

Analysis of C₁, C₂, and C₁₀ through C₃₃ particle-phase and semi-volatile organic compound emissions from heavy-duty diesel engines

Z. Gerald Liu^{a,*}, Devin R. Berg^a, Victoria N. Vasys^a, Melissa E. Dettmann^a,
Barbara Zielinska^b, James J. Schauer^c

^a Department of Research and Development, Cummins Emission Solutions, 1801 U.S. Highway 51, Stoughton, WI 53589, USA

^b Division of Atmospheric Sciences, Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, USA

^c Department of Civil and Environmental Engineering, University of Wisconsin-Madison, 660 North Park St, Madison, WI 53706, USA

ARTICLE INFO

Article history:

Received 8 June 2009

Received in revised form

17 November 2009

Accepted 18 November 2009

Keywords:

Organic compound emissions

Particulate matter emissions

Heavy-duty diesel engines

Aftertreatment technology

Diesel particulate filter

Chemical speciation

ABSTRACT

To meet increasingly stringent regulations for diesel engines, technologies such as combustion strategies, aftertreatment components, and fuel composition have continually evolved. The emissions reduction achieved by individual aftertreatment components using the same engine and fuel has been assessed and published previously (Liu et al., 2008a,b,c). The present study instead adopted a systems approach to evaluate the net effect of the corresponding technologies for model-year 2004 and 2007 engines. The 2004 engine was equipped with an exhaust gas recirculation (EGR) system, while the 2007 engine had an EGR system, a crankcase emissions coalescer, and a diesel particulate filter. The test engines were operated under the transient federal test procedure and samples were collected with a source dilution sampling system designed to stimulate atmospheric cooling and dilution conditions. The samples were analyzed for elemental carbon, organic carbon, and C₁, C₂, and C₁₀ through C₃₃ particle-phase and semi-volatile organic compounds. Of the more than 150 organic species analyzed, the largest portion of the emissions from the 2004 engine consisted of formaldehyde, acetaldehyde, and naphthalene and its derivatives, which were significantly reduced by the 2007 engine and emissions technology. The systems approach in this study simulates the operation of real-world diesel engines, and may provide insight into the future development of integrated engine technology. The results supply updated information for assessing the impact of diesel engine emissions on the chemical processes, radiative properties, and toxic components of the atmosphere.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Increasingly stringent regulations placed upon diesel engine emissions have made it necessary to implement exhaust aftertreatment technology to lower the emission levels of criteria pollutants, including nitrogen oxides (NO_x) and particulate matter (PM). In 2004, the U.S. Environmental Protection Agency (EPA) implemented emission standards of 0.13 g (KW^{*h})⁻¹ (0.1 g (bhp^{*h})⁻¹) for PM and 3.35 g (KW^{*h})⁻¹ (2.5 g (bhp^{*h})⁻¹) for NO_x plus non-methane hydrocarbons. More stringent regulations include the recent Euro IV standards of 0.02 g (KW^{*h})⁻¹ for PM and 3.5 g (KW^{*h})⁻¹ for NO_x and the EPA's 2007 emissions standards of 0.013 g (KW^{*h})⁻¹ (0.01 g (bhp^{*h})⁻¹) for PM and 0.27 g (KW^{*h})⁻¹ (0.2 g (bhp^{*h})⁻¹) for NO_x (phased in by 2010). To meet these regulations, current approaches use engine optimization strategies for either PM or NO_x abatement, and then apply

Selective Catalytic Reduction (SCR) or Diesel Particulate Filters (DPF) respectively to address the PM–NO_x tradeoff. This study reflects the latter approach in the 2007 engine, which includes an EGR system, a crankcase emissions coalescer, and a diesel particulate filter.

The basic function of the DPF is its ability to filter PM mass emissions with a high level of efficiency. Diesel PM filtration generally involves the processes of diffusion and interception, coupled with other forces such as thermophoresis and electrophoresis. The filtration efficiency is known to increase as the PM loading accumulates on the filter, which comes at the cost of restricted gas flow, corresponding to inhibited performance in the form of engine power and fuel economy (Eastwood, 2000). Therefore, it becomes necessary to regularly remove the PM that has collected on the filter in order to maintain optimal engine performance. This is typically accomplished through a process known as passive or active regeneration, in which the PM collected on the filter is oxidized, usually involving reactions with O₂, NO₂, or hydrocarbons.

Besides NO_x and PM, diesel emissions also contain a large variety of organic compounds present in both the particle and gas phase

* Corresponding author. Tel.: +1 608 877 3802; fax: +1 608 873 1550.
E-mail address: jerry.z.liu@cummins.com (Z. Gerald Liu).

(Eastwood, 2000; Schauer et al., 1999; De Abrantes et al., 2004). These organic species are most commonly derived from the diesel fuel, which contains C₁₀–C₂₅ hydrocarbons, and lubrication oil, which contains primarily higher molecular weight hydrocarbons (Schauer et al., 1999; Johnson and Kittelson, 1994; Voss et al., 1997). Additionally, the hydrocarbon species present within the diesel fuel and lubrication oil may produce thermally-altered byproducts during in-cylinder combustion or during DPF regeneration when temperatures exceed 250 °C (Schauer et al., 1999; Rogge et al., 1993). This would suggest that diesel engine exhaust may contain a wide variety of organic species, whether present in diesel fuel and lubrication oil or produced by thermal alteration. A program known as the Advanced Collaborative Emissions Study (ACES), in collaboration with the U.S. Department of Energy, U.S. Environmental Protection Agency, the California Air Resources Board, the American Petroleum Institute, the Engine Manufacturers Association, the Health Effects Institute, and the Coordinating Research Council, has identified more than 650 chemical compounds that may be present in the emissions from diesel engines, the majority of which are part of the complex mixture of organic species. These compounds have been selected according to the risks posed to public health and environmental concerns.

The emissions reduction achieved by individual aftertreatment components using the same engine and fuel has been assessed and published previously (Liu et al., 2008a,b,c). These studies have documented that DPFs significantly reduce the emissions of the major PM constituents, including elemental carbon, organic matter (OM), inorganic ions, and metallic compounds. The same DPF also decreased emissions of many classes of organic compounds: PAHs, aromatics, aldehydes, hopanes, steranes, and n-alkanes. However, real-world diesel engines are integrated systems, and understanding the net reductions achieved by combustion strategies, aftertreatment components, fuel composition, and other technologies requires a systems approach, as adopted by the present study. This paper evaluated the net effect of the corresponding technologies for model-year 2004 and 2007 engines. The 2004 engine was equipped with an exhaust gas recirculation (EGR) system, while the 2007 engine had an EGR system, a crankcase emissions coalescer, and a diesel particulate filter.

The goals of this study included a detailed understanding of the hydrocarbon speciation from the 2004 engine and an assessment of the emissions reduction between the 2004 and 2007 systems. Using the transient federal test procedure and a source dilution sampling system designed to simulate atmospheric cooling and dilution conditions, samples were analyzed for elemental carbon, organic carbon, and C₁, C₂, and C₁₀ through C₃₃ particle-phase and semi-volatile organic compounds. Of the more than 150 organic species analyzed, the largest portion of the emissions from the 2004 engine consisted of formaldehyde, acetaldehyde, and naphthalene and its derivatives, which were significantly reduced by the 2007 engine and emissions technology. The systems approach in this study represents the operation of real-world diesel engines, and may provide insight into the future development of integrated engine technology. The results supply updated data, applicable to atmospheric models of chemical transport, climate, and receptors, which assess the impact of diesel engine emissions on the chemical processes, radiative properties, and toxic components of the atmosphere.

2. Experimental methods

2.1. Engine configurations

For each test engine, the diesel fuel was certified for the corresponding year. The 2004 fuel was Chevron Phillips Low Sulfur

Table 1
Properties for 2004 and 2007 certified diesel fuels.

Property	2004 Fuel	2007 Fuel
API gravity	36.2	36.2
Cetane number	47	42
Sulfur content (ppm)	308.5	9.2
PM content (mg L ⁻¹)	0.1	3.3
Aromatics (LV%)	29.5	32.0
Saturates (LV%)	67.9	63.6
Viscosity @ 40 °C (cSt)	2.6	2.2
Distillation 5% (°C)	202	197
Distillation 95% (°C)	333	312

Certified #2 Diesel and the 2007 fuel was Chevron Phillips Ultra-Low Sulfur Certified Diesel for which the fuel properties can be found in Table 1. With the exception of the sulfur content, the two fuels have similar properties. It is expected that the effect of the two fuels on organic compound emissions would be marginal. However, the lower sulfur content of the 2007 fuel would reduce the formation of particle-phase sulfates that contribute to PM mass and number emissions (Kweon et al., 2003). The lubrication oil used for each engine was Valvoline Premium Blue 15W-40 with a sulfated ash content of less than 1%.

Two similar 15 L heavy-duty diesel engines, compliant with EPA regulations for the corresponding model-year, were used in order to compare the effects of 2004 and 2007 emissions technology. The 2004 engine was equipped with an EGR system for NO_x reduction, which recycles a fraction of the exhaust gas into the engine intake to dilute the O₂ concentration and lower the flame temperature of the working fluid within the cylinder. In contrast, the 2007 engine had an EGR system, DPF, and crankcase emissions coalescer for NO_x and PM reduction. The DPF used in the present study consisted of two stages. The first stage was a diesel oxidation catalyst (DOC), a ceramic flow-through monolith with a precious metal coating designed to aid in the reduction of CO and hydrocarbon (HC) emissions as well as assist with filter regeneration through the exothermic oxidation of dosed diesel fuel and the conversion of NO to NO₂. The second stage was a catalyzed soot filter (CSF) designed to reduce PM emissions, lower the soot oxidation temperature, and remove the fuel residuals. Composed of porous cordierite material, the extruded wall-flow monolithic CSF had alternating plugs. Diesel particles accumulate on the surface of the filter media, and as the soot cake layer builds in thickness, filtration efficiency improves and the restriction increases, which eventually requires regeneration. Previous studies have documented that the combined DOC and CSF reduce the emissions of both particle-phase and semi-volatile organic compounds (Liu et al., 2008a,c).

Crankcase emissions, which include both gaseous and particulate components resulting from chemical, thermal, and mechanical processes, have become a necessary constituent of the total emissions analysis due to their inclusion in the EPA's 2007 regulations. For the 2007 engine, crankcase emissions were filtered using a coalescer as part of an open crankcase ventilation (OCV) system. The coalescer was primarily designed to remove large oil droplets generated mechanically with a secondary function of removing chemically and thermally generated sub-micron oil mist from the gas fumes exiting the crankcase before they are vented to the atmosphere.

2.2. Testing procedure

In preparation for testing, the engines were warmed up for 2 h on ISO mode 8, corresponding to 50% load and intermediate speed. For each configuration, the engine was run over the transient

Federal Test Procedure (FTP) cycle, which has a duration of 20 min. The FTP cycle consists of four stages designed to simulate the highly transient operating conditions that heavy-duty engines often encounter on American road ways. Each configuration was tested at least three times to determine the measurement variation. Blank substrates were exposed during each step of the process to monitor for contamination from dilution air, background conditions, handling, storage, and transportation.

Engine exhaust samples were collected with a source dilution sampling (SDS) system which consisted of a constant volume primary dilution tunnel, a secondary micro-diluter, a residence time chamber (RTC), isokinetic sampling probes, multiple sampling trains, and control devices. A detailed discussion of the design, operating principles, and quality assurance and quality control (QA/QC) procedures for the SDS system can be found in the literature (Liu et al., 2008d). In summary, HEPA filters and activated carbon removed particles and organic compounds, respectively, from the dilution air prior to mixing with the engine exhaust. The dilution air had significantly lower particle number concentrations than the ambient air of the Emissions Laboratory, according to the measurements from the Scanning Mobility Particle Sizer (SMPS). The mixture of dilution air and engine exhaust was further diluted to simulate atmospheric conditions and sampled with a full-partial-full method to minimize particle loss. A variety of media were used for sample collection including baked quartz filters, polytetrafluoroethylene (PTFE) membrane filters, XAD resin cartridges, polyurethane foam (PUF), thermal desorption (TD) tubes, and dinitrophenylhydrazine (DNPH) cartridges. Upstream of the sample collection media, $PM_{2.5}$ cyclone separators pre-classified the PM in

the exhaust flow. Fig. 1a shows the testing setup and the components of the SDS system, while Fig. 1b shows the sampling train configurations and collection media. Before testing, the system was cleaned and the substrates were prepared according to applicable QA/QC practices.

2.3. Analysis methods

Samples collected at the Cummins Emission Laboratory were analyzed for chemical species, using a variety of established methods, by the Wisconsin State Laboratory of Hygiene and the Desert Research Institute. Particulate emissions of EC, OC, and particle-phase organics, were captured using quartz and Teflon impregnated glass fiber (TIGF). EC and OC in the particulate matter samples were analyzed using a thermal–optical method described by Birch and Cary (1996). The samples were heated to 870 °C under a helium atmosphere to evolve OC, which was then oxidized to CO_2 and reduced to methane before being measured by a flame ionization detector (FID). The sample was then cooled and re-heated in a helium and oxygen atmosphere to remove all carbon from the filter. The evolved carbon is corrected for pyrolysis carbon formed during the initial analysis stage and the elemental carbon in the sample is quantified. OC is reported as the sum of the carbon evolved during the initial stage of the analysis plus the pyrolysis carbon. Two corrections were made to the resulting OC mass. The measurement from the second filter was subtracted from the first to correct for non-adsorbed gaseous OC emissions (Kolodziej et al., 2007). Also, the OC mass was multiplied by 1.2 to correct for oxygen, hydrogen, and nitrogen constituents of the total organic

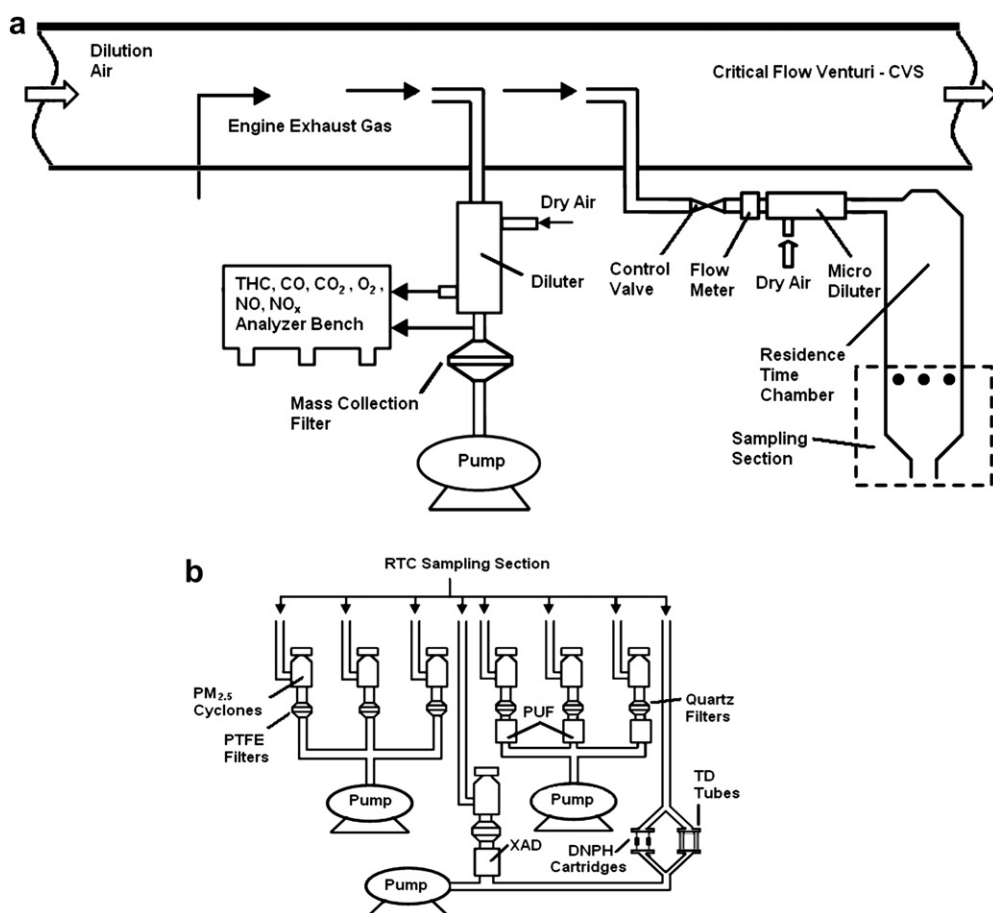


Fig. 1. Schematic of sample collection apparatus showing (a) the full-partial-full source dilution sampling system and (b) the sampling trains found in the sampling section of the RTC.

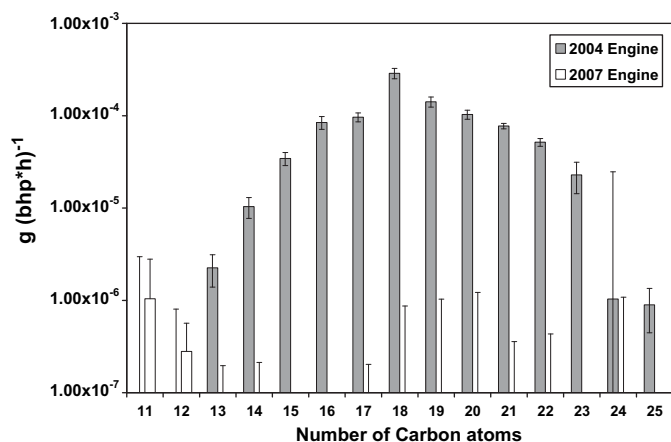


Fig. 2. Comparison of alkane emissions arranged by carbon number.

matter (OM) adsorbed onto the EC particles (Seinfeld and Pandis, 1998). Although Turpin and Lim (2001) suggested that a 1.4 factor can be the lowest reasonable estimate and a 1.6 factor appears more accurate for urban aerosol, Bae et al. (2006) concluded that vehicle emissions have an OM-to-OC ratio closer to 1.2, a result of less oxygenated organics in vehicle emissions compared to atmospheric particulate matter.

Further analysis for particle-phase compounds was performed on the baked quartz and TIGF filters. Organic species, including PAHs, PAH derivatives, and aromatics were analyzed using gas chromatography/mass spectrometry (GC/MS) in addition to the gaseous samples collected on XAD resins as described below (Zielinska et al., 2004; Fujita et al., 2007). Further, hopanes and steranes, which were collected on quartz filters, were analyzed using GC/MS. Prior to sampling, the quartz filters were baked at 550 °C for 12 h to ensure that there were no preexisting organics.

Gaseous volatile organic compounds (VOCs) including PAHs, aldehydes, and n-alkanes were also analyzed in the present study. Gaseous samples were collected on TD tubes, DNPH cartridges, and XAD resin packed cartridges that were situated behind a TIGF filter during sample collection. TD tubes and DNPH cartridges were used for the collection of gaseous samples to be analyzed for aldehydes and alkanes. TD tubes were analyzed by a modified National Institute of Occupational Safety and Health (NIOSH) method 2549 in which the organic compounds were quantified by GC/MS, after being conditioned to ambient temperature (Eller, 1994). DNPH cartridges were desorbed with acetonitrile and analyzed using high performance liquid chromatography (HPLC), which utilized a NOVA-PAK C18 column and UV detection (Winberry et al., 1999).

XAD cartridges were extracted with dichloromethane, combined with TIGF filter extracts, and analyzed for PAHs, and PAH derivatives by GC/MS interfaced with an ion trap operating under electron impact ionization mode (Varian CP-3800 GC equipped with a CP8400 autosampler and interfaced to a Varian Saturn 2000 Ion Trap), as described in the literature (Zielinska et al., 2004; Fujita et al., 2007). Quantification of the individual compounds was obtained using the selective ion storage technique, monitoring the most characteristic ions of each compound of interest and the corresponding deuterated internal standard from the Desert Research Institute. Six-point calibration curves for the GC/MS quantification were made for the most abundant and characteristic ion peaks of the compounds of interest using the deuterated species most closely matched in volatility and retention characteristics as internal standards from the Desert Research Institute (Zielinska et al., 2004). The calibration check (using median calibration standards) was run every 10 samples to verify the accuracy of analyses. If the relative

accuracy of measurement, defined as a percent difference from the standard value, was less than 20%, the instrument was recalibrated. The minimum detection limit (MDL) for PAH and derivatives is 0.02 ng μL^{-1} , which corresponds to approximately 4 ng sample⁻¹.

Nitro-PAHs were analyzed using negative ion chemical ionization with a triple quadrupole GC/MS/MS system (Varian 1200), which allowed for structural elucidation of unknown compounds with precursor, product and neutral loss scan as well as sensitive analyses of complex mixtures. Quantification of the individual compounds was performed by similar methods as for PAHs, but instead using the multiple ion detection technique. For each analysis, a six- to eight-level calibration was performed for each compound of interest and a calibration check was run every 10 samples as described above. The MDL for nitro-PAH is 0.0005 ng μL^{-1} , which corresponds to approximately 0.1 ng sample⁻¹.

3. Results and discussion

3.1. Particulate emissions

The experimental design also measured the criteria pollutants, including PM, NO_x, CO, total hydrocarbons, as well as O₂, CO₂, etc., but the discussion of these compounds were out of the scope of this paper. EC and OM, the latter of which encompasses the hydrocarbon species in this paper, represent two of the largest constituents of the total PM emissions. Both were analyzed in this study and their values are shown in Table 2. From the 2004 engine, EC emissions comprise approximately 48% of the total PM mass while the OM contributes another 44%. However, from the 2007 engine, PM mass emissions contain roughly 21% EC and 35% OM. The remaining portion of the PM mass emissions, 8% for the 2004 engine and 44% for the 2007 engine are composed of inorganic ions, primarily sulfate, ammonia, and nitrate, as well as trace metallic emissions. This implies that the 2007 engine and emissions technology dramatically reduced the emissions of EC and OM, resulting in a larger composition from other sources, such as inorganic ions. Since OM is such a large portion of the total PM mass emissions, it is important to gain a more in depth understanding of the organic species which contribute to the total OM mass.

3.2. Organic emissions

As part of the present study, gaseous and particle-phase samples collected from the test engines were analyzed and more than 150 organic compounds were quantified. PAHs and aliphatic aldehydes make up the largest portions of the total semi-volatile and particle-phase organic compound mass emissions, of which formaldehyde, acetaldehyde, and naphthalene and its derivatives predominate. Additional compounds, such as alkanes, nitro-PAHs, and hopanes and steranes, were also quantified and a summary of the amounts detected and the reductions can be found in Table 2. When a compound failed to be detected, the symbol "<" indicates the corresponding detection limit.

Organic compounds analyzed in the present study included C₁, C₂, and C₁₀ through C₃₃ particle-phase and semi-volatile organic compounds. Low molecular weight hydrocarbons such as those below C₂₂ are frequently derived from diesel fuel, while high molecular weight hydrocarbons are present in lubrication oil (Johnson and Kittelson, 1994; Voss et al., 1997) although significant overlap exists (Zielinska et al., 2004). The majority of organic hydrocarbons in Table 2 have a low molecular weight and therefore are believed to be from fuel-derived sources and most displayed a reduction of greater than 90%. The fuel-derived portion of the hydrocarbons typically exists in the gas phase at catalyst operating temperatures, while the soluble organic fraction (SOF) portion of

Table 2
Organic species emissions comparison from a 2004 and a 2007 heavy-duty diesel engine.

Compound (carbon number)	2004 Engine ^a		2007 Engine ^a		% Reduced		
Elemental carbon	49 700	±	3550	150	±	38.2	99.7 ± 7.2
Organic carbon	37 800	±	4360	213	±	101	99.4 ± 11.8
Organic mass	45 300	±	5230	256	±	121	99.4 ± 11.8
n-Alkanes							
n-Undecane (11)	< 0.01	±	2.97	1.04	±	1.76	–
n-Dodecane (12)	<0.01	±	0.795	0.279	±	0.286	–
n-Tridecane (13)	2.25	±	0.859	<0.01	±	0.186	>99.6 ± 46.4
n-Tetradecane (14)	10.4	±	2.64	<0.01	±	0.203	>99.9 ± 27.3
n-Pentadecane (15)	34.4	±	5.52	<0.01	±	0.00	>99.9 ± 16.0
n-Hexadecane (16)	84.6	±	13.4	<0.01	±	0.00	>99.9 ± 15.8
n-Heptadecane (17)	96.5	±	10.7	<0.01	±	0.193	>99.9 ± 11.3
n-Octadecane (18)	68.8	±	12.7	<0.01	±	0.413	>99.9 ± 19.1
n-Nonadecane (19)	52.3	±	10.0	<0.01	±	1.02	>99.9 ± 21.1
n-Eicosane (20)	75.0	±	7.46	<0.01	±	0.931	>99.9 ± 11.2
n-Heneicosane (21)	68.5	±	4.88	<0.01	±	0.348	>99.9 ± 7.6
n-Docosane (22)	48.1	±	4.63	<0.01	±	0.423	>99.9 ± 10.5
n-Tricosane (23)	19.3	±	8.48	<0.01	±	0.00	>99.9 ± 43.9
n-Tetracosane (24)	0.0127	±	2.37	<0.01	±	1.07	–
Branched alkanes							
Norpristane (18)	215	±	34.6	<0.01	±	0.754	>99.9 ± 16.4
Pristane (19)	89.4	±	14.6	<0.01	±	0.0725	>99.9 ± 16.4
Phytane (20)	28.3	±	9.02	<0.01	±	0.768	>99.9 ± 34.6
Saturated cycloalkanes							
Dodecylcyclohexane (18)	4.26	±	2.67	<0.01	±	0.00	>99.8 ± 62.7
Pentadecylcyclohexane (21)	8.92	±	1.91	<0.01	±	0.00	>99.9 ± 21.4
Hexadecylcyclohexane (22)	3.52	±	1.85	<0.01	±	0.00	>99.7 ± 52.6
Heptadecylcyclohexane (23)	3.53	±	1.05	<0.01	±	0.00	>99.7 ± 29.7
Octadecylcyclohexane (24)	1.02	±	1.02	<0.01	±	0.00	>99.0 ± 100
Nonadecylcyclohexane (25)	0.896	±	0.451	<0.01	±	0.00	>98.9 ± 50.3
Aromatics							
Biphenyl (12)	140	±	11.4	47.7	±	14.2	65.9 ± 18.3
2-Methylbiphenyl (13)	13.3	±	2.09	54.3	±	28.6	–
3-Methylbiphenyl (13)	288	±	29.5	152	±	64.0	47.2 ± 32.5
4-Methylbiphenyl (13)	62.5	±	5.52	18.8	±	5.10	69.9 ± 17.0
PAHs, POM, and Derivatives							
Naphthalene (10)	719	±	79.6	122	±	129	83.0 ± 29.0
2-Methylnaphthalene (11)	1290	±	144	82.7	±	52.1	93.6 ± 15.2
1-Methylnaphthalene (11)	543	±	52.5	46.1	±	26.1	91.5 ± 14.5
Dimethylnaphthalenes (12)	1460	±	113	89.0	±	18.6	93.9 ± 9.0
Trimethylnaphthalenes (13)	935	±	45.9	38.8	±	3.95	95.9 ± 5.3
1-Ethyl-2-methylnaphthalene (13)	115	±	14.1	4.25	±	1.18	96.3 ± 13.3
2-Ethyl-1-methylnaphthalene (13)	6.83	±	1.59	0.673	±	0.193	90.1 ± 26.1
Anthracene (14)	7.38	±	1.00	0.862	±	0.385	88.3 ± 18.8
Phenanthrene (14)	78.6	±	11.3	12.3	±	3.62	84.4 ± 19.0
Methylphenanthrenes (15)	85.4	±	9.49	3.30	±	0.460	96.1 ± 11.7
Dimethylphenanthrenes (16)	66.9	±	5.33	1.17	±	0.239	98.3 ± 8.3
Fluorene (13)	131	±	20.6	12.9	±	3.54	90.2 ± 18.4
Methylfluorenes (14)	0.00	±	0.00	10.9	±	3.91	–
Fluoranthene (16)	4.31	±	0.137	1.13	±	0.564	73.8 ± 16.3
Pyrene (16)	11.7	±	1.20	0.979	±	0.649	91.6 ± 15.8
Acenaphthalene (12)	30.5	±	1.88	2.18	±	1.42	92.9 ± 10.8
Acenaphthene (12)	45.5	±	6.55	22.0	±	21.1	51.6 ± 60.8
Chrysene + triphenylene (18)	1.05	±	0.133	0.123	±	0.109	88.3 ± 23.0
Benz[a]anthracene (18)	0.586	±	0.0579	0.0632	±	0.0698	89.2 ± 21.8
Benzo[g,h,i]fluoranthene (18)	0.607	±	0.593	0.258	±	0.270	57.5 ± 142
Benzo[b + k + j]fluoranthene (20)	0.240	±	0.0735	0.00776	±	0.00715	96.8 ± 33.6
Benzo[a]pyrene (20)	0.0797	±	0.0378	0.00613	±	0.00469	92.3 ± 53.3
Benzo[e]pyrene (20)	0.232	±	0.0575	0.00374	±	0.0983	98.4 ± 67.2
Benzo[g,h,i]perylene (22)	0.0724	±	0.0240	0.0168	±	0.00885	76.8 ± 45.4
Nitro-PAHs							
1-Nitronaphthalene (10)	0.361	±	0.0701	0.0858	±	0.0198	76.2 ± 24.9
2-Nitronaphthalene (10)	0.531	±	0.0896	0.0478	±	0.00914	91.0 ± 18.6
Methylnitronaphthalenes (11)	0.719	±	0.110	0.0232	±	0.00393	96.8 ± 15.8
2-Nitrobiphenyl (12)	0.0228	±	0.00974	0.00166	±	0.00087	92.7 ± 46.5
4-Nitrobiphenyl (12)	0.0103	±	0.00644	0.000117	±	0.00009	98.9 ± 63.4
1-Nitropyrene (16)	0.0550	±	0.0154	<0.00025	±	0.00	99.5 ± 28.0
9-Nitroanthracene (14)	0.192	±	0.00914	0.0403	±	0.00931	79.0 ± 9.6
Oxygenated PAHs							
Acenaphthenequinone (12)	29.1	±	2.68	0.945	±	1.49	96.8 ± 14.3
9-Fluorenone (13)	13.9	±	2.29	6.54	±	1.59	52.9 ± 27.9
Xanthone (13)	8.75	±	3.94	0.386	±	0.0908	95.6 ± 46.1

Table 2 (continued)

Compound (carbon number)	2004 Engine ^a		2007 Engine ^a			% Reduced	
Perinaphthanone (13)	29.7	±	4.33	1.01	±	0.288	96.6 ± 15.5
Anthraquinone (14)	5.16	±	0.886	1.30	±	0.506	74.8 ± 27.0
9-Anthraaldehyde (15)	1.56	±	0.829	0.0388	±	0.0291	97.5 ± 55.0
Benanthrone (17)	1.89	±	0.109	0.0154	±	0.00973	99.2 ± 6.3
Aliphatic aldehydes							
Formaldehyde (1)	5160	±	2440	<0.01	±	58.1	>99.9 ± 48.4
Acetaldehyde (2)	1480	±	783	<0.01	±	43.1	>99.9 ± 55.8
Hopanes							
17 α (H)-22,29,30-Trisnorhopane (27)	0.430		0.0658	<0.01		0.00	97.7 ± 15.3
17 α (H),21 β (H)-Hopane (30)	1.67		0.0558	0.0109		0.0109	99.3 ± 4.0
22S-17 α (H),21 β (H)-29-Homohopane (31)	0.925		0.0309	<0.01		0.00	98.9 ± 3.3
22R-17 α (H),21 β (H)-29-Homohopane (31)	0.545		0.284	<0.01		0.00	98.2 ± 52.1
22S-17 α (H),21 β (H)-29,30-Bishomohopane (32)	2.11		1.60	<0.01		0.00	99.5 ± 75.8
22R-17 α (H),21 β (H)-29,30-Bishomohopane (32)	0.288		0.144	<0.01		0.00	96.5 ± 50.0
22R-17 α (H),21 β (H)-29,30,31-Trishomohopane (33)	5.33		5.33	<0.01		0.00	—
Steranes							
20S-5 α (H),14 α (H),17 α (H)-Cholestane (27)	5.89		4.87	<0.01		0.00	99.8 ± 82.7
20R-5 α (H),14 β (H),17 β (H)-Cholestane (27)	0.576		0.0438	<0.01		0.00	98.3 ± 7.6
20S-5 α (H),14 β (H),17 β (H)-Cholestane (27)	0.749		0.0729	<0.01		0.00	98.7 ± 9.7

^a Values are reported in $\mu\text{g (bhp}^*\text{h)}^{-1}$, uncertainty is given as the standard error of the test results.

the PM consists primarily of lubrication oil-derived hydrocarbons adsorbed onto carbon particles (Eastwood, 2000; Farrauto and Voss, 1996). It is apparent from Table 2 that the modern engine and emissions technology significantly reduces both low molecular weight and high molecular weight hydrocarbons.

Low molecular weight organic species consist primarily of PAHs and n-alkanes. Emissions of alkanes are $751 \mu\text{g (KW}^*\text{h)}^{-1}$ ($560 \mu\text{g (bhp}^*\text{h)}^{-1}$) and $1.77 \mu\text{g (KW}^*\text{h)}^{-1}$ ($1.32 \mu\text{g (bhp}^*\text{h)}^{-1}$) from the 2004 and 2007 engines, respectively, representing a reduction in excess of 99%. Commonly found in crude oil, from which diesel fuel derives, branched alkanes may serve as diesel exhaust tracers during air quality analysis (Schauer et al., 1999). Branched alkane species in the present study, which included norpristane, pristane, and phytane (C₁₈–C₂₀), are each reduced to levels below the detection limits of $0.013 \mu\text{g (KW}^*\text{h)}^{-1}$ ($0.01 \mu\text{g (bhp}^*\text{h)}^{-1}$). For the 2004 engine, C₁₈ norpristane has the largest concentration of the alkane species at $288 \mu\text{g (KW}^*\text{h)}^{-1}$ ($215 \mu\text{g (bhp}^*\text{h)}^{-1}$), followed by C₁₇ n-heptadecane at $129.4 \mu\text{g (KW}^*\text{h)}^{-1}$ ($96.5 \mu\text{g (bhp}^*\text{h)}^{-1}$). The reduction of alkanes (also shown in Fig. 2 as arranged by carbon number), like many of the other hydrocarbon species, primarily occurs through gas-phase oxidation, although filtration can make a minor contribution (Johnson and Kittelson, 1994; Voss et al., 1997; Bagley et al., 1998).

Most low molecular weight polycyclic aromatic hydrocarbons (2–3 rings) consist of fuel-derived hydrocarbons, typically present in the engine exhaust and in the gas phase (Zielinska et al., 2004). These and other combustion derived PAHs also originate from the crankcase due to leakage around the piston rings and possible absorption into the crankcase oil (Zielinska et al., 2004; Fujita et al., 2007). The concentrations of the tailpipe PAHs from the 2004 engine and combined tailpipe and crankcase PAHs from the 2007 engine are displayed in Fig. 3, arranged by the number of aromatic rings. The highest PAH emissions from the 2004 engine are observed for methyl and dimethyl substituted naphthalene derivatives, both displaying emissions of greater than $1877 \mu\text{g (KW}^*\text{h)}^{-1}$ ($1400 \mu\text{g (bhp}^*\text{h)}^{-1}$). As can be seen in Fig. 3, the emission rates of 2 through 6-ring PAHs displayed significant reductions for the 2007 engine, but low initial emission levels of 5 and 6-ring PAHs resulted in larger relative error. Species of particular concern are the 5 ring PAHs such as the highly toxic benzo[a]pyrene. The 2007 engine achieved significant reductions of the majority of these compounds with no observed production of any 5 ring PAHs. Reduction of these

PAH species from the 2007 engine likely proceeded through the oxidation and filtration mechanisms of the DOC and CSF. It has been shown that high fuel sulfur content impairs the performance of the oxidation catalyst (Eastwood, 2000); therefore the ultra-low sulfur content of the 2007 fuel allows for optimal conversion efficiency and reduced PAH emissions from the oxidation catalyst. Methyl and dimethyl substituted PAHs were reduced at a greater rate than their unsubstituted counterparts. Previous studies have suggested the process of thermal dealkylation as an explanation (Schauer et al., 1999; Tancell et al., 1995). The effects of thermal dealkylation should also be seen under high exhaust temperatures during DPF regeneration.

Additionally, exposure of PAH compounds to gaseous NO_x, such as NO₂, emissions can produce nitro-PAHs. The PAH nitration reactions occur in the atmosphere, during combustion, or within aftertreatment devices. Airborne nitro-PAHs account for a substantial portion of the total mutagenic properties of fine particles (Harley et al., 2006). Fig. 3 also displays the emission levels of the nitro-PAH compounds from the 2004 and 2007 heavy-duty diesel engines, arranged by the number of aromatic rings. Of the 14 nitro-PAHs analyzed during the present study, the majority are reduced significantly for the 2007 engine, except for

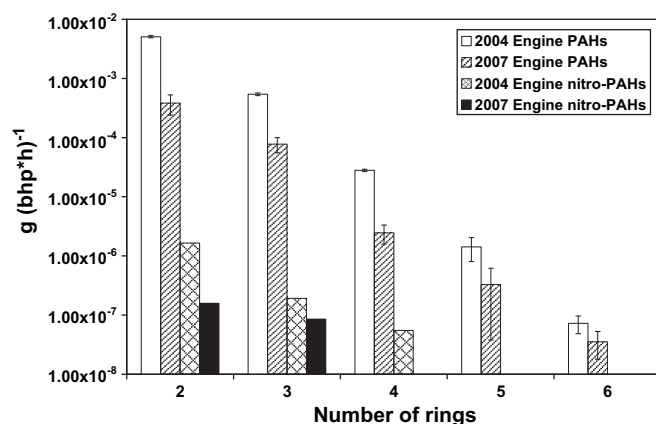


Fig. 3. Comparison of PAH and nitro-PAH emissions arranged by number of aromatic rings.

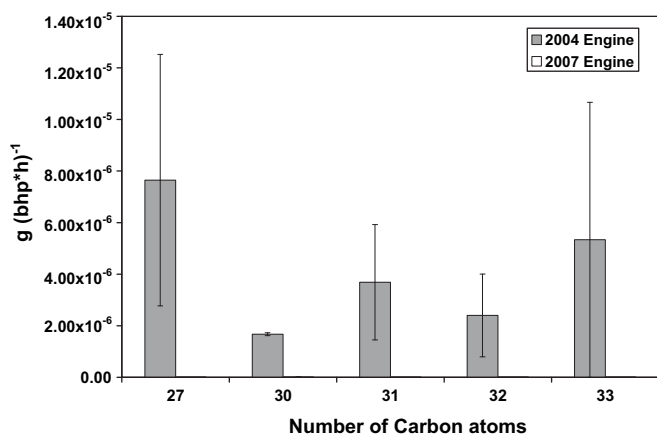


Fig. 4. Comparison of hopane and sterane emissions arranged by carbon number.

a small increase for 9-nitrophenanthrene. The mechanisms of this increase remain unknown; however, it is speculated that the selective nitration of phenanthrene occurs within the DPF or results from sampling artifacts caused by the extended exposure of the sampling substrates to the gaseous NO_x in the exhaust stream.

High molecular weight organic species in the present study consist of lubrication oil-derived compounds, including saturated cycloalkanes, hopanes, steranes, and a few 6-ring PAHs; however, some of these compounds partition between the gas and particle phases (Schauer et al., 1999; Johnson and Kittelson, 1994; Fujita et al., 2007). Hopanes and steranes are often found in crude oil due to the decomposition of biomass materials (Zielinska et al., 2004). These species, previously used as tracers for diesel PM emissions (Schauer et al., 1999; Zielinska et al., 2004; Fujita et al., 2007), contribute to the SOF in the form of particulate hydrocarbons. Consequently, the reductions seen in Fig. 4 were attributed to particulate filtration mechanisms over the CSF and subsequent combustion during filter regeneration. The high molecular weight, 6-ring PAH compounds analyzed in the present study were emitted at low levels, with the largest contribution from benzo[*g,h,i*]perylene. With an emission rate of 0.0971 μg (kW^h)⁻¹ (0.0724 μg (bhp^h)⁻¹) from the 2004 engine, benzo[*g,h,i*]perylene was reduced in excess of 75% by the 2007 emissions technology. For sufficiently high exhaust temperatures, the oxidation catalyst may remove a portion of the SOF emissions before they adsorb onto the primary carbon particles eventually filtered out by the CSF (Eastwood, 2000).

3.3. Conclusion

The results from this study, along with other studies in the literature, suggest that the 2007 heavy-duty diesel emissions technology is capable of reducing elemental carbon, organic carbon, and also the majority of particle-phase and semi-volatile organic compounds present in diesel engine exhaust. Fig. 5 summarizes the reduction efficiency of the 2007 technology over the 2004 technology for PAHs, alkanes, and hopanes and steranes, whose details are shown in Table 2. There is no apparent relationship between carbon number and the reduction efficiency, suggesting that the reduction efficiency is more dependent upon each individual compound's molecular structure and subsequent reactivity. The significant reductions observed for formaldehyde, acetaldehyde, PAHs, and nitro-PAHs are of particular importance due to the carcinogenic and mutagenic properties of these compounds (Eastwood, 2000; Code of Federal Regulations, 2006).

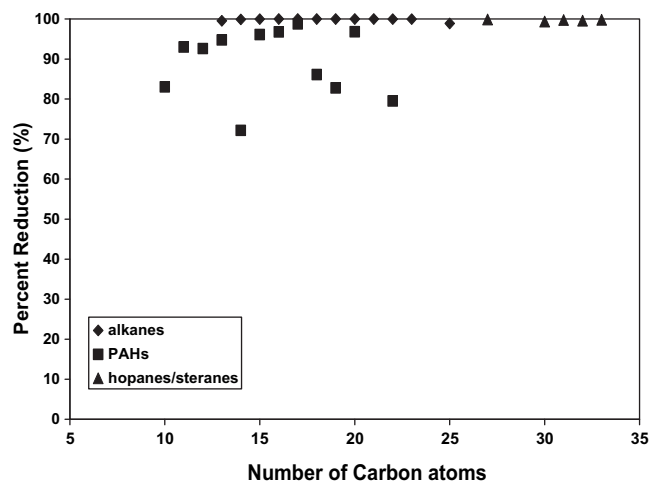


Fig. 5. Percent reductions found for the 2007 engine over the 2004 engine for alkanes, PAHs, and hopanes and steranes arranged by carbon number.

The PAHs, which have the less consistent reduction efficiencies, can be thermally altered, while the hopanes and steranes are mainly destroyed in both the combustion process and within the after-treatment devices.

Acknowledgements

The authors acknowledge Dr. Roger McClellan, Prof. John Johnson and Prof. Susan Bagley of Michigan Technological University, Prof. David Kittelson of the University of Minnesota, Dr. Doug Lawson of the National Renewable Energy Laboratory, Prof. David Foster of the University of Wisconsin-Madison, Dr. Glynis Lough and Dr. Michael Hays of the U.S. EPA, and Dr. John Wall, Dr. Wayne Eckerle, and Dr. Shirish Shimpi of Cummins Inc. for their valuable discussions. We also acknowledge Thaddeus Swor and Tom Wosikowski of Cummins Emission Solutions for their help with sample collection as well as Anna Cunningham and Mark McDaniel of the Desert Research Institute, and Jeff DeMinter, Steve Strebel, and Steve Geis of the Wisconsin State Laboratory of Hygiene for their help with the chemical analysis.

Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2009.11.036.

References

- Bagley, S.T., Gratz, L.D., Johnson, J.H., McDonald, J.F., 1998. Effects of an oxidation catalytic converter and a biodiesel fuel on the chemical, mutagenic, and particle size characteristics of emissions from a diesel engine. *Environmental Science and Technology* 32, 1183–1191.
- Bae, M.S., Schauer, J.J., Turner, J.R., 2006. Estimation of the monthly average ratios of organic mass to organic carbon for fine particulate matter at an urban site. *Aerosol Science and Technology* 40, 1123–1139.
- Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology* 25, 221–241.
- Code of Federal Regulations, 2006. Control of Hazardous Air Pollutants from Mobile Sources: 40 CFR Parts 59, 80, 85, and 86. U.S. Government Printing Office, Washington.
- De Abrantes, R., De Assuncao, J.V., Pesquero, C.R., 2004. Emissions of polycyclic aromatic hydrocarbons from light-duty diesel vehicles exhaust. *Atmospheric Environment* 38, 1631–1640.
- Eastwood, P., 2000. Critical Topics in Exhaust Gas Aftertreatment. Research Studies Press Ltd., Baldock.

- Eller, P.M., 1994. NIOSH Manual of Analytical Methods, fourth ed. U.S. Department of Health and Human Services, Cincinnati.
- Farrauto, R.J., Voss, K.E., 1996. Monolithic diesel oxidation catalysts. *Applied Catalysis B* 10, 29–51.
- Fujita, E.M., Zielinska, B., Campbell, D.E., Arnott, W.P., Sagebiel, J.C., Mazzoleni, L., Chow, J.C., Gabele, P.A., Crews, W., Snow, R., Clark, N.N., Wayne, W.S., Lawson, D. R., 2007. Variations in speciated emissions from spark-ignition and compression-ignition motor vehicles in California's south coast air basin. *Journal of the Air and Waste Management Association* 57, 705–720.
- Harley, R.A., Hooper, D.S., Kean, A.J., Kirchstetter, T.W., Hesson, J.M., Balberan, L.T., Stevenson, E.D., Kendall, G.R., 2006. Effects of reformulated gasoline and motor vehicle fleet turnover on emissions and ambient concentrations of benzene. *Environmental Science and Technology* 40, 5084–5088.
- Johnson, J.E., Kittelson, D.B., 1994. Physical Factors Affecting Hydrocarbon Oxidation in a Diesel Oxidation Catalyst. SAE 941771.
- Kolodziej, C., Wirojsakunchai, E., Foster, D.E., Schmidt, N., Kamimoto, T., Kawai, T., Akard, M., Yoshimura, T., 2007. Comprehensive Characterization of Particulate Emissions from Advanced Diesel Combustion. SAE 2007-01-1945.
- Kweon, C.B., Okada, S., Stetter, J.C., Christenson, C.G., Shafer, M.M., Schauer, J.J., Foster, D.E., 2003. Effect of Fuel Composition on Combustion and Detailed Chemical/physical Characteristics of Diesel Exhaust. SAE 2003-01-1899.
- Liu, Z.G., Berg, D.R., Schauer, J.J., 2008a. Detailed Effects of a Diesel Particulate Filter on the Reduction of Chemical Species Emissions. SAE 2008-01-0333.
- Liu, Z.G., Berg, D.R., Schauer, J.J., 2008b. Effects of a zeolite-selective catalytic reduction system on comprehensive emissions from a heavy-duty diesel engine. *Journal of the Air and Waste Management Association* 58, 1258–1265.
- Liu, Z.G., Berg, D.R., Swor, T.A., Schauer, J.J., 2008c. Comparative analysis on the effects of diesel particulate filter and selective catalytic reduction systems on a wide spectrum of chemical species emissions. *Environmental Science and Technology* 42, 6080–6085.
- Liu, Z.G., Swor, T.A., Schauer, J.J., Debilzen, J., Severance, C., 2008d. A source dilution sampling system for characterization of engine emissions under transient or steady-state operation. *Aerosol Science and Technology* 42, 270–280.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental Science and Technology* 27, 636–651.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R., 1999. Measurement of emissions from air pollution sources. 2. C₁ to C₃₀ organic compounds from medium duty diesel trucks. *Environmental Science and Technology* 33, 1578–1587.
- Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. John Wiley & Sons, Inc., New York.
- Tancell, P.J., Rhead, M.M., Pemberton, R.D., Braven, J., 1995. Survival of polycyclic aromatic hydrocarbons during diesel combustion. *Environmental Science and Technology* 29, 2871–2876.
- Turpin, B.J., Lim, H.J., 2001. Species contributions to PM_{2.5} mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* 35, 602–610.
- Voss, K.E., Wildman, T.D., Gorel, A., Norris, M.G., Rotolico, T., Fabel, A., 1997. Zirconia Based Ceramic, In-cylinder Coatings and Aftertreatment Oxidation Catalysts for Reduction of Emissions from Heavy Duty Diesel Engines. SAE 970469.
- Winberry, W.T., Tejada, S., Lonneman, B., Kleindienst, T., 1999. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. EPA/602/R-96/010b.
- Zielinska, B., Sagebiel, J., McDonald, J.D., Whitney, K., Lawson, D.R., 2004. Emission rates and comparative chemical composition from selected in-use diesel and gasoline-fueled vehicles. *Journal of the Air and Waste Management Association* 54, 1138–1150.