Abstracts

Session 5 – Environmental Science and Health Impacts

U.S. DEPARTMENT OF ENERGY'S STUDIES OF WEEKDAY/WEEKEND POLLUTION IN SOUTHERN CALIFORNIA

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Over the past 3-year period, the U.S. Department of Energy (DOE) and others have sponsored a series of coordinated studies to investigate the relationships between emissions of hydrocarbons and nitrogen oxides on ambient ozone and particulate nitrate levels. This presentation will summarize those studies and discuss DOE's future projects in increasing our fundamental understanding of the connection between emissions and ambient air quality.

Ambient ozone concentrations in California's South Coast Air Basin (SoCAB) can be as much as 55 percent higher on weekends than they are on weekdays under comparable meteorological conditions. This is paradoxical because emissions of ozone precursors (hydrocarbons, carbon monoxide, and nitrogen oxides) are lower on weekends relative to weekdays. Day-of-week emissions activity data were collected and analyzed to investigate the hypothesized causes of the "weekend ozone effect." Emissions activity data were collected for various mobile, area, and point sources throughout the SoCAB, including on-road vehicles, lawn and garden equipment, barbecues, fireplaces, solvent use, and point sources with continuous emissions monitoring (CEM) data.

Survey results indicate that significant differences exist between weekday and weekend emissions activity patterns and emissions. The combined effect of these differences resulted in a 12-18 percent decrease in reactive organic gases (ROG) and a 35-41 percent decrease in NO_x emissions on Saturdays and Sundays, respectively, relative to weekdays, in the summer of 2000. These changes in emissions resulted in an increase of the ROG to NO_x ratio of more than 30 percent on weekends compared to weekdays, which, along with lower NO_x emissions, increases ozone production on weekends relative to weekdays.

OFFICE OF HEAVY VEHICLE TECHNOLOGIES' WEEKEND/WEEKDAY OZONE STUDY IN THE SOUTH COAST AIR BASIN

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Many urban locations in the United States experience higher ozone on weekends than on weekdays, despite lower ozone precursor emissions of hydrocarbons, carbon monoxide, and nitrogen oxides. This presentation summarizes the results from a study designed to test hypotheses regarding the cause(s) of high weekend ozone levels in the South Coast Air Basin (SoCAB) of Los Angeles, California. In Phase 1 we analyzed existing ambient and meteorological data for the SoCAB to refine our working hypotheses. We performed time-resolved measurements during Phase 2 to test the hypothesized relationship between emissions sources and the weekend ozone effect.

Analysis of the existing ambient data indicates that the intensity and spatial extent of the weekend ozone effect are correlated with day-of-week variations in the extent of ozone inhibition due to titration with nitrous oxide (NO) and rates of ozone accumulation. Lower NO-mixing ratios and higher NO_2/NO_x ratios on weekend mornings allows ozone to begin accumulating about an hour earlier on weekends compared to weekdays. The weekday/weekend differences in the duration of ozone accumulation have remained relatively constant from 1981 to 2000. In contrast, the rate of ozone accumulation decreased by one-third to one-half over the same period with the largest reductions occurring in the central basin on weekdays.

Trends in mixing ratios of ozone precursors show a transition in the SoCAB to lower VOC/NO_x ratios due to greater reductions in VOC emissions. Reductions in VOC/NO_x ratios were greater on weekdays resulting in higher VOC/NO_x ratios on weekends relative to weekdays. Trends in VOC/NO_x ratios parallel the downward trend in peak ozone levels, a shift in the location of peak ozone from the central to eastern portion of the SoCAB, and an increase in the magnitude and spatial extent of the weekend ozone effect in the SoCAB. Lower NO_x emissions from diesel exhaust are the most important factor in weekday-weekend differences in ambient levels of NO_x and VOC/NO_x ratios.

The decrease in weekend ozone precursor emissions of VOC and NO_x provides a natural test case for investigating the response of ozone levels to specific changes in precursor emissions. This study demonstrates that ozone will increase in the urbanized areas of the SoCAB if NO_x emissions are decreased at current levels of VOC until weekend NO_x mixing ratios are decreased by roughly 90 percent. The study also shows

weekend ozone would be even higher were it not for concomitant weekend emission reductions of VOC's.

Because the SoCAB is hydrocarbon limited and mobile sources are the predominant source of hydrocarbons, the most effective means for reducing ozone in the SoCAB is to reduce emissions from the portion of the motor vehicle fleet responsible for the greatest amount of hydrocarbon emissions. The development of accurate weekend emission inventories by government agencies is urgently needed so air quality models can accurately assess the effects of current and future ozone control regulations.

PHYSICAL AND CHEMICAL CHARACTERISTICS OF DIESEL EXHAUST PARTICLES

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Exhaust particles from modern diesel engines without aftertreatment are found in two distinct, but overlapping size modes: a mainly volatile nuclei mode and a mainly solid accumulation mode in roughly the 3-30 and 30-500 nm diameter ranges, respectively. These particles have been characterized through size-fractionated measurements of volatility, hygroscopicity, density, and chemical composition using a tandem differential mobility analyzer (TDMA), an aerosol particle mass analyzer (APM) and a thermal desorption particle beam mass spectrometer (TDPBMS).

Volatility measurements showed that nuclei and accumulation mode particles are externally mixed across a wide size range, with the chemical components being distributed between two particle types: “less volatile” (probably comprised of an elemental carbon core with a small organic component) and “more volatile.” The volatility experiments showed that, except for the smallest particles, heating could differentiate volatile and solid particles. The fraction of solid particles decreased as particle size decreased, and only a volatile mode was detectable for the smallest particles tested (7 nm). More than 97 percent of the volume of the volatile constituents of 12- and 30-nm particles disappeared on heating to 400°C. The volatility was found to resemble that of C24-C32 normal alkanes, which implies a significant contribution of lubricating oil to the volatile particles.

APM mass and density measurements showed fractal-like behavior with particle mass increasing with approximately the $D_p^{2.4}$ (D_p = mobility diameter) and effective density decreasing from about 1 to 0.3 g/cm^3 in the 50-300 nm diameter range.

TDMA hygroscopicity experiments and TDPBMS analysis suggest the presence of sulfuric acid in diesel nanoparticles when a 350-ppm sulfur fuel was used, but not when a 96-ppm sulfur CA fuel was used. Hygroscopic measurements found that the smallest particles were the most hygroscopic, suggesting enrichment with sulfuric acid. TDPBMS measurements showed that the organic component of total diesel particulate matter and nanoparticles appears to be comprised predominantly of unburned lubricating oil, while the fuel contribution to the total organic component appears to be negligible. The major organic compound classes (alkanes, cycloalkanes, and aromatics) appear to be distributed fairly uniformly across the volatility spectrum. Low-volatility oxidation products (e.g., organic acids) and PAH’s do not appear to be a major portion of the organic mass. The oil that forms particles appears to be derived primarily

from material evaporated from the cylinder walls, although there may also be a significant component from atomization. Nanoparticles formed using 410-ppm sulfur fuel contained small amounts of sulfuric acid, which may enhance nucleation. No sulfuric acid was detected in nanoparticles formed using 96-ppm sulfur or Fischer-Tropsch (< 1 ppm sulfur) fuel. These results are consistent with hygroscopicity measurements.

MEASUREMENT OF ON-ROAD AND LAB DIESEL PARTICLE SIZE

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Particle-size distributions measured in the CRC/DOE E-43 project will be described. The project was designed to determine if modern diesel engines produce size distributions with a significant nuclei mode (particles with diameter less than about 30 nm) under real-world, on-road conditions; to establish laboratory dilution conditions that give size distributions similar to those measured on-road; and to compare the tendency to produce nanoparticles (a nuclei mode) of newer and older technology engines. Other objectives included determination of the chemical composition of these particles and their lifetime in the atmosphere. The first three of these goals are discussed in this presentation.

Field studies were carried out using four test trucks powered by Caterpillar and Cummins engines. On-road chase studies were carried out in Minnesota, and CVS performance cell and chassis dynamometer studies were carried out at Caterpillar and Cummins. A wind tunnel study was also carried out at the National Aeronautics and Space Administration's Langley Wind Tunnel. U.S. Environmental Protection Agency certification and a market-basket blend of California fuels were used.

On-road dilution is rapid (1,000:1 in 2 seconds), and the test vehicles produced bimodal distributions with nuclei mode and accumulation mode geometric number mean diameters ranging from 6 to11 nm and 52 to 62 nm, respectively. Number and volume fractions in the nuclei mode ranged from 37 to 87 percent and 0.3 to 2.1 percent, respectively. Nuclei mode particles were found to consist primarily of volatile material. Lower sulfur fuel produced a smaller nuclei mode under most conditions, but the accumulation modes produced by all fuels were similar. Cold temperatures favored nuclei mode formation. Both old and new technology engines produced nuclei modes of similar magnitude, but the older technology engines produced larger accumulation modes. Nuclei mode properties were highly variable due in part to changes in engine, fuel, and environmental conditions and in part due to on-road experimental uncertainties.

Laboratory exhaust samples were obtained using a mini two-stage ejector dilutor, a partial flow CVS system followed by an ejector dilutor, and a Sierra BG-1 dilutor followed by an ejector dilutor. Although it was not possible to duplicate all individual on-road size distributions in the laboratory, composite average on-road size distributions were similar to those obtained using the CVS or BG-1 systems. Our results suggest that rather than attempting to simulate on-road formation of nuclei mode particles, which takes place under highly variable ambient conditions, the best laboratory sampling strategy might be to adjust conditions to evaluate the tendency of an engine/fuel/operating condition to form nanoparticles.

OVERVIEW OF DETAILED CHEMICAL SPECIATION AND PARTICLE SIZING FOR DIESEL EXHAUST, BOTH REAL-TIME AND FILTER-BASED MEASUREMENTS

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U.S Environmental Protection Agency ambient air-quality measurement protocols have been incorporated into the exhaust measurement system of a research single-cylinder diesel engine. To allow more detailed assessment of the individual chemical components of the diesel particulate matter (PM), the exhaust dilution system includes a residence time chamber (RTC) to allow for residence times of 30-60 seconds in the second stage of dilution before sampling. Measurements have been performed using the more normal approach of catching the particulate matter on filters and then analyzing the filters and also using an aerosol time of flight mass spectrometer (ATOFMS), which is capable of analyzing individual particles for size and composition at a rate of up to 150 particles per minute for a particle size range from 0.15 to 5 micrometers. Additional data on particle size were obtained using a scanning mobility particle sizer (SMPS).

Samples have been collected on a range of different filters where mass loading, elemental and organic carbon (ECOC), trace metals, sulfate ions (SO_4), volatile organic compounds, and semi-volatile organic compounds have been evaluated. Using the SMPS, particle-size distributions have been measured for the different operating conditions and for different exhaust gas residence times in the RTC.

This paper gives an overview of the results obtained with the different measurement techniques for the range of engine operating conditions covered by the CARB 8 mode test. Results show that the chemical composition and size distribution of the particulate matter are highly dependent on the engine operating conditions. There is a dramatic shift in the ratio of elemental to organic carbon and in the sulfate ions (SO_4) when the engine is traversed across a load and speed range. Similarly, there is a shift in the particle-size range for which there is virtually no impact on the mass loading, and the nanoparticle size distribution, at a fixed dilution ratio and temperature, is a function of the time spent in the RTC. Trace metal concentrations in the particulate vary significantly with load and speed and are treated as indicative of oil consumption.

Results of the filter-based measurements are being compared to those obtained using the ATOFMS, which have been widely used to study atmospheric aerosols, but have only seen limited use for assessing internal combustion engine exhaust emissions.

Using the ATOFMS to make fundamental measurements of chemical composition and particle size in engine exhaust has the potential to offer unique insights into the impact of changes in engine operating conditions on the resultant changes in the exhaust characteristics.

DEVELOPMENT OF REMOTE SENSING INSTRUMENTATION FOR NO_X AND PM EMISSIONS FROM HEAVY-DUTY TRUCKS

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Researchers at Oak Ridge National Laboratory (ORNL) are developing prototype instruments to remotely and non-intrusively measure the NO_x and particulate matter (PM) emissions from heavy trucks. An ultraviolet (UV) absorption method and a modified LIDAR method are being employed to measure NO_x and PM concentrations, respectively, in the exhaust plumes of moving trucks.

To couple the concentration measurements to the truck on a gram-per-mile basis, an innovative approach to determining engine operating conditions with remote sensing is being employed. This is accomplished by using sensitive listening equipment to acquire acoustic signatures as the truck passes.
Acoustic signature analysis will devolve data about the truck's operating parameters, such as engine speed, turbine speed, and number of cylinders. The combined results will be used to make estimates of the instantaneous exhaust flow rate, which, when coupled with the emission concentration measurements, vehicle speed, acceleration, and load, lead to emissions data in terms of grams
per mile. These three technologies represent extensions and modifications of existing measurement sciences into this new application, and much of the challenge is the development of algorithms for interpreting data from each.

This effort is part of a larger project concept dealing with truck emissions and their impacts on local air quality. The Watt Road Environmental Laboratory Initiative is a joint effort between ORNL and the University of Tennessee, Knoxville, to develop a field laboratory for comprehensive studies of truck emissions in a 2.5-mile corridor along Interstate 40 in Knox County, Tennessee.

COMPARATIVE TOXICITY OF COMBINED PARTICLE AND SEMI-VOLATILE ORGANIC FRACTIONS OF GASOLINE AND DIESEL ENGINES

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This study was conducted to: (1) evaluate a range of mutagenicity and lung toxicity parameters for testing collected emission samples and (2) compare the bacterial mutagenicity and non-cancer lung toxicity of combined particulate matter (PM) and semi-volatile organic compound (SVOC) fractions of emissions from normal- and high-emitting gasoline and diesel vehicles.

PM and SVOC samples were collected from in-use, light- and medium-duty vehicles, including: a composite group of five gasoline normal emitters; a composite group of three diesel current technology (1998-2000) normal emitters; and one each black smoker gasoline, white smoker gasoline, and high-emitting diesel. Vehicles were operated with fuel and crankcase oil "as received" on chassis dynamometers on the California Unified Driving Cycle. Both "normal emitter" groups were sampled while operating at either 72°F or 30°F. PM was collected on filters, and SVOC was collected in polyurethane foam/XAD resin traps.

Both fractions were extracted from collection media in solvent, sent to Lovelace Respiratory Research Institute for testing, recombined in their original collection ratios, and administered to the biological test systems in multiple doses. Bacterial (Ames) mutagenicity was tested using Salmonella strains TA98 and TA100 with and without metabolic activation. Rats were instilled intratracheally, and cellular and chemical constituents of lung washings and histopathology were evaluated at multiple doses and times after administration. The potencies of the samples were compared on the basis of the slopes of dose-response curves.

Most biological response parameters gave dose-response slopes that clearly demonstrated a range of potency among the samples. Mutagenic potency differed between the two bacterial strains, although they reflected similar general patterns of samples having greater and lesser potency. There was generally good agreement among the sample rankings indicated by multiple parameters reflecting cytotoxicity, inflammation, and lung tissue changes, allowing the selection of a more limited set of

parameters for future studies. The parameters selected for oxidative injury and macrophage function yielded little useful information.

Some important general conclusions could be drawn from the aggregate lung toxicity results: (1) the toxicity per unit PM+SVOC mass was similar for normal-emitting gasoline and diesel vehicles; (2) operating temperature did not appear to cause systematic differences in toxicity; (3) high-emitters not only emitted more mass, but the toxicity per unit of mass was also greater than that of normal-emitters.

IN VITRO GENOTOXICITY OF GASOLINE AND DIESEL ENGINE VEHICLE EXHAUST PM2.5 PARTICULATE AND SEMI-VOLATILE ORGANIC COMPOUND MATERIALS

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Three categories of *in vitro* genotoxicity were measured for acetone extracts of exhaust materials from a set of gasoline-engine automobiles and from a set of diesel-engine autos or light trucks supplied by a vehicle exhaust studies program sponsored by the U.S. Department of Energy. Acetone-washed filter samples of exhaust particulate matter with equivalent aerodynamic diameter less than 2.5 micrometers and XAD resin-sorbed semi-volatile organic compounds (SVOC) sampled at 72°F from modern, in-tune vehicles operated on the "Unified Driving Cycle" for light-duty vehicles were provided to the National Institute for Occupational Safety and Health (NIOSH) of the Centers for Disease Control and Prevention.

These samples were prepared for assay by filtration, evaporation, and re-suspension in TWEEN-80. National Institute of Standards and Technology Standard Reference Material 1650a was similarly treated and assayed. Mutagenicity testing *in vitro* used the *Salmonella typhimurium* histidine reversion micro-suspension assay with tester strains YG1024 and YG1029, with and without S9 microsomal activation of samples. Each sample preparation was tested at four or more concentrations, with duplicate tests at each concentration, and with a repetition of the entire experiment. Micronucleus induction assay for chromosomal damage used Chinese hamster lung fibroblasts (V79 cells), which were challenged for 24 hours, and 3000 cells from each treatment were scored for micronucleated cells. The single cell, gel-electrophoresis assay (SCGE) for DNA migration was used as a measure of DNA single- and double-strand breaks in V79 cells challenged for 24 hours. Each sample preparation was tested at four or five concentrations.

Results are presented for gasoline vehicle PM2.5, gasoline vehicle SVOC, diesel PM2.5, and diesel SVOC for the three sets of genotoxicity tests with dose expressed in terms of both extracted mass and normalized to equivalent vehicle miles.

PRO-INFLAMMATORY CYTOKINE RESPONSES TO EXPOSURE TO DIESEL SOOT

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Inhalation of particulate material (PM) of many types causes inflammation in the lung. The mechanisms by which PM activates the cellular and molecular processes resulting in recruitment of white blood cells (leukocytes) into the air spaces of the lung are not fully understood, but clearly involve stimulation of the production of small proteins called chemokines, which are chemoattractants for leukocytes.

This study was conducted to investigate the role of chemokines in the pro-inflammatory cascade following exposure to diesel soot (DS). Studies were conducted by intratracheal instillation of DS into rat lungs and exposure of a human alveolar epithelial cell line (A549 cells) in cell culture to the same material. In both systems, toxicity was assessed by measuring release of the intracellular enzyme, lactate dehydrogenase (LDH). Lung inflammation following instillation was measured by counting the numbers of leukocytes in the lung washes.

Doses of DS between 0.1 and 1 mg/rat increased the amount of the chemokine Macrophage Inflammatory Protein-2 (MIP-2) measured in the lung washes, but at higher doses, less MIP-2 was detected. In contrast, the number of inflammatory cells continued to increase throughout the dose range. Small increases in LDH were observed, reaching a plateau at doses above 1 mg/rat.

Similar results were observed in cultured A549 cells. Increased Interleukin-8 (IL-8: a human chemokine analogous to rat MIP-2) was measured in cells exposed to DS over the range of 0.03-1 $\mu g/cm^2$, but reduced levels of the chemokine were detected at higher doses. DS had little effect on the release of LDH. This indicates that DS was not acutely toxic to the cells and that the suppressed response at high doses in both systems was unlikely to be due to acute toxicity. Instead, DS may adsorb the chemokines, making them unavailable for assay.

ARB'S STUDY OF EMISSIONS FROM DIESEL AND CNG HEAVY-DUTY TRANSIT BUSES

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The identification of diesel particulate matter (PM) as a Toxic Air Contaminant (TAC) in California triggered the development of control strategies under the Diesel Risk Reduction Program (DRRP), which was recently approved by the California Air Resources Board (ARB). The DRRP aims to reduce PM emissions from diesel-fueled engines, and it includes numerous control measures to be phased in over the next several years. These measures are meant to substantially curtail emissions from new and existing on-road and off-road sources.

Approaches to reducing the risk of exposure to diesel PM include the use of alternative fuels, like compressed natural gas (CNG), and advanced aftertreatment control for existing and new diesel engines. Buses fueled by CNG or using diesel particulate filters (DPF) are two "green" alternatives to conventional diesels. These alternatives have been demonstrated to reduce PM emissions. However, additional information is needed on their effect on the
emissions profiles of non-regulated species, toxic and otherwise.

For this reason, the ARB embarked on a research effort to collect emissions data from two late-model, heavy-duty transit buses in three different configurations. These were: (1) a CNG bus equipped with a 2000 DDC Series 50G engine, (2) a diesel bus equipped with a 1998 DDC Series 50 engine and a catalyzed muffler, and (3) the same diesel vehicle retrofitted with a Johnson Matthey Continuously Regenerating Technology (CRT™) DPF in place of the muffler. The CNG bus in this study was certified for operation without oxidation catalyst. The diesel bus configurations ran on ARCO's (a BP company) Emission Control Diesel (EC-D 1) fuel with a measured sulfur content of 11 ppm.

The objectives of the study were: (1) to assess driving cycle effects, (2) to characterize the types and amounts of several toxic substances emitted for the various configurations, and (3) to investigate total PM and ultrafine (<100 nm) particle emissions. This study has shown that, in terms of PM mass, CNG and trap-equipped diesel buses are significantly superior to the conventional diesel bus. However, no single "green" technology is clearly superior to the other for every pollutant indicator measured. Measurable levels of toxic compounds in the exhaust suggest that neither the CNG nor the trap-equipped bus may be clearly superior to the other in all aspects. Most importantly, possible technology improvements were identified.

A COMPARISON OF TWO GASOLINE AND TWO DIESEL CARS WITH VARYING EMISSION-CONTROL TECHNOLOGY

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The transport sector contributes significantly to air pollution and particularly influences local air quality. Besides the question of air quality, the consumption of fossil fuels in the transport sector and the CO_2-emissions from this use are increasingly important issues.

For a long period of time, the emissions from light-duty vehicles have been in focus, and a lot of measures have been taken to reduce the emissions from these vehicles.

The market penetration for light-duty diesel cars has been increasing in most markets in Europe and is now over 30 percent (2001). In Sweden, however, the market share for diesel cars has decreased the last 3 years and is now slightly above 5 percent.

The issue of whether petrol or diesel fuel should be used as fuel in passenger cars has been the subject of lively debates during the last years, particularly in Sweden, especially the particle emissions from diesel cars. This study is an attempt to contribute with some more facts to the subject.

The study presented in this paper is built on new investigations of two petrol and two diesel cars with varying emission-control strategies. Tests have been carried out both in the European driving cycle and in other driving cycles. Besides the regulated substances, analysis has been made on unregulated substances as well. The data have also been compared with data from earlier studies.