

## **SOURCE APPORTIONMENT AND RECEPTOR MODELING**

### **37) TITLE: Determination of the Spatial and Temporal Variability of Size-Resolved PM<sub>2.5</sub> Composition and Mixing State in Multiple Regions in California**

**PROBLEM:** In order to develop effective control strategies, one must further understand the major sources of particles in different regions of California. An understanding of the major sources contributing to PM<sub>2.5</sub> in California is limited to several major areas over short time periods.

**PREVIOUS WORK:** Most of the research on PM<sub>2.5</sub> composition has been limited to major field campaigns which focus on a relatively small period of time in a specific region. These studies have given us a much better idea of the particle composition in southern and central California. However, these represent extremely short snapshots in time of particle chemistry and the ability to apportion sources has been limited. Single particle analysis techniques have evolved to become quantitative and to include the ultrafine PM fraction. Data processing has become automated and allows one to unambiguously distinguish diesel and gasoline-derived particles.

**OBJECTIVE:** This objective is to perform particle characterization as well as measure other criteria pollutants in a number of regions of California impacted by PM<sub>2.5</sub> including major cities, agricultural areas, and transport sites. Single particle fingerprints will be used to relate PM to various sources, especially sources producing the carbonaceous fraction such as biomass burning and vehicles. Seasonal dependence of the fraction of secondary PM at different locations will also be examined.

**DESCRIPTION:** Analysis of single particles by mass spectrometry produces size-resolved composition, providing information on sources as well as subsequent atmospheric processing leading to secondary organic aerosols. ATOFMS has been used to develop source fingerprints of diesel and gas vehicles, brake and tire wear, power plants, wood and other biomass burning aerosols, fine dust, and sea salt. By comparing these signatures with ambient particle mass spectra, the relative fractions of particles from different sources can be determined. New profiles will be developed for charbroiling operations and CNG buses. Sampling needs to be conducted in as many locations as feasible due to the high degree of spatial and temporal variability of PM<sub>2.5</sub>. A mobile lab will be equipped with two ATOFMS and sizing (SMPS, APS), aethelometer, mass concentration, visibility, and trace gas (CO, ozone, and NO<sub>x</sub>) instruments. Sampling at current California air quality stations will provide a historical basis for comparison and access to meteorological data. The mobile lab will provide the flexibility necessary to move to various locations, and allow for "target of opportunity" sampling during PM<sub>2.5</sub> events.

**BENEFITS:** The proposed field studies will provide a long term picture of the temporal and spatial variability of particle composition in a number of major regions in California. The preliminary results should be available by early to mid 2007 for use in PM<sub>2.5</sub> SIP development (2008). A more complete picture will be obtained of the major sources impacting annual-average PM<sub>2.5</sub> violations in California, allowing better control strategies to be established.

Furthermore, as current diesel PM and other regulations are being implemented, this long-term record will provide feedback on how these control programs are affecting air quality.

**38) TITLE: Advanced Factor Analysis of STN Data for Apportionment of Gasoline and Diesel Emission Contributions**

**PROBLEM:** The PM<sub>2.5</sub> National Ambient Air Quality Standards are likely to be exceeded in a number of locations in California. Improved methods are needed to identify the important sources and then these methods can be applied to provide input to the state implementation planning process. Of particular interest is the resolution of traffic-related carbonaceous particle sources into the contributions from gasoline vehicles and diesel engines. Diesel exhaust is suggested to be more toxic and have more influence on adverse health effects. Currently there are samplers in the Speciation Trends Network (STN) in urban areas collecting chemical composition data for PM<sub>2.5</sub> samples. However, it has been generally thought that it is necessary to obtain specific chemical components (molecular markers) in order to apportion diesel and gasoline engine emissions. It would be of great value both in terms of air quality strategy development and epidemiology, if such a resolution were possible based on the STN data.

**PREVIOUS WORK:** Improved source identification as well as separation of traffic-related carbonaceous particle sources into gasoline vehicles and diesel engines using temperature resolved carbon fractions has been demonstrated for Atlanta, Georgia, Washington, DC, and Brigantine, New Jersey. However, the STN network does not provide these fractions. The use of an expanded factor analysis model has been applied to a particulate matter data set from Atlanta and successfully separated diesel emissions from gasoline vehicle sources.

**OBJECTIVE:** The objective is to use advanced factor analysis approaches to analyze the data obtained by the STN network and any other comparable data to resolve the sources of PM<sub>2.5</sub> with a particular emphasis on the separation of gasoline and diesel fueled vehicle emissions.

**DESCRIPTION:** In the expanded analysis, the bilinear model is augmented by an additional complex equation that contains modeling information. This expanded model can be applied to the variety of STN data from samples collected in California to identify the sources and apportion the mass to those sources with the expectation that gasoline and diesel sources can be accounted for separately.

**BENEFITS:** The project will yield several major benefits including providing a means to more fully utilize the STN data and to provide a resolution of motor vehicle emissions into gasoline and diesel without the need for high cost sampling and analysis for molecular marker compounds. These results will be helpful for both implementation planning and for future epidemiological studies.

**39) TITLE: Identification and Atmospheric Reactions of Polar Products of Selected Aromatic Hydrocarbons**

**PROBLEM:** The polar, oxygenated and nitrated, photooxidation products of aromatic hydrocarbons are poorly understood. While aromatics are known to be significant precursors to

secondary organic aerosols, their reaction products in many cases have not been identified, and their toxicity and subsequent fate in the atmosphere are unknown.

**PREVIOUS WORK:** Using Solid Phase MicroExtraction (SPME) techniques, the formation of hydroxycarbonyl products from two biogenic alcohols and a series of *n*-alkanes has been investigated. Additionally, the formation and reaction of an unsaturated di-aldehyde, HOCH<sub>2</sub>CH=CHCHO, from the OH radical-initiated reaction of 1,3-butadiene has also been investigated. From its time-dependent concentration, a formation yield of □22% and a rate constant for its reaction with OH radicals of □5.3 x 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (which is 80% of its parent, 1,3-butadiene) has been derived.

**OBJECTIVES:** To identify and, whenever possible, quantify dicarbonyl and hydroxycarbonyl products formed from the atmospheric reactions of selected aromatic hydrocarbons (including polycyclic aromatic hydrocarbons, PAH). The reaction rates of these carbonyl-containing products with hydroxyl radicals and their photolysis rates will be measured, as will the products of these processes.

**DESCRIPTION:** SPME fibers pre-coated with PFBHA [O-(2,3,4,5,6-pentafluorobenzyl) hydroxyl-amine hydrochloride] will be used to allow on-fiber derivatization of carbonyl-containing compounds with subsequent thermal desorption and gas chromatographic analysis of these carbonyl compounds as their oximes. Identification will be made by GC-MS and analysis by GC-FID during OH + aromatic reactions will provide the time-concentration behavior of the carbonyl product(s). These data allow the rate constants for reaction (with OH radicals and/or photolysis) of the product(s) to be determined. This approach will allow the investigation into the formation and reactions of carbonyl-containing products (unsaturated 1,4-dicarbonyls such as C(O)CH=CHCH=CHCHO and possibly di-unsaturated dicarbonyls and unsaturated epoxy-1,6-dicarbonyls) from the OH radical-initiated reactions of aromatic hydrocarbons such as toluene and xylenes and selected PAHs. Many of these compounds are not commercially available and cannot be analyzed by gas chromatographic methods without prior derivatization.

**BENEFITS:** This project will provide data needed for assessments of the human health risk associated with sources of aromatic hydrocarbons, such as gasoline and diesel fuels, as well as provide atmospheric chemistry data needed to formulate more scientifically accurate computer models of air pollution, including the formation of secondary organic aerosols.

#### **40) TITLE: Source Apportionment of Fine and Ultrafine Particulate Matter**

##### **ABSTRACT**

A review of source apportionment studies for airborne particulate matter reveals that unique chemical tracers are only available for a few general source categories including wood combustion, motor vehicle exhaust, coal combustion, meat cooking, crustaceous seafood cooking, candle combustion, tobacco smoke, and leaf abrasion. Unique chemical profiles can be constructed for many more sources, but their interpretation requires the uses of complex source apportionment models. Ten models that calculate the contribution that different sources make to air borne particulate matter are reviewed: Tracer Analysis, Chemical Mass Balance, Principal Component Analysis, Factor Analysis, Positive Matrix Factorization, Empirical

Orthogonal Functions, Chemical Mass Balance / Factor Analysis, Target Transformation Factor Analysis, Emissions Inventory Analysis, and Source-oriented Chemical Transport Models. The mathematical basis, assumptions, and limitations for each source apportionment model are summarized. The source apportionment methods are shown to provide a continuous spectrum of capabilities with increasingly detailed information provided as the amount of input data expands.

A protocol to characterize source contributions to primary and secondary airborne particulate matter concentrations in a region of interest is recommended. Ambient data sets can first be analyzed using bilinear statistical models to identify approximate source identities and contributions. After important source profiles have been measured, linear statistical models can be applied to calculate source contributions to primary particulate matter at receptor locations. If regional source contributions to airborne particulate matter and / or source contributions to secondary particulate matter are important, emissions inventories can be developed for the region of interest and source-oriented chemical transport models can be used to identify important source contributions to these features of airborne particulate matter.

Link to final report: <ftp://ftp.arb.ca.gov/carbis/research/apr/past/00-332.pdf>

#### **41) TITLE: Comparison of >C10 Polar Organics in Size-Segregated Particles for Source Apportionment of Diesel and Gasoline Emissions.**

**PROBLEM:** The ARB has classified particulate matter from diesel exhaust as a toxic air contaminant (TAC). Molecular speciation of organics in diesel particles is critical to evaluating the effectiveness of control strategies and investigating whether specific chemicals, or signature patterns of chemicals, can serve as markers of diesel emissions for source apportionment.

**PREVIOUS WORK:** Some studies suggest that the signature of >C10 hydrocarbons in diesel- and gasoline-derived particles can be used for source apportionment. This project will focus on the oxygenated combustion products found in PM, specifically carbonyls and multi-functional carbonyls. Existing methods can measure gas-phase carbonyls but do not provide information on carbonyls found in the particle phase. In a previous study, carbonyls in particles were measured in the Caldecott tunnel. Preliminary results indicate possible differences between multi-functional carbonyls in PM associated with gasoline and diesel exhaust.

**OBJECTIVE:** To develop the capability to characterize >C10 carbonyls and multi-functional carbonyls in size-segregated diesel and gasoline particles; measure the composition of >C10 polar organics in diesel- and gasoline-derived particulate matter; and evaluate whether specific high-molecular weight chemicals, or patterns of specific chemicals, can be used as markers for source apportionment.

**DESCRIPTION:** Impaction substrates and materials to coat the substrate to reduce particle bounce will be evaluated. To test this method of reducing particle bounce, particles segregated into seven different size cuts will be collected in the heavy-duty bore of the Caldecott tunnel. Carbonyls and other polar organics will be measured by using derivatization followed by GC-MS (PFBHA/GC/ITMS) methods. If necessary, experiments will be conducted to refine the method to provide sampling times of ½ hour or less. After development of the method,

samples of size-segregated particles will again be collected in the heavy- and light-duty bores of the Caldecott tunnel. The data will be analyzed to determine whether the composition of >C10 organics on size-segregated particles can be used to differentiate between diesel- and gasoline-derived particles.

**BENEFITS:** This project will develop a method to measure carbonyls and multifunctional carbonyls in PM. It will also examine size-segregated particle-phase samples for compounds, which can serve as markers for diesel exhaust. Information from this study will provide vital corroboration for diesel exhaust risk assessment and diesel and gasoline PM source apportionment. The project will also investigate a possible sampling artifact, which could have an impact on future PM chemical speciation.

**42) TITLE: A Study to Validate Concentrations Estimated from Air Dispersion Modeling for Source-To-Receptor Distances of Less Than 100 Meters**

**ABSTRACT**

Currently available dispersion models used to estimate dispersion in urban areas were developed using data from experiments conducted at source-receptor distances ranging from 50 m to 16km. The rural dispersion curves are based on the Prairie Grass experiment (Barad, 1958) where the source-receptor distances ranged from 50 m to 800 m. The urban dispersion curves are based on the St. Louis Dispersion Study (Mc. Elroy and Pooler, 1968) where the nearest receptor was 800 m from the source. Regulatory programs require the assessment of potential health impacts from exposures to air toxics from urban sources, such as gasoline stations, dry cleaners, and automotive repair facilities, where human receptors are typically within fifty meters from the critical need to validate dispersion tools at this distance. ARB has responded to this need by sponsoring UCR to develop a new dispersion model that can be used to estimate the impact of urban sources at source-receptor distances of tens of meters. The model has been developed using data from the Prairie Grass experiment (Barad, 1958), and an experiment conducted in this project have been compared with tracer concentrations measured under a variety of meteorological conditions in the vicinity of an urban source located at a parking lot on the College of Engineering, Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside. In addition, the performance of the model has been compared with those of ISC, ISC-PRIME, and AERMOD-PRIME, models that are currently used in regulatory practice. The statistics used to quantify model performance ranks the models in the following order: Proposed model, AERMOD-PRIME, ISC, and ISC-PRIME. The relative performance of these models indicates that a reliable model for near source dispersion in urban areas needs to use site-specific meteorology, incorporate upwind dispersion under low wind speed conditions, and reduce source height to account for building downwash

Link to full report: <ftp://ftp.arb.ca.gov/carbis/research/apr/past/99-319.pdf>

**43) TITLE: Validation of Toxic Air Contaminant Concentrations Estimated from Air Dispersion Modeling for Distances Less Than 100 Meters from the Source**

**PROBLEM:** Air dispersion modeling is used to estimate the downwind concentration of a Toxic Air Pollutant (TAP) emitted from a facility. Conventional Gaussian-based air dispersion models are designed to estimate concentrations from 100 meters to 1 kilometer from the source. Currently, modeling for distances less than 100 meters from the source is based on extrapolation of the Pasquill-Gifford dispersion curves. Human activity commonly occurs within 10 meters of a source, and risk assessment and risk management decisions impacting business costs, practices, and public relations are commonly based on estimated concentrations much closer to the source than 100 meters. Air dispersion modeling algorithms need to be validated or revised to address near-source concentrations of TAPs.

**PREVIOUS WORK:** None at the Air Resources Board and none published by the U.S. EPA.

**OBJECTIVE:** To produce a valid air dispersion model for pollutant concentrations between the source and 100 meters.

**DESCRIPTION:** Analytical methods to estimate TAP concentrations between the source and 100 meters would be developed. This could include a review of the literature, an air monitoring program, or development of new air dispersion modeling algorithms to assess previous work.

**BENEFITS:** Because current risk assessment practices are based on air dispersion modeling results, it is important that the modeling be reliable and as accurate as possible. Valid modeling would enable us to better estimate the human health risks associated with exposure to TAPs. This study would be a key component in assessing a facility's potential exposure and risk. This study would also address a component of the Risk Assessment Advisory Committee's recommendations to help improve the characterization of uncertainty in exposure assessment.

#### **44) TITLE: Physical and Chemical Characterization of Size-Segregated Particulate Matter Emissions from Gasoline- and Diesel-Powered On-Road Motor Vehicles**

**PROBLEM:** Particulate Matter (PM) emissions have become a concern worldwide. The U.S. EPA recently promulgated PM<sub>2.5</sub> standards for fine particulate matter, and a recent university study identified potential health concerns with ultrafine (<0.1 μm) and nanoparticle (< 0.05 μm) PM emissions from diesel engines. Members of the European community who have been studying the entire size domain of PM have proposed both ambient and occupational health standards for PM. The European studies point to the need for establishing standardized methods for measuring ultrafine and nanoparticle PM emissions.

**PREVIOUS WORK:** In September 1996, a study by the Health Effects Institute (HEI) found that a later 1 model year diesel engine had lower mass PM emissions than an earlier engine, but the newer engine produced many times greater numbers of particles, especially small, primary particles. At an August 1997, European conference on internal combustion engine nanoparticle measurement, the consensus was that measurements of ultrafine and nanoparticle emissions are influenced by dilution ratio, humidity, and temperature parameters for which no standardized measurement methods exist.

**OBJECTIVE:** To develop appropriate methods for sampling the entire size domain of gasoline- and diesel-fueled vehicle PM exhaust emissions under conditions that are representative of

those that PM exhaust emissions experience in the atmosphere. If test procedures can be readily developed, a small fleet of gasoline- and diesel-powered vehicles would be tested using these new methods to obtain emission data from different classes of on-road motor vehicles.

**DESCRIPTION:** The contractor would identify existing studies regarding the fate of motor vehicle ultrafine and nanoparticle PM emissions in ambient air, perform data analysis, and do one of the following: a) If the data permit, propose test procedures for accurately representing these conditions, and then procure and test a small fleet of gasoline-powered light-duty autos and heavy-duty diesel-powered vehicles; or b) if data are lacking, recommend additional data collection of vehicle emissions in ambient air, collect these emission data, perform data analysis, and develop representative test procedures.

**BENEFITS:** The size-segregated and chemically characterized ambient PM data would provide ARB health effects staff with representative ambient exposure data. The motor vehicle exhaust PM emissions data would provide ARB emissions inventory and air quality modeling staff with a small set of vehicle-specific, size-segregated, chemically-characterized vehicle exhaust PM emissions data as a function of engine and fuel type, vintage, and mileage.