# Analysis of Organic Molecular Markers in Atmospheric Fine Particulate Matter: Understanding the Impact of "Unknown" Point Sources on Chemical Mass Balance Models

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## Abstract

   Particle-phase organic tracers (molecular markers) have been shown to be an effective method to assess and quantify the impact of sources of carbonaceous aerosols. These molecular markers have been used in chemical mass balance (CMB) models to apportion primary sources of organic aerosols in regions where the major organic aerosol source categories have been identified. As in the case of all CMB models, all important sources of the tracer compounds must be included in a Molecular Marker CMB (MM-CMB) model or the MM-CMB model can be subject to biases. To this end, the application of the MM-CMB models to locations where reasonably accurate emissions inventory of organic aerosols are not available, should be performed with extreme caution. Of great concern is the potential presence of industrial point sources that emit carbonaceous aerosols and have not been well characterized or inventoried. The current study demonstrates that emissions from industrial point sources in the St. Louis, Missouri area can greatly bias molecular marker CMB models if their emissions are not correctly addressed. At a sampling site in the greater St. Louis Area, carbonaceous aerosols from industrial point sources were found to be important source of carbonaceous aerosols during specific time periods in addition to common urban sources (i.e. mobile sources, wood burning, and road dust). Since source profiles for these industrial sources have not been properly characterized, method to indentify time periods when point sources are impacting a sampling site, needs to avoid obtaining biases source apportionment results. The use of real time air pollution measurements, along with molecular marker measurements, as a screening tool to identify when point sources are impacting a receptor site is presented.

**Key words** : Organic Molecular Marker, Chemical Mass Balance, Source, EC, OC

# 1. INTRODUCTION

   Understanding the composition of atmospheric organic aerosols is necessary for identifying their sources and predicting their effect on various atmospheric processes. Hundreds of particle-phase individual organic compounds have been identified over the past few decades and have been quantified in ambient air using gas chromatograph/mass spectro-

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metry (Wang et al., 2009; Lee et al., 2008; Olson and Norris 2008; Sheesley et al., 2004; Sheesley et al., 2003; Schauer et al., 2002a; Allen et al., 1999; Schauer et al., 1999a; Simoneit et al., 1999). Although only between 10% to 30% of the total particulate organic compound mass can be quantified as individual organic species, particle-phase organic compounds have been used in source apportionment receptor models to quantify the impact of key sources of organic aerosols including diesel trucks, gasoline vehicles, wood smoke, road dust, meet cooking, vegetative detritus, and natural gas combustion (Jaeckels et al., 2007; Bae et al., 2006; Sheesley et al., 2003; Zheng et al., 2002; Schauer and Cass, 2000; Schauer et al., 1996).

On this basis of the law of mass conservation, a chemical mass balance (CMB) receptor model seeks to find the best-fit linear combination of source profiles that can best represent the chemical composition of chosen atmospheric samples (Kang et al., 2008; Lee et al. 2008; Bae et al., 2006; Schauer and Cass, 2000; Schauer et al., 1996). However, unknown sources that are not included in the source profiles violate the mass balance assumption and tend to bias the model results. Although the use of multivariate models, such as Positive Matrix Factorization (PMF), can often avoid the problems associated with unknown sources, such models require a large datasets of observations to obtain useful relates that can related model derived factors with air pollution sources. For this reason, there is a need to develop strategies to identify when unknown point sources are impacting the sampling sites for a short period, which can be used as a screening tool for Molecular Marker CMB (MM-CMB) models.

The current study uses real time measurements and molecular marker measurements to demonstrate how these measurements can be used as a screening tool to determine when point sources are likely to bias MM-CMB models. The methods are demonstrated using data collected at the St. Louis Supersite between June 22 and July 31, 2001 to identify the impact of the point sources that are important contributors to carbonaceous particulate matter. These results show how unknown point sources of atmospheric fine

organic aerosol can be identified and how they can bias MM-CMB models.

## 2. CARBONENOUS AEROSOL SAMPLING COLLECTION AND ANALYSIS

Fig. 1 and 2 present schematic of organic and Organic Carbon (OC) and Elemental Carbon (EC) samplers and extraction method for GC/MS analysis at St. Louis Supersite for measurement of fine particle organic carbon speciation.

### 2.1 24-hour integrated EC/OC

Fine particulate matter samples were collected at the St. Louis Supersite (Bae et al., 2004a) for daily 24-hour integrated average Organic Carbon (OC) and Elemental Carbon (EC). All integrated samples for EC/OC analysis were collected downstream of $PM_{2.5}$ cyclones that operated at flowrate of 24 liters per minute (lpm) on quartz fiber filters that were pre-baked at $550°C$ for at least 12 h before sample collection. Before and after sampling, filters were stored in petri dishes with baked aluminum foil liners. After sample collection the filters were stored at freezer conditions until they were analyzed. The laboratory based thermal-optical EC/OC analyzer (Sunset Laboratory) was used to analyze the quartz fiber filters using the same protocol that was employed for the ACE-Asia EC/OC intercomparison study (Schauer et al., 2003). As previously discussed by Bae et al. (2004b), an organics denuder that was fabricated with replaceable parallel charcoal-impregnated filter strips to collect gas-phase organic compounds was used the downstream quartz fiber filter (Bae et al., 2004b; Sullivan et al., 2004).

### 2.2 Semi-continuous EC/OC

In addition to the 24-hour average EC/OC measurements, two semi-continuous EC/OC instruments were operated using a one hour sample collection period followed by a one hour chemical analysis period to collect and analyze on alternating hours to allow continuous sample collection. The semi-conti-
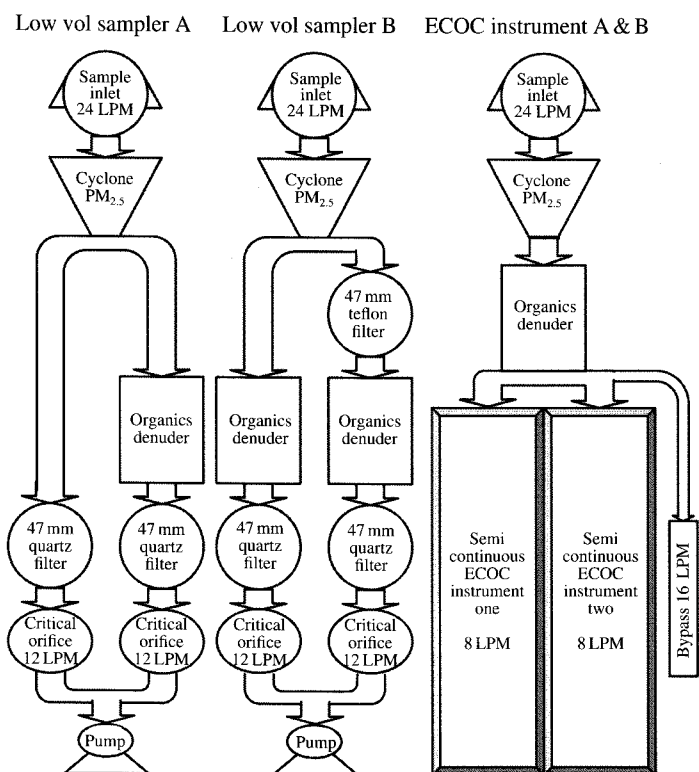
**Fig. 1. Schematic of 24-hour integrated EC/OC samplers and semi-continuous EC/OC instruments at the St. Louis Supersite.**

nuous EC/OC Instruments operated with the same cyclone and denuder system, which was used for the 24 hour integrated EC/OC samplers. Filter blanks and instrument blanks were performed once every week along with two different external calibrations. A new filter was installed weekly and was spiked with a sugar solution during loading as an external calibration. In addition, an external source of methane gas was injected as a secondary calibration. Details of the semi-continuous EC/OC analyzer have been previously described (Bae et al., 2004a, b). Briefly, the particle-laden filter was heated in an oxygen-free ultra high purity helium atmosphere. As organic compounds were vaporized, they were immediately oxidized to carbon dioxide and passed through a methanator to reduce the $CO_2$ to methane. The methane was then quantified by a flame ionization detector (FID). After the completion of the oxygen-free heating stages, the oven was cooled and the pure

helium oven purge gas was switched to a 2% oxygen/helium mixture. During this phase, both the original EC and that produced by the pyrolysis of organics during the first heating stages were burned in the presence of oxygen to form carbon dioxide. The carbon dioxide was then converted to methane and detected by the FID. During this initial heating cycle some of the organic carbon pyrolytically converted to EC. The pyrolytic conversion was continuously monitored by measuring the transmission of a 660 nm wavelength laser that passed through the filter (Huebert and Charlson, 2000). This pyrolysis that is darkening of the filter deposit can be corrected by the amount of light transmittance by a laser beam. The point during the second heating cycle where the laser beam transmission through the sample returned to the original sample transmission was used to define the split between OC and EC.

A single-channel Aethalometer (Magee Scientific

Company, Berkeley, CA) eq uipped with a $PM_{2.5}$ inlet impactor was operated to measure the aerosol Black Carbon (BC) concentrations at the same sampling site. Air samples drawn by the Aethalometer operated through a quartz-fiber tape determined by the light-absorbance.

### 2. 3  Organic Molecular Markers

Samples collected for molecular marker analysis were collected downstream of $PM_{2.5}$ cyclones that operated at flowrate of 92 lpm in medium volume samplers (Bae et al., 2006; Sheesley et al., 2004). Flow through the medium volume samplers were controlled using critical orifices and were checked before and after each sample was collected and were equipped with timers to start and stop sample collection at midnight each day. The inlets of the all samplers were equipped with a rain hat to avoid rain and snow from entering the sampler. All integrated samples for molecular marker analysis were collected on quartz fiber filters that were prebaked at 550°C for at least 12 hours before sample collection and were placed in petri dishes lined with baked aluminum foil liners.

### 2. 3. 1  Quantification of Organic Compounds

The methods and procedures for the organic speciation have been previously reported (Sheesley et al., 2003; Schauer et al., 2002a,b, 1999b; Mazurek et al., 1987). Before extraction, each sample which consisted of one half of the 90 mm quartz filters from the medium volume sampler, was spiked with set of internal standards that included dodecane-$D_{26}$, decanoic Acid-$D_{19}$, phthalic Acid 3,4,5,6-$D_4$, acenaphthene-$D_{10}$, hexadecane-$D_{34}$, levoglucosan-U-13$C_6$ (carbon 13 uniform labeled compound), eicosane-$D_{42}$, heptadecanoic Acid-$D_{33}$, 4,4'-dimethoxybenzophenone-$D_8$, chysene-$D_{12}$, octacosane-$D_{58}$, aaa-20R-cholestane-$D_4$, cholesterol-2,2,3,4,4,6-$D_6$, dibenz[ah]anthracene-$D_{14}$, and hexatriacontane-$D_{74}$.

As shown in Fig. 2, the sample were extracted a total of 4 times using sonication. The samples were sonicated 2 times with 30 mL of high purity dichloromethane for 10 minutes and then were sonicated twice with 30 mL of high purity methanol for 10
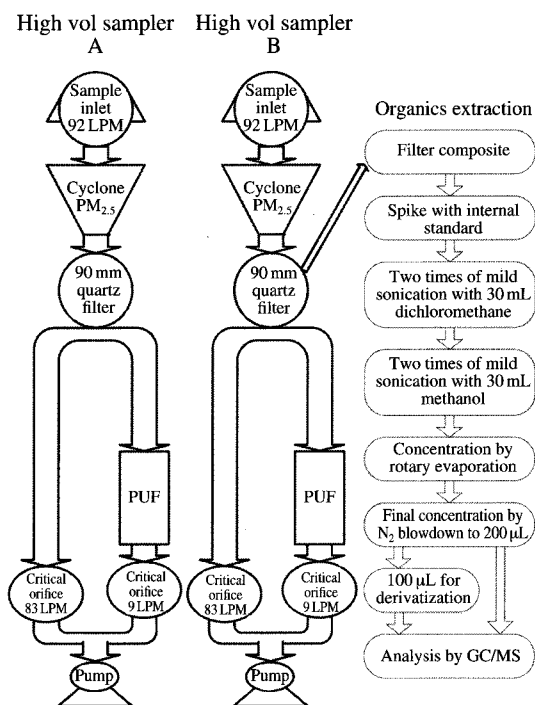


Fig. 2. Schematic of medium volume samplers used for samples collected for organic molecular marker analysis by solvent extraction for GC/MS analysis at St. Louis Supersite for measurement of fine particle matter.

minutes in each jar. The two extracts were combined and reduced in volume to approximately 5 mL using a vacuum rotary evaporator. The samples were then filtered into a graduated test tube throughout a PTFE syringe filter. As a final step, the samples were reduced in volume using nitrogen blow down to a final volume that yielded a final concentration of the internal standards in the extract equivalent to the internal standard spike and the internal standard concentrations in the quantification standards. Half of the final extract volume was methylated using diazomethane (1-methyl-3-nitro-1-nitrosoguanidine, MNNG) (Ngan and Toofan, 1991). The other half volume of extract was reacted with silylation reagent to derivatize levoglucosan and cholesterol to their trimethylsilylderivatives (TMS-derivatives). After the derivation, the samples were reconcentrated to the pre-derivatization final volume. Table 1 summarized the average

**Table 1. Organic Molecular Markers analyzed by GC/MS from June 22 to July 31 in 2001.**

| Organic molecular marker | Average[1] | Std error[2] | Organic molecular marker | Average[1] | Std error[2] |
|---|---|---|---|---|---|
| Tetracosane | 3.22 | 0.62 | Benzenetricarboxylic acid | 1.00 | 0.09 |
| Pentacosane | 4.44 | 0.60 | Benzenetetracarboxylic acid | 0.26 | 0.02 |
| Hexacosane | 2.19 | 0.40 | Butanedioic acid | 8.28 | 1.48 |
| Heptacosane | 3.11 | 0.52 | Pentanedioic acid | 1.78 | 0.20 |
| Octacosane | 1.54 | 0.53 | Hexanedioic acid | 1.76 | 0.36 |
| Nonacosane | 2.67 | 0.45 | Heptanedioic acid | 0.71 | 0.16 |
| Triacontane | 2.77 | 1.88 | Octanedioic acid | 2.01 | 0.38 |
| Hentriacontane | 3.04 | 1.20 | Nonanedioic acid | 1.23 | 0.17 |
| Dotriacontane | 1.21 | 0.72 | 17a(H)-22,29,30-Trisnorhopane | 0.15 | 0.02 |
| Tritriacontane | 1.19 | 0.49 | 17b(H)-21a(H)-30-Norhopane | 0.56 | 0.04 |
| Tetratriacontane | 1.36 | 0.69 | 17a(H)-21b(H)-Hopane | 0.48 | 0.03 |
| Pentatriacontane | 1.20 | 0.66 | 22S, 17a(H),21b(H)-30-Homohopane | 0.24 | 0.02 |
| Hexatriacontane | 1.32 | 0.68 | 22R, 17a(H),21b(H)-30-Homohopane | 0.20 | 0.02 |
| iso-Nonacosane | N/D | N/D | 22S, 17a(H),21b(H)-30-Bishomohopane | 0.14 | 0.01 |
| anteiso-Triacontane | 0.25 | N/D | 22R, 17a(H),21b(H)-30-Bishomohopane | 0.10 | 0.01 |
| iso-Hentriacontane | N/D | N/D | 22S, 17a(H),21b(H)-30,31,32-Trishomohopane | 0.12 | 0.01 |
| anteiso-Dotriacontane | N/D | N/D | 22R, 17a(H),21b(H)-30,31,32-Trishomohopane | 0.07 | 0.01 |
| iso-Tritriacontane | N/D | N/D | 20R, 5a(H),14b(H), 17b(H)-Cholestane | 0.14 | 0.01 |
| Pentadecylcyclohexane | 0.26 | 0.12 | 20S, 5a(H),14b(H), 17b(H)-Cholestane | 0.09 | 0.01 |
| Hexadecylcyclohexane | 0.15 | 0.02 | 20R, 5a(H),14a(H), 17a(H)-Cholestane | 0.11 | 0.01 |
| Heptadecylcyclohexane | 0.23 | 0.03 | 20R, 5a(H),14b(H), 17b(H)-Ergostane | 0.07 | 0.01 |
| Octadecylcylcohexane | 0.25 | 0.03 | 20S, 5a(H),14b(H), 17b(H)-Ergostane | 0.09 | 0.01 |
| Nonadecylcyclohexane | 0.19 | 0.02 | 20R, 5a(H),14b(H), 17b(H)-Sitostane | 0.11 | 0.01 |
| Tetradecanoic acid | 2.02 | 0.64 | 20S, 5a(H),14b(H), 17b(H)-Sitostane | 0.10 | 0.01 |
| Pentadecanoic acid | 2.65 | 0.89 | Fluoranthene | 0.18 | 0.03 |
| 9-Hexadecenoic acid | 0.50 | 0.11 | Acephenanthrylene | 0.02 | 0.00 |
| Hexadecanoic acid | 12.95 | 3.11 | Pyrene | 0.12 | 0.02 |
| Heptadecanoic acid | 1.64 | 0.36 | methyl substituted MW 202 PAH | 0.22 | 0.04 |
| 9,12-Octadecanedienoic acid | 0.23 | 0.05 | Benzo(ghi)fluoranthene | 0.52 | 0.06 |
| 9-Octadecenoic acid | 0.50 | 0.22 | Cyclopenta(cd)pyrene | 0.36 | 0.07 |
| Octadecanoic acid | 17.91 | 5.04 | Benz(a)anthracene | 0.12 | 0.05 |
| Nonadecanoic acid | 0.38 | 0.03 | Chrysene/Triphenylene | 0.17 | 0.03 |
| Eicosanoic acid | 0.55 | 0.06 | methyl substituted MW 226 PAH | 0.26 | 0.05 |
| Heneicosanoic acid | 0.19 | 0.02 | methyl substituted MW 228 PAH | 0.32 | 0.05 |
| Docosanoic acid | 0.59 | 0.07 | Benzo(b,k)fluoranthene | 0.51 | 0.11 |
| Tricosanoic acid | 0.28 | 0.03 | Benzo(j)fluoranthene | 0.05 | 0.02 |
| Tetracosanoic acid | 1.05 | 0.12 | Benzo(e)pyrene | 0.22 | 0.06 |
| Pentacosanoic acid | 0.38 | 0.14 | Benzo(a)pyrene | 0.10 | 0.02 |
| Hexacosanoic acid | 0.89 | 0.09 | Perylene | 0.04 | 0.01 |
| Heptacosanoic acid | 0.20 | 0.02 | Indeno(cd)pyrene | 0.15 | 0.03 |
| Octacosanoic acid | 1.02 | 0.11 | Dibenz[a,h]anthracene | 0.04 | 0.01 |
| Nonacosanoic acid | 0.18 | 0.03 | Benzo(ghi)perylene | 0.20 | 0.03 |
| Triacontanoic acid | 1.21 | 0.18 | Coronene | 0.19 | 0.03 |
| Pimaric acid | 12.31 | 3.44 | Retene | 0.10 | 0.03 |
| Isopimaric acid | 0.10 | 0.04 | 1H-Phenalen-1-one | 0.24 | 0.03 |
| Sandaracopimaric acid | 11.57 | 4.71 | Anthracen-9,10-dione | 0.45 | 0.07 |
| 8,15-Pimaredienoic acid | 0.57 | 0.50 | Benz(de)anthracen-7-one | 0.09 | 0.01 |
| Dehydroabietic acid | 13.27 | 7.54 | Benz(a)anthracene-7,12-dione | 0.18 | 0.03 |
| 7-Oxodehydroabietic acid | 28.62 | 2.28 | 1,8-Naphthalic anhydride | 0.73 | 0.24 |
| Abieta-6,8,11,13,15-pentae-18-oic acid | 12.57 | 1.36 | Levoglucosan | 60.48 | 12.04 |
| Abieta-8,11,13,15-tetraen-18-oic acid | 0.31 | 0.09 | Cholesterol | 0.76 | 0.12 |
| Abietic acid | 3.60 | 2.31 | Stigmasterol | 1.42 | N/D |
| 1,2-Benzenedicarboxylic acid | 1.79 | 0.15 | Bis(2-ethylhexyl)phthalate | 16.58 | 1.87 |
| 1,4-Benzenedicarboxylic acid | 4.98 | 0.78 | Dibutylphthalate | 21.88 | 2.32 |
| 1,3-Benzenedicarboxylic acid | 0.43 | 0.04 | 1,2-Dimethylphthalate | 4.85 | 0.62 |
| 4-Methyl-1,2-benzenedicarboxylic acid | 0.46 | 0.03 | Squalene | 0.73 | 0.15 |

[1] Unit: ng/m³, [2] Standard error

concentrations of organic molecular markers for this study.

### 2.3.2 Gas Chromatography Mass Spectrometer

The same GC/MS protocols were used to analyze the neutral extracts, the methylated extracts, and the silylated extracts. A 5MS GC column (ultra low bleed 5%-diphenyl, 95%-dimethylsiloxane copolymer) was used for the measurements as this column has low bleed that improves sensitivity for all compounds. Calibration for GC/MS analysis was performed using three-point calibration curves referenced to internal standards for more than 100 target organic compounds previously identified as useful molecular markers. The quantification standards including n-alkanes, n-alkanoic and aromatic acids, PAH, levoglucosan, hopanes, steranes, and cholesterol (Schauer and Cass, 2000; Schauer et al., 1996). These standards contain a variety of molecular markers that have been used as tracers for source apportionment modeling including the following sources: meat cooking, motor vehicles, vegetative detritus, and cigarette smoke. The methodology for addressing the completeness of sources has been presented by Schauer et al. (1996).

### 2.4 Cheminal Mass Balance (CMB) Receptor Modeling By Organic Molecular Markers

The molecular marker chemical mass balance (MM-CMB) model developed by Schauer et al. (1996), which uses specific organic compounds as molecular markers to apportion source contributions to atmospheric fine particle mass and atmospheric fine particle organic carbon concentrations, was employed to quantify sources of OC at the St. Louis Midwest Supersite. The CMB solution was obtained using the US EPA CMB8.2 software to compute the effective variance least square solution (Watson et al., 1984). Ambient and source profiles used in the MM-CMB calculation consisted of molecular markers that were analyzed by GC/MS, elemental carbon, silicon, and aluminum. The source emission profiles used in the present study were obtained from previous source testing efforts that used the same analytical methods for source profiling of diesel trucks, gaso-

line-powered cars, smoking vehicles, wood smoke, road dust, vegetative detritus, and natural gas combustion (Lough et al., 2005; Schauer et al., 2002a, b, 1999a, b; Rogge et al., 1994, 1993a, b, c, d; Hildemann et al., 1991) Fig. 3 presents examples of source profiles used for apportionment with MM-CMB. The fitting species which were EC, Si, Al, n-alkanes (n-$C_{29}$ through n-$C_{33}$), hopanes, steranes, levoglucosan, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo [e]pyrene, indeno(cd)pyrene, dibenz[a,h] anthracene, and benzo(ghi)perylene (Jaeckels et al., 2007; Bae et al., 2006; Zheng et al., 2002).

## 3. RESULT AND DISCUSSION

### 3.1 Daily Organic Molecular Marker Concentrations

Fig. 4 and 5 present the temporal variation of daily source contribution by MM-CMB and the average variation of OC (solid line) and EC (dotted line) from June 22 to July 31 in 2001 along with the 24-hour average concentrations of organic compounds that are the primary emission markers at the St. Louis Supersite. The molecular marker concentrations on June 30 and July 26 are not shown due to malfunction of samplers, which prevented the collection of samplers, and analysis failure. The annual-average OC and EC concentration for calendar year 2002 at the St. Louis Supersite was measured to be 3.88 and 0.70 μg m$^{-3}$, respectively (Bae et al., 2004a). The average OC concentration for the 39 days shown in Fig. 5 is 10% higher than the reported 2002 annual averages measured and was 4.26 μg m$^{-3}$. However, the average EC concentration for these 39 days was the same level as the reported 2002 annual averages measured as 0.70 μg m$^{-3}$.

During 39 days sampling period, the highest 24-hour average OC concentration was 11.9 μg m$^{-3}$ and the highest 24-hour average EC concentration was 2.97 μg m$^{-3}$. Previous study shows the monthly average EC to OC ratio varied noticeably over the course of 2002 with the highest ratio in the winter and lowest in summer. The lower EC to OC ratio in the summer is believed to be from higher concentrations of

Organic molecular markers
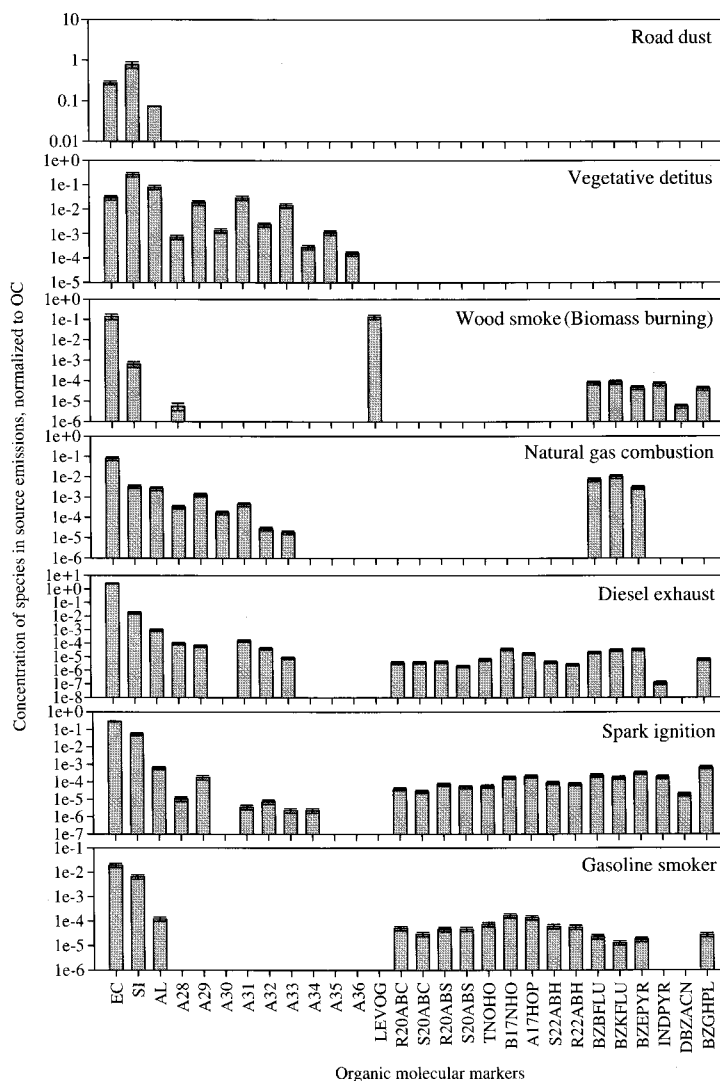
| EC | Elemental Carbon | S20ABC | 20S, 5a(H),14b(H), 17b(H)-cholestane |
| SI | silicon | R20ABS | 20R, 5a(H),14b(H), 17b(H)-sitostane |
| AL | aluminum | S20ABS | 20S, 5a(H),14b(H), 17b(H)-sitostane |
| A28 | octacosane | TNOHO | 17a(H)-22,29,30-trisnorhopane |
| A29 | nonacosane | B17NHO | 17b(H)-21a(H)-30-norhopane |
| A30 | triacontane | A17HOP | 17a(H)-21b(H)-hopane |
| A31 | hentriacontane | S22ABH | 22S,17a(H),21b(H)-30-homohopane |
| A32 | dotriacontane | R22ABH | 22R,17a(H),21b(H)-30-homohopane |
| A33 | tritriacontane | BZBFLU | benzo(b)fluoranthene |
| A34 | tetratriacontane | BZKFLU | benzo(k)fluoranthene |
| A35 | pentatriacontane | BZEPYR | benzo[e]pyrene |
| A36 | hexatriacontane | INDPYR | indeno[cd]pyrene |
| LEVOG | levoglucosan | DBZACN | dibenz[a,h]anthracene |
| R20ABC | 20R, 5a(H),14b(H), 17b(H)-cholestane | BZGHPL | benzo[ghi]perylene |

**Fig. 3. Source Profiles used for apportionment with Chemical Mass Balance Model (Note: mass of Species normalized to mass of organic carbon).**
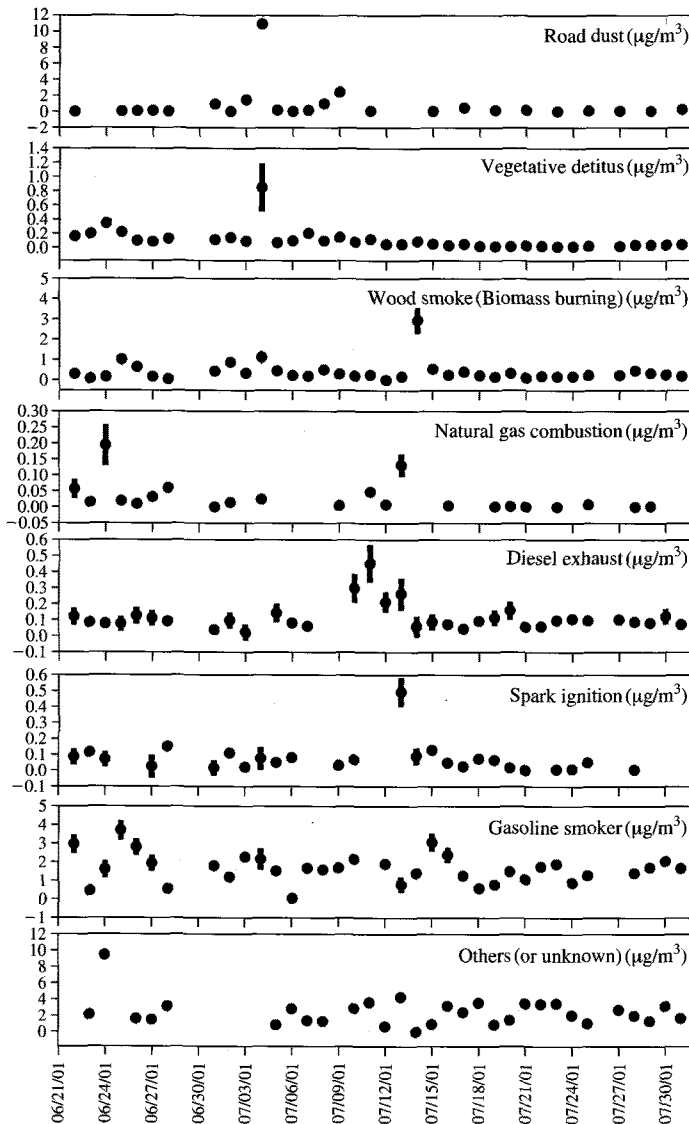
Fig. 4. Temporal variation of Daily Source Contributions by Organic Molecular Marker Chemical Mass Balance Model.

secondary organic aerosol. Likewise, the higher EC to OC ratios in winter are believed to result from wood burning and changes in vehicular emissions. In addition, a comparison of the daily average EC and OC concentrations demonstrates different daily source trends as well. As a result, the EC to OC ratio varied noticeably over the course of the 39 days shown in Fig. 5 with the highest ratio, 0.65 on July 11 and lowest, 0.04 on June 24. The variations in EC

to OC ratio are believed to results from the emissions of local point sources of organic and elemental carbon. In this context, we hope to understand the unknown sources through the examination of the chemical compositions of PM on days impacted by these point sources and existing correlation between OC and daily changes of organic molecular markers.

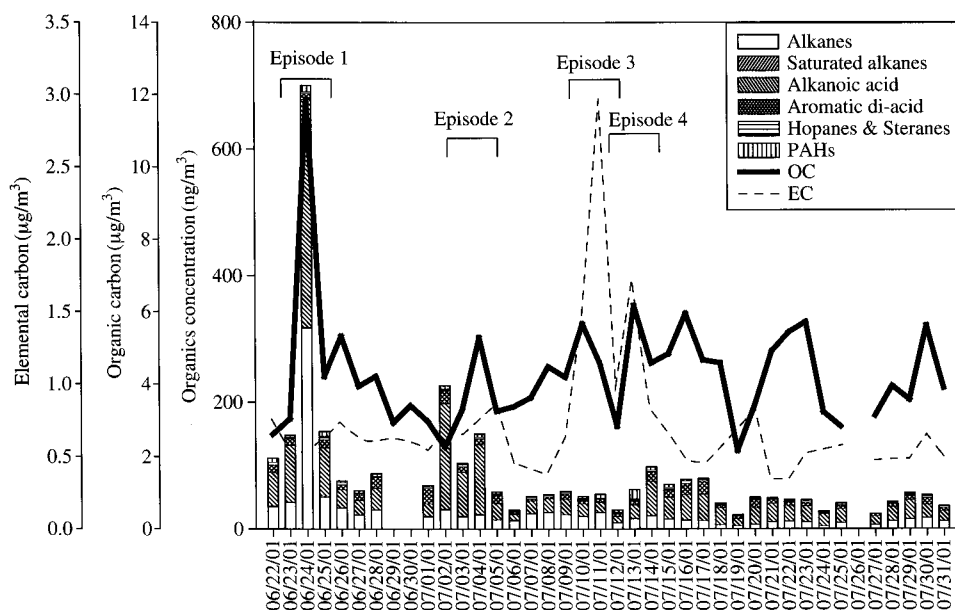Four air pollution Episodes were identified by significant short term increases in OC or EC, as would

**Fig. 5. Temporal variation of 24-hour integrated OC (solid line) and EC (dotted line) from June 22 to July 31 in 2001 along with concentrations of grouped organic compounds that are the primary emission markers at the St. Louis Super-site.**

be expected from the impact of a plume form a local emissions source. Episode 1 occurred on June 24 and was characterized by high organic carbon concentrations. Episode 2 was on July 4, which is a holiday in the United States. Episode 3 occurred on July 11 as was characterized by high elemental carbon concentrations. Finally, Episode 4 occurred on July 13 and was characterized by both high organic and elemental carbon concentrations.

Fig. 6 shows the daily patterns in n-alkanes ($C_{24}$-$C_{32}$) concentrations. The average sum of individually analyzed n-alkane ($C_{24}$-$C_{36}$) in this study was 2.08 ng $m^{-3}$ per alkane over the 39 day period. A previous study in Los Angeles found that while no single compound could serve as a suitable tracer for vegetative detritus, these compounds provided a fingerprint that could be used to quantify the contributions of vegetative detritus to fine particle organic carbon. ($C_{23}$-$C_{33}$) (Rogge et al., 1993c). However, it is important to note that other anthropogenic activities such as cigarette smoking, wildfires, etc., also contribute to these high molecular weight n-alkanes to the urban atmo-

sphere (Rogge et al., 1994).

Episode 1 contained remarkably large variations in n-alkanes concentrations, which were coincident with OC concentration changes. On June 24, the highest concentration of total n-alkanes (sum of $C_{24}$-$C_{36}$) for the 39 days was observed at 317 ng $m^{-3}$. In contrast, the EC concentrations follow a different pattern with EC concentrations being relatively lower on June 24. These results suggest that the changes in sources significantly impacted OC concentration on June 24 over a relatively short time period as indicated by the OC concentrations.

Fig. 6, also, shows the daily patterns in PAH concentrations: benzo[ghi]fluoranthene, cyclopenta[cd] pyrene, benz(a)anthracene, chrysene/triphenylene, benzo(b,k)fluoranthene, benzo[j]fluoranthene, benzo [e]pyrene, benzo[a]pyrene, perylene, indeno(cd)pyrene, dibenz[a,h]anthracene, benzo(ghi)perylene, and coronene. It is important to note that PAHs are important features of fine particle emissions from some natural gas combustion and from motor vehicles (Schauer et al., 2002b; Rogge et al., 1993d), and since
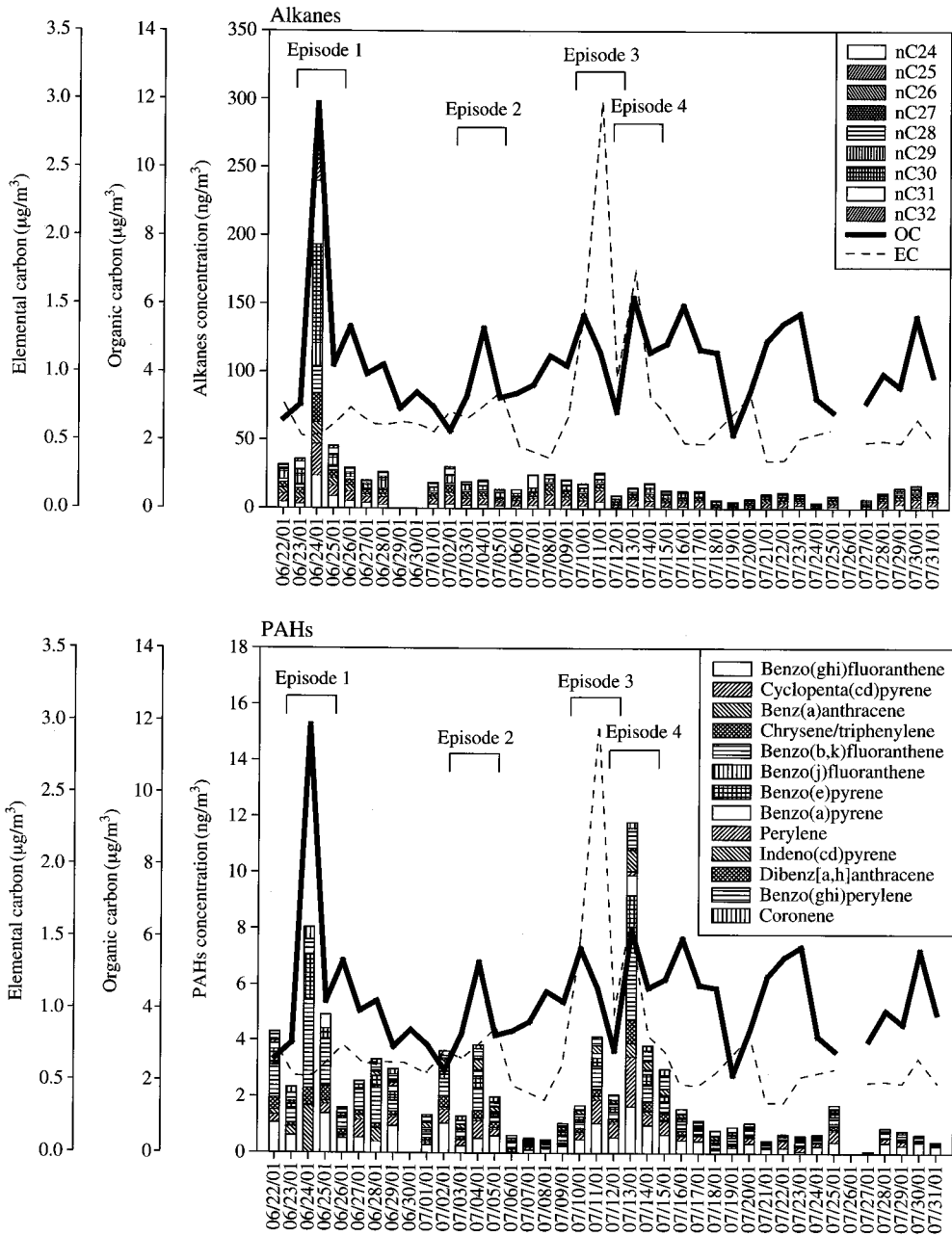
Fig. 6. Daily patterns in n-alkanes ($C_{24}$-$C_{32}$) and PAH concentrations in fine particulate matter from June 22 to July 31 in 2001 at the St. Louis Supersite.

these did not correlate with OC changes during episode 1, it is not expected that the OC changes during episode 1 resulted from mobile sources of natural gas combustion. In contrast, PAH concentrations during Episode 4 increased to a level that was 5.4 times higher PAH concentrations than the 39 day
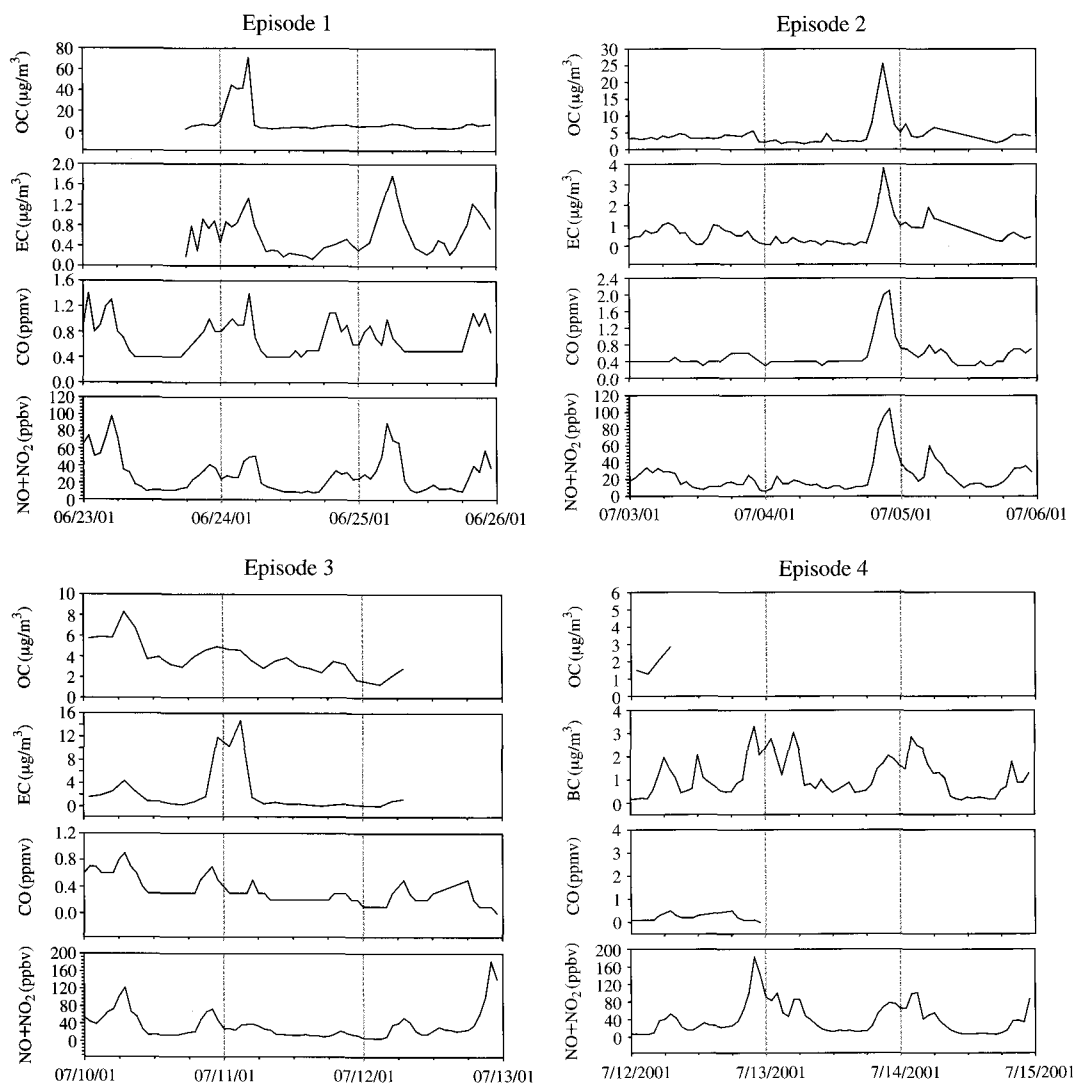
**Fig. 7.** OC, EC, CO, NO, and NO$_2$ concentration patterns for selected multi-day episodes in 2001 at the St. Louis Supersite.

average, which coincided with increases in OC and EC concentrations associated a point source plume. The correlation of OC and EC plumes with high concentrations of specific molecular markers suggests that primary emissions from local point sources are important drivers in temporal changes in OC and EC. A more detail analysis of the four study episodes is presented below.

### 3.1.1 Episode 1

In order to identify when point sources are impacting carbonaceous aerosol concentrations at the Midwest St. Louis Supersite and to identify their impacts on OC concentrations, semi-continuous measurements and integrated 24-hr molecular marker concentrations were examined for Episode 1, 2, 3, and 4. Fig. 7 presents EC, CO, and NO$_x$ (NO+NO$_2$) concentrations patterns for Episode 1 that span a three
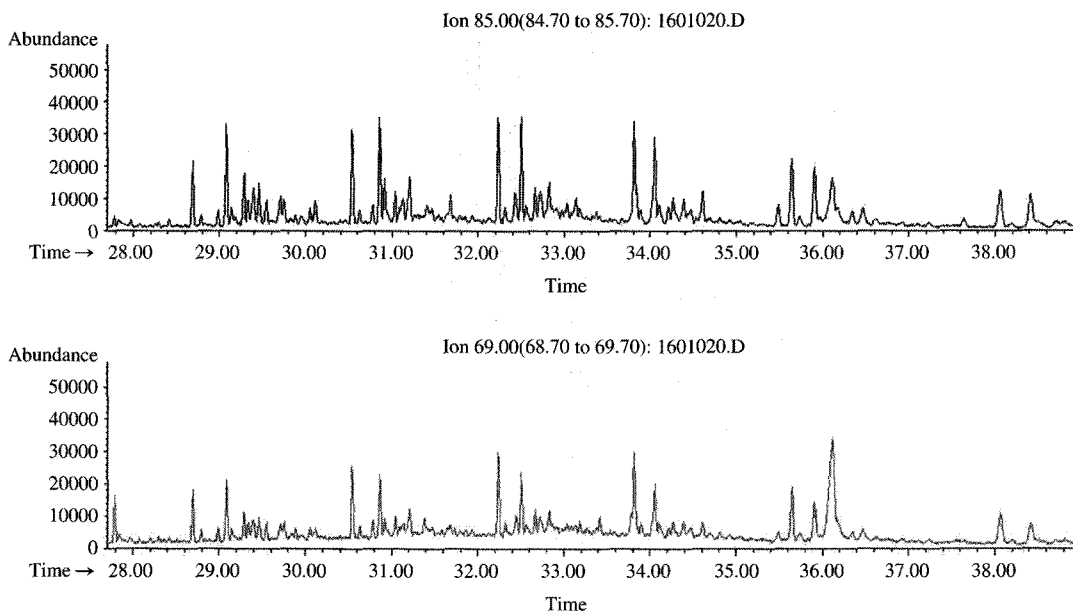
Fig. 8. Mass fragment ions (*m/z*) of 85 and 69 by GC/MS for Unknown Compound. (Note: An analysis of the GC/MS chromatogram for the analysis of the sample from June 24, showed the presence of a homologous series of organic compounds that had key mass fragment ions (*m/z*) of 85 and 69).

day period from June 23 through June 25. Missing OC and EC data from June 23 was due to operational problem with the EC/OC instrument. The extremely high OC concentration observed on June 24, which reached a maximum hourly concentration of 71.2 μg m$^{-3}$ between 5:00-6:00 AM, which has the time dependent characteristics of an impact from a local point source. The peak of OC concentration on this day is 6 times higher than the 24-hour average concentration of 11.87 μg m$^{-3}$ and 19 times higher than the 2002 annual averages of 3.88 μg m$^{-3}$. Elevated EC and CO concentrations were also observed between 5:00-6:00 AM on June 24, however, the relative increases were much smaller indicating that the relative impact of the point source on OC and EC concentrations are much smaller compared to the impact on OC. The EC to OC ratio during the plume event was 0.019, which is remarkably lower than the annual average at this site, which was 0.18 in 2002. These results indicate that caution should be used in using EC to OC ratios to estimate secondary organic aerosols during periods when local sources such as

observed in this study can impact carbonaceous aerosol concentrations. On June 25, a more traditional pattern in EC concentrations was observed with a diurnal pattern in hourly EC and CO concentrations that is not coincident with OC concentrations. The patterns on June 24 indicate the absence of a significant point source impact and are more characteristic of traditional mobile source impacts.

Molecular marker data was used to better understand the nature of the point sources impacting the sampling site. As shown in Fig. 5 and 6, the n-alkane and n-alkanoic acid concentrations on June 24 are 4 times higher than the day before or after June 24. However, hopanes & steranes follow a different pattern with higher concentrations on June 25 as compared to June 23 and 24. These results suggest that wax n-alkanes are likely associated with this local point source at the Midwest St. Louis Supersite. An analysis of the GC/MS chromatogram for the analysis of the sample from June 24, showed the presence of a homologous series of organic compounds that had key mass fragment ions (*m/z*) of 85 and 69 as
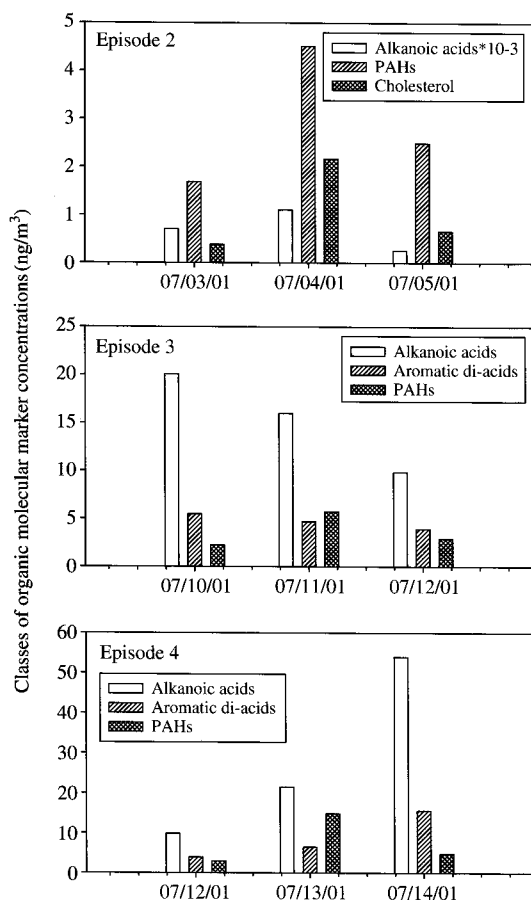
**Fig. 9. Classes of daily organic molecular markers for selected multi-day episodes in 2001 at the St. Louis Supersite.**

shown in Fig. 8. Although these compounds could not be identified, the homologous series is suggestive of a polymeric-like material. As discussed in more detail in a later section of this manuscript, the presence of this point source would lead to biases in the a CMB model if the model did not include a profile for the local point source since the n-alkanes, which are impacted by the local point source, are often used as tracers in MM-CMB models.

### 3.1.2 Episode 2

As seen in Fig. 7, a significant increase in the OC, EC, CO, NO, and $NO_2$ concentrations were observed in the evening of July 4, which is the US Holiday celebrating Independence Day. During this episode, OC concentrations rose to an hourly average of 25.6 $\mu g\ m^{-3}$ between 9:00 to 10:00 PM, which is consistent with the large usage of fireworks on the US Independence Day. This peak hourly average OC concentration was 5 times higher than the day averages measured as 5.29 $\mu g\ m^{-3}$ and 7 times higher than the reported 2002 annual averages of 3.88 $\mu g\ m^{-3}$. The EC to OC ratio was 0.15 during the peak OC concentration on July 4 is slightly lower with the reported average of 0.18 in 2002. In addition, alkanoic acid, cholesterol, and PAHs significantly increased on July 04 as compared to the concentrations of these compounds on the day before and the day after July 4 (Fig. 9). However n-alkanes, aromatic/aliphatic acid, and hopanes/steranes have no daily significant changes before/after days of July 04, which is quite different than Episode 1.

### 3.1.3 Episode 3

Episode 3 is also presented in Fig. 5, and shows a significant increase in EC concentrations in the later hours of July 10 and the early hours of July 11. It should be noted that OC and EC of daytime on July 12, 2001 are not available as the EC/OC instrument underwent routine maintenance at this time. The peak hourly EC concentration was 14.1 $\mu g\ m^{-3}$ between 3:00 to 4:00 AM on July 11. Due to the fact that the EC concentrations increase in the absence of parallel increases in $NO_x$ and CO, the increase cannot be attributed diesel engine emissions, gasoline vehicles or other common urban sources. The peak hourly EC concentration is 8 times higher than the 24-hr average concentration of 2.97 $\mu g\ m^{-3}$ and 20 times higher than the reported 2002 annual averages of 0.70 $\mu g\ m^{-3}$. It is interesting to note that the increase in OC concentration during Episode 3 is much smaller than the EC increase. The OC concentration was 4.6 $\mu g\ m^{-3}$ during the peak EC concentration hour, which yields a very high EC to OC ratio of 3.20. This EC to OC ratio is remarkably higher throughout the St. Louis Supersite sampling period with the reported average of 0.18 in 2002. In addition, 2 times higher PAHs are measured on July 11, 2001 than the concentrations of before/after days. However alkanoic
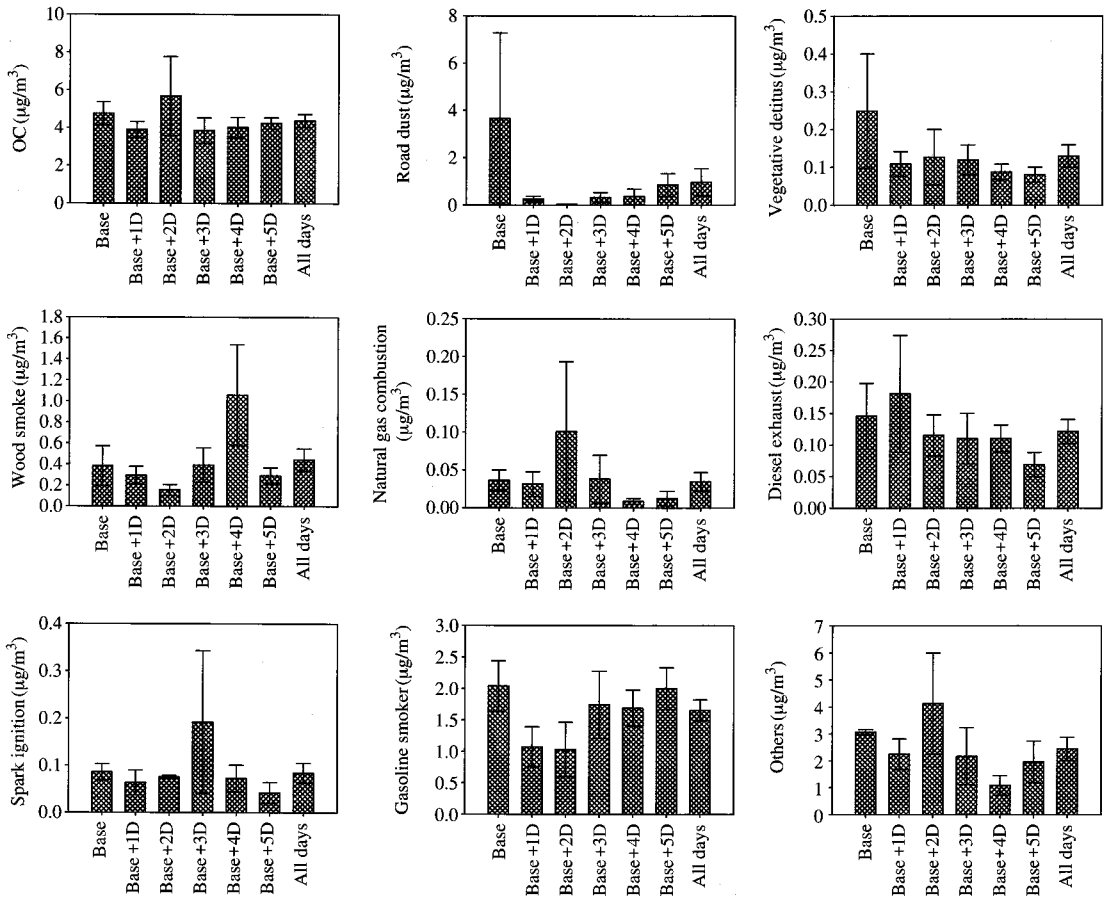
**Fig. 10. Average concentration with standard error of MM-CMB results using six different representations of the every sixth day measurements from June 22 through July 21 in 2001 (Base includes Episode 2, Base+1D includes Episode 3, Base+2D includes Episode 1, and Base+3D includes Episode 4). All Days in the last bar indicates total average of daily concentrations.**

acid, aromatic & aliphatic acid, alkylcyclohexanes, and hopanes & steranes do not follow the EC trend (Fig. 9). Again, the impact of the local source observed in Episode 3 would yield a significant bias in a MM-CMB modeling analysis without a suitable source profile for the non-traditional local source impacting EC during this period.

### 3.1.4 Episode 4

On July 12, high distributions of Black Carbon (BC) measured by an Aethalometer were observed at 7:00 AM in the morning, 1:00 PM in the middle of day and 10:00 PM in the evening (see Fig. 7). In

addition, on July 13, the peaks of BC and NOx appear at 2:00 AM, 5:00 AM, and 10:00 PM in the evening with higher 24 hour integrated concentrations of OC and EC. Although it is not clear if these spikes are all associated with a single source but the PAH concentrations on July 13 are 4 times higher than the concentrations on the days before and after July 13 (Fig. 9). These characteristics of Episode 4 are much different than the other episodes.

### 3.2 1-in-6 Day Representations

As previously stated, the impact of the local sources resulting in the trends seen in the four episodes
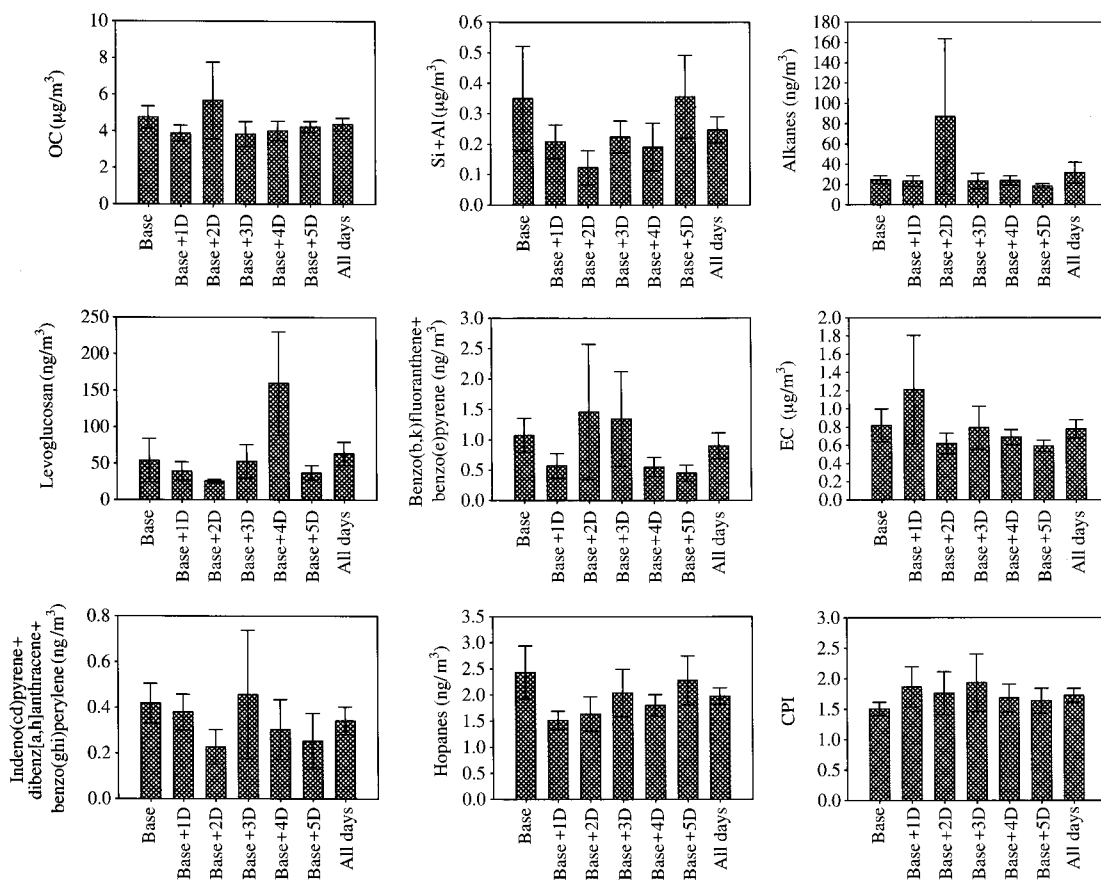
**Fig. 11. Average concentration with standard error of selected molecular markers using six different representations of the every sixth day measurements from June 22 through July 21 in 2001 (a case of average 1 includes Episode 2, a case of average 2 includes Episode 3, a case of average 3 includes Episode 1, and a case of average 4 includes Episode 4). (Note: CPI, Carbon Preference Index=$(C_{25}+C_{27}+C_{29}+C_{31}+C_{33}+C_{35})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32}+C_{34}+C_{36})$ for n-alkanes).**

discussed above is expected to have a significant bias on MM-CMB results without properly addressing these local sources. To further explore such biases, a sensitivity test was conducted to compare the MM-CMB results for the episode days to the MM-CMB results for non-episode days during the periods of June 22 to July 21, 2002 at the St. Louis Midwest Supersite.

Fig. 10 and 11 present average concentrations with standard error (the uncertainty of the sample mean) of MM-CMB results and organic molecular markers using six different representations of the every sixth day measurements from June 22 through July 21 in

2001 with true average of daily concentrations in the last bar indicated as "All days". The first bar represents the average in the first case of the every sixth day measurements (hereafter termed the "Base" days). The Base days included June 22, June 28, July 4 (Episode 2), July 10, and July 16. The second bar shows the average of the days that lag one day after base days, and the remaining bars represent the remaining independent 1-in-6 days. The Base+1D included June 23, June 29, July 5, July 11 (Episode 3), and July 17. The Base+2D and Base+3D include Episode 1 and Episode 4, respectively.

These plots reveal that every sixth day analysis for

MM-CMB results can be very biased by the events by the local sources given the expectation that the monthly averages based on samples from every 6th day should be relatively constant. The Base Days, which includes Episode 2 have much higher road dust and vegetative detritus source contributions than the other averages. Results from bias associated with the high aluminum and silicon concentrations believed to be associated with the a local point source that was not included in the model.

In addition, plant wax n-alkanes exhibit a strong odd carbon number predominance and thus, a high Carbon Preference Index (CPI) value (Rogge *et al.*, 1993e). The input of anthropogenic contaminants reduces the CPI, such that values of near 1 reflect the significant introduction of contaminants with human origin. In the present study the CPI values $(C_{24}-C_{36})$ was in the range 0.74-3.76, suggesting that most of the measured n-alkanes were of anthropogenic in origin. The Base+1D includes Episode 3, which has much higher contributions from diesel exhaust that results from the excess EC associated with a local source, which again is not included in the model. The Base+2D, which includes Episode 1 is biased to have high contributions from natural gas combustion due to high PAH associated with benzo (b,k)fluoranthene/benzo(e)pyrene, and high other, and also small increment of vegetative detritus due to high n-alkanes. A case of Base+3D includes Episode 4 (higher spark ignition due to indeino(cd)pyrene, dibenz[a,h]anthracene, & benzo(ghi)perylene). A case of Base+4D includes higher wood smoke concentrations due to high levoglucosan concentration (433 ng m$^{-3}$) on July 14.

# 4. SUMMARY AND IMPLICATIONS

The current study demonstrates that sources including local point sources can impact OC and EC concentrations if they are not properly addressed in MM-CMB models. For this reason, a screening tool that uses supplemental real time measurements and molecular organic marker data to identify when uncharacterized point sources are influencing a receptor

site has been developed and demonstrated. It is important that these tools should be applied before molecular marker CMB efforts are used in locations where local point source, which are not well characterized, can potentially impact the receptor site.

As efforts to use molecular marker CMB models in the Korean Peninsula are pursued for air quality management and health studies, efforts are needed to better characterize local sources and to employ the screening tools presented here to avoid biased source apportionment results.

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