

Carleton College

Carleton Digital Commons

Faculty Work

Chemistry

2005

Stability of Single Particle Tracers for Differentiating Between Heavy- and Light-Duty Vehicle Emissions

Deborah S. Gross
Carleton College

Alexander R. Barron
Carleton College

Ellen M. Sukovich
Carleton College

Benjamin S. Warren
Carleton College

Julia C. Jarvis
Carleton College

See next page for additional authors

Follow this and additional works at: https://digitalcommons.carleton.edu/chem_faculty

 Part of the [Chemistry Commons](#)

Recommended Citation

Gross, Deborah S., Alexander R. Barron, Ellen M. Sukovich, Benjamin S. Warren, Julia C. Jarvis, David T. Suess, and Kimberly A. Prather., "Stability of Single Particle Tracers for Differentiating Between Heavy- and Light-Duty Vehicle Emissions". *Atmospheric Environment*. 2005, 39: 2889-2901. Available at: <https://doi.org/10.1016/j.atmosenv.2004.12.044>. Accessed via Faculty Work. Chemistry. *Carleton Digital Commons*. https://digitalcommons.carleton.edu/chem_faculty/4
The definitive version is available at <https://doi.org/10.1016/j.atmosenv.2004.12.044>

This Article is brought to you for free and open access by the Chemistry at Carleton Digital Commons. It has been accepted for inclusion in Faculty Work by an authorized administrator of Carleton Digital Commons. For more information, please contact digitalcommons.group@carleton.edu.

Article Author

Deborah S. Gross, Alexander R. Barron, Ellen M. Sukovich, Benjamin S. Warren, Julia C. Jarvis, David T. Suess, and Kimberly A. Prather



Stability of single particle tracers for differentiating between heavy- and light-duty vehicle emissions

Deborah S. Gross^{a,*}, Alexander R. Barron^a, Ellen M. Sukovich^a,
Benjamin S. Warren^a, Julia C. Jarvis^a, David T. Suess^b, Kimberly A. Prather^c

^aDepartment of Chemistry, Carleton College, 1 North College Street, Northfield, MN 55057, USA

^bDepartment of Chemistry, University of California-Riverside, Riverside, CA 92521, USA

^cDepartment of Chemistry, University of California-San Diego, La Jolla, CA 92093, USA

Received 2 September 2004; received in revised form 15 December 2004; accepted 15 December 2004

Abstract

To determine the size and chemical composition of particles derived from on-road vehicle emissions, individual particles were sampled continuously with an aerosol time-of-flight mass spectrometer (ATOFMS) at the Caldecott Tunnel in Northern California. In this tunnel, traffic is segregated, such that in theory only light duty vehicle emissions or a mix of heavy- (HDV) and light-duty vehicle (LDV) emissions can be sampled separately. Two studies were carried out, one in November 1997 and a second in July 2000, time periods with average ambient temperatures of 10–15 and 26–32 °C, respectively, with the instrument operating at ambient outdoor temperatures. Analysis of the chemical composition of the particles sampled in these studies shows that sampling conditions can strongly impact the determination of suitable markers for identifying particles emitted from different vehicle types during ambient studies. Differences in the results of these two studies are shown to be related to the different ambient temperatures at which the measurements were carried out. Particles sampled from HDV-influenced traffic in the 1997 study were 16 times more likely to have mass spectra containing peaks at both m/z 128 (naphthalene) and 156 (dimethylnaphthalene/naphthaldehyde) and 51 times more likely to have mass spectra containing peaks at both m/z 156 and 170 (trimethylnaphthalene/methylnaphthaldehyde) than were particles sampled from the LDV-only traffic tunnel. The peaks corresponding to m/z 156 and 170 are on average 2 and 4 times more intense in the mass spectra of the HDV-influenced data set than in the LDV-only data set. In contrast, in the 2000 experiment, the peaks at m/z 128 and 156 were present in ~1% and ~2% of the particles, respectively, with no preference for traffic type. These results show the usefulness of naphthalene and its derivatives for identification of the vehicle source of particulate emissions, under appropriate conditions, and highlight the fact that ambient conditions can strongly affect potential marker ions for source apportionment studies, necessitating a combination of controlled laboratory and field measurements for identification of stable marker ions.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Aerosol particle; Polycyclic aromatic hydrocarbon; Semivolatile; Vehicle emissions; Diesel

*Corresponding author. Tel.: +1 507 646 5629; fax: +1 507 646 4400.

E-mail address: dgross@carleton.edu (D.S. Gross).

1. Introduction

The development of single-particle methods has made it possible to analyze the chemical composition of individual ambient aerosol particles in real-time (Suess and Prather, 1999, and references therein; Middlebrook et al., 2003). These instruments have been deployed in a wide variety of studies (Sipin et al., 2003), including investigations of: ambient particulate matter in the troposphere in urban and rural areas; particulate matter in the tropopause and lower stratosphere; particle properties and chemistry, via laboratory and ambient studies; and characterization of particulate emissions from a variety of sources known to be important in the atmosphere. Because of the wide variety of chemical compositions observed for ambient particulate matter using single-particle techniques, source characterization studies are of tremendous importance in order to clearly identify and apportion the types of particles observed in ambient measurements. When potential markers for specific sources are identified, it is imperative to characterize the conditions under which a specific marker ion is indeed indicative of the source.

Vehicle emissions are a source of ambient particulate matter which adversely impact both urban and rural areas, and can make up a significant fraction of the aerosol mass in a given location (Schauer et al., 1996; Schauer and Cass, 2000). The health effects of vehicle emissions are becoming better understood, and there is now increasing proof of a variety of mechanisms for adverse health effects due to exposure to these emissions (Samet et al., 2004). There are a number of reports in the literature of investigations of vehicle exhaust by single-particle mass spectrometric techniques (Silva and Prather, 1997; Reilly et al., 1998; Gross et al., 2000; Suess and Prather, 2002; Okada et al., 2003; Vogt et al., 2003). These studies are focused on the determination of the chemical signatures and variability of the particle emissions from internal combustion engines. One of the goals of these studies is to attempt to identify differences in the size and/or composition signature of individual particles emitted from vehicles burning diesel fuel versus vehicles burning gasoline. Being able to distinguish individual particle signatures from various sources will provide a more accurate determination of the source contributions to ambient particulate matter sampled in many locations, and will help elucidate the potential health effects of specific particle sources.

Vehicle emission studies over the years have investigated metals in emissions, particularly lead prior to its phase-out in gasoline. Since the phase-out of leaded gasoline, attention has focused on organic compounds in vehicle emissions (Fraser et al., 1998, 1999; Carlsson et al., 1999; Schauer et al., 2002a), with the goal of finding appropriate tracer species for identification of vehicle emissions in air and particulate matter samples.

A wide range of organic compounds has been identified as components of raw fuel and vapor and/or particle phase vehicle emissions, which has improved our understanding of the concentrations of species emitted from vehicles under specific conditions, and has proven useful in urban airshed models (Schauer et al., 1996; Schauer and Cass, 2000; Schauer et al., 2002b).

Researchers have used a variety of methods for sampling emissions from vehicles. These range from roadside studies in which the instrumentation samples in real-time to collecting emissions in large bottles or bags, which are then transported to instruments. Laboratory-based dynamometer studies have also been used successfully, as they provide the most control over vehicle types and operating conditions (see for example Sodeman et al., 2004b). Sampling in a roadway tunnel is a variant of roadside studies that has proven extremely successful, due to the high concentration of vehicle emissions in the sampled air (El-Fadel and Hashisho, 2001). Tunnel studies have the benefit that air is sampled directly from inside the tunnel bore, and therefore is not subject to wind or other environmental processes that could further dilute or vary the emissions. In particular, certain tunnels which employ traffic restrictions can segregate vehicles by size, which results in segregation largely by the type of fuel consumed (i.e. heavy-duty vehicle (HDV) typically consume diesel fuel, passenger cars (light-duty vehicle (LDV)) typically consume gasoline). The Caldecott Tunnel in Berkeley, CA, runs East/West between Berkeley, CA and Orinda, CA, and segregates HDV into only two of three two-lane tunnel bores (one running from West to East, and another running from East to West). Light-duty vehicles are permitted in both of these bores, as well as in the middle bore, which alternates between running East to West (morning rush-hour) and West to East (afternoon rush-hour). In two studies carried out at the Caldecott Tunnel, during November 1997 and July 2000, we sampled air from the two West to East tunnel bores at the Caldecott Tunnel, obtaining data from either mixed HDV + LDV traffic or LDV-only traffic using aerosol time-of-flight mass spectrometry (ATOFMS). Preliminary results of the 1997 study are presented elsewhere (Gross et al., 2000; Allen et al., 2001). Here we present further progress in identifying marker ions, to obtain information about the differences in emissions between HDV and LDV influenced emissions, and to examine the applicability of these marker ions for identifying the vehicle-type source of particles sampled during other seasons.

While there are many chemical compounds of interest in vehicle emissions, a very important class of organic compounds, from the health perspective, is polycyclic aromatic hydrocarbons (PAHs). There are a large number of molecules in this broad structural classification, and many of them are suspected or known

carcinogens (Denissenko et al., 1996). Depending on their molecular weight and structure, PAHs range from the semi-volatile, which are able to partition onto and off of particles depending on external conditions, to being almost exclusively found in the condensed phase. Because of their health effects and ability to exist both in the gas and particle phase, it is important to understand how PAHs behave when sampled with a real-time technique, such as a single-particle mass spectrometer, and how their detection varies as a function of ambient conditions.

The ultimate goal of this research was to develop a set of marker ions in single-particle mass spectra that can be used to identify the vehicle type that emitted an individual particle sampled in ambient air. One can then simply employ necessary instrument calibration factors to correct for biases in particle sampling as a function of particle size (Allen et al., 2000) and count the number of particles from each type of vehicle to directly determine the relative source contributions to ambient particulate matter. An example of this approach is given by Sodeman et al. (2004a). However, this task is complicated by seasonal variations in the composition of aerosol particles, which can vary with changes in meteorological conditions as well as emission and transformation rates of the species within the particles (Limbeck et al., 2004).

Here results from two studies carried out under different ambient conditions at the same location show that care must be exercised in the choice of the marker ions used to attribute single-particle mass spectra to specific vehicle types, and emphasizes the importance of taking into consideration the possibility of seasonal variations affecting their occurrence.

2. Experimental

2.1. Aerosol time-of-flight mass spectrometry

The aerosol time-of-flight mass spectrometer (ATOFMS), used in both of these studies, has been described in detail elsewhere (Noble and Prather, 1996; Gard et al., 1997). Briefly, aerosol particles are introduced into the ATOFMS vacuum system through a convergent nozzle and two skimmers, which collimate the particles into a beam and accelerate them to a terminal velocity, determined by their aerodynamic diameter. The aerodynamic diameters of the particles are measured from their flight time over a known distance (6 cm) between two orthogonal continuous wave lasers (Nd:YAG pumped diodes, Brimrose Corp., Baltimore, MD, 532 nm). The start and stop times are determined by a timing/logic circuit, triggered by light scattered from the particles and collected with photomultipliers. When the particles cross the second laser

beam, the timing/logic circuit stops, reverses, and counts down, triggering a pulsed Nd:YAG laser (Continuum, Santa Clara, CA for 1997 study and Big Sky Lasers, Bozeman, MT for 2000 study, both at 266 nm) to fire when the particle is in the center of the source of the dual collinear-reflectron time-of-flight mass spectrometer. Both speed (which is converted to aerodynamic particle size using an empirical calibration curve) and chemical composition (positive and negative ions) of each particle are obtained. Typical desorption/ionization laser fluence during the 1997 experiment was $\sim 2 \times 10^7 \text{ W cm}^{-2}$ (0.3 mJ/pulse, 7 ns pulse-length, 0.4 mm laser spot diameter). During the 2000 experiment, it was $\sim 2 \times 10^8 \text{ W cm}^{-2}$ (1.5 mJ pulse⁻¹, 7 ns pulse-length, 0.4 mm laser spot diameter). Differences are due to the affect of ambient temperature on the energy output of the desorption/ionization laser. The ATOFMS instrument was located at ambient outdoor temperature, which was in the range of 10–15 °C in November 1997 and in the range of 26–32 °C in July 2000. The temperature sensitive desorption/ionization laser used in the 1997 study was replaced with a thermally stabilized desorption/ionization laser for the 2000 study.

2.2. Sampling at the Caldecott tunnel

In both experiments, the ATOFMS instrument was located in the East Fan Room, directly above the eastern exit of the Caldecott Tunnel. In the 1997 experiment, a sample line (copper, 150 ft length, 0.25 in i.d.) brought air and particles directly to the instrument from a vent in the roof of the tunnel, about 2–4 in above the tops of the tallest vehicles. The sample line was co-located with filter and impactor samplers located in the ventilation duct, as well as with an optical particle counter (OPC) inlet. In the 2000 experiment, a modified sampling system brought air at $\sim 50 \text{ L min}^{-1}$ from the tunnel bore through a sample line (copper, 150 ft length, 0.625 in i.d.) into a chamber from which all sampling equipment, including the ATOFMS, pulled particle-laden air. In both experiments, the sample lines were located ~ 50 ft before the ventilation ducts for the two East-bound tunnels merged. Given that the prevailing air flow, due to the ventilation fans, was toward the East, we expect that minimal mixing of the emissions occurred prior to emissions sampling. We cannot completely rule out the possibility that some species partitioned onto the particles during transport through the sampling lines. The residence time of the particles within the sampling lines was ~ 1.6 min during the 1997 study, and ~ 1.7 min during the 2000 study, so there should not be significant differences due to residence times in the sampling lines. The temperature of the sampling line was maintained at ambient temperature.

Vehicles traversing the tunnel were counted and identified as HDV or LDV in both experiments. The

percentage of HDV vehicles in the HDV influenced traffic was 6.8% and 4.5%, in the 1997 and 2000 studies, respectively. In the LDV-only traffic, these percentages were reduced to 0.2% and <0.8%, respectively.

2.3. Tunnel sampling protocol

Particles were sampled from the two eastbound bores of the three-bore Caldecott Tunnel. In the 1997 experiment, sampling was carried out on mixed traffic (mix of light-duty vehicles (LDV) and heavy-duty vehicles (HDV)) from 12:00 to 15:00 on 17/11/1997 and 18/11/1997. Particles were sampled from LDV-only traffic in the middle bore from 15:30 to 18:30 on 19/11/1997 and 20/11/1997. This report focuses on the results obtained on 18/11/1997 and 20/11/1997. In the 2000 experiment, sampling was essentially continuous from 23/7/2000 to 1/8/2000. Approximately 140 h was spent sampling mixed HDV + LDV traffic, and approximately 40 h was spent sampling LDV-only traffic. The longer sampling of mixed traffic emissions was due to road construction: most nights there was only one, mixed, eastbound traffic bore. The particles sampled included background sea-salt particles (containing peaks for Na^+ (m/z 23), K^+ (m/z 39), and Na_2Cl^+ (m/z 81 and 83)) as well as vehicle emissions particles. For the analysis conducted here, sea-salt particles, which comprised approximately 50% of sampled particles due to the higher detection efficiency of larger particles versus smaller particles in the ATOFMS, were excluded based on their composition. All other particles were considered vehicle emissions particles, and these are the only particles considered in the remainder of this paper.

2.4. Laboratory experiments

In order to aid in the interpretation of the field data, laboratory experiments were carried out to examine the effect of laser fluence on PAH molecular ion and fragment ion distributions. Anthracene (Aldrich Chemical Company, St. Louis, MO, USA) was dissolved in methanol at near-saturation. Particles were generated with a constant output atomizer (Model 3076, TSI, Shoreview, MN, USA), dried by passing them through a silica gel diffusion drier, and sampled into a commercial ATOFMS instrument (Model 3800, TSI, Shoreview, MN, USA). The laser fluence was systematically varied between $1.0 \pm 1.1 \times 10^6$ and $1.5 \pm 0.2 \times 10^8$ W/cm², and the resulting mass spectra were analyzed for the presence of molecular and fragment ions.

3. Results and discussion

A general examination of the size distributions and speciation of the individual particles sampled at the

Caldecott Tunnel in 1997 has already been reported in Gross et al. (2000). The size distributions of vehicle emissions particles sampled in the 2000 study are shown in Fig. 1. The size distribution of particles observed in the 2000 study is quite different from that observed in 1997 (Gross et al., 2000). Note that the size distributions shown in both our previous paper and this work are unscaled, and therefore do not correct for size-biases in the ATOFMS particle inlet. More vehicle emissions particles are observed in the $\sim 1\text{--}3\ \mu\text{m}$ size range in the 2000 data, and there are more particles observed at sizes below $\sim 0.3\ \mu\text{m}$, although this is likely due to the significantly larger number of particles sampled in the 2000 study. A significant fraction of particle spectra detected in 1997 contained polycyclic aromatic hydrocarbons (PAH), and estimates suggest that each HDV emits significantly more particles than each LDV as it travels through the tunnel, consistent with previous studies (Dreher and Harley, 1998; Miguel et al., 1998).

In this paper, as compared to our previous analysis, we have used a different data analysis method to improve the calibration of the single particle mass spectra, and therefore to obtain more detailed information about the chemical signatures of the particles observed in the two tunnel bores during both studies. The general trends in the data are in good agreement with the previous work (Gross et al., 2000) as determined by comparing the number of particles whose mass spectra contain specific ions, but now a more comprehensive analysis of the differences between the particles in the two bores of the tunnel is possible, with an emphasis on PAH species which could be used as marker ions for HDV versus LDV emissions, as described below. We compare the results obtained in the 1997 study with results from the July 2000 study, when the ambient conditions were dramatically

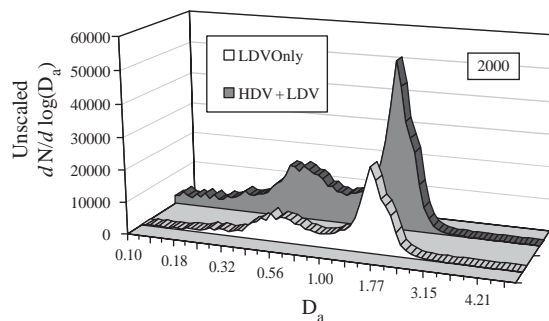


Fig. 1. Size distributions of vehicle emissions particles observed in both HDV + LDV traffic and LDV-only traffic during the 2000 study. Note that the size distribution has not been scaled to correct for the inherent size biases in the ATOFMS sampling. Particles identified as sea-salt, assumed to be from the ambient background, have been subtracted from these size distributions.

different, to try to discern the effect of the ambient conditions on any potential marker ions.

3.1. The presence of PAH species in ambient particles

As shown in Tables 1 and 2, many of the particles sampled from each tunnel bore contained molecular ions attributed to a variety of PAH species ($\geq 128m/z$). In this work, we will focus mainly on the lower mass PAH species, as discussed below. Dramatic differences in the percentage of particles containing PAH molecular ions can be seen when comparing the 1997 and 2000 data sets. There are a number of possible explanations for the greater percentage of particles containing PAH molecular ions seen in the 1997 study: (1) there could be more particles containing PAH species in the 1997 data versus the 2000 data, (2) there could be PAH compounds present in the particles in the 2000 study which are not observed in the single-particle mass spectra due to fragmentation in the desorption/ionization process, or (3) there could be some other light-absorbing compound in the particles detected in the 1997 study that enhances the ionization of PAHs in single-particle mass spectrometry experiments. The first two possibilities can be differentiated through a close examination of the single-particle mass spectra. If there are fewer PAH molecular ions in one data set, but there are significant PAH

fragment ions, then it is likely that the interaction between the desorption/ionization laser and the particles was different, leading to fragmentation of existing PAH species. If there are fewer PAH molecular ions *as well as* fewer PAH fragment ions in one data set, it is likely that the PAH content of the particles is lower. The third option requires additional measurements to fully explore. The most likely light-absorbing species is elemental carbon (EC). Dynamometer studies show differences in the EC emitted by HDV versus LDV, especially in the carbon chain-length observed in the single-particle mass spectra (Sodeman et al., 2004a). This could affect the light-absorbing properties of the aerosol, and warrants further study under controlled laboratory conditions.

To distinguish between the first two possibilities, we compared the mass spectral patterns of a PAH in laboratory generated particles as a function of laser fluence, as well as the fragment ions from the PAH molecules in the mass spectra obtained in the tunnel. Fig. 2a shows averaged spectra resulting from laboratory experiments in which pure anthracene (molecular weight 178 amu) particles were generated and sampled by the ATOFMS, as a function of desorption/ionization laser fluence, to investigate the fraction of spectra containing molecular ion and specific fragment ions. The averaging process makes it easier to see the overall effects of changing the laser fluence on the intensity of high versus low m/z peaks, but also makes the ability to see specific peaks within the figure more difficult. Laser fluences were chosen such that the minimum was below that used in the 1997 tunnel study, and the maximum was close to that used in the 2000 tunnel study. As seen in Fig. 2b, which shows the percent of particles containing selected fragment ions in the anthracene spectra, the percent of particles containing the molecular ion due to anthracene is relatively unchanged at $74 \pm 6\%$, across the entire range of laser fluences investigated here, although there are significant changes in the area of each of the peaks (Fig. 2a).

A comparison of the percent of particles containing fragmentation products in these laboratory generated particles versus those sampled in the tunnel can help distinguish whether the particles in the two tunnel studies actually had different amounts of associated PAH, or if the PAH in the 2000 study were merely fragmented. Note that the PAHs observed in tunnel particles are not found pure, in single-component aerosol particles, as is the case for the laboratory generated particles. Light absorption by the other components of the particles should decrease the observed fragmentation of the PAHs in the tunnel particles, as not all of the energy from the laser is available to the PAH. Thus, these laboratory experiments provide an upper limit to the extent of fragmentation we should observe in the tunnel particles.

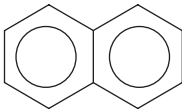
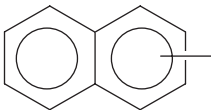
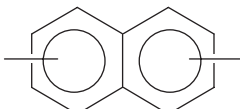
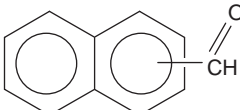

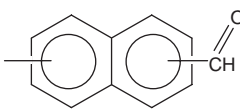
Table 1

Frequency of occurrence of aromatic fragments and naphthalene derivatives in mixed HDV + LDV emissions and LDV-only emissions, in both the 1997 and 2000 studies

m/z Present in mass spectra	% of particles in HDV + LDV	% of particles in LDV only	Ratio $\frac{(HDV+LDV)}{(LDV \text{ only})}$
November 1997 study			
77	20.8	8.6	2.4
91	16.9	6.2	2.7
128	24.6	12.6	2.0
142	12.9	1.5	8.6
156	32.2	4.6	7.0
170	34.3	4.2	8.2
128 + 156	14.7	0.9	16
142 + 156	9.2	0.2	46
156 + 170	20.2	0.4	51
July 2000 study			
77	6.4	6.1	1.0
91	1.3	1.3	1.0
128	1.1	1.3	0.8
142	3.0	3.4	0.9
156	2.1	2.2	1.0
170	0.08	0.07	1.1
128 + 156	0.06	0.04	1.3
142 + 156	0.02	0.04	0.5
156 + 170	0.005	0.014	0.3

Table 2

Ion formulae and possible identification of PAH ions and fragments. The location of substituents on PAHs cannot be determined, and thus the structures do not indicate specific sites of attachment

m/z present in mass spectra	Proposed chemical formula	Structure	Compound name
128	$C_{10}H_8^+$		Naphthalene
142	$C_{11}H_{10}^+$		Methylnaphthalene
156	$C_{12}H_{12}^+$		Dimethylnaphthalene
		or	
	$C_{11}H_8O^+$		Naphthaldehyde
170	$C_{13}H_{14}^+$		Trimethylnaphthalene
		or	
	$C_{12}H_{10}O^+$		Methylnaphthaldehyde

We focus here only on the percent of particle spectra containing specific peaks rather than peak intensity, due to the lower dynamic range of the ATOFMS detection system used in the 1997 and 2000 studies, which resulted in truncation of high intensity peaks. A range of carbon-containing fragment ions observed in the spectra of anthracene particles can be seen in Fig. 2a. Fig. 2b shows that the percent of particles containing the fragment ion corresponding to C_3^+ (m/z 36) is relatively unchanged until very low laser fluences, approximately equivalent to those used in the 1997 study. Similar results are found for other C_n^+ ions ($n = 2-5$). The fraction of the smallest observed fragment ion, due to C^+ (m/z 12), declines below approximately 6.4×10^7 W/cm² laser fluence, indicating that sufficient energy is not being imparted to the molecule to fragment it to this extent.

Additionally, we investigate the aromatic fragment ions indicative of aromatic (and hence PAH) species, specifically m/z 63, 77 and 91, corresponding to $C_5H_3^+$, $C_6H_5^+$ and $C_7H_7^+$, respectively (McLafferty, 1973).

While the spectra seen here for anthracene (Fig. 2a) is qualitatively different from the electron-impact spectrum of anthracene (NIST Mass Spec Data Center, S.E.S., director, 2003), these specific ions will have the same structural origin. These fragment ions are significantly more common in the 1997 dataset, with a greater fraction of particles containing these ions in HDV influenced emissions (Table 1). In combination with the larger fraction of particles containing various PAH molecular ions in the 1997 data set, this is consistent with the presence of more PAH-containing species associated with the particles in 1997. The fragment ions at m/z 63, 77 and 91 were also investigated in the laboratory generated anthracene particles. The peak at m/z 91 was found in <10% of particles, at all laser fluences, but this is expected for polycyclic aromatic compounds such as anthracene. However, the peaks at m/z 63 and 77 were observed in a relatively large fraction of particles, as seen in Fig. 2. The percentage of particles containing m/z 77 was highest in the $2-9 \times 10^7$ W/cm² range of laser fluences, at

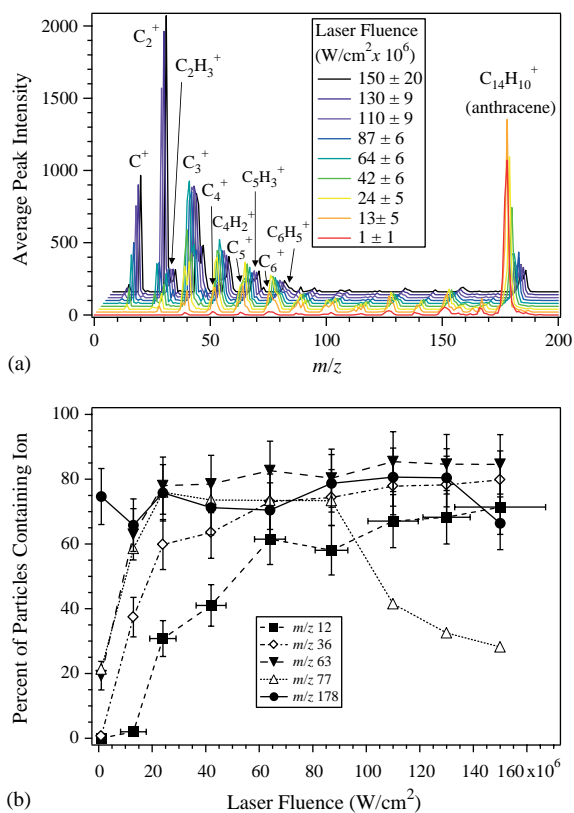


Fig. 2. (a) Average mass spectra of laboratory generated particles of pure PAH (anthracene, molecular weight 178). Spectra are averages of 500 particles for all except the lowest and highest laser fluences, which are averages of ~ 100 spectra, making it difficult to pick out specific peaks. The spectra are offset for clarity, with the spectrum in front corresponding to the lowest laser fluence. The major peaks are labeled. (b) Percentages of particle spectra containing selected ions. The x -error bars indicate the range ($\pm 1\sigma$) of laser energies obtained in a given experiment, and are shown on only the m/z 12 data, for clarity. The x -error bars are identical for all points at the same laser fluence in this plot. The y -error bars are simply based on \sqrt{N} , where N is the number of sampled particles containing the ion. Ions shown are C^+ (m/z 12, \blacksquare), C_3^+ (m/z 36, \diamond), $C_5H_3^+$ (m/z 63, \blacktriangle), $C_6H_5^+$ (m/z 77, \triangle), and the molecular ion (m/z 178, \bullet). Note that the molecular ion is present in a relatively constant percentage of these laboratory generated particles, regardless of desorption/ionization laser pulse energy.

$74 \pm 1\%$ of particles, it was also commonly observed at higher laser fluences, with a peak at m/z 77 observed in $34 \pm 7\%$ of particles. The decrease in the percentage of particles containing this ion at the higher laser fluences studied suggests that this relatively large fragment ion is itself fragmented at higher desorption/ionization energies, while at lower laser energies, it is not readily formed due to the small degree of fragmentation that is observed

for the anthracene ion overall. A similar trend is observed for C_n^+ ions with $n = 6-12$.

Taken together, these laboratory experiments demonstrate that the PAH molecular ion should be present in a high fraction of single particle spectra if the particles contain PAH molecules, regardless of whether low or high desorption/ionization laser fluences are used. The most common fragment ions observed for anthracene in ATOFMS spectra, corresponding to C_n^+ and $C_nH_m^+$ ions and fragment ions indicative of aromatic and polyaromatic structures, are also present in the particle spectra at both low and high laser fluences. Finally, even at the higher desorption/ionization laser fluence, the PAH ions are not completely fragmented to very small carbon-number fragments. These findings support the hypothesis that an absence of peaks corresponding to PAH molecular ions and significant fragment ions indicates a decrease in PAH species associated with the sampled particles in the 2000 data set. This difference is most likely due to the different ambient temperatures during the 1997 and 2000 studies, and suggests that either the species are partitioning onto the particles from the gas phase before we sample them (1997 study) or are evaporating from the particles before we sample them (2000 study). Differentiating these two possible cases will require additional measurements with vehicles on a dynamometer, under controlled temperature conditions, that are beyond the scope of this work. Either case has implications for seasonal differences in human exposure to particulate PAHs.

3.2. Identification of alkylated polycyclic aromatic hydrocarbons

Mass spectra of PAH-containing particles obtained via ATOFMS are identified by peaks with $>0.5\%$ of the total spectrum area at m/z values which correspond to the molecular ion of the PAH (the unfragmented PAH molecule). These PAH molecules are also detected in methylated forms in the mass spectra (e.g. phenanthrene, at 178 m/z , is often detected in the same particle as a methylated phenanthrene, which appears at 192 m/z). As mentioned previously (Gross et al., 2000), the detection of so many PAH molecules in the 1997 data set is a direct result of the low ambient temperature during the study.

The temperature can influence the partitioning of the semivolatile PAH species. Thus, we would expect more of the higher-volatility PAH molecules to be associated with the particles sampled in the 1997 study than in the 2000 study. In the 1997 study, very clear differences in the PAH signatures are observed in the particles sampled from the HDV-influenced traffic versus those from the LDV only traffic. These differences make it possible to differentiate particles which likely originate from an HDV versus those from an LDV on the basis of

the chemical composition determined from the mass spectra obtained. However, the differences between these studies indicate that differences observed in one season may not apply when the sampling is repeated at a different time of year, under different ambient conditions.

3.2.1. Identification of alkylated PAHs in 1997 study

In our analysis of this data set, we observed a variety of ion peaks corresponding to many PAH molecules, including the simple PAH naphthalene and alkylated naphthalene derivatives, which we will focus on here. Peaks observed correspond to the molecular ions of the PAH naphthalene and its derivatives up to trimethylnaphthalene/methylnaphthaldehyde (m/z 128–170). We are unable to conclusively distinguish between the methyl and aldehyde-substituted forms using time-of-flight mass spectrometry, as they are isomers and have the same chemical formula and therefore molecular mass, although there are spectral clues to the most likely type of derivative.¹ We are also unable to determine the specific substituent sites on these PAH molecules (see Table 2). Various studies have identified both the aldehyde derivatives and the alkyl derivatives of naphthalene in samples of diesel exhaust, and show that the alkyl derivatives are significantly more abundant (Jensen and Hites, 1983; Schauer et al., 1999, 2002a). Jensen and Hites tested the emissions of a single-cylinder test engine under various load conditions. They observed naphthalene in its unsubstituted form and with up to six additional carbon atoms in the particulate matter from the engine. In addition, small amounts of naphthalenecarboxaldehydes were also detected (Jensen, 1983). Rogge et al. (1993a, b) also found naphthalenecarboxaldehyde (formylnaphthalene) in auto emissions, although none was detected in their diesel samples. Schauer et al. (1999) identified a wide range of organic

¹Although we cannot definitely identify the isomeric species, we can get indications from fragment ions observed in these mass spectra. A significant fraction of single-particle mass spectra in the HDV influenced data set also contain fragment ions at m/z 115 and 141 (20% and 19% of particles, respectively) compared to the LDV-only data set (6% and <1% of particles, respectively). These ions are characteristic fragments of alkylated naphthalenes, corresponding to the loss of all of the alkylated substituents except one methyl group from alkylated naphthalenes (m/z 141) and the loss of all substituents and a CH group from one of the naphthalene rings (m/z 115) (McLafferty, 1973). These peaks are seen in the 70 eV electron impact (EI) spectra of all of the various alkylated derivatives (NIST Mass Spec Data Center, 2003). These fragment ions are not observed in the EI mass spectra of the aldehyde-substituted naphthalenes (NIST Mass Spec Data Center, 2003). Thus, the evidence in the single-particle mass spectra suggests that a significant portion of the substituted naphthalene peaks are alkylated.

compounds in medium-duty diesel truck emissions. They reported trimethylnaphthalenes ($130 \mu\text{g}$ emitted per km driven ($\mu\text{g km}^{-1}$)) and tetramethylnaphthalenes ($98.6 \mu\text{g km}^{-1}$) with naphthalene, methylnaphthalene and dimethylnaphthalenes also detected in the vapor phase and as constituents of diesel fuel (especially dimethylnaphthalenes which were 2 mg g^{-1} of fuel). Work by Arey and coworkers has determined the rate constants for reactions between commonly observed alkylated naphthalenes and the atmospherically relevant nitrate and hydroxyl radicals (Phoussongphouang and Arey, 2002, 2003).

The four species with $m/z = 128, 142, 156,$ and 170 are often detected together in the single particle mass spectrum of an individual particle, as shown in Fig. 3, however not all derivatives appear together in all particles. Fig. 4 is a histogram of the peaks in all particles from the HDV + LDV data set which contain the m/z 156 peak, showing the fraction of dimethylnaphthalene-containing particles which contain all other m/z values. Carbon-containing fragments are predominant in both the positive and negative ion mass spectra. Our results are not consistent with these ions originating from alkyl-nitronaphthalenes, such as those recently observed in ambient air by Arey and coworkers (Reisen et al., 2003), given the very small fraction (<3%) of alkylated naphthalene-containing particles which also contain a characteristic NO_2^- fragment ion ($m/z -46$). The

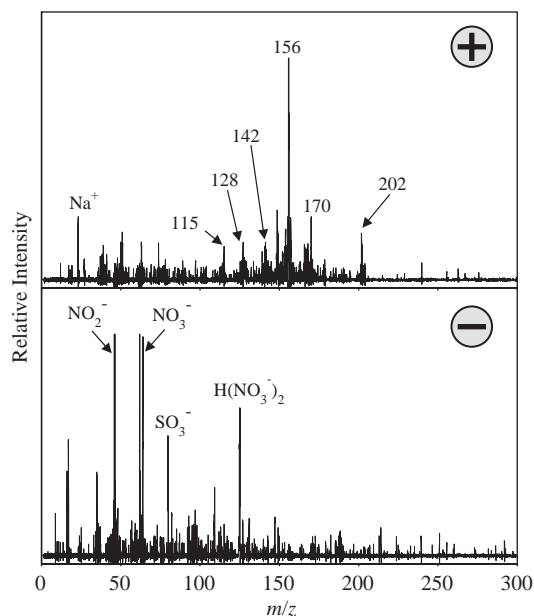


Fig. 3. A single-particle mass spectrum of (a) positive ions and (b) negative ions from a PAH containing particle sampled in 1997 from HDV + LDV traffic. Peaks due to PAH ions are labeled. Note specifically the significant signal due to di- and trimethylnaphthalene (PAHs with m/z 156 and 170).

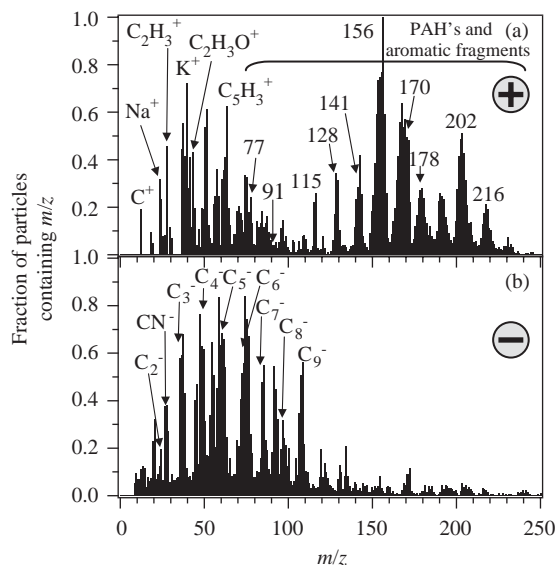


Fig. 4. Histograms of all peaks appearing in (a) positive and (b) negative ion mass spectra of only those particles sampled in 1997 which contain the m/z 156 peak due to di-methylnaphthalene. These histograms count the fraction of particles which contain a peak at each m/z value with relative intensity $>0.50\%$.

m/z 156 peak is usually the most intense in this series of naphthalenes. This observation is consistent with Jensen and Hites' study of aromatic emissions from a diesel engine (Jensen and Hites, 1983). They found that under normal conditions, the di- and trimethylnaphthalenes in the particulate phase were roughly four times more abundant than any other naphthalene homologue, with an average of 2.4 alkyl carbons per naphthalene observed.

3.2.2. Identification of alkylated PAHs in 2000 study

The situation was different in the data from the 2000 study, where very few particles were found to contain the naphthalene ions described above. Characteristic fragments of the alkylnaphthalenes (see footnote 1) were observed in only 0.8% and 4%, respectively, of particles sampled from the mixed HDV + LDV traffic, and 0.7% and 4%, respectively, of particles, sampled from the LDV-only traffic. However, these abundances are comparable in magnitude to those of the substituted naphthalenes themselves (see below), and therefore are still consistent with the species being alkylated.

3.3. Abundances of alkylated naphthalenes

The occurrence of the various naphthalene derivatives in the ATOFMS mass spectra varies dramatically depending on the traffic type sampled in the 1997 data

set, but not in the 2000 data set where the absolute number of particles containing naphthalene derivatives was quite small. Table 1 shows the relative frequency of various naphthalene homologue peaks in the results from mixed HDV + LDV traffic versus from the LDV-only traffic, in both studies.

3.3.1. Abundances of alkylated naphthalenes in 1997 study

In the 1997 data (Gross et al., 2000), as in previous studies (Miguel et al., 1998), we observed that lower molecular weight PAHs and their methylated derivatives were more prevalent in the HDV-influenced data set. Histograms of the frequency of occurrence of each m/z value up to 250 in the positive ion mass spectra of all particles sampled from mixed HDV + LDV traffic and from LDV-only traffic, sampled in 1997, are shown in Figs. 5a and b, respectively. Histograms of ion frequency in both data sets are generally similar, with a combination of low mass fragments and inorganic ions, in addition to a distribution of high mass PAH ions. However, there are also several striking differences of note. Both show inorganic ions at m/z 23 (Na^+) and m/z 39 (K^+) in the majority of particles and PAHs at m/z 178 and 202 in between 20% and 50% of the particles sampled. However, organic ions and lower mass PAH ions are more frequently observed in the HDV-influenced emissions, while higher mass PAH ions occur more frequently in the particles in the LDV-only emissions. The naphthalene derivatives with m/z 128, 142, 156, and 170 appear to be largely contributed by HDVs. Additionally, the fragment ions at m/z 115 and 141, which are consistent with alkylated naphthalenes (see footnote 1) are 14% and 18% more frequent in the HDV-influenced emissions, respectively.

The peaks at m/z 156 and 170 were often detected in the same particle, and were most commonly seen in the HDV + LDV data. The final column in Table 1 shows the ratio of the percentage of particles containing each naphthalene-series ion in the HDV + LDV samples versus in the LDV-only samples. The ratios are between 2.0 and 16, indicating that there is a significantly larger fraction of particles containing these ions in the HDV-influenced bore of the tunnel, in the time periods compared in this study. An even more striking difference between the two types of emissions is seen in the combined occurrence of the ions pairs of m/z 128 and 156, m/z 142 and 156, and m/z 156 and 170. These pairs of peaks are observed in individual particle mass spectra 16, 46, and 51 times more often, respectively, in the HDV-influenced emissions than in the LDV-only emissions. Thus, if we see the combination of m/z 156 and 170 peaks in vehicle emissions data, we can be at least 98% sure that the particle came from HDV influenced emissions. A particle sampled from ambient air that contains these specific combinations of peaks is quite

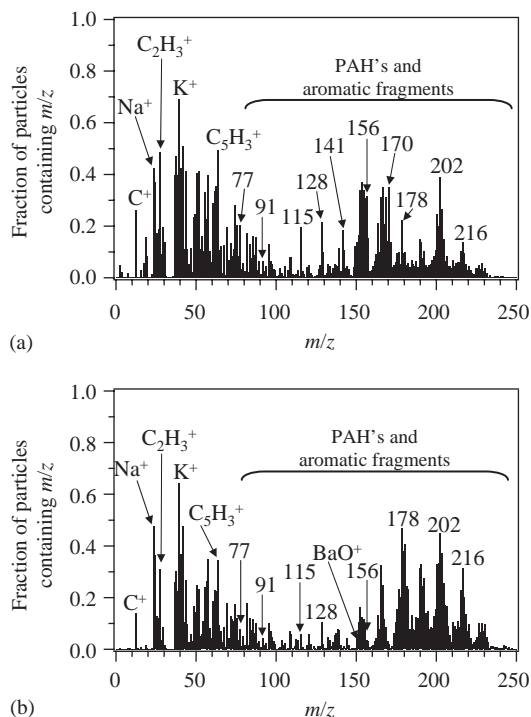


Fig. 5. Histograms of all peaks appearing in positive ion mass spectra obtained from (a) 1997 HDV + LDV emissions and (b) 1997 LDV-only emissions. These histograms count the fraction of particles which contain a peak at each m/z value with relative intensity $>0.50\%$.

likely derived from HDV influenced emissions, under the conditions of this sampling where the ambient temperature is low. Given that semi-volatile species partition onto particles rapidly upon dilution and cooling at the tailpipe, we can assume that the particles that contain these species were emitted by HDV. Dynamometer studies at controlled temperatures are required to confirm this.

In addition to occurring more frequently in the HDV-influenced data set, alkylated naphthalenes are also more intense in the mass spectra of the particles from the HDV-influenced data set. Given the spread in signal/noise values in each single-particle mass spectrum, it is difficult to state a peak area threshold above which it is likely that the particle arose from HDV influenced emissions, and below which it is likely that it arose from LDV emissions. The differing intensities of the alkylated naphthalenes, expressed as normalized relative peak areas, are shown in Fig. 6. The m/z 128 and 142 peaks have similar intensities in the two data sets, while the m/z 156 and 170 peaks are much more intense in the HDV + LDV data set. Peaks at m/z 156 were, on average 3.4 times more intense while those at m/z 170 were 2.8 times more intense than were these peaks in the LDV

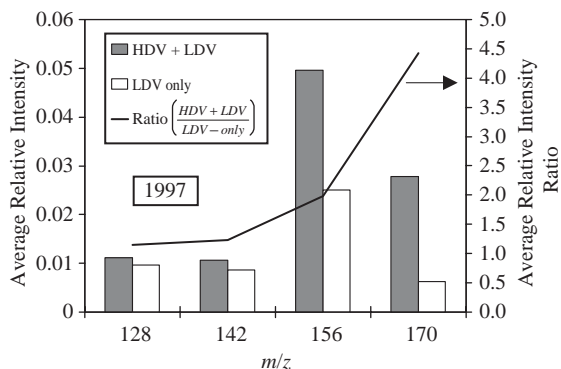


Fig. 6. Average relative mass spectral peak intensity of naphthalene and methylated naphthalene ions in single particle data obtained in 1997. HDV + LDV data is gray and LDV-only data is white. The graph shows the higher average relative intensity for di- and tri-methylnaphthalene (PAHs with m/z 156 and 170). The solid line indicates the ratio of the relative intensity for each m/z ion in HDV + LDV versus LDV-emissions (right-hand axis).

only data set. The average peak areas of both the m/z 156 and 170 peaks are significantly different in the HDV + LDV versus LDV only data sets from 1997, at the 99.9% confidence level ($v_{\text{calc}} = 97$ and 261 for these ions, respectively).

3.3.2. Abundances of alkylated naphthalenes in 2000 study

In the 2000 data set, the trends noted above are much less apparent. Figs. 7a and b show the histograms of all positive ions present up to m/z 250 in the HDV + LDV and LDV-only data sets acquired in the 2000 study. Again, the histograms of the positive ions from both traffic types are generally similar, and show a greater number of lower-mass ions than in the 1997 data, consistent with the higher desorption/ionization laser fluence under which the 2000 data set was acquired. The m/z distributions which appear at approximately m/z 140 and 155 are in fact overlaps of distributions of particles containing peaks due to Ba^+ (m/z of most abundant isotope is 138), the fragment ion at m/z 141, and the methylnaphthalene at m/z 142 as well as peaks due to $\text{BaO}^+/\text{BaOH}^+$ (m/z of most abundant isotopes are 154/155) and the dimethylnaphthalene ion at m/z 156. The barium containing peaks are likely due to brake wear (Rogge et al., 1993a, b; Gross and Schauer, 2004). Only about 6% of the particles sampled from each traffic type contain the m/z 202 PAH, in contrast to $\sim 40\%$ of particles from each traffic type sampled in 1997. The differences between the data acquired from the two traffic types in 2000 are also less pronounced than in 1997. However, under the higher desorption/ionization laser fluence conditions, we see that positively

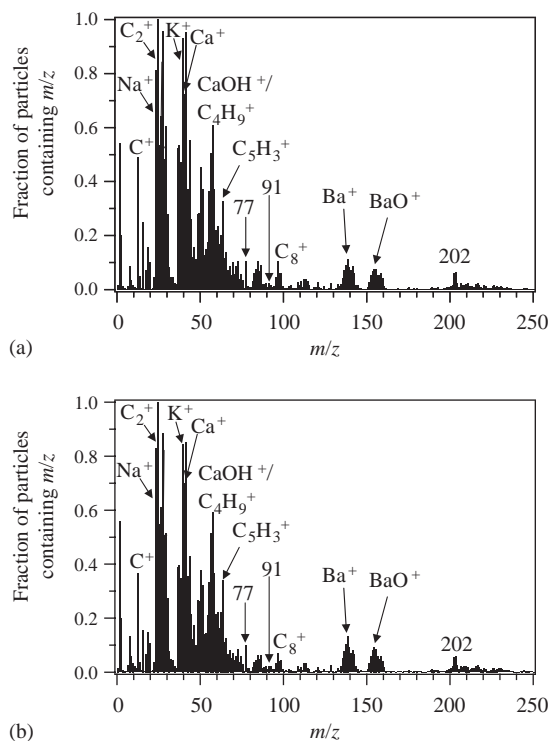


Fig. 7. Histograms of all peaks appearing in positive ion mass spectra obtained from (a) 2000 HDV + LDV emissions, (b) 2000 LDV-only emissions. These histograms count the fraction of particles which contain a peak at each m/z value with relative intensity $>0.50\%$.

charged carbon-containing fragments, especially those due to C_n^+ ($n = 1, 3-12$) ions are slightly more common in HDV influenced emissions, while barium-containing particles are slightly (but not significantly) more prevalent in the LDV-only emissions.

The naphthalene-series ions (m/z 128, 142, 156, and 170) that were so prevalent in the 1997 data set are also observed in the 2000 data, as shown in Table 1. However, their frequency of occurrence is approximately equal in data acquired from both traffic types, and they appear approximately 10 times less frequently than in the 1997 data. The ratios of the combinations of m/z 128 and 156, m/z 142 and 156, and m/z 156 and 170 in each traffic type should not be interpreted as an indication of a trend opposite to that seen in the 1997 data, as they were observed in only a very small number of particles (e.g. 2 particles contained m/z 156 and 170 out of the total 41,474 HDV + LDV particles sampled, and three out of the 20,053 LDV-only particles sampled contained these ions). Thus, under the conditions of this experiment, with higher ambient temperature and higher desorption/ionization laser fluence, the potential marker ion combinations observed in the 1997 data disappear.

4. Conclusion

The unique setup of the Caldecott Tunnel's bores provides for the opportunity to extrapolate the contribution of HDVs to the emissions in the mixed HDV + LDV traffic data (Miguel et al., 1998; Gross et al., 2000). We have analyzed two data sets obtained in the tunnel for promising marker ions for HDV emissions, and found that the presence of the most promising marker ions is very dependent on ambient conditions. Based on the results presented in Figs. 5 and 6, we suggest that, under the right circumstances, the series of alkylated naphthalenes (m/z 128, 142, 156, 170) provides a suite of chemical markers characteristic of HDV emissions, but they will only be detected under appropriate ambient conditions. In the 1997 data set, taken at colder ambient temperatures, all members of this sequence of alkylated naphthalene derivatives are significantly more abundant in the HDV-influenced emissions (Table 1). In particular, the presence of two or more members of the sequence in the same particle spectrum occurs almost exclusively in the HDV-influenced data set. In addition to their more frequent occurrence, m/z 156 and 170 peaks are also more intense in the mass spectra of particles sampled from the HDV-influenced bore of the tunnel (Fig. 6). These trends are not maintained in particles sampled at significantly higher ambient temperatures.

It is the combination of high signal intensity and frequency of occurrence in the HDV-influenced data that make the alkylated naphthalenes strong marker ions, indicating HDV emissions as the particle source, as seen in the 1997 data. This is especially true of the combination of m/z 156 and 170. These ions have not been observed in published filter/impactor studies of particulate-phase diesel emissions, presumably due to the combination of the relatively high vapor pressure of the compounds and the long sample collection times needed for bulk analysis. This highlights an advantage of real-time single particle mass spectrometry methods which analyze each particle within microseconds of sampling, enabling the study of semivolatile organic compounds. The potential for using these ions as chemical markers needs to be compared against results from tests of vehicular emissions from a variety of well-characterized vehicles on a dynamometer under controlled conditions of temperature, desorption/ionization laser fluence, etc. The fact that under certain conditions there is a significant difference in the alkylated naphthalene content in the single-particle mass spectra obtained from particulate emissions influenced by heavy duty vehicles is promising for future identification of the vehicle types which contribute to ambient particulate pollution. The differences in the two studies, carried out under different ambient conditions, highlight the need to consider the ambient conditions, and their effect on

semivolatile species, when determining source markers in environmental data. Thus, we recommend the combined use of controlled (laboratory or dynamometer) studies with ambient measurements for establishing stable markers for ambient source apportionment studies.

Acknowledgements

We thank the National Renewable Energy Laboratory and California Air Resources Board for funding for this study, as well as the Caltrans staff at the Caldecott Tunnel for their assistance in making the tunnel studies a success. The authors thank Dr. Markus Gälli, Sylvia H. Pastor, and Philip J. Silva for their part in the data collection. A.R.B. and B.S.W. thank Carleton College for funding during the analysis of the 1997 data. E.M.S. and J.C.J. thank Sigma Xi, The Scientific Research Society, for Grants in Aid of Research, which partially funded their field work in 2000.

References

- Allen, J.O., Fergenson, D.P., Gard, E.A., Hughes, L.S., Morrical, B.D., Kleeman, M.J., Gross, D.S., Gaelli, M.E., Prather, K.A., Cass, G.R., 2000. Particle detection efficiencies of aerosol time-of-flight mass spectrometers under ambient sampling conditions. *Environmental Science and Technology* 34, 211–217.
- Allen, J.O., Mayo, P.R., Hughes, L.S., Salmon, L.G., Cass, G.R., 2001. Emissions of size-segregated aerosols from on-road vehicles in the Caldecott tunnel. *Environmental Science and Technology* 35, 4189–4197.
- Carlsson, H., Westerholm, R., Ostman, C., 1999. Particulate and semivolatile associated aliphatic hydrocarbon exhaust emission from heavy duty diesel vehicles. *Toxicological and Environmental Chemistry* 68, 413–428.
- Denissenko, M.F., Pao, A., Tang, M.S., Pfeifer, G.P., 1996. Preferential formation of benzo[a]pyrene adducts at lung cancer mutation hotspots in P53. *Science* 274, 430–432.
- Dreher, D.B., Harley, R.A., 1998. A fuel-based inventory for heavy-duty diesel truck emissions. *Journal of the Air and Waste Management Association* 48, 352–358.
- El-Fadel, M., Hashisho, Z., 2001. Vehicular emissions in roadway tunnels: a critical review. *Critical Reviews in Environmental Science and Technology* 31, 125–174.
- Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 1998. Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. *Environmental Science and Technology* 32, 2051–2060.
- Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 1999. Particulate organic compounds emitted from motor vehicle exhaust and in the urban atmosphere. *Atmospheric Environment* 33, 2715–2724.
- Gard, E., Mayer, J.E., Morrical, B.D., Dienes, T., Fergenson, D.P., Prather, K.A., 1997. Real-time analysis of individual atmospheric aerosol particles: design and performance of a portable ATOFMS. *Analytical Chemistry* 69, 4083–4091.
- Gross, D.S., Schauer, J.J., 2004. Personal Communication.
- Gross, D.S., Gaelli, M.E., Silva, P.J., Wood, S.H., Liu, D.Y., Prather, K.A., 2000. Single particle characterization of automobile and diesel truck emissions in the Caldecott Tunnel. *Aerosol Science and Technology* 32, 152–163.
- Jensen, T.E., Hites, R.A., 1983. Aromatic diesel emissions as a function of engine conditions. *Analytical Chemistry* 55, 594–599.
- Limbeck, A., Rendl, J., Heimbürger, G., Kranabetter, A., Puxbaum, H., 2004. Seasonal variation of palladium, elemental carbon and aerosol mass concentrations in airborne particulate matter. *Atmospheric Environment* 38, 1979–1987.
- McLafferty, F.W., 1973. *Interpretation of Mass Spectra*. W. A. Benjamin, Reading, MA.
- Middlebrook, A., Murphy, D.M., Lee, S.-H., Thomson, D.S., Prather, K.A., Wenzel, R.J., Liu, D.-Y., Phares, D.J., Rhoads, K.P., Wexler, A.S., Johnston, M.V., Jimenez, J.L., Jayne, J.T., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., 2003. A comparison of particle mass spectrometers during the 1999 Atlanta supersite project. *Journal of Geophysical Research, [Atmospheres]* 108, 8424.
- Miguel, A.H., Kirchstetter, T.W., Harley, R.A., Hering, S.V., 1998. On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. *Environmental Science and Technology* 32, 450–455.
- NIST Mass Spec Data Center, S. E. S., director, 2003. *Mass Spectra*. In: Linstrom, P.J., Mallard, W.G. (Eds.), *NIST Chemistry Webbook*. NIST Standard Reference Database Number 69. National Institute of Standards and Technology, Gaithersburg, MD <http://webbook.nist.gov/>.
- Noble, C.A., Prather, K.A., 1996. Real-time measurement of correlated size and composition profiles of individual aerosol particles. *Environmental Science and Technology* 30, 2667–2680.
- Okada, S., Kweon, C.-B., Stetter, J.C., Foster, D.E., Shafer, M.M., Christensen, C.G., Schauer, J.J., Schmidt, A.M., Silverberg, A.M., Gross, D.S., 2003. Measurement of trace metal composition in diesel engine particulate and its potential for determining oil consumption: ICPMS (inductively coupled plasma mass spectrometer) and ATOFMS (aerosol time of flight mass spectrometer) measurements. *Society of Automotive Engineers [Special Publication] SP SP-1737*, 59–72.
- Phouongphouang, P.T., Arey, J., 2002. Rate constants for the gas-phase reactions of a series of alkylnaphthalenes with the OH radical. *Environmental Science and Technology* 36, 1947–1952.
- Phouongphouang, P.T., Arey, J., 2003. Rate constants for the gas-phase reactions of a series of alkylnaphthalenes with the nitrate radical. *Environmental Science and Technology* 37, 308–313.
- Reilly, P.T.A., Gieray, R.A., Whitten, W.B., Ramsey, J.M., 1998. Real-time characterization of the organic composition and size of individual diesel engine smoke particles. *Environmental Science and Technology* 32, 2672–2679.

- Reisen, F., Wheeler, S., Arey, J., 2003. Methyl- and dimethyl-ethyl-nitronaphthalenes measured in ambient air in Southern California. *Atmospheric Environment* 37, 3653–3657.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993a. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental Science and Technology* 27, 636–651.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993b. Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environmental Science and Technology* 27, 1892–1904.
- Samet, J.M., DeMarini, D.M., Malling, H.V., 2004. Biomedicine: do airborne particles induce heritable mutations? *Science* 304, 971–972.
- Schauer, J.J., Cass, G.R., 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental Science and Technology* 34, 1821–1832.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A.R., Christensen, C.G., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30, 3837–3855.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 2. C-1–C-30 organic compounds from medium duty diesel trucks. *Environmental Science and Technology* 33, 1578–1587.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2002a. Measurement of emissions from air pollution sources. 5. C1–C32 organic compounds from gasoline-powered motor vehicles. *Environmental Science and Technology* 36, 1169–1180.
- Schauer, J.J., Fraser, M.P., Cass, G.R., Simoneit, B.R.T., 2002b. Source reconciliation of atmospheric gas-phase and particle-phase pollutants using organic compounds as tracers. *Environmental Science and Technology* 36, 3806–3814.
- Silva, P.J., Prather, K.A., 1997. On-line characterization of individual particles from automobile emissions. *Environmental Science and Technology* 31, 3074–3080.
- Sipin, M.F., Guazzotti, S.A., Prather, K.A., 2003. Recent advances and some remaining challenges in analytical chemistry of the atmosphere. *Analytical Chemistry* 75, 2929–2940.
- Sodeman, D.A., Toner, S.M., Prather, K.A., 2004a. Determination of single particle mass spectral signatures from light duty vehicle emissions, submitted for publication.
- Sodeman, D.A., Toner, S.M., Shields, L.G., Suess, D.T., Gross, D.S., Prather, K.A., 2004b. Comparison of light duty and heavy duty vehicle emissions from dynamometer and tunnel studies using ART-2a, submitted to *Environmental Science and Technology*, submitted.
- Suess, D.T., Prather, K.A., 1999. Mass spectrometry of aerosols. *Chemical Reviews* 99, 3007–3035.
- Suess, D.T., Prather, K.A., 2002. Reproducibility of single particle chemical composition during a heavy duty diesel truck dynamometer study. *Aerosol Science and Technology* 36, 1139–1141.
- Vogt, R., Kirchner, U., Scheer, V., Hinz, K.P., Trimborn, A., Spengler, B., 2003. Identification of diesel exhaust particles at an Autobahn, urban and rural location using single-particle mass spectrometry. *Journal of Aerosol Science* 34, 319–337.