# Organic Speciation of Vehicle Exhaust Particulates: Gasoline and Light Duty Diesel Vehicles

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## Introduction

On road vehicle emissions are a major source of particulate matter pollution, especially in urban areas. In this study, organic speciation of fine particulate matter (PM2.5, d≤2.5 um) was carried out on 18 light-duty vehicles tested from July, 2005 to May, 2006 on a chassis dynamometer over different driving cycles. Twelve gasoline vehicles were evaluated including a gasoline-electric hybrid. Two of the vehicles operated on compressed natural gas (CNG), and four were diesel vehicles. Three gasoline vehicles were tested with both summer and winter fuels. A detailed chemical profile was constructed for the vehicle exhaust particulates collected from each vehicle and fuel type. More than 100 organic molecular marker compounds were quantified by gas chromatograph/mass spectrometry (GC/MS). The major organic components identified were n-alkanes, PAH (polycyclic aromatic hydrocarbons), hopane, sterane, n-alkanoic acids and benzoic acids.

**Goals**

- Updated emission profiles for light-duty diesel and gasoline-powered vehicles
- Mass balance relationships for vehicle molecular markers to EC and OC mass emission rates
- Identify molecular markers for CMB modeling

## Sampling of Vehicular Particulates

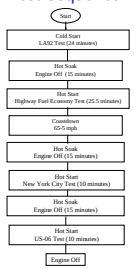
**Light duty dynamometer**

**Vehicle selection** availability, engine characteristics, age/ mileage, type of service, repeatability

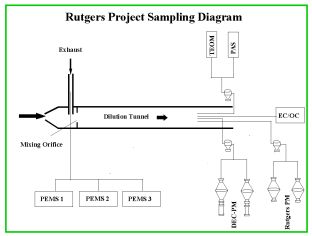
**Species measured** HC, CO, $CO_2$, $NO_x$, PM2.5 (filter & real-time), EC, OC, gas & particle-phase PAHs, PM surface area

### NYSDEC Automotive Emissions Lab Test Sequence

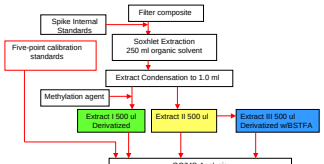
| Vehicle Make/Type | Model Year | No. of Cylinders | Engine Displacement (L) | Rated Power (hp) | Odometer (mi) | Test Wt. (lb) |
|---|---|---|---|---|---|---|
| **Gasoline** | | | | | | |
| Ford Taurus | 2005 | 6 | 3 | 155 | 36,362 | 3625 |
| Honda Civic Hybrid | 2004 | 4 | 1.2 | 85 | 27,800 | 3000 |
| Chevrolet Cavalier | 2004 | 4 | 2.2 | 140 | 28,892 | 3375 |
| Chevrolet Venture Minivan | 2002 | 6 | 3.4 | 185 | 54,939 | 4000 |
| Ford Windstar Minivan | 2001 | 6 | 3.8 | 200 | 58,720 | 4500 |
| Ford Crown Victoria | 2000 | 8 | 4.6 | 200 | 55,782 | 4250 |
| Jeep Cherokee | 1998 | 6 | 4 | 185 | 93,839 | 3875 |
| Oldsmobile Achieva | 1997 | 4 | 2.4 | 150 | 173,270 | 3250 |
| Jeep Grand Cherokee | 1995 | 8 | 5.2 | 230 | 171,033 | 4000 |
| Chevrolet Astro Cargo Van | 1994 | 6 | 4.3 | 190 | 165,274 | 4500 |
| Jeep Cherokee | 1992 | 6 | 4 | 185 | 229,106 | 3875 |
| Dodge Ram Van | 1990 | 8 | 5.2 | 140 | 154368 | 3750 |
| **CNG** | | | | | | |
| Chevrolet Cavalier | 2004 | 4 | 2.2 | 140 | 28,892 | 3375 |
| Ford Crown Vic | 1999 | 8 | 4.6 | 200 | 34915 | 4500 |
| **Diesel** | | | | | | |
| Volkswagon Jetta | 2003 | 4 | 1.9 | 90 | 74391 | 3500 |
| Volkswagon New Beetle | 2001 | 4 | 1.9 | 90 | 64546 | 3250 |
| Ford F350 | 1999 | 8 | 7.3 | 350 | 115515 | 4500 |
| Dodge Ram | 1999 | 10 | 8 | 300 | 101745 | 4500 |
| **Grease** | | | | | | |
| Ford F350 | 1999 | 8 | 7.3 | 350 | 115515 | 4500 |
| **Bio-diesel** | | | | | | |
| Ford F350 | 1999 | 8 | 7.3 | 350 | 115515 | 4500 |




### Constant volume sampling (CVS) system




### Analytical protocol GCMS markers




Extract I: Organic acids | Extract II: Neutral compounds | Extract III: Polar compounds

**Alkanes**
n-pentacosane
n-hexacosane
n-heptacosane
n-octacosane
n-nonacosane
n-triacontane
n-hentriacontane
n-dotriacontane
anteiso-triacontane
iso-hentriacontane
anteiso-hentriacontane
iso-dotriacontane
anteiso-dotriacontane
iso-tritriacontane
phytane
pristane

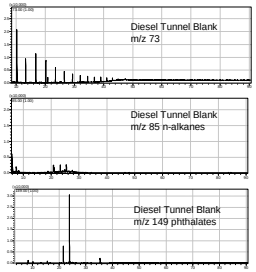
**PAHs**
benzo[b]fluoranthene
benzo[k]fluoranthene
benzo[e]pyrene
indeno[1,2,3-cd]pyrene
indeno[1,2,3-cd]fluoranthene
retene
coronene

**Acids**
21 n-alkanoic acids (with $C_{10}$ to $C_{30}$)
10 aliphatic dicarboxylic acids ($C_3$ to $C_{10}$)
1 aromatic polycarboxylic acid
cis-9-n-octadecenoic acid

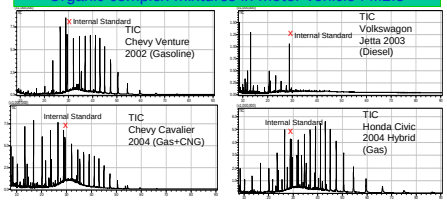
**Other**
hopanes
steranes
nonanal
diterpenoids
sterols
cholesterol
7H-benz[de]anthracen-7-one
benz[a]anthracene-7,12-dione

Molecular markers in CMB Model

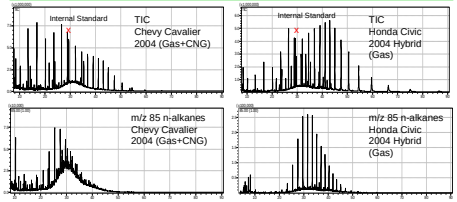
### Test system QA/QC



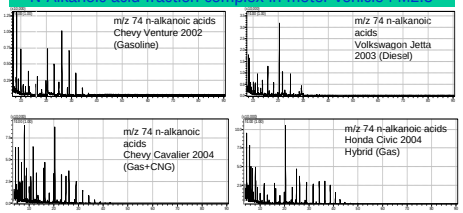

### Organic complex mixtures in motor vehicle PM2.5



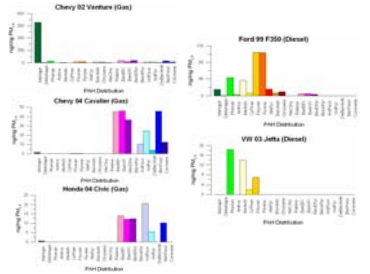

### Hydrocarbon fraction complex in motor vehicle PM2.5



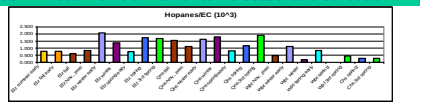

### N-Alkanoic acid fraction complex in motor vehicle PM2.5

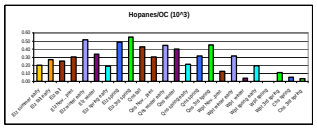



### PAH mixtures in motor vehicle PM2.5




### SOAP Motor vehicle marker to EC seasonal distribution




## Results & Discussion

- Organic extracts from vehicles tested fuel type, vehicle age widely variable chemical compositions
- Distributions or chemical profiles distinct patterns for key molecular markers used in CMB modeling; new, updated source profiles enhance accuracy model output
- Chemical emission profiles important for NE U.S. state emissions inventories and SIPs
- Vehicle chemical emission profiles will be incorporated into state-of-the-science transportation simulation models to better predict the impact of motor vehicle emissions on urban airsheds from transportation systems

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