Pyrene-d_{10}, Benz[a]anthracene-d_{12}, Coronene-d_{12}, Cholestane-d_4, n-C_{15}-d_{32}, n-C_{20}-d_{42}, n-C_{24}-d_{50}, n-C_{30}-d_{58}, n-C_{32}-d_{66} and n-C_{36}-d_{74}. A standard mixture (PMSTD#12, Wisconsin State Laboratory of Hygiene, WI, USA) was used for quantification during GC–MS analysis. The PMSTD#12 includes n-alkanes from C_8 to C_{40}, cyclic and branched alkanes.

2.3. Extraction and analysis

2.3.1. Pressurized liquid extraction

The sampled filters were extracted using the Accelerated Solvent Extraction system (ASE; ASE 350, Thermo Scientific Dionex, CA, USA). The method developed for deconvoluting and quantifying the UCM was tested using the National Institute of Standards and Technology standard reference material for urban dust (NIST SRM 1649b, Gaithersburg, MD, USA). Each batch of CalNex filters (batch = 10), included one SRM (0.008–0.01 g) and one lab blank. Cells were preconditioned using the following ASE parameters: mixture of 1:1 methanol:DCM, temperature at 100 °C, 5 min heat time, 5 min static time, 120% rinse volume, three cycles and purged with Nitrogen for 100 s. The sampled filter was then placed inside the conditioned ASE cell and spiked with IS#6 and allowed to come to equilibrium for 60 min. Filter samples were extracted using the same protocol as the preconditioning except a sequential extraction of methanol followed by DCM was used. The methanol and DCM