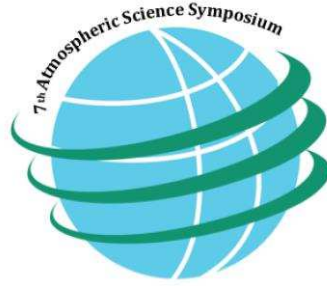


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DIURNAL VARIATION OF ORGANIC AEROSOL IN URBAN EAST ST. LOUIS, IL

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ABSTRACT

Despite significant efforts, the formation, evolution, properties, and removal mechanisms of organic aerosol remain uncertain. Current drawbacks in SOA formation models are related to detailed aerosol processes and the lack of field measurements that can be used as test or constraint. Diurnal variation of organic aerosol provides insight into secondary organic aerosol (SOA) transformation pathways and data can be used to evaluate SOA production models. However, analytical difficulties complicate the identification and quantification of OA components. In this work, a comprehensive method was developed and applied to investigate the diurnal variation of OA in the urban area of East St. Louis, IL. Aerosols were collected every 4-5 hours during the day and overnight with a high-volume air sampler, derivatized with a multi-step derivatization method, and analyzed with multidimensional gas chromatography (GC×GC-ToF-MS). Concentrations of functionalized species showed a diurnal variation, with highest levels at 0600-1400 h. Lower concentrations were observed in the afternoon. Variation in OA concentrations is influenced by diurnal changes of temperature, solar radiation, fresh emissions of OA precursors, and mixed layer height. The novel application of Van Krevelen diagrams to high temporal resolution samples was useful to evaluate diurnal variations in the degree of oxygenation of the OA. A clear dispersion of O:C ratios was observed throughout the day. The lowest O:C ratios were observed at 0600-1000 h, whereas the highest O:C ratios at 1000-1400 h. The study presented here provides the basis to better understand functionalization, fragmentation, and oligomerization processes and SOA formation pathways.

Keywords: diurnal variation, East St. Louis, multidimensional gas chromatography, secondary organic aerosol

ÖZET

Organik aerosolların oluşumu, gelişimi, özellikleri ve yokolma mekanizmaları üzerine önemli çalışmalar yapılmasına rağmen bu konularda belirsizliğini koruyan birçok nokta bulunmaktadır. Buna ek olarak, ikincil organik aerosol (SOA) oluşumu modellerinde mevcut olan eksiklikler, ayrıntılı aerosol süreci ve yeterli olmayan arazi ölçüm sonuçları ile yakından ilgilidir. Organik aerosollardaki günlük değişim, SOA'ların oluşum mekanizmaları hakkında fikir vermektedir ve elde edilen veriler SOA oluşumu modellerini değerlendirmede kullanılabilir. Fakat analitik zorluklar, OA bileşenlerinin ve miktarının belirlenmesi işlemlerini karmaşık hale getirmektedir. Yapılan bu çalışmada, doğu St. Louis, IL kentinin mücavir alanındaki OA'ların günlük değişimini incelemek üzere kapsamlı bir metod geliştirilmiştir. Aerosollar, yüksek hacimli örnekleyici kullanılarak tüm gün boyu 4-5 saat aralıklarla toplanmış, çok aşamalı türev dönüştürme metodu ile türevine dönüştürülmüş ve çok boyutlu gaz kromatograf (GC×GC-ToF-MS) ile analiz edilmiştir. Fonksiyonel grup konsantrasyonları günlük değişim göstermiş ve en yüksek seviyelerine sabah erken saatlerde (0600-1400) ulaşmıştır. Öğleden sonra ise bu değerlerde düşüş gözlenmiştir. Bu değişim, günlük sıcaklık değişimi, güneş ışınımı, yeni OA oluşumu ve karışım tabakası yüksekliği faktörlerinden etkilenmektedir. Oksijenlenme seviyesindeki değişimlerin anlaşılması amacıyla Van Krevelen diyagramları hızlı zaman çözünürlük numunelerine uygulanmıştır. Toplanan numunelerin O:C oranında tüm güne yayılan bir dağılım gözlenmiştir. En düşük ve en yüksek O:C oranı sırasıyla 0600-1000 ve 1000-1400 saatleri arası toplanan numunelerden elde edilmiştir. Sunulan çalışma, SOA oluşumu için önemli olan fonksiyonelleştirme, fragmentasyon ve oligomerizasyon işlemlerinin anlaşılması için bir temel oluşturmayı amaçlamaktadır.

1.INTRODUCTION

Aerosols have diverse effects on human health, climate, and ecosystems. Fine and ultrafine particles can penetrate into the circulatory system and cause health issues such as acute respiratory problems, congestive heart

failure, and long-term effects such as lung cancer and increase non-accidental morbidity (Kennedy, 2007). Aerosols also have an important role in radiation balance and lifetime and properties of clouds by absorbing and scattering solar radiation and acting as cloud condensation nuclei. Organic aerosol (OA) comprises a large fraction of the atmospheric aerosol mass that varies from 20% to 90%. The sources, formation mechanisms, removal processes, and climate and health effects are highly uncertain (Jimenez et al., 2009), which is partly due to the lack of suitable methodologies to quantitatively measure and identify the thousands of compounds with very different physicochemical properties that comprise the OA (Alves, 2008). In addition, OA is transported globally, thus the chemical composition, mass, and physicochemical properties are continually evolving (Jathar et al., 2015). OA is emitted directly by primary natural and anthropogenic sources (POA) and formed in the atmosphere through series of oxidation reactions of volatile organic compounds (VOC) to form secondary organic aerosol (SOA). The VOCs can be oxidized through two pathways: (1) oxygenated functional groups are incorporated into the parent VOC and (2) the molecule of the parent VOC undergoes fragmentation followed by functionalization. The oxygenated functional groups that can be added to the parent VOC are carbonyl (-C=O), hydroxyl (-OH), nitrate (-CONO_2), hydroperoxy (=COOH), carboxyl (-COOH), peroxy-carboxyl (-C(O)OOH), and ester (-C(O)OR) (Ziemann and Atkinson, 2012). The levels of oxygenation determines hygroscopicity (i.e., water uptake), cloud nucleating ability, phase, and light absorption and scattering.

Current drawbacks in SOA formation model forecasts are related to detailed aerosol processes such as fragmentation, oxidation reactions, and ice formation in mixed-phase clouds which are important in the development of precipitation, the behavior of aerosols at high relative humidity, and finally, the lack of field measurements performed under realistic ambient conditions that can be used as test or constraint (Jathar et al., 2015; Murphy, 2013). Laboratory chamber studies have been used to develop models of SOA production. However, only the first few generations of oxidation can be studied in a chamber, and thus, SOA production is typically underpredicted (Jathar et al., 2015). A number of 2-D and 3-D frameworks have been proposed to describe and/or model SOA formation pathways. Donahue et al., (2006) suggested a 2-D diagram of average carbon oxidation state (OS_c) and saturation vapor concentration to represent partitioning distributions. Pankow and Barsanti (2009) proposed a carbon number polarity grid of carbon number (n_c) and a measure of total molecular polarity based on enthalpy of vaporization to understand fragmentation, oxidation at constant n_c , accretion, and polymerization. Kroll et al., (2011) proposed a 2-D diagram of OS_c and n_c to represent functionalization, oligomerization, and fragmentation (Kroll et al., 2011) and more recently Flores and Doskey (2014) proposed a 3-D framework to group GC×GC data according to functionality. Two- and three-dimensional Van Krevelen diagrams of n_c , and elemental O:C and H:C ratios have been used to describe average properties of atmospheric OA (Daumit et al., 2013). Here we use a comprehensive methodology for identification and quantification of OA species in high-temporal resolution samples collected in a light urban/industrial area of East St. Louis (IL). Diurnal variation of functionalized OA and Van Krevelen diagrams are presented.

2. METHODS

2.1 Chemicals

All chemicals and solvents were purchased in the highest purity available from MP Biomedicals (Santa Ana, CA), Wako Chemicals (Richmond, VA), Sigma-Aldrich Chemical Co. (St. Louis, IL), and Burdick and Jackson (Muskegon, MI). Derivatizing reagents are 1% (v/v) Trimethylchlorosilane (TMCS) in Bis(trimethylsilyl)-

trifluoroacetamide (BSTFA), 98% O-methoxyamine hydrochloride (MHA), and a 2 M solution of trimethylsilyl-diazomethane (TMSD) in hexane (Sigma-Aldrich Chemical Co.). A total of 34 authentic standards that represent the varying complexity of organic aerosol were selected (Figure 2). The chemicals used as model compounds were organized according to functional groups as follows: Group 1: -OH, Group 2: -COOH, Group 3: -C=O, -COOH, Group 4: -COOH, -OH, and Group 5: -C=O, -OH. The authentic standards were stored in the dark and under dry conditions at 25°C. Stock standards of model compounds were prepared in a series of dilutions in either Methanol or 1:1 (v/v) dichloromethane (DCM)/acetonitrile (ACN) and stored at 4°C.

2.2 Sample collection

Samples were collected at the St. Louis – Midwest Supersite located in East St. Louis, IL (latitude: 38.6122, longitude: 90.16028, elevation: 184 m). The site is located approximately 3 km east of the city of St. Louis (IL) central business district in a light residential/industrial area near a highway with high loading of light- and heavy-duty vehicle traffic. The Ozarks forest in Missouri, which is known for high isoprene emissions, is located approximately 15 km west of the sampling site. A Tisch PNY1123 (Tisch Environmental, Cleves, OH) high-volume air sampler was used to collect 4-5 h samples of aerosol during the day beginning at 0600 h, 1000 h, 1400 h, and an 11 h sample overnight starting at 1900 h. The sampler was calibrated with a variable orifice prior to each 24-h sample period. Quartz fiber filters were individually wrapped in aluminum foil and pre-combusted at 450°C prior to sampling, and stored at 4°C before sampling, immediately after sampling, and during transport to avoid losses of semi-volatile compounds. Filter blanks were handled like samples for quality control purposes.

2.3 Sample processing and analysis

2.3.1 Extraction

All laboratory glassware (i.e., vials, flasks, Pasteur pipettes, thimbles, Soxhlet extractor, etc) was washed with a 5% solution (v/v) of ultrapure soap, rinsed three times with distilled water, oven-dried overnight, and pre-combusted at 450°C prior to use. Whole quartz filter samples were carefully cut into small strips and placed in glass thimbles of the Soxhlet extractor with tweezers. The filters were extracted with a 1:1 (v/v) mixture of DMC:MeOH for 24 h. Prior to sample analysis, six blank filters were spiked with a solution containing 600 ng of stock standards for quality control and evaluation of method performance. Extraction efficiencies and corresponding standard errors obtained from six replicate analysis can be found in Table 1. Following extraction, samples were allowed to stabilize to room temperature and the volume was reduced to approximately 5-ml with a vacuum-operated rotary evaporation unit. Extracts were then dried over sodium sulfate (Na_2SO_4) and proceeded to complete dryness under a gentle stream of ultrapure nitrogen. Dried extracts were stored at 4°C prior to derivatization.

2.3.2 Derivatization

The oxygenated functional groups of interest in organic aerosol that require derivatization prior to gas chromatographic analysis are -C=O, -COOH, and -OH. The functional groups were derivatized in a series of steps as follows: (1) -C=O was converted to a methyloxyme (R-N=O-CH_3) with 20 μL of MHA in ACN at 70°C for 60 min, (2) -COOH was converted a methyl ester (R-C(O)O-CH_3) with 6 μL of TMSD and 3.3 μL of MeOH with sonication for 20 min at room temperature, (3) -OH was converted to a trimethylsilyl (TMS) derivative (R-

OSi(CH₃)₃) with 180 µL of 1% TMCS in BSTFA (v/v) at 70°C in 60 min. The extracts were allowed to stabilize to room temperature and stored at 4°C until analysis, which was performed within 24 h following derivatization. The amounts of derivatizing reagents were selected based upon stoichiometric amounts suggested by Kowalewski and Gierczak (2011). Derivatization yields were obtained considering the average instrumental response of derivatization experiments performed in triplicate according to the maximum stoichiometric amounts (Kowalewski and Gierczak, 2011). Details of the method development, a discussion regarding advantages of the three-step derivatization method, and discussion regarding choice of solvents can be found elsewhere (Flores, 2013; Flores and Doskey). Table 1 shows derivatization efficiencies and corresponding standard errors for a series of studies performed in triplicate.

2.3.3 GC-analysis

Conventional GC and multidimensional GC×GC analyses were performed on a Leco Pegasus 4D GC×GC coupled to a time-of-flight (ToF) mass spectrometer (Pegasus IV, Leco, St Joseph, MI). The primary and secondary columns for analysis were a 30 m × 0.25 mm I.D. column coated with 0.25-µm-film-thickness of (50%-Trifluoropropyl)-methylpolysiloxane (DB-210; Agilent Technologies, Santa Clara, CA) and a 10 m × 0.10 mm I.D. column coated with 0.10-µm-film thickness of Polyethylene Glycol in a Sol-Gel matrix (SolGel-WAX; SGE Analytical Science, Austin, TX). The choice of columns was based on 3-D theoretical retention diagrams generated for the separation of a complex mixture of derivatized SOA species on 37 liquid and ionic commercially available GC stationary phases (Flores and Doskey, 2014). The multidimensional GC × GC was equipped with a Gerstel (GERSTEL, Inc., Linthicum Heights, MD) programmable temperature vaporizer (PTV) inlet that allows flexible temperature programs for quantitative transfer of sample components to the GC. The GC contains 2 ovens (i.e., main and secondary) for independent control of the temperature ramps for the primary and secondary columns and a thermal modulator that modulates the effluent from the primary column to the secondary column. After separation, the sample analytes are directed through the ion source and ToF detector for identification and quantification. Details on the selection of the PTV, GC, and MS programs can be found elsewhere (Flores and Doskey, 2014). Briefly, the PTV was held at 60 °C for 0.2 min and then increased to 240 °C. The GC oven was held at 60 °C for 1 min and increased to 180, 200, and 240 °C at 20, 11, and 8 °C min⁻¹, respectively. The ToF-MS was operated at -70 eV in positive electron ionization (EI) mode and mass spectra were acquired from 50 to 500 m/z at 200 Hz. A series of dilutions of derivatized model compounds (see Fig. 2) were analyzed 6 times to calculate instrumental detection limits (Flores, 2013; Flores and Doskey). Average detection limits (ng m⁻³) are reported in Table 1.

2.4 Data processing

For the analysis reported here, samples were limited to integration of 500 compounds. Identification of compounds was performed by comparison of true mass spectra with a personalized mass spectral library built upon derivatized model compounds, commercially available NIST mass spectral library, and mass spectra reported in the literature. Only the identified species that provided a similarity match above 70% were considered. Analytes were quantified according to their unique mass fragment ion (UI). Identified species were organized according to functional groups and concentrations were calculated by solving linear calibration curves of model compounds as follows: (1) -COOH with dodecanoic acid, (2) -2COOH with pentanedioic acid,

hexanedioic acid, heptanedioic acid, and nonanedioic acid, (3) $-\text{COOH}$, $-\text{OH}$ with tartaric acid, (4) $-\text{C}=\text{O}$, $-\text{COOH}$ with ketoglutaric acid, (5) 4-5-OH with meso-erythritol, (6) $-\text{OH}$ with hexadecanol, (7) cyclic $-\text{C}=\text{O}$, 3OH with levoglucosan, (8) cyclic $-\text{C}=\text{O}$ with nopinone, (9) aromatic $-\text{COOH}$ with p-toluic acid, and (10) aromatic $-\text{COOH}$, $-\text{OH}$ with 4-hydroxybenzoic acid. Average concentrations of identified species in organic aerosol are reported in Table 1. Van Krevelen diagrams were obtained by calculating the O:C and H:C ratios of identified species with structures corrected for adduct groups from the 3-step derivatization method. The resultant diagram of a diurnal sample is shown in Fig. 4

3. RESULTS AND DISCUSSION

3.1 Extraction yield

Aerosol samples were subjected to a number of required processing steps in preparation for analysis. The nature of the processing steps compromise the qualitative and quantitative results. The sample extraction and processing method were evaluated by spiking a known amount of stock solutions of authentic standards of the model compounds (Fig. 2) on clean pre-combusted quartz fiber filters. Table 1 shows average extraction yields (%), which also include solvent reduction steps by rotary evaporation and nitrogen blowdown, and standard error of model compounds organized by functional group for 6 experiments. A mixture of 1:1 (v/v) DCM and MeOH was observed to be the optimal combination of solvents, which provided the best extraction efficiency for the highest number of derivatized species (Flores and Doskey). The best recoveries of model compounds were obtained by species containing single functionalities $-\text{OH}$ and $-\text{COOH}$ (89.61 and 85.93 %, respectively) followed by species containing $-\text{C}=\text{O}$, and $-\text{COOH}$ (79.30 %). High recoveries of species containing single functionalities were expected due similar interaction with the extraction solvents. The lowest recovery was obtained for species containing $-\text{C}=\text{O}$ and $-\text{OH}$ (43.96%), followed by $-\text{COOH}$ and $-\text{OH}$ (52.15%). The species that contributed to the low extraction efficiencies were S-S-2-Hydroxy-3-pinanone ($-\text{C}=\text{O}$, $-\text{OH}$), L-Tartaric acid (2- COOH , 2- OH), and Gallic acid (aromatic, $-\text{COOH}$, $-\text{OH}$) (7.77, 4.55, and 2.011 %, respectively). Recovering species containing multi- and poly-functionalities which represent a continuum of vapor pressures and polarities is extremely challenging. The average standard error for all model compounds was 20.5% and is acceptable considering the number and complexity of processing steps. Future work involves studying recoveries with other mixtures of solvents and alternative extraction methods like accelerated solvent and supercritical fluid extraction.

3.2 Derivatization

A three-step derivatization method performed in series was evaluated. The polar functionalities, $-\text{C}=\text{O}$, $-\text{COOH}$, and $-\text{OH}$, were converted to their methyloxime, methyl ester, and trimethylsilyl derivatives to increase the volatility of the analyte and facilitate transfer through the GC system. The average derivatization yield for all model compounds was 78.1 % with an average error of 6.92 % (Fig. 2). Lowest recoveries were obtained for compounds containing $-\text{C}=\text{O}$ (57.4 %) and $-\text{C}=\text{O}$, $-\text{OH}$ (75.7 %), however, precision is within acceptable values. Also, there are several advantages to using MHA rather than O-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA-HCl) as the derivatizing reagent to derivatize $-\text{C}=\text{O}$ (Kowalewski and Gierczak, 2011). Future work will involve using greater amounts of derivatizing reagent to increase the yields levels of oxygenated analytes in OA.

3.3 Diurnal variation of functionalized OA species.

Aerosol samples were collected on August 22-26, 2011. Average volumes of air collected during the day and night were 35.36 m³ and 97.68 m³, respectively. Table 2 and Fig. 3 show average concentrations of species identified in OA organized by functional group. The general trend among the identified oxygenated species was high concentrations in the morning from 0600 h until 1400 h due to fresh emissions of precursors and photooxidation throughout the morning to midday. The decrease in concentrations that is observed later in the afternoon is likely due to dilution by an expanded mixed layer (Ding et al., 2012). Maximum concentrations were observed for compounds with -COOH, -OH (29.19 ng m⁻³ and 39.13 ng m⁻³ at 0600-1000 h and 1000-1400 h, respectively). Peak concentrations of fatty acids (-COOH) and fatty alcohols (-OH) were 0.87 and 0.03 ng m⁻³, respectively, which are approximately 2 orders of magnitude smaller than those reported in the megacities of Xi'an and New Delhi (Li et al., 2014). Dicarboxylic acids (2 -COOH) and polyols (4, and 5 -OH) were more than 2 orders of magnitude less than those found in the megacities of Mumbai and Hong Kong (Aggarwal et al., 2013; Li and Yu, 2005a). Ketocarboxylic acids (-C=O, -COOH) ranged from below detection limits to 370 ng m⁻³ in seven locations in Hong Kong (Li and Yu, 2005b) whereas in this study the highest concentrations were 1.5 ng m⁻³ in an early morning sample. Concentrations of polyols (i.e., 2-Methyltetrols) and other multifunctional SOA tracers have variable ranges from below instrumental detection limits to 784 ng m⁻³ in a number of locations with various biogenic and anthropogenic sources around the world (Claeys et al., 2004; Ding et al., 2008; Ion et al., 2005; Kleindienst et al., 2007; Kourtchev et al., 2005; Lewandowski et al., 2008; Xia and Hopke, 2006). Factors that influence diurnal variations in OA composition and concentration include the following: emission rates, reaction rates, ambient temperature, solar radiation, and height of mixed layer (Ding et al., 2012). Thus, comprehensive studies of emissions, seasonal variations of OA, and comprehensive characterization of OA species in high temporal-resolution samples are necessary to understand SOA formation pathways and improve SOA production models.

3.4 Variation of oxygenation levels

Molecular formulas of oxygenated species identified in samples collected on August 22, 2011 were determined to calculate H:C and O:C ratios. Van Krevelen diagrams for samples collected during the day (0600-1000 h, 1000-1400 h, and 1400-1900 h) and overnight (1900-0600 h) are shown in Fig. 4. Average O:C ratios were 0.4, 0.6, 0.5, and 0.5 for samples collected at 0600 h, 1000 h, 1400 h, and overnight, respectively. Average H:C ratios were 1.8, 1.8, 1.7, and 1.7 for samples collected at 0600 h, 1000 h, 1400 h, and overnight, respectively. The O:C ratios observed in East St. Louis are comparable to those found in Heshan, China, Sacramento, USA, Hong Kong, China, New York City, USA, and Kaiping China (Gong et al., 2012; He et al., 2011; Huang et al., 2011; Setyan et al., 2012; Sun et al., 2011 in Daumit et al., 2013). Other heavily industrialized cities and megacities around the world exhibited higher O:C ratios that ranged 0.65-1.02 (Daumit et al., 2013). The average elemental H:C ratios observed in East St. Louis were comparable to the locations reported above (1.12-1.49). Variations in O:C ratios in high time resolution samples can be used to evaluate diurnal variations in SOA formation by determining the spread of data in Fig. 4. Box plots were created to quantify the magnitude of the spread of data (Fig. 5a). The O:C ratios in samples collected overnight were low due to the low O content in freshly-emitted SOA precursors. The OA species further oxidize in the presence of sunlight, which can be observed by a higher average O:C and larger spread of data in the sample collected at 1000-1400 h. The O:C values remain relatively

constant in samples collected at 1400-1900 h and 1900-0600 h; however, the minimum oxygenation levels are larger than the sample collected early in the morning, which indicates the species collected after 1400 h are already oxygenated. Approximately 43 % of the total identified species in the sample collected at 0600-1000 h has an O:C ratio between 0.0 and 0.2 (Fig. 5b). The total number of identified species is 187, 154, 150, and 149 in samples collected at 0600-1000 h, 1000-1400 h, 1400-1900 h, and 1900-0600 h respectively. A more detailed molecular analysis is required to better understand functionalization, fragmentation, and oligomerization processes, and SOA formation pathways.

4. CONCLUSION

A novel approach for comprehensive molecular analysis of diurnal variations in OA composition and concentration in a light residential and industrial area of East St. Louis, (USA) was presented. Complete characterization of OA with high-temporal resolution requires the following: (1) a high-volume air sampler to collect sufficient mass for molecular analysis over a 4-h time period, (2) a 3-step derivatization method for unambiguous identification of substances containing polar functionalities, and (3) a GC×GC-ToF-MS, which provides high peak capacity and rapid data collection to separate, identify, and quantify molecular species in OA. Temperature changes during the day, solar radiation, fresh emissions of OA during the day, and changes in the mixed layer height influence photochemical reactions and a diurnal variation of organic aerosol was clearly observed. Variable meteorological conditions throughout the sampling period suggest local sources of OA from light and heavy vehicular traffic and possibly emissions from the Ozarks Forest located west of the sampling station impacted East St. Louis. Highest concentrations of functionalized species in OA were observed early in the morning between 0600 and 1400 h. Lower concentrations later in the afternoon are likely due to dilution by an expanded mixed layer. Application of Van Krevelen diagrams to high-temporal resolution aerosol samples was used to evaluate diurnal variations in the degree of oxygenation of the OA. Increases in O:C ratios for aerosol samples collected in the morning and middle of the day suggest photooxidation of volatile species. The O:C ratio of OA collected overnight increased and is likely due to the decrease in boundary layer height during the night. Average O:C ratios (i.e., 0.4-0.6) observed during the day are consistent with other field studies. Future work includes application of the strategy developed here to elucidate SOA formation pathways in heavily urbanized areas with variable sources of OA in megacities like Istanbul and Mexico City. Application of the method has important implications for the advancement of SOA production models and elucidation of OA sources for air pollution control purposes.

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Table 1. Average method extraction yields, derivatization yields, and detection limits of model compounds considered in this study. Species identifications are shown in Figure 2.

Functional Group	Extraction yield (%)	Extraction standard error (%)	Derivatization yield (%)	Derivatization standard error (%)	Detection Limit (ng m ⁻³) ³
-C=O	8.611	1.240	57.400	6.880	0.054
-OH	89.617	22.224	90.017	7.440	0.007
-COOH	85.932	18.839	80.236	7.187	0.011
-C=O, -COOH	79.289	17.445	77.110	5.593	0.011
COOH, OH	52.156	18.274	88.125	6.172	0.010
C=O, OH	43.961	17.234	75.706	8.267	0.026

Table 2. Diurnal variation of oxygenated species in organic aerosol. Data represents average concentration (ng m⁻³) of OA collected on Aug 22-26, 2011 in a light urban/industrial area in East St. Louis, IL

COOH	2COOH	COOH, C=O	4,5-OH	cycli c 3OH, C=O	COOH aromatic	OH, COOH aromatic	COOH , OH	C=O cyclic	OH
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³ 30 m³ of collected air were assumed in the calculation

6-10am	3.816	5.181	3.667	0.697	7.107	1.492	2.886	29.188	15.48 1	1.05 2
10-2pm	4.350	6.879	2.802	0.084	6.646	1.414	1.973	39.133	9.674	1.19 2
2-7pm	2.493	5.746	1.637	<QL	3.723	0.953	2.332	21.129	11.46 8	0.65 6
7-6am	1.148	3.660	0.921	0.413	1.869	0.838	1.548	8.892	13.23 3	0.16 8

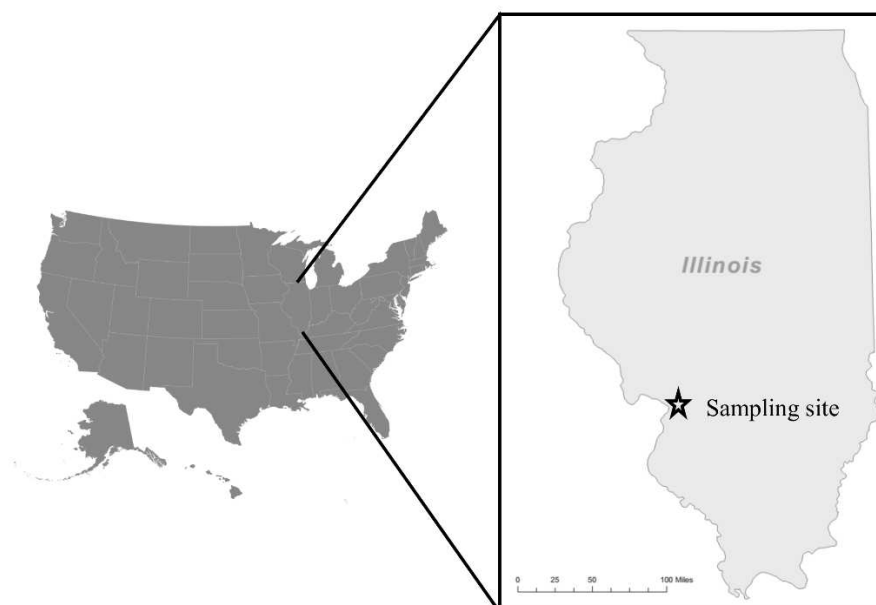


Fig. 1. Sampling site located in the US EPA Midwest Supersite in East St. Louis, IL (USA)

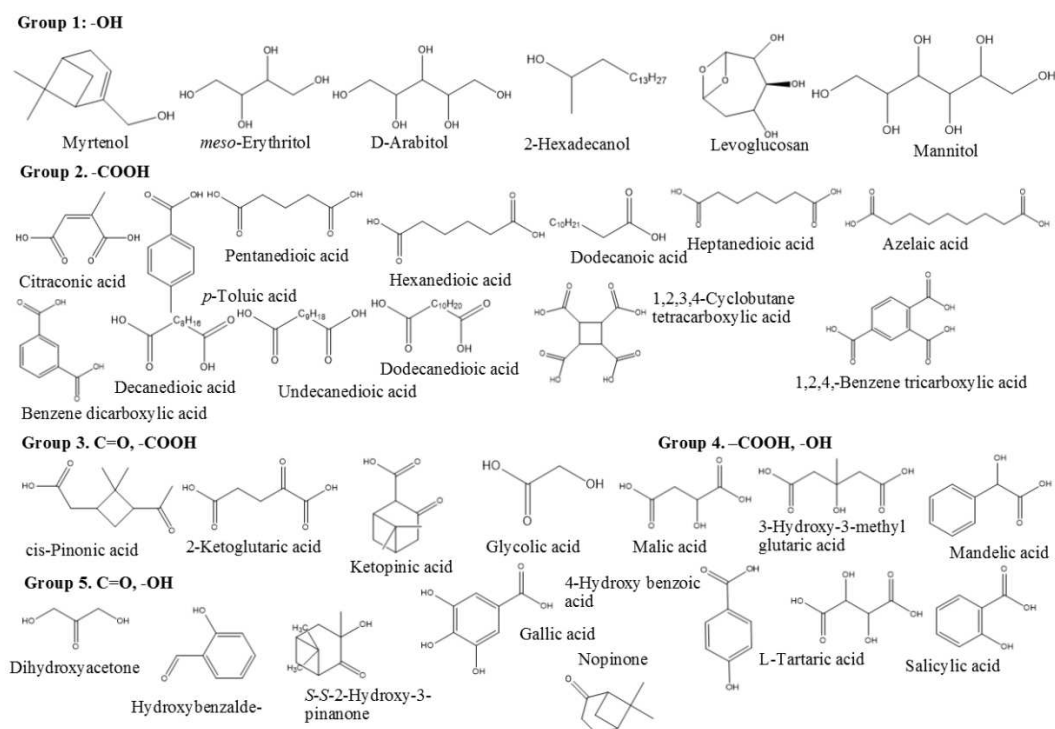


Fig. 2. Model compounds used in this study to estimate extraction and derivatization yields

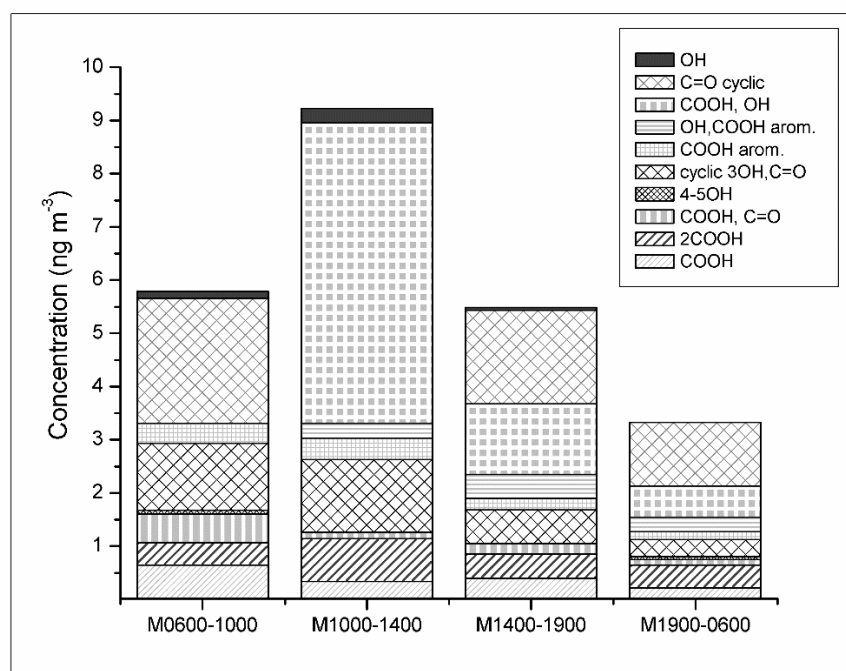


Figure 3. Average concentrations of functionalized OA species collected on August 22, 2011

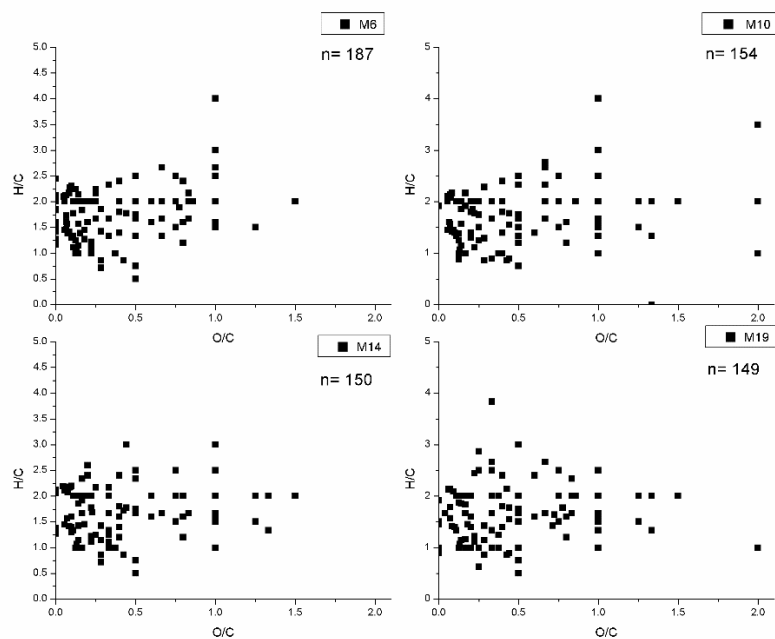


Fig. 4. Van Krevelen diagrams of samples collected diurnally on August 22, 2011.

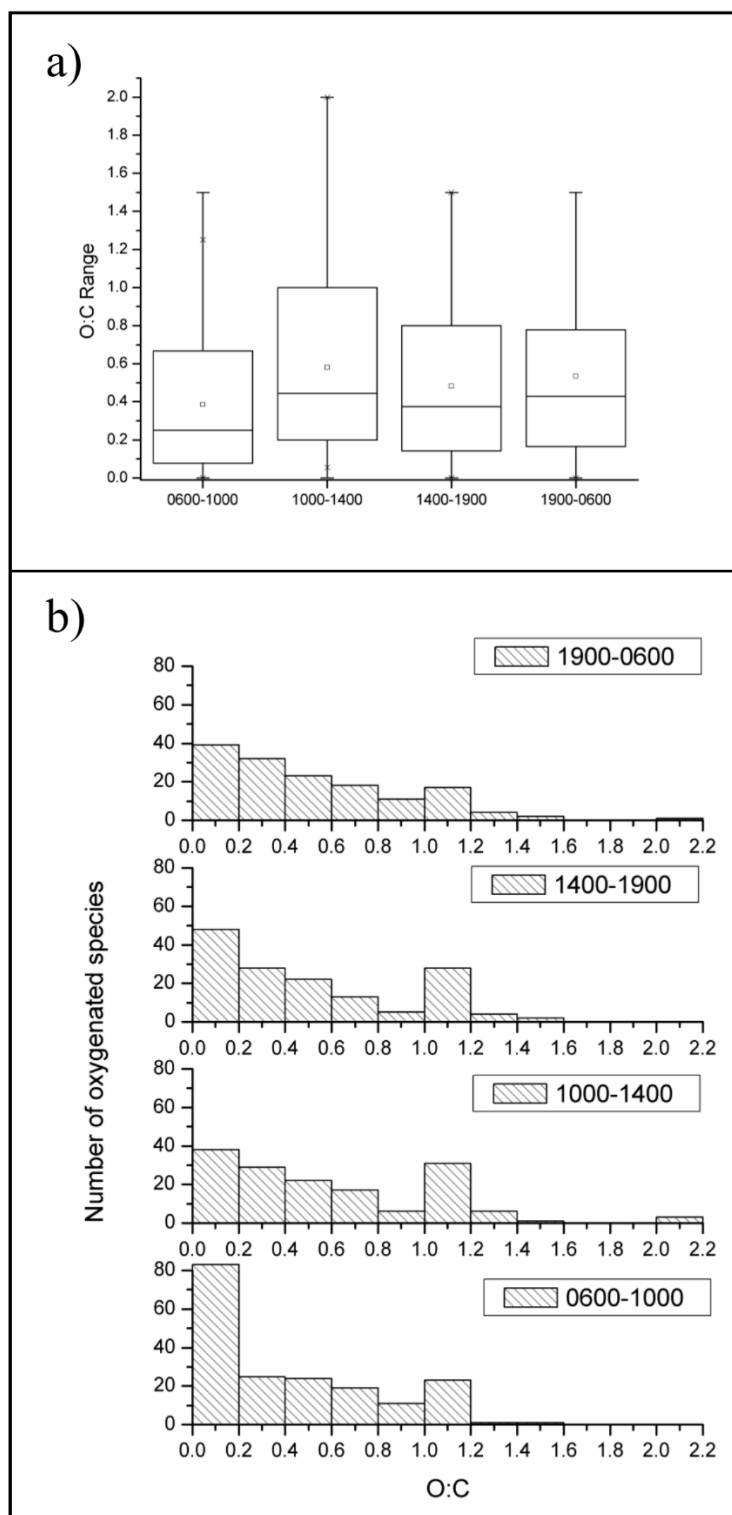


Fig. 5a, b. Frequency distribution of oxygenated OA species for the highly-timed resolved sample collected on August 22, 2011