Abstracts

Session 9 – Environmental Science and Health Impacts

THE WEEKEND OZONE EFFECT - THE WEEKLY AMBIENT EMISSIONS CONTROL EXPERIMENT

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ABSTRACT

Since the mid-1970s, ozone concentrations in California's South Coast Air Basin (SoCAB) have been higher on weekends than on weekdays. Despite significantly lower ozone precursor levels on weekends, 20 of all 78 southern California sites show statistically significant higher mean ozone levels on Sundays than on weekdays ($p<0.01$); 49 of the remaining 50 sites show no significant differences between mean weekday and Sunday peak ozone levels. The weekend effect has generated strong interest because of its implications for development of air-quality control strategies.

To investigate the possible causes of higher weekend ozone compared to weekday ozone in the SoCAB, the National Renewable Energy Laboratory (NREL), with support from DOE's Office of FreedomCAR and Vehicle Technologies, and the Coordinating Research Council (CRC) sponsored a multiphase effort beginning in 1999 to collect and analyze weekday and weekend air-quality, emissions, and meteorological data to formulate hypotheses likely to explain the causes of elevated weekend ozone in the SoCAB.

As part of the field study, on-road mobile source emissions activity data were collected in close proximity to each ambient air-quality monitoring site. These emissions-activity data include daily diurnal vehicle count figures for selected surface streets and Caltrans Weigh-in-Motion data collected on major freeways. Surveys also were conducted to acquire data about business and residential activities on weekdays and weekends.

The ambient air-quality field program was conducted during September and October 2000. Measurements were used to attribute weekday/weekend changes in the temporal and spatial patterns of volatile organic compounds (VOC's) and NO_x concentrations to major sources of ozone precursor emissions. While exhaust emissions from on-road gasoline and diesel vehicles are the primary sources of interest, detailed speciation of VOC's also allowed for attribution of other sources of volatile organic compounds.

Air-quality simulation modeling explained the observed weekend ozone effect very well. Changes to the mass of motor vehicle emissions were the main contributor to ozone differences rather than changes to the timing of motor vehicle emissions. Ozone increases on weekends are caused by lower NO_x emissions because ozone formation is strongly VOC-limited throughout most of the Los Angeles area. Carryover of precursors and/or ozone is not an important factor in explaining the relationships between emission changes and ozone effects.

GASOLINE VEHICLE EXHAUST PARTICLE SAMPLING STUDY

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ABSTRACT

The University of Minnesota collaborated with the Paul Scherrer Institute, the University of Wisconsin (UWI), and Ricardo, Inc., to physically and chemically characterize the exhaust plume from recruited gasoline spark ignition (SI) vehicles. The project, supported by DOE's Office of FreedomCAR and Vehicle Technologies, had four primary objectives:

- Measure representative particle-size distributions from on-road SI vehicles and distinguish between SI and diesel emissions.
- Compare the information obtained from on-road tests to a small subset of light-duty gasoline vehicles tested on a chassis dynamometer under steady-state cruise conditions and using the Unified Cycle at both room temperature and 0°C.
- Characterize bulk and size-segregated chemical composition of the particulate matter (PM) emitted in the exhaust from the gasoline vehicles.
- If results from objectives 1 and 2 do not agree with regard to PM-size distribution, utilize the latest information on particle formation and dilution to explain the differences.

Particle number concentrations and size distributions are strongly influenced by dilution and sampling conditions. Laboratory methods were evaluated to dilute SI exhaust in a way that would produce size distributions that were similar to those measured during experiments. Size fractionated samples were collected for chemical analysis using a nano-microorifice uniform deposit impactor (nano-MOUDI). In addition, bulk samples using Teflon and quartz fiber filters followed by polyurethane foam were collected and analyzed by the UWI researchers.

Data were also collected during cold, cold start idle tests, laboratory tests to determine the impact of lube oil consumption on particulate matter emissions and during an on-road study to compare weekday with weekend air quality around the Twin Cities area. This portion of the study resulted in the development of a method to apportion the diesel and SI contribution to on-road aerosol.

A mixture of low-, mid-, and high-mileage vehicles was recruited for testing during the study. Under steady highway cruise conditions, a significant particle signature above background was not measured, but during hard accelerations number weighted size distributions for the test fleet were similar to modern heavy-duty diesel vehicles. Number emissions were much higher at high speed and during cold starts, and fuel-specific number emissions range from 10^{12} to 3 x 10^{16} particles/kg fuel. A simple relationship between number and mass emissions was not observed. Other results will be discussed.

DOE'S GASOLINE/DIESEL PARTICULATE MATTER (PM) SPLIT STUDY – CHARACTERIZATIONS OF THE VARIATIONS IN CHEMICAL COMPOSITION OF $PM_{2.5}$ IN THE SOUTH COAST AIR BASIN

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ABSTRACT

DOE's Gasoline/Diesel Particulate Matter (PM) Split Study is being conducted to quantify the relative contributions of tailpipe emissions from gasoline-powered motor vehicles and diesel-powered motor vehicles to the ambient concentrations of fine particulate matter ($PM_{2.5}$) in the urbanized region of Southern California using an organic compound-based chemical mass balance model (CMB). This study involves several groups working cooperatively on sample collection and quality assurance aspects of the study, but working independently, at least initially, on chemical analysis and data analysis. Groups participating in the study include California's Bureau of Automotive Repair, the South Coast Air Quality Management District, the U.S. Environmental Protection Agency, Ralph's Groceries, the Clean Air Vehicle Technology Center, the West Virginia University, the University of Wisconsin at Madison (UWM), and the Desert Research Institute (DRI).

Source testing of 59 light-duty vehicles (including 2 diesel vehicles) was completed in June 2001; ambient measurements were performed in July; and the testing of 34 heavy-duty vehicles was completed in September. DRI used sample collection and chemical analysis methods consistent with those employed during the Northern Front Range Air Quality Study. Parallel samples were collected by UWM using methods consistent with previous PM studies in Los Angeles. This paper describes the variations in the chemical composition of the ambient samples collected by DRI.

Twenty-four hour samples were collected on Teflon and quartz filters and Teflon-impregnated glass fiber (TIGF) filters followed by polyurethane foam (PUF) plugs and XAD-4 resin cartridges for 28 consecutive days at air-monitoring stations in downtown Los Angeles and Azusa. Teflon filters were analyzed for gravimetric mass, elements, and ions, and quartz filters were analyzed for organic and elemental carbon by thermal optical reflectance (TOR) and thermal optical transmittance (TOT) using both IMPROVE and NIOSH protocols. The TIGF/PUF/XAD samples were combined and extracted together by day of the week, and analyzed for polycyclic aromatic hydrocarbons, hopanes, steranes, alkanes, methoxyphenols, lactones, sterols, and polar organic compounds.

A third set of ambient samples was collected from a mobile sampling van at several regionally representative sites and at locations with expected higher proportions of PM emissions from diesel trucks (e.g., Terminal Island, truck stop, highway truck routes) and from gasoline vehicles (e.g., congested freeways during commuter rush hours, surface streets during weekends, and a parking lot at major sporting events). Black carbon and total PM were monitored continuously by photoacoustic and DustTrak instruments. As a prelude to the CMB analysis, we examined the variations in relative abundances of key marker compounds in the source-dominated ambient samples relative to corresponding variations in the samples from regional air-quality monitoring sites by day of the week. This work was supported by the DOE's Office of FreedomCAR and Vehicle Technologies through the National Renewable Energy Laboratory.

RELATIONSHIP BETWEEN COMPOSITION AND TOXICITY OF ENGINE EMISSION SAMPLES

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ABSTRACT

Differences in the lung toxicity and bacterial mutagenicity of samples from gasoline and diesel vehicle emissions were reported previously and have been published (Seagrave *et al*., *Toxicological Sciences* 70:212-226, 2002). Although the toxicity rankings provided important information, the ultimate goal was to determine the physical-chemical species responsible for the differences. The relationships between sample composition and toxicity have now been analyzed.

Filter and semi-volatile organic compound (SVOC) samples were collected from normal and high-emitter gasoline and diesel vehicles operated on chassis dynamometers on the Unified Driving Cycle. Seven vehicle-operating temperature conditions were tested. The composition of extracted filter and SVOC material was measured in detail. The filter and SVOC fractions were combined in their original mass collection ratios, and the toxicity of the seven samples was compared by instillation into rat lungs followed by measures of inflammation and tissue damage and by the Ames bacterial mutagenicity test. There was good coherence among multiple measured variables in ranking the samples and demonstrating a five-fold range in toxicity.

The relationship between chemical composition and toxicity was analyzed by principal component analysis (PCA) and projection to latent surfaces (PLS, also known as partial least squares). The stepwise PCA-PLS analysis revealed the chemical constituents co-varying most strongly with toxicity and gave predictions of relative toxicity with good accuracy. The results, which will be described in detail, suggest that selected, but not all, nitro-aromatic compounds most strongly influenced mutagenicity, and that organic compounds, especially particle-associated organics, most strongly influenced the lung inflammatory response.

THE EFFECT OF CHANGES IN DIESEL EXHAUST COMPOSITION AND AFTERTREATMENT TECHNOLOGY ON LUNG INFLAMMATION AND RESISTANCE TO VIRAL INFECTION

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ABSTRACT

Diesel engine exhaust changes in composition with modification of engine operation/configuration, including the addition of emission reduction technologies, such as low-sulfur fuel and catalyzed ceramic traps. While previous studies have shown that diesel exhaust can cause inflammation in rodents and humans and decreased resistance to respiratory infection in mice (Harrod et al., *Am. J. Resp. Cell Mol. Biol*., vol. 28, pp. 451-463), there is little information on the impact of changes in exhaust composition (resulting from change in engine operation) and aftertreatment technology on these effects.

To address this, identical inflammation and respiratory infection assessments were conducted after exposure of mice to diesel exhaust generated from a single-cylinder diesel engine generator under three steady-state operating conditions: 1) high-load operation, #2 certified fuel, diluted to 200 $\mu g/m^3$ particulate matter (PM), 2) low-load operation, #2 certified fuel, diluted to 200 $\mu g/m^3$ PM, and 3) high-load operation with ultra-low sulfur fuel and catalyzed ceramic trap, with same dilution rate as condition 1.

Changing the operation (load) of the engine resulted in a twofold change in particle organic content and a fourfold difference in particle size. Comparative results of the compositions of these three exposure atmospheres and the biological effects will be discussed.

IN VITRO GENOTOXICITY OF PARTICULATE AND SEMI-VOLATILE ORGANIC COMPOUND EXHAUST MATERIALS FROM A SET OF GASOLINE AND A SET OF DIESEL ENGINE VEHICLES OPERATED AT 30^0F

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ABSTRACT

Extracts of engine exhaust particulate material (PM) or of exhaust semi-volatile organic compound material (SVOC) pooled from a set of gasoline engine automobiles or from a set of diesel engine autos or light trucks, all operated at 30^0 F, were assayed *in vitro* for three measures of genotoxic activity. Materials supplied by the U.S. Department of Energy from modern vehicles operated on the Unified Driving Cycle for light-duty vehicles were acetone extracted and re-suspended into TWEEN-80.

Both diesel and gasoline vehicle PM extracts were significantly active for the induction of gene mutation at dose concentrations from 5 to 120 microgram extract/ml, and both displayed a positive dose-response in the *Salmonella typhimurium* histidine reversion micro-suspension assay with tester strains YG1024 and YG1029, with and without S9 microsomal activation of samples. The diesel vehicle PM extract was about twice as active as the gasoline vehicle PM extract on a mass basis.

Chinese hamster lung fibroblasts (V79 cells) were assayed for chromosome damage and for DNA damage at doses from 50 to 125 microgram extract/ml. For chromosome damage determined by the micronucleus induction assay, the maximum activity expressed by gasoline vehicle PM extract was about three times that of the maximum diesel vehicle PM extract. For DNA damage measured by the single cell gel-electrophoresis (comet) assay, the gasoline vehicle PM extract was significantly active at all but the lowest dose. The diesel vehicle PM extract did not express significant activity at any of the doses.

In general, the SVOC extracts were severalfold less active than their PM extract counterparts in all assays. Results are compared with those of a National Institute of Standards and Technology Standard Reference Material diesel exhaust particulate sample, and with those of a similar study of these gasoline and diesel vehicles operated at 70^0F.

COMPARISON OF DIRECT EXPOSURE OF HUMAN LUNG CELLS TO MODERN ENGINE EXHAUST PARTICLES

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ABSTRACT

Cultured human lung cells have been exposed in situ to dilute exhaust from two different vehicles, a gasoline spark-ignited vehicle equipped with a three-way catalyst and a light-duty diesel equipped with a catalyzed diesel particulate filter. Both of these vehicles have extremely low particulate mass emissions, on the order of 5 mg/mile. Particle size and number concentrations are monitored by a scanning mobility particle sizer.

As in previous reports to DEER, the cells are grown in transwell membranes, and dilute exhaust is pumped through the chamber, allowing exhaust nanoparticles to interact individually with the cells. Measurements of cell inflammatory response, including interleukin-8 production and LDH, are reported for time-resolved exposures up to 6.5 hours in duration. A cold start is included in each test sequence.

AN ENGINE EXHAUST PARTICLE SIZER FOR TRANSIENT EMISSION PARTICLE MEASUREMENTS

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ABSTRACT

The measurement of particle emissions from vehicles has been a compromise based on which parameters were most important for the particular measurement. There has been increased interest in obtaining size-distribution data during transient engine operation where total number concentrations can change dramatically. For measuring submicrometer particle sizes, currently the most common technique, scanning mobility particle sizer (SMPS), relies on electrical mobility. The SMPS gives high size resolution but requires an aerosol to be stable with time to make a particle-size distribution measurement.

This paper describes a new instrument, the engine exhaust particle sizer (EEPS), which has high time resolution, uses electrical mobility for classifying the particles, and was designed specifically for measuring engine exhaust. The measurement is based on the particles' electrical mobility similar to what is used in the SMPS system.

Particles entering the instrument are charged to a known charge level. The particles then are repelled outward by the voltage from a central column. When the particles reach an outer cylindrical (a column of rings), they create a current on one of the rings that is measured by an electrometer. The electrometer currents are measured multiple times per second to give high time resolution.