

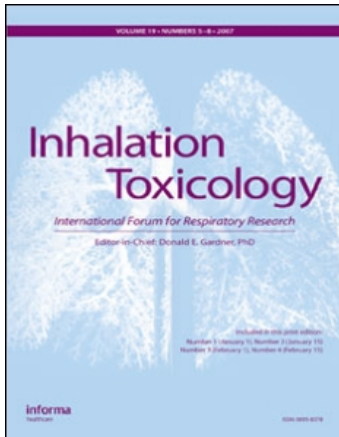
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Generation and Characterization of Gasoline Engine Exhaust Inhalation Exposure Atmospheres

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Generation and Characterization of Gasoline Engine Exhaust Inhalation Exposure Atmospheres

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Exposure atmospheres for a rodent inhalation toxicology study were generated from the exhaust of a 4.3-L gasoline engine coupled to a dynamometer and operated on an adapted California Unified Driving Cycle. Exposure levels were maintained at three different dilution rates. One chamber at the lowest dilution had particles removed by filtration. Each exposure atmosphere was characterized for particle mass, particle number, particle size distribution, and detailed chemical speciation. The majority of the mass in the exposure atmospheres was gaseous carbon monoxide, nitrogen oxides, and volatile organics, with small amounts of particle-bound carbon/ions and metals. The atmospheres varied according to the cycle, with the largest spikes in volatile organic and inorganic species shown during the “cold start” portion of the cycle. Ammonia present from the exhaust and rodents interacted with the gasoline exhaust to form secondary inorganic particles, and an increase in exhaust resulted in higher proportions of secondary inorganics as a portion of the total particle mass. Particle size had a median of 10–20 nm by number and approximately 150 nm by mass. Volatile organics matched the composition of the fuel, with large proportions of aliphatic and aromatic hydrocarbons coupled to low amounts of oxygenated organics. A new measurement technique revealed organics reacting with nitrogen oxides have likely resulted in measurement bias in previous studies of combustion emissions. Identified and measured particle organic species accounted for about 10% of total organic particle mass and were mostly aliphatic acids and polycyclic aromatic hydrocarbons.

INTRODUCTION

Gasoline engine exhaust (GEE) is among the least studied environmental source emissions. This is intriguing considering its importance as a source of environmental exposure, and the myr-

iad studies that have linked roadway emissions and proximity to roadways (proxy for exposure to engine emissions) to increased morbidity and mortality (Finkelstein et al., 2004; Hoek et al., 2002; Janssen et al., 2003; Peters et al., 2004; Riediker et al., 2004; Seagrave et al., 2006). In fact, source attribution studies have shown that GEE is often the largest contributor to ambient carbonaceous particulate matter (PM) in metropolitan areas (Fujita et al., 1998, 2007). GEE contributes a large proportion of the volatile organic emissions (including many designated as hazardous air pollutants by the US Environmental Protection Agency) that are rarely assessed in ambient measurements. The majority of the GEE-derived pollutants in the atmosphere are emitted from a small portion of poorly maintained vehicles and from emissions during start-up before the catalyst is operating properly (e.g. Fujita et al., 1998).

In contrast to GEE, diesel engine exhaust (DEE) is among the most studied environmental source emissions. Laboratory studies suggest that vapor and particle extracts of DEE may not

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be any more (or less) responsive in toxicology assays than GEE (Seagrave et al., 2002). Despite this, the concern and debate over roadway pollution continues to be focused primarily on DEE. This includes both attribution of health effects as well as assessments of exhaust composition. Only a handful of studies have characterized the chemical composition of GEE in detail (e.g., Fraser et al., 1998; Knapp et al., 2003; Phuleria et al., 2006; Robert et al., 2007; Schauer et al., 2002, 2008; Zielinska et al., 2004), but there have been many studies that have characterized DEE (reviewed in Lloyd & Cackette, 2001). Many of the chemical components of interest in DEE are also present in GEE. However, there are also some key composition contrasts that make GEE unique, such as the shift of the majority of the mass of the organic emissions to the gas phase.

As previously reviewed (McDonald et al., 2007), only a small number of inhalation toxicology studies have been conducted on GEE. Reports of the studies conducted to date present limited information on the inhalation systems, engines, fuels, lubricants, engine operation, and detailed composition of the atmosphere. The limited information makes comparison among studies difficult and evaluation of the composition/health response linkages implausible.

The National Environmental Respiratory Center (NERC) was established at the Lovelace Respiratory Research Institute (LRRI) to conduct laboratory research improving our understanding of the contributions of individual air contaminants and their combinations to the health effects associated with exposures to complex air pollution mixtures. The NERC research strategy (www.nercenter.org) involves conducting a series of inhalation toxicology studies of common source emissions having different, but overlapping, compositions. Both the composition of the exposure atmospheres and a range of health effects are measured in detail using identical protocols, allowing the combination of results from all studies into a single composition-concentration-response database. NERC studies have been conducted for contemporary diesel emissions (Campen et al., 2003; Harrod et al., 2003, 2004; McDonald et al., 2004; Reed et al., 2004), hardwood smoke (Barrett et al., 2006; McDonald et al., 2006; Reed et al., 2006), and gasoline engine emissions (Lund et al., 2007; McDonald et al., 2007). McDonald et al. (2007) reported the overall approach to developing the GEE exposure atmosphere and a few preliminary biological results. This manuscript provides a detailed description of the exposure atmosphere development and composition, and companion manuscripts summarize experimental design, rodent husbandry and health responses.

MATERIALS AND METHODS

This study included three dilutions of GEE, one atmosphere at the lowest dilution with particles removed by filtration, and one clean air control. The dilutions were selected to complement dilutions used in the LRRI NERC diesel study (McDonald et al., 2004). That study used dilutions ranging from 10:1 to 90:1, which corresponded to PM concentrations of 1,000 $\mu\text{g}/\text{m}^3$ down

to 30 $\mu\text{g}/\text{m}^3$. The GEE study reported here utilized a \sim 10:1 dilution rate at the highest exposure level (H), and two additional dilutions at 15:1 mid (M) and 90:1 low (L), respectively. The 15:1 dilution yielded a 30- $\mu\text{g}/\text{m}^3$ PM concentration, and was thus selected to provide overlap with the same concentration of PM in the previous DEE study.

Exhaust was generated from two 1996 General Motors 4.3-L V6 gasoline engines (initial mileage 50–70 $\times 10^3$) equipped with stock exhaust systems (including muffler and catalyst) obtained from in-use vehicles (Chevrolet S-10 light-duty pickup trucks) purchased in Albuquerque, NM. The two vehicles were selected based on their comparable mileage and acceptable performance at a local emissions inspection facility. The vehicles were first operated on a chassis dynamometer at Southwest Research Institute (San Antonio, TX) using the California Unified Driving Cycle (California Code Regulations, 1996) to further ensure normal emissions and to obtain critical operating specifications (engine speed, throttle position, manifold pressure) that would permit adapting the chassis dynamometer cycle to the engine stand dynamometer at LRRI. At LRRI, the engines were connected to eddy current dynamometers (Model Alpha 240, Zöellner, Kiel, Germany) and linked to a dynamometer interface (Type DTC-1, Dyne Systems Co., LLC, Germantown, WI) that was controlled by a custom software program (Cell Assistant, Dyne Systems Co.).

The final engine cycle was adapted from the emissions testing protocol to one that would fit an inhalation exposure paradigm. The final cycle included one 5-min “cold start” followed by a 19-min “hot stabilized” portion of the cycle. Exposures were started immediately after engine ignition. After the initial engine cycle, the 24-min engine cycle was repeated continuously for a total time of 3 h. At 3 h, the first engine was shut down and the process was repeated for the second engine. Two engines were used each exposure day to provide two cold starts. The engines were fueled with regular unleaded gasoline blended to the average USA composition for the summer of 2001 and winter of 2001–2002 of non-oxygenated, non-reformulated fuel (survey by TRW, Livonia, MI). The fuel was blended in a single batch (ChevronPhillips Specialty Fuels Division, Borger, TX), delivered in barrels, and stored under controlled conditions until used. The fuel characteristics are shown in Table 1. The crankcase oil (10W-30, Pennzoil Products Company, Houston, TX) and oil filter (Duraguard PF52, AC Delco, Detroit, MI) were changed every 122 h (equivalent to 3,000 miles) of engine operation.

Exhaust was immediately diluted with charcoal-filtered and HEPA-filtered air at the tailpipe in a dilution exposure system as previously described for DEE (McDonald et al., 2004). Exhaust was diluted to approximately 10:1 (high - H), 15:1 (medium - M), and 90:1 (low - L) prior to entering the 2- m^3 whole-body inhalation exposure chambers (H2000, Lab Products, Inc., NJ). The primary dilution was conducted with a constant flow of clean air that was from the same source as used for the clean-air control group (C). A high filtered (HF) exposure atmosphere contained the 10:1 dilution with particles removed by a HEPA

TABLE 1
Characteristics of fuel used to generate the GEE inhalation exposure atmospheres^a

Tests	Results
Specific gravity, 60/60°F	0.7495
Reid vapor pressure at 100°F, psia	8.47
Sulfur content (ppm)	331.5
Distillation range °F at 760 mm Hg	
10% evaporated	126
50% evaporated	215
90% evaporated	333
Composition vol %	
Aromatics	33.2
Olefins	7.6
Saturates	59.2
Research octane number	91.6
Motor octane number	82.4
Anti-knock index (R+M)/2	87

^aTests performed according to standard methods and provided by the fuel vendor (Chevron Phillips).

filter. Dilutions were monitored and controlled by monitoring nitrogen oxides (NO_x) directly from the exposure chambers as described (McDonald et al., 2004). Exposure targets were set to achieve GEE NO_x concentrations of 2 (L), 12 (M), and 18 (H) ppm.

The exposure atmospheres were characterized in detail as previously described (McDonald et al., 2004, 2006). Table 2 summarizes the observables, measurement techniques, sampling conditions, analysis frequency, and analytical lab for the chemical analysis of test atmospheres. In brief, sample collection strategies were developed to capture and measure gas, semivolatile, and particle phases for a broad spectrum of chemical classes. Inorganic gases were analyzed by chemiluminescence (NO_x), photoacoustic infrared spectroscopy (CO₂), ion chromatography after collection on to selective adsorbants (NH₃, SO₂), liquid chromatography/mass spectrometry after collection on to selective adsorbants (volatile acids and carbonyls), and gas chromatography/mass spectrometry after collection into SUMMA canisters (volatile organic hydrocarbons). Particle chemistry was determined from material collected on quartz filters for analysis of carbon (elemental carbon (EC)), organic carbon, by thermal/optical reflectance (Chow et al., 1993, 2007) and inorganic ions (sulfate, nitrate, ammonium) by ion chromatography after aqueous extraction (Chow & Watson, 1999). Organic carbon was normalized to organic mass (OM) by multiplying the measured value by 1.2 to account for unmeasured hydrogen and other elements. Metals were analyzed by inductively coupled plasma mass spectrometry after acid digestion of ultra-clean Teflon membrane filters. Semivolatile and particle-phase organics were analyzed by gas chromatography/mass spectrometry in organic extractions of an XAD-

4 coated diffusion denuder (gas phase) followed by a Teflon-coated glass-fiber filter followed by 10 g of XAD-4.

In each case, sampling media (e.g., filters, canisters, etc.) were pre-cleaned and consisted of both laboratory and field blanks, where laboratory measurement blanks ensured cleanliness of the analytical and (where applicable) extraction systems, and field blanks ensured that no contamination was introduced during the sample handling procedures. Laboratory blank background values were subtracted from the sample values, and field blanks were inspected to evaluate the importance of sample handling on data reported (no significant concentrations were measured in field blanks). All flow measurements were conducted using flow standards that were verified annually according to standards traceable to the National Institute of Standards and Technology.

SUMMA canister samples were obtained subsequent to passing through an approximately 6-×40-cm-long custom denuder containing steel rods (1 cm wide) coated with a saturated solution of Co(NO₃)₂ in water and dried at room temperature. The denuder was heated to 400°C with a flow of approximately 300 ml/min of air for 8 to 10 h, and oxidation of the cobalt was confirmed by the elution of NO₂ from the denuder. The denuder served to reduce NO_x concentrations so that reactive organic compounds would not be degraded within the canisters after sampling. This technique has recently been reported for sampling combustion emissions into SUMMA canisters (EPA, 2008), and the use of CoO to react with NO_x was previously reported (Braman et al., 1986).

Particle size distribution was measured with a fast mobility particle sizer (FMPS; TSI, St. Paul, MN), which measures particle count from ~5–500 nm with 1-s time resolution. Samples were collected during an entire 6-h exposure period directly from the breathing zone of the rodents.

Several exposure-generation system performance characteristics were examined as a part of the pre-study performance verification. These included the homogeneity of material within exposure chambers, the stability of the exposure atmospheres, and determination of atmosphere concentrations during non-exposure hours when the engines were not in operation. The characterization included measurements of PM, NO_x, hydrocarbon (HC), and semivolatile organics as described above. Non-exposure monitoring was conducted both overnight (beginning 1 h after system shutdown) after a 6-h engine operation (to match typical exposure operation) and during the day after a 48-h period when the engine was not operating.

RESULTS

Pre-Study System Verification

As expected, pre-study system tests for homogeneity of material within the exposure atmosphere showed that the material was well distributed, with less than 10% variability between reference ports located throughout the exposure chamber. The stability of the exposure atmospheres from day to day and among exposure levels was acceptable according to prescribed

TABLE 2
Summary of exposure atmosphere characterization measurements and measurement conditions

Observables	Collection device	Collection media	Collection point	Sample flow rate (L/m)	Analytical instrument	Analysis allocation
Gravimetric mass	Aluminum in-line filter holder	TIGF	Chamber/Plenum	4	MB	LRRI
Continuous mass	Dust-Trak nephelometer	NA	Chamber	2	NA	LRRI
NOx	Chemiluminescence analyzer	NA	Chamber	0.4	NA	LRRI
Particle Size	Fast-mobility particle sizer	NA	Chamber	10	NA	LRRI
CO/CO ₂ /THC	Photoacoustic analyzer	NA	Chamber	1	NA	LRRI
THC	Flame ionization detector	NA	Chamber	1	NA	LRRI
Organic/elemental carbon	Aluminum in-line filter holder	Quartz filter (1)	Plenum	20	TOR	DRI
Ions (sulfate/nitrate/ammonium)	Aluminum in-line filter holder	Quartz filter (2)	Plenum	20	IC, AC	DRI
SO ₂	Aluminum in-line filter holder	K ₂ CO ₃ -impregnated cellulose fiber filter	Chamber	2-5	IC	DRI
NH ₃	URG denuder (20 cm, 4 channel)	Citric acid-coated cellulose fiber filter	Chamber	5	AC	DRI
Metals and other elements	Teflon in-line filter holder	Teflon filter (2)	Plenum	20	ICPMS/ICPOES	WSLH
Volatile hydrocarbons (C ₁ -C ₁₂)	Volatile organic sampler	Electropolished canister	Chamber	0.1	GCMS/GCFID	DRI
Volatile carbonyls	Volatile organic sampler	DNPH cartridge	Chamber	0.3	LC/DAD/MS	DGA, Inc.
Volatile organic acids	Aluminum in-line filter holder	KOH-impregnated quartz filter	Chamber	1-2	LC/DAD/MS	DGA, Inc.
Semivolatile/fine particle organics (1)	Tisch environmental PUF sampler	Quartz filter/PUF/XAD-4/PUF	Plenum	80	GCMS	LRRI
Semivolatile/fine particle organics	URG denuder (60 cm, 8 channel)	XAD-coated/filter/PUF/XAD-4/PUF	Plenum	80	GCMS	LRRI

Chemical species: CO = carbon monoxide; CO₂ = carbon dioxide; SO₂ = sulfur dioxide; NH₃ = ammonia; NOx = nitric oxides; THC = total hydrocarbons

Instruments/collection devices: URG = URG Corporation; TIGF = Teflon-impregnated glass fiber filter; NA = not applicable; DNPH = dinitrophenylhydrazine; PUF = polyurethane foam; MB = microbalance; TOR = thermal/optical reflectance; IC = ion chromatography; AC = automated colorimetry; ICPMS = inductively coupled plasma mass spectrometry; ICPOES = inductively coupled plasma optical emission spectroscopy; GCMS = gas chromatography mass spectrometry; GCFID = gas chromatography flame ionization detector; DNPH = dinitrophenylhydrazine; LC/DAD/MS = liquid chromatography/diode array/mass spectrometry.

Organizations: LRRI = Lovelace Respiratory Research Institute; DRI = Desert Research Institute; WSLH = Wisconsin State Laboratory of Hygiene; DGA, Inc. = Daniel Grosjean and Associates, Inc.

TABLE 3

Summary of overnight sampling results after the end of a 6-h generation of GEE in the dilution tunnel and exposure chambers

Name	Units	Exhaust at 10:1 dilution	Overnight	48 h after exhaust
Particle mass	$\mu\text{g}/\text{m}^3$	80.0	ND ^a	ND
NOx	ppm	24.0	<LOQ ^b	<LOQ
Vapor Hydrocarbons	ppm	7.6	0.4	0.5
Speciated Semivolatile Organics				
2-methylnaphthalene	ng/m^3	2528.6	20.0	39.8
1-methylnaphthalene	ng/m^3	1167.9	-3.2	7.5
Biphenyl	ng/m^3	84.3	-0.1	0.6
1,2-dimethylnaphthalene	ng/m^3	59.9	-0.4	-0.8
phenanthrene	ng/m^3	212.9	13.7	5.3
anthracene	ng/m^3	31.9	-0.2	-0.2
fluoranthene	ng/m^3	5.0	0.3	0.5

^aNot detected.

^b<LOQ, below limit of quantitation.

performance criteria. In addition, the concentrations of PM, NOx, HC and speciated organics during non-exposure hours (Table 3) were present at concentrations that have been previously observed in background air during monitoring of clean-air exposure atmospheres (e.g., McDonald et al., 2004).

Exposure Atmosphere Composition

Figure 1 shows the summary (average) compositions at each exposure level based on data provided in Table 4. Note that individual compound concentrations for speciated metals and organics are not included but are available from the NERC database at www.nercenter.org. All averages are composites of repeated transient engine cycles (and two cold starts) from two separate engines. The composition within the exposure chambers was constantly changing throughout the engine duty cycle. To illustrate this, Figure 2 shows the change in PM in real time during an hour of exposure at the H level. Figure 3 shows the concentrations of total hydrocarbons in real time, illustrating that the peak concentrations occur during the two cold starts. Note that the peaks during those cold starts had little impact on the final reported average concentrations, which were more of a reflection of the lower levels during the remainder of the cycle. Real-time data are not available for all analytes, so all data are reported as exposure averages. Errors are standard deviation among repeated measurements.

As previously reported for DEE (McDonald et al., 2004) and hardwood smoke (McDonald et al., 2006), the gaseous component of GEE accounted for the majority of the mass of material emitted from the engine and subsequently found within the inhalation atmosphere. This is illustrated particularly well by comparing all of the constituents expressed in mass units. In Table 4, the concentration of the most commonly measured constituents

of GEE in each exposure atmosphere is given both in units of mass/ m^3 . Table 4 and Figure 1 show that the majority of the mass of GEE in these exposure atmospheres was composed of gaseous material, especially CO and NOx (~94% NO and ~6% NO₂). SO₂ and NH₃ accounted for a small portion of the overall mass, but approximately 16–30 times more than the PM mass. NH₃ was contributed from both the rodents and GEE. In contrast with the NERC diesel and hardwood smoke atmospheres however, the primary source of NH₃ in the chambers was the GEE (not the rodents).

Volatile Organic Carbon

Volatile organic carbon (VOC), reported here as the non-methane VOC (NMVOC), was present in the inhalation exposure atmospheres due to both GEE and animal emissions. Of course the majority of the material, especially at lower dilutions, is attributable to GEE, as illustrated by the increase in total mass concentration and the shift in relative composition of individual chemical species. As indicated in Figure 3, the VOCs were especially high in concentration during the cold starts, but then stabilized to less than 10 ppm at the H exposure level. Note the H and HF levels showed approximately 25–30% differences in average concentrations. The samples were not taken concurrently from these exposure levels, and the higher concentrations reported for the HF are biased by a day on which the total hydrocarbon concentrations were higher than when the H samples were taken. The contribution of chemical classes to NMVOCs were ranked as alkane > aromatic > isoalkene > alkene > alkyne > carbonyls > acids > oxygenates (ethanol, ethers). The number of individual compounds that were summed to account for each of these classes differed, but in general all classes were dominated by the lower molecular weight compounds from C₂–C₆ (e.g., ethane, pentane and methyl pentanes, butane, hexanes and their carbonyl derivatives), with high but lesser amounts of the higher molecular weight compounds. This VOC profile is consistent with previous reports that have linked emissions to the relative abundance of these compounds in the fuel (Fraser et al., 1998). Benzene, toluene, and the xylenes were the most abundant aromatics. The concentrations of these higher concentration aromatics at the H exposure level ranged from ~500–1000 $\mu\text{g}/\text{m}^3$. Another compound of interest was 1,3-butadiene, a putative carcinogen that was present at concentrations in the 10–40 $\mu\text{g}/\text{m}^3$ range at the H exposure level.

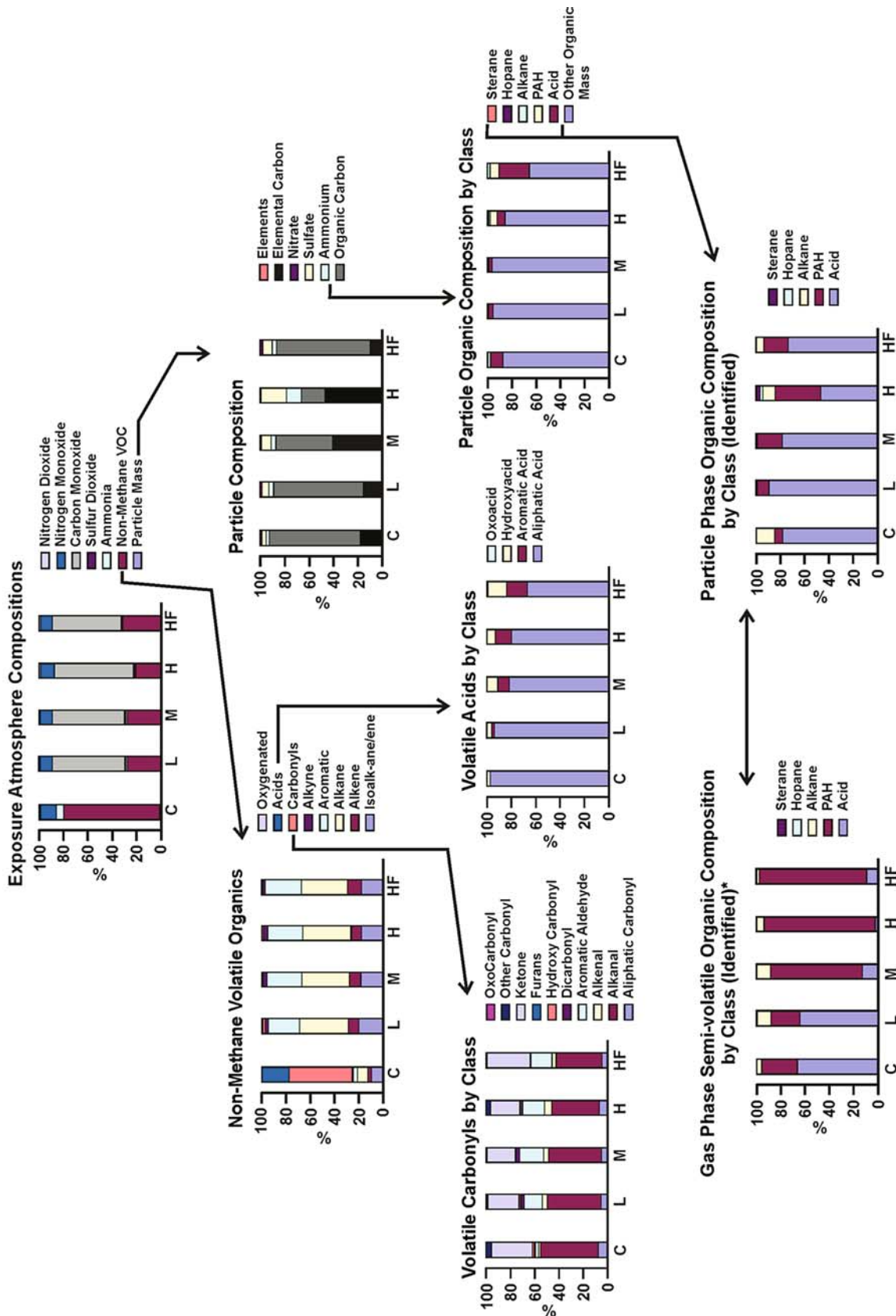
An important consideration in evaluating the concentrations of 1,3-butadiene and other reactive compounds (e.g., styrene, alkenes) are the reactions with NOx during storage of VOCs in SUMMA canisters prior to analysis (EPA, 2008). To address these reactions, some samples were collected in parallel using either a preconditioning of the aerosol through a CoO denuder (to remove NOx) or with no preconditioning. Figure 4 shows results for selected chemicals from the analysis of these samples. The concentrations of benzene and toluene, relatively unreactive compounds in the absence of sunlight, were similar with and without removal of NOx. However, the reactive

TABLE 4
Composition of Gasoline Engine Exhaust Exposure Atmospheres

Exposure atmosphere composition	Units	C ^a	L ^b	M ^c	H ^d	HF ^e
Particle mass	$\mu\text{g}/\text{m}^3$	2.5 ± 2.9	6.6 ± 3.7	30.3 ± 11.8	59.1 ± 28.3	2.3 ± 2.6
Particle count	particle/cm ³	1472.8	2.6×10^4	2.6×10^5	5.0×10^5	1.1×10^4
Non-methane VOC	$\mu\text{g}/\text{m}^3$	101.9	1912.2	10,860.4	15,952.9	25,876.6
Ammonia	$\mu\text{g}/\text{m}^3$ (ppm)	$20.0 (0.03) \pm 0.1$	$219.1 (0.38) \pm 0.9$	$1149.5 (1.98) \pm 6.0$	$1957.7 (3.37) \pm 8.1$	$1241.5 (2.14) \pm 6.1$
Sulfur dioxide	$\mu\text{g}/\text{m}^3$ (ppm)	$1.1 (0.0) \pm 0.1$	$193.5 (0.09) \pm 7.9$	$862.6 (0.38) \pm 35.3$	$1366.8 (0.62) \pm 56.0$	$1051.1 (0.47) \pm 43.0$
Carbon monoxide	mg/m ³ (ppm)	$0.0 (0.0) \pm 0.2$	$12.2 (12.8) \pm 0.5$	$70.1 (73.2) \pm 1.6$	$102.8 (107.3) \pm 3.3$	$99.5 (103.9) \pm 1.6$
Nitrogen monoxide	mg/m ³ (ppm)	$0.04 (0.04) \pm 0.1$	$2.1 (2.0) \pm 0.5$	$12.2 (11.9) \pm 1.1$	$18.4 (18.0) \pm 2.8$	$17.2 (16.7) \pm 1.9$
Nitrogen dioxide	mg/m ³ (ppm)	$0.0 (0.0) \pm 0.0$	$0.13 (0.1) \pm 0.0$	$0.7 (0.5) \pm 0.1$	$1.4 (0.9) \pm 0.3$	$1.7 (1.1) \pm 0.2$
Particle composition						
Elemental carbon	$\mu\text{g}/\text{m}^3$	1.1 ± 0.4	5.1 ± 2.6	22.8 ± 2.7	31.0 ± 6.6	1.5 ± 1.1
Organic mass	$\mu\text{g}/\text{m}^3$	7.2 ± 2.0	16.8 ± 2.4	9.5 ± 0.5	12.6 ± 2.1	11.3 ± 2.5
Ammonium	$\mu\text{g}/\text{m}^3$	0.2 ± 0.0	0.7 ± 0.1	1.2 ± 0.5	8.3 ± 2.3	0.5 ± 0.1
Sulfate	$\mu\text{g}/\text{m}^3$	0.2 ± 0.1	1.3 ± 0.1	2.4 ± 1.0	13.7 ± 3.6	1.2 ± 0.1
Nitrate	$\mu\text{g}/\text{m}^3$	0.1 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	0.6 ± 0.1	0.3 ± 0.0
Sum of elements	ng/m ³	0.12	0.10	0.25	1.42	0.60
Non-methane volatile organics						
Isoalk-ane/ene	$\mu\text{g}/\text{m}^3$	8.4	375.4	1994.7	2866.2	4823.2
Alkene	$\mu\text{g}/\text{m}^3$	2.5	163.4	993.5	1370.1	2292.3
Alkane	$\mu\text{g}/\text{m}^3$	7.7	770.3	4290.2	6373.4	9974.2
Aromatic	$\mu\text{g}/\text{m}^3$	2.8	489.9	3089.4	4565.3	8051.4
Alkyne	$\mu\text{g}/\text{m}^3$	0.7	42.6	369.8	584.1	566.6
Oxygenated	$\mu\text{g}/\text{m}^3$	4.0	7.6	1.5	7.9	3.3
Carbonyls	$\mu\text{g}/\text{m}^3$	46.0	42.4	107.2	162.5	152.5
Acids	$\mu\text{g}/\text{m}^3$	29.8	20.6	14.3	23.4	13.3
Volatile carbonyls by class						
Aliphatic carbonyl	$\mu\text{g}/\text{m}^3$	5.3	2.4	5.2	16.2	6.1
Alkanal	$\mu\text{g}/\text{m}^3$	21.5	19.4	48.1	57.8	56.9
Alkenal	$\mu\text{g}/\text{m}^3$	0.4	1.5	5.6	12.1	5.8
Aromatic aldehyde	$\mu\text{g}/\text{m}^3$	1.1	7.0	22.1	30.7	29.0
Dicarbonyl	$\mu\text{g}/\text{m}^3$	0.7	0.3	0.6	1.7	0.5
Hydroxy carbonyl	$\mu\text{g}/\text{m}^3$	0.3	0.2	0.3	1.8	0.3
Furans	$\mu\text{g}/\text{m}^3$	0.0	0.0	0.0	0.4	0
Ketone	$\mu\text{g}/\text{m}^3$	15.8	11.4	24.9	35.2	53.3
Other carbonyl	$\mu\text{g}/\text{m}^3$	0.9	0.2	0.4	6.3	0.4
Oxocarbonyl	$\mu\text{g}/\text{m}^3$	0.0	0.0	0.0	0.3	0.2
Volatile organic acids by class						
Aliphatic acid	$\mu\text{g}/\text{m}^3$	28.9	19.4	11.8	18.8	8.9
Alkenoic acid	$\mu\text{g}/\text{m}^3$	0.0	0.0	0.0	0.0	0.0
Aromatic acid	$\mu\text{g}/\text{m}^3$	0.1	0.4	1.3	3.0	2.2
Hydroxyacid	$\mu\text{g}/\text{m}^3$	0.8	0.8	1.2	1.5	2.1
Oxoacid	$\mu\text{g}/\text{m}^3$	0.0	0.1	0.0	0.1	0.1
Semivolatile organic carbon-gas phase						
Acid	ng/m ³	1194.8	2167.9	993.8	499.7	1735.2
PAH	ng/m ³	522.9	800.9	5878.8	18857.3	16863.2
Alkane	ng/m ³	72.8	389.1	898.6	1209.2	466.6
Hopane	ng/m ³	nd ^f	nd	nd	nd	nd
Sterane	ng/m ³	nd	nd	nd	nd	nd
Semivolatile organic carbon-particle phase						
Acid	ng/m ³	819.2	381.0	438.1	815.7	2876.0
PAH	ng/m ³	67.8	40.5	116.1	664.2	791.6
Alkane	ng/m ³	161.0	4.7	5.4	170.3	258.0
Hopane	ng/m ³	20.2	nd	nd	66.9	54.4
Sterane	ng/m ³	nd	nd	nd	nd	nd

^aControl = clean air; ^bLow; ^cMid; ^dHigh; ^eHigh filtered; ^fNot detected.

GASOLINE ENGINE EXHAUST ATMOSPHERE



6769-1a

*Semi-Volatile Organics not included in Mass Balance Above

FIG. 1. Composition (weight fraction) of gasoline engine exhaust and clean air exposure atmospheres.

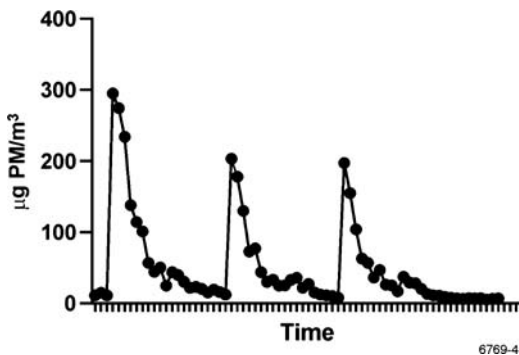


FIG. 2. Real-time particle mass concentration in the H exposure level chamber. Data represent approximately 1 h of monitoring in the breathing zone of the rodent.

compounds, such as 1,3-butadiene and styrene, are decreased when NO_x is not removed. This has implications for all results of exhaust samples measured from SUMMA canisters to date. Because it is not standard practice to precondition gas samples to remove NO_x, the majority of measured reactive NMVOCs reported in the literature are likely biased significantly low. This includes results from the NERC diesel study (McDonald et al., 2004), where no preconditioning of the aerosol was done. To address this, those measurements are currently being repeated and updated in the NERC database available at www.nercenter.org.

Particulate Matter

Measurement of PM from GEE is challenging due to the low PM concentration in the presence of large amounts of vapors that will adsorb to filters and contribute to the mass interpreted as PM. Prior to the study, several sampling conditions and filter types were evaluated to define the most appropriate technique for daily sampling of PM. A Teflon membrane filter was chosen after initial trials because it yielded the lowest measured mass at the H exposure level (5060 µg/m³) compared with Teflon-coated glass fiber filters (80–100 µg/m³). This lower adsorption of vapor organics on Teflon filters has resulted in converting to

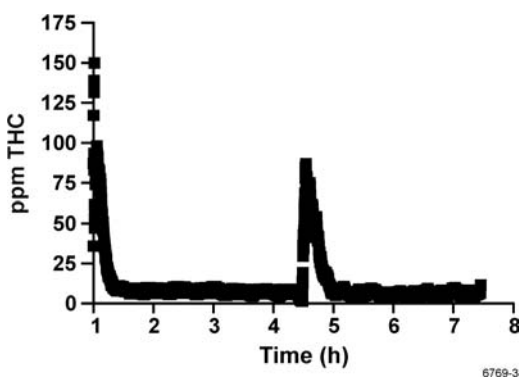


FIG. 3. Real-time hydrocarbon concentration (THC) at the H exposure level.

these filters from the previously used Teflon-coated glass fiber filters in the standardized measurement of DEE PM for regulatory purposes (40 CFR, 2007). GEE PM is not measured for regulatory purposes, so there is no associated standard. The average PM concentrations were 7, 30, and 59 µg/m³ in the L, M, and H exposure atmospheres. The concentrations of PM in the C and HF atmospheres were 2.5 µg/m³.

Size measurement of GEE particles is complicated due to the relatively low concentrations, small size, and high concentrations of vapor (that can lead to filter artifacts). In addition, because of the nature of the engine cycle, the particle number and size changed in real time throughout the day. To address this, an FMPS that measured particle number and size from ~5–500 nm in real time was used after analysis by a micro-orifice uniform deposition impactor (MOUDI) revealed little mass of PM above 500 nm. Figure 5 shows the particle size and concentration in the H exposure atmosphere as a function of time. As expected, the particle number and size changed throughout the duty cycle. While the measurements were not traced as a function of point in the duty cycle, in general it was observed that larger particle size and higher concentration were associated with the higher workloads. The particle size ranged from 5.5–150 nm, with the majority of the particles between 5–20 nm. The mass median diameter was approximately 150 nm. The median diameter ranged from ~10 nm at the higher dilution levels to 15–20 nm at the lowest dilution. Particle count (shown in Table 4 as the average across repeated engine cycles, including cold start) was $\sim 2.6 \times 10^4$, 2.6×10^5 , and 5×10^5 particles/cm³ in the L, M, and H exposure atmospheres, respectively. It is of note that the HF exposure atmosphere contained approximately 1×10^4 particles/cm³, which was above C (10^3) but substantially less than any of the other exposure atmospheres and 98% less than the particle count at the same dilution without filtration.

The fractional abundance of the primary PM constituents (EC, OM, inorganic ions (sulfate/nitrate)) differed among the GEE exposure chambers because of variation in the proportions of particle-bound inorganic species in these chambers. The PM in the C chamber was composed of nearly 100% OM that likely consisted of a combination of rodent dander and exhaled organic vapor that adsorbed onto the quartz filter and was weighed as organic carbon. EC in the unfiltered GEE exposure atmospheres accounted for ~20–50% of the PM, with negligible amounts of EC in the HF and C atmospheres. OM accounted for the majority of the mass in the C, L, and HF atmospheres. However, the portion of OM, as a fraction of PM, decreased as a function of decreasing dilution. At the M level OM was ~50%, and it only accounted for ~20% at the H level. The absolute amounts of OM did not increase as a function of exposure level. Much of the OM, especially at the lowest exposure levels, can be attributed to adsorption of organic vapors onto the quartz filters. This explains the poor agreement between measured gravimetric mass and sum of measured species for the L and HF groups, where organic vapor adsorption accounted for a large amount of mass.

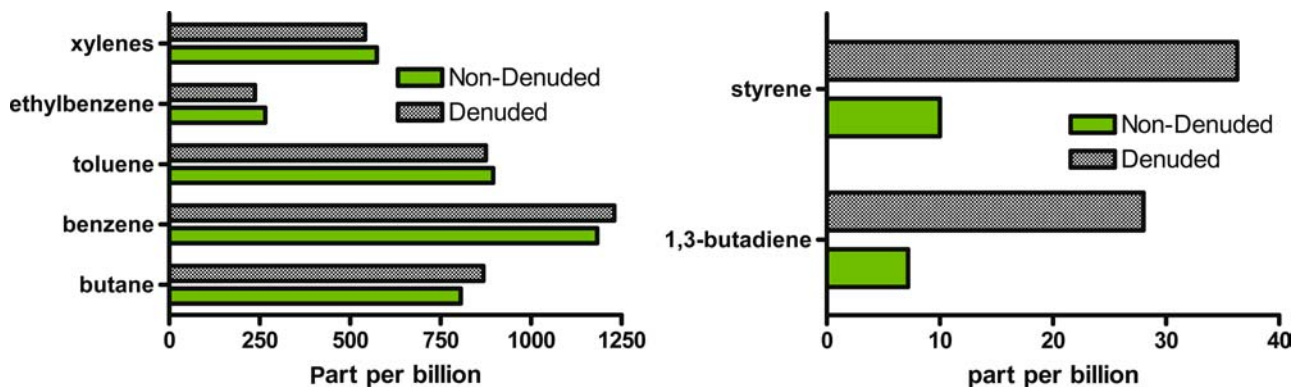


FIG. 4. Concentration of VOCs captured from the L dilution level in SUMMA canisters and analyzed by gas chromatography/mass spectrometry. Samples were collected in parallel with and without a scrubber to denude the NO_x that can react inside the canister. (A) The moderate reactivity compounds did not change in the presence or absence of NO_x. (B) The reactive compounds styrene and 1,3-butadiene were approximately five times higher in the absence of NO_x.

In contrast, EC trended precisely with the changes in dilution. At the lowest dilution, the remainder of the mass was accounted for by sulfate and ammonium, presumably as (NH₄)₂SO₄. Elements (mostly metals) accounted for <5% of the PM mass. The most abundant elements (in descending order) were Ca, Fe, Al, K, Zn, Cu, and Mg, ranging in concentration from 500–20 ng/m³ at the H level. Among these metals, all scaled with dilution except for K. Notably K was also observed in the HF exposure in appreciable concentrations, accounting for the observation of metals at that exposure level. The remaining metals at that exposure level were similar in concentration to the C concentrations (data not shown).

Gas and Particle-Bound Semivolatile Organic Compounds

The organic classes analyzed in semivolatile organic compounds (SVOCs) included the n-alkanes from C₁₃–C₃₀, acids from C₁₃–C₂₀, polycyclic aromatic hydrocarbons (PAHs), oxygenated/sulfur containing PAHs, hopanes, steranes, methoxy-lated phenols, and sugar derivatives. These classes were chosen based on components that have been shown in previous studies to be abundant constituents in emissions from air pollution sources, and many of these classes have been used to distinguish among different sources in ambient air by source/receptor models (e.g., Fujita et al., 1998; Schauer et al., 1996). All classes mentioned above were assessed but some are not

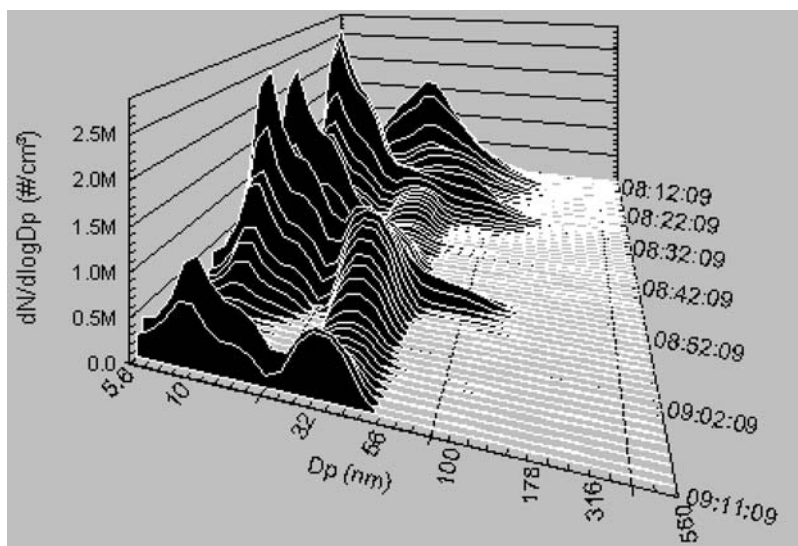


FIG. 5. FMPS plot of particle number size distribution as a function of time. This plot shows 1 h of data collected directly from the breathing zone of the rodents in the inhalation chamber. Note the particle size changes every second of the engine cycle.

shown here (yet are retained in the NERC database) because they were not present at detectable levels (e.g., methoxylated phenols, sugar derivatives). In many cases, the same compound existed simultaneously in the particle and gas phases, and the portions are included in both the gas phase semivolatile organic composition or particle organic portion of Figure 1.

The majority of the mass of the SVOCs was gas phase. Only a small portion of the particle OM (~10%) was accounted for by SVOC by direct measurement. This poor mass balance was consistent with other comprehensive measurements of GEE PM, and also consistent with results reported for the NERC diesel atmosphere (McDonald et al., 2004). The quantified OM consisted largely of straight-chain aliphatic acids (likely combustion products of alkanes) and PAHs.

DISCUSSION

The GEE exposure system was designed to produce exposure atmospheres that contained exhaust approximately consistent in physical-chemical composition with contemporary (circa 2004) fleet average on-road and laboratory emissions. A detailed assessment of the chemical and physical composition of the exposure atmosphere revealed that this was accomplished by purchasing in-use vehicles of a type accounting for a significant fraction of the on-road light duty truck fleet at the time of the study. The duty cycle simulated operation of these vehicles on a chassis dynamometer. The cold starts were included because the largest emissions of nearly all constituents occur during this phase of the driving cycle, as described below.

The largest peak in concentrations of emissions (especially gas phase) occurred during the cold start portions of the exposure day before the catalyst reached operating temperature. The peak concentration in the exposure atmospheres during the cold start was approximately five to ten times higher than the peak concentrations during the remainder of the day. This was observed for hydrocarbons, NO_x, and CO. However, the cold start only accounted for 3% of the exposure time (5 min per engine), and as a result the spike in concentrations had very little impact on the average exposure concentrations.

The study characterized the composition of GEE at a level of detail consistent with or exceeding the most detailed characterizations to date (e.g., Allen et al., 2001; Fujita et al., 2007; Gillies et al., 2001; Phuleria et al., 2006; Robert et al., 2007; Schauer et al., 2002). This was done because the overall goal of the NERC program is to identify the physical-chemical species causing various health effects (www.nercenter.org). As a result, this was the first known detailed characterization of a GEE inhalation exposure atmosphere. The work revealed and/or confirmed several measurement challenges for gaseous organics and PM in complex mixtures. These challenges apply to emissions testing as well as the characterization of inhalation exposure atmospheres. Volatile organics such as 1,3-butadiene were shown to react in the presence of NO_x, decreasing measured concentrations by factors of approximately five. This was alleviated by

the use of a newly developed NO_x denuder during sampling. The measurement of low levels of PM in the presence of high vapor concentrations was complicated due to vapor artifacts that could influence PM concentration by a factor of two. This was minimized by the use of Teflon membrane filters that are less susceptible to vapor adsorption. The majority of the GEE particles were less than 20 nm in diameter, and were changing in both concentration and size throughout the engine cycle. A recently developed FMPS was applied to measure particles in real time.

During the NERC diesel study, it was documented that not all constituents of the atmosphere scaled precisely with changes in dilution (McDonald et al., 2004). That study showed that nitrate (likely nitric acid) emitted from the engine reacted with ammonia that was attributed in large part to the presence of the animals. The reaction occurred at a higher rate at the lowest dilutions, leading to larger relative proportions of inorganic ions as a fraction of total PM as exposure concentration increased. A similar phenomenon was observed in the GEE exposures. However, in GEE the primary inorganic anion was sulfate, and the majority of ammonia was derived from the GEE. As previously shown (e.g., Allen et al., 2001), modern three-way catalysts contribute to ammonia emissions from GEE. In this study there was a dilution-dependent increase in ammonia, confirming that the dominant source was GEE and not the animals. This was not the case for the NERC diesel study, in which the major source of ammonia was the animals.

The increased fraction of sulfate with increased exposure level suggests in part that sulfate was formed within the exposure chambers from oxidation of SO₂. The other evidence is that sulfate typically only accounts for less than 5% of PM from motor vehicle emissions (e.g., Allen et al., 2001; Fujita et al., 2007; Gillies et al., 2001; Phuleria et al., 2006; Robert et al., 2007; Schauer et al., 2002). It is possible that the formation was highest in the high exposure level because this level had the highest relative humidity. The H exposure level, because it was diluted with less dry air, typically had a humidity of approximately 60–70%, 20–30% higher than the lower exposure levels. SO₂ reaction rates are substantially increased in the presence of humidity (Seinfeld & Pandis, 1998).

Metals in the exposure atmospheres were primarily composed of Ca, Fe, Al, K, Zn, Cu, and Mg. The concentrations of these elements were higher than those observed in the NERC DEE study, perhaps in part due to the use of mid-mileage gasoline engines obtained from vehicles exposed to ambient wear and tear as opposed to the new diesel engines used for the NERC DEE study. In fact, the DEE study found that Ca and Zn, two fuel and lubrication additives, were the only metals (with the exception of low levels of Hf) associated with DEE. With the exception of K, the remaining metals mentioned above are found in engine exhaust due to wear of the engine and after-treatment (Docekal et al., 1992).

Organic speciation of SVOCs (gas and particle phase) showed that the majority of the mass was in the gas phase. Similar to DEE and to a lesser extent wood smoke, only a small portion

(~10%) of the total particle-phase OM can be accounted for by detailed organic measurements. Of the identified and measured compounds, PAHs and alkanolic acids were the most abundant. These proportions were similar to the compositions of catalyst-equipped gasoline emissions reported by Schauer et al. (2002). The PAHs are perhaps the most well studied organic combustion by-products. Many of the environmental PAHs are typically attributed to DEE, often ignoring contributions from other sources such as wood smoke and GEE. PAHs were present in GEE at similar or higher concentrations than in the NERC DEE study (McDonald et al., 2004). In fact, the concentrations of many of the putative "toxic" PAHs, such as benzo(a)pyrene, were much higher in GEE (~30 ng/m³) than reported in DEE (~5 ng/m³) at the same dilutions. This may be due to the presence of more aromatics in the gasoline fuel than in diesel fuel.

This study included a filtered atmosphere to remove PM and allow assessment of the contribution of PM to the health effects. The use of a filter to remove material from a complex mixture presents challenges. The ability to filter even the smallest particles proved to be 98%, with small breakthrough of particles only less than 50 nm. A concern was the potential for the gas phase to preferentially adsorb or desorb from the filter during exposures, creating a filtered atmosphere having a gas phase qualitatively different from that of its unfiltered counterpart. While this may have happened to some degree, the similar concentrations for the majority of the measured gaseous constituents between the HF and H atmospheres suggest that the goal of changing only the PM concentration was successfully achieved. Any observed differences between the two atmospheres' non-PM components were within the day-to-day variability of the concentrations.

This study was the first to provide a detailed characterization of GEE inhalation exposure atmospheres. The atmospheres were successfully generated 7 days/week for over 200 days of exposures without loss of an exposure day. Each engine accumulated the equivalent of ~25,000 miles during the course of the exposures. The target dilutions were achieved, which provided overlaps in dilution and concentration with previous NERC atmospheres. This study revealed new information about the composition of GEE and advanced measurement technologies, and showed again the dynamic nature of inhalation exposure atmospheres of complex mixtures that react during aging within the exposure chamber. Combined with the companion papers on the health effects of GEE, this work has served to help place GEE in the context of other important environmental source emissions and will offer opportunities to evaluate the role of physical and chemical composition on health response to complex mixtures.

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