Ethanol Work Plan

ARB Work Plan for Conducting an Airborne Environmental Fate and Transport Analysis of Ethanol Containing Gasoline

Objective

Executive Order D-5-99, Task 10, states "the California Air Resources Board (ARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water, and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA), shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline, and any resulting secondary transformation products. These reports are to be peer reviewed and presented to the Environmental Policy Council by December 31, 1999, for its consideration."

Proposed Action

To assist OEHHA, ARB staff will conduct a preliminary analysis to identify the directional change in ambient air concentrations of potentially detrimental contaminants of exhaust components and subsequent reaction products that would result from substituting ethanol-based gasoline for gasoline containing methyl tertiary-butyl ether (MTBE). Subsequently, staff will conduct modeling and data analyses of the air quality impacts of the fuels and provide OEHHA quantitative estimates of changes in ambient air concentrations for the various contaminants. The main focus of the analyses will be on ethanol, acetaldehyde, peroxyacetyl nitrate (PAN), MTBE, formaldehyde, benzene, and 1,3-butadiene. Other compounds under investigation include isobutene, toluene, xylene isomers, n-hexane, and others that may be identified by OEHHA, external review, and literature searches. A report of the results will be written and submitted for peer review to the University of California and subsequently submitted to the Air Resources Board.

Proposed Approach

Emission and air quality impacts will be evaluated for the following five fuels:

- Pre-1996 Cleaner Burning Gasoline (Pre-CBG)
- Current MTBE-Based Cleaner Burning Gasoline (CBG)
- Ethanol-Based Fully Complying Fuel (With Oxygen Content of 3.5%)
- Ethanol-Based Fully Complying Fuel (With Oxygen Content of 2.0%)
- A Non-Oxygenated Fully Complying Fuel

Emission Inventory Component

Total mass emissions of volatile organic compounds (VOC), oxides of nitrogen (NOx), and carbon monoxide (CO) for pre-CBG and CBG will be based on the mobile source emission factor model, EMFAC7G. The VOC speciation profiles for these two fuels were previously developed from ARB surveillance data and presented at a public workshop in September 1998.

For the three fully complying non-MTBE fuels, the Predictive Model constrains the total mass emissions of VOC and NOx to be no more than the emissions from CBG. Adjustments for mass emissions of CO, if any, will be developed. Available data on VOC speciation from existing emission test programs will be reviewed to identify those that best represent the fuels. Adjustments will be developed that can be applied to the VOC speciation profiles for the CBG base fuel in order to produce profiles for the three fully complying non-MTBE fuels.

CO emissions and speciated VOC data from the following test programs will be used:

- Auto / Oil Program (Multiple Programs)
- ARB Surveillance Program
- ARB 12-Car Ethanol / MTBE Test Program

VOC speciation profiles will be developed for each of the substitute fuels for the following processes and applied to all gasoline-related emission inventory categories (e.g., passenger cars, motorcycles, heavy-duty vehicles, fuel spillage, etc.):

- Cold Start Exhaust -- Catalyst and Non-Catalyst
- Hot Stabilized Exhaust -- Catalyst and Non-Catalyst
- Diurnal and Resting Evaporative
- Hot Soak and Running Evaporative
- Liquid fuel.

The VOC speciation profiles will be peer reviewed by Professor Robert Harley of the University of California at Berkeley. Professor Harley will also calculate headspace vapors from the liquid fuel speciation profiles as a check on the ones developed in-house.

In order to determine if the VOC speciation profiles for the three fully complying non-MTBE fuels are reasonable, ARB staff plan to conduct complete exhaust speciation tests for multiple vehicles using two prototype non-MTBE regular-grade gasolines currently being produced and sold commercially in California. One is an non-oxygenated gasoline and the other contains ethanol at about a two percent

oxygen level. Both fuels fully comply with California's current CBG regulations. The liquid fuels and headspace vapors will also be speciated. It is anticipated that full-scale production of fully complying non-MTBE gasoline will result in blends different from those being produced today. However, the results from these tests are expected to yield valuable insights into the directional effects of using ethanol-containing and non-oxygenated gasolines, providing a reality check for the profiles prepared in-house using limited test data.

Air Quality Modeling Component

The Urban Airshed Model with the Flexible Chemical Mechanism interface (UAM-FCM) will be applied for the August 27-29, 1987 ozone episode in the South Coast Air Basin (SoCAB) using special meteorological and air quality data collected during the Southern California Air Quality Study. Emission inventories for calendar years 1993, 1997, and 2003 will be simulated using the meteorology from the 1987 episode. Fixing the meteorological conditions in this way allows the effects of fuel change to be directly calculated. The SAPRC-97 photochemical mechanism will be used to simulate atmospheric transformations. The mechanism includes explicit treatments of the chemistry for ethanol, acetaldehyde, PAN, MTBE, formaldehyde, benzene, and 1,3-butadiene. SAPRC-97 currently lumps isobutene, toluene, xylene isomers, and n-hexane with similarly reacting compounds. If necessary, specific chemical mechanisms for these and other compounds will be added based on discussions with Dr. William Carter of the University of California at Riverside, developer of the SAPRC series of mechanisms.

To establish baseline conditions, 1993 and 1997 mass emissions will be simulated with the VOC speciation profiles for pre-CBG and CBG, respectively. Calendar year 2003 will be evaluated for CBG and the three fully complying non-MTBE fuels. Boundary conditions will be assumed to be invariant with the calendar year and fuel because these background concentrations presumably reflect marine air. Model results for the first day of the simulation (i.e., August 27) are greatly influenced by the initial conditions for ozone and its precursors. Therefore, only the results for the second and third days of the simulations will be reported.

Model results for pre-CBG (1993) and CBG (1997 and 2003) will be reported for the peak one-hour average and 24-hour average concentrations (for both the second and third days of the simulations) for ethanol, acetaldehyde, PAN, MTBE, formaldehyde, benzene, 1,3-butadiene, and other compounds of interest. Concentrations will be calculated for the nineteen CO monitoring sites used in the data analysis, as described in the next section. Results for the three fully complying non-MTBE fuels will be presented as percent increases or decreases from the 2003 CBG baseline for the nineteen sites. Secondary formation of acetaldehyde and formaldehyde will be tracked separately from the contribution of direct emissions. Due to the constraint of the Predictive Model that total mass

emissions of VOC and NOx remain fixed, ozone, nitrogen dioxide, and nitric acid (a precursor to PM10 and PM2.5) are not expected to change, although this will be checked with the model. Peroxypropionyl nitrate (PPN) is often observed in ambient air along with PAN. While PPN is not expected to change as a result of the introduction of non-MTBE fuels, this will be verified through use of the explicit treatment of PPN chemistry in SAPRC-97.

Data Analysis Component

A preliminary analysis of the directional change in ambient air concentrations of potentially detrimental contaminants of exhaust components and subsequent reaction products for the three fully complying non-MTBE fuels will be conducted. This will be based on a literature review of atmospheric chemistry studies and areas (e.g., Albuquerque, Brazil, Denver) that have measured air quality before and after large-scale implementation of ethanol as a motor fuel.

OEHHA has requested peak one-hour average and 24-hour average concentrations for ethanol, acetaldehyde, PAN, MTBE, formaldehyde, benzene, and 1,3-butadiene in the SoCAB, as well as population-weighted annual average concentrations for the SoCAB. The general approach used to determine these levels will be to: 1) establish relationships between the compound of interest and CO for CBG; 2) determine the peak observed one-hour average and 24-hour average CO concentrations in the SoCAB in 1997; 3) determine the population-weighted annual average CO in the SoCAB in 1997 using standard interpolation -- inverse square of distance from the monitoring site to the centroid of the census tract and a 50 kilometer radius of influence -- of the 19 CO monitoring sites and 1997 population projections by census tract; 4) estimate the 1997 baseline by applying the relationship with CO to the peak one-hour average, peak 24-hour average, and population-weighted annual average CO concentrations; 5) estimate the 2003 baseline by ratioing the 1997 baseline with the 1997 and 2003 UAM-FCM model results; and 6) estimate the effects for the three fully complying non-MTBE fuels with percent changes from the model. Data from 1996 to 1998 will be used to represent 1997 in order to account for natural year-to-year meteorological fluctuations. The three microscale CO monitoring sites (i.e., North Long Beach, Pomona, Riverside-Magnolia) will be included in the analysis to maximize the spatial coverage.

The following databases will be used to determine the relationships with CO:

- ARB emission inventory for 1997
- ARB Toxic Air Contaminant network in the SoCAB in 1996 to 1998
- Desert Research Institute VOC monitoring study in the SoCAB in 1996
- Desert Research Institute Sepulveda Tunnel study in 1996
- UC Berkeley Caldecott Tunnel studies in 1996 and 1997

- UC Berkeley and others will measure ethanol, carboxylic acids, and other speciated VOC in the Caldecott Tunnel as part of a previously planned study of criteria pollutants and ammonia in July 1999

Secondary formation of acetaldehyde and formaldehyde will be separated from the contribution of direct emissions by two methods. First, a stepwise regression with CO (to represent direct emissions) and ozone (to represent secondary formation) or total oxidant (sum of ozone and nitrogen dioxide) will be attempted. If successful, the six-step procedure described earlier will be applied for both CO and ozone (or total oxidant). Otherwise, a relationship with CO and the aldehyde from early morning measurements and tunnel studies will be used to calculate direct emissions. The difference between the total aldehyde and the direct emissions will be assumed to be from secondary formation. The limitation of this latter approach is that it can only be applied to the five sites with year-around formaldehyde and acetaldehyde data.

It is not yet clear how the ethanol baseline will be established, as available measurements are limited to the summer of 1996 and they are not expected to correlate with CO. Dr. Daniel Grosjean will establish the PAN baseline concentrations using measurements from the 1987 Southern California Air Quality Study, the 1997 Southern California Ozone Study-NARSTO, and other special studies. He will attempt to predict PAN levels from acetaldehyde, nitric oxide, nitrogen dioxide, ozone, and temperature data. ARB staff will conduct box modeling with SAPRC-97 to assist the effort.

A qualitative analysis will be conducted for particulate matter. PM2.5 can be approximated as the sum of nitrates, sulfates, organic carbon, elemental carbon, and secondary organic carbon. PM10 is roughly the sum of PM2.5 and coarse dust. The proportions of these various components are available for the SoCAB for 1995. Gasoline-fueled motor vehicles are a relatively small contributor to sulfates and elemental carbon in the SoCAB, so these components can be assumed to be fixed. Nitrates and organic carbon are not expected to change because NOx and VOC emissions are fixed. Vehicle activity is not likely to vary with the fuel, so coarse dust can be assumed to be constant as well. Secondary organic carbon will vary as a function of the aromatic content of the fuel, and to a lessor extent from high molecular weight alkanes. The directional change in PM2.5 and PM10 can be estimated from aromatic and alkane content of the VOC speciation profiles and the 1995 chemically resolved ambient data.

Proposed Work Schedule

June 8	VOC speciation profiles submitted to Professor Harley for peer review.

June 23	Professor Harley submitted peer review of VOC speciation profiles to ARB.
June 25	Preliminary analysis submitted to OEHHA.
July 12	Joint Cal/EPA, ARB, SWRCB, and OEHHA public workshop to review draft work plans.
Mid-July	Information submitted to Cal/EPA for selection of peer reviewers.
Late July	Preliminary Comments from Peer Reviewers on Work Plan
Early August	Draft quantitative analysis submitted to OEHHA.
Early September	Draft Report Available to Public
Mid-September	ARB public workshop to review the draft report.
Early October	Draft report submitted to University of California for final peer review.
Late October	Final Comments from Peer Reviewers
Mid-November	Final Draft Report and Notice for Board Hearing Available to Public
December 10-11	Final draft report presented to the Air Resources Board.

Late December	Final report submitted to Cal/EPA.

Ethanol Fate, Transport, and Health Risk Analysis