Potential Addition to MATES-III:
Analysis of Organic Compounds within Collected PM$_{2.5}$ Samples for Source Apportionment

Preliminary Draft for Discussion at MATES-III Technical Advisory Group

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I.   Introduction

During MATES-II the concentration of diesel exhaust was estimated by applying a factor of 1.04 to the elemental carbon concentration measured upon collected 24 hour PM_{10} filter samples. The factor of 1.04 was determined from diesel source profiles and fine particle studies conducted in 1982 (Gray, 1986). From this 1982 study it was determined an average of 67 percent of elemental carbon mass in the Los Angeles atmosphere comes from diesel engine exhaust and diesel exhaust has an average of 64 percent elemental carbon (67%/64% = 1.04).

It was later determined that applying a factor of 1.04 to measured EC concentrations may have underestimated the concentration of diesel exhaust for MATES-II (MATES-II Final Report, 2000). This underestimate may have partially resulted from not using current emission inventories. Changes in the vehicular fleet and fuel compositions have changed their emission contributions to the elemental carbon concentration over time (Christoforou *et al.*, 2000). Using the 1998 $PM_{2.5}$ emissions inventory suggested a factor of 1.24 might have been more appropriate (MATES-II Final Report, 2000).

An issue for the MATES-II estimate of diesel concentration was the use of elemental carbon alone to determine a concentration of diesel particulate matter. A unique characteristic of diesel exhaust is the emission of large amounts of elemental carbon. However; there are other sources of elemental carbon which may be significant. Some identified sources of elemental carbon within the South Coast Basin are automobile exhaust, meat charbroiling, road dust (includes tire wear particles, organometallic brake lining, fine paved road dust), wood smoke (biomass burning) and fuel oil (ship emissions).

Another issue for the MATES-II estimate of diesel exhaust was the application of a single factor to each sampling location throughout the year long study period. The contribution of other elemental carbon sources varies between sampling location and time of year. For instance, the contribution of elemental carbon from fireplace wood smoke will be greater in the wintertime and may not be equally distributed throughout all the sampling locations. Sample locations nearby residential areas could have a much heavier influence of elemental carbon from fireplace wood burning than those located within industrial settings. Applying a single factor to elemental carbon concentrations does not take the seasonal or spatial contributions of other sources of elemental carbon into consideration.

There are two strategies available to account for other sources of elemental carbon and the variability of these sources as a function of sampling location and time. These strategies are: (1) the use of a source apportionment model that utilizes the measurement of particle bound organic compounds and metals as tracers for sources of elemental carbon and (2) the development of an emissions inventory for elemental carbon (Schauer, J., 2003). The use of an emission inventory of elemental carbon has been shown effective in determining contributing sources to sampling locations over long periods of time and large spatial areas (Gray and Cass, 1998). This method is dependent upon a good emission inventory for elemental carbon and does not work well within microenvironments. Currently the most established technique of

determining other sources of elemental carbon is to analyze for particulate bound organic compounds and metals that act as tracers to identify and apportion contributing sources. This technique relies upon updated source profiles of all major contributors of elemental carbon and reconciles sources using a chemical mass balance model. The apportionment of other similar sources of elemental carbon such as automobile exhaust allows for both the elemental and organic carbon concentration of diesel exhaust to be estimated. Doing this provides a better estimate of the diesel concentration within a filter since the ratio of elemental carbon to organic carbon within diesel exhaust is highly variable with respect to operating conditions, temperature, fuel, engine load, engine size, etc (Christoforou, 2000; Fraser and Lakshmanan, 2002; Shah *et al.*, 2004).

Several receptor source reconciliation studies have been conducted using the multiple organics, metal, and elemental carbon analysis approach in conjunction with a chemical mass balance model (Schauer *et al*, 1996; Watson *et al*, 1998; Schauer and Cass, 2000; Schauer *et al.*, 2002; Zheng *et al*, 2002; Fine *et al*, 2004). Notably this approach was applied to PM_{10} filter samples collected in 1995 as part of the Southern California Children's Health Study (Manchester-Neesvig *et al*, 2003). During this study PM_{10} filter samples were compiled at each of the 12 sampling locations for three seasons and analyzed for 94 organic compounds along with Elemental Carbon (EC) and Organic Carbon (OC). Source contributions to PM_{10} samples were quantified for six sources: gasoline-powered motor vehicle exhaust, diesel vehicle exhaust, wood smoke, vegetative detritus, tire wear, meat smoke, and natural gas combustion. The results from this apportionment are shown in Figure 1.
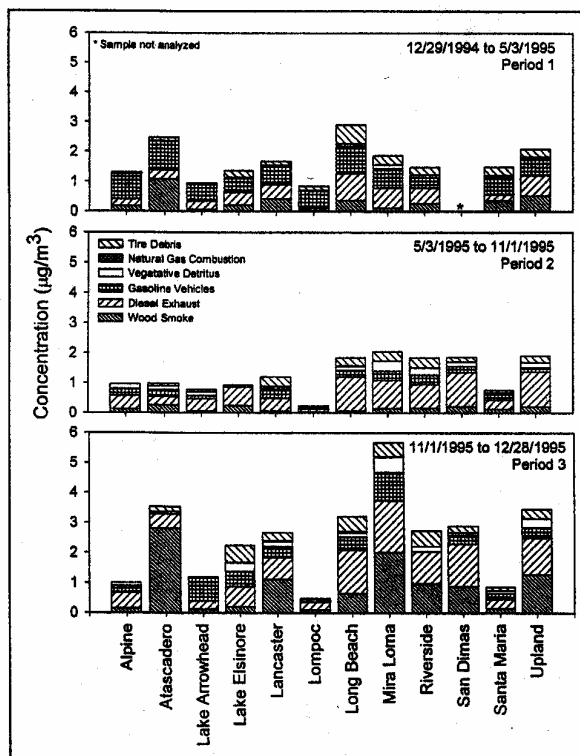

Figure 1: Source contributions to PM_{10} samples collected in 1995 as part of the Southern California Children's Health Study (Adapted from Manchester-Neesvig *et al*, 2003)

Analyzing for organic compounds and metals in conjunction with elemental carbon upon collected particulate samples can very clearly determine certain contributing sources. For instance, levoglucosan is a specific indicator of wood burning (McDonald *et al.*, 2000). Additional highly specific organic compounds emitted from wood burning may be used to differentiate between hardwood and softwood combustion (Schauer *et al.*, 2001). However, determining the difference between gasoline and diesel contributions to a collected particulate filter is not as clearly defined. A study conducted in a roadway tunnel underneath the Houston ship channel utilized the multiple organics technique along with a chemical mass balance model to determine how accurately diesel emissions could be distinguished from gasoline vehicles ([2]Fraser *et al.*, 2003). Collected filter samples within the tunnel were analyzed for elemental carbon, silica, alumina, and 11 organic compounds. Modeled results from the collected filters were found to be apportioned correctly with the observed traffic volume of gasoline and diesel vehicles in the tunnel. To determine the minimum amount of compounds or elemental constituents needed to correctly separate diesel and gasoline, the CMB model was run with a variety of inputs. This exercise determined that three classes of organic compounds along with Al, Si, and EC were required to correctly separate gasoline and diesel particulate matter.

II. MATES-III

Due to issues with solely using elemental carbon as an estimate of diesel exhaust, the MATES-III technical advisory group has suggested a supplemental analysis of organic compounds upon the MATES-III collected $PM_{2.5}$ samples. Analysis of organic compounds and elemental carbon would be used with recent source profiles and a chemical mass balance model to better estimate the concentration of diesel within collected ambient filter samples. From this recommendation the AQMD has looked into the possibilities of utilizing organic tracers for the MATES-III study, reviewed several studies involving the measurement of particle bound organic compounds, and contacted several scientists with experience in the analysis of particulate bound organic compounds. These scientists include individuals from University of Southern California, Desert Research Institute and The University Wisconsin Madison.

Based upon these findings approximately 30 organic compounds would need to be analyzed upon collected $PM_{2.5}$ quartz filter samples for MATES-III to apportion sources of elemental carbon. Sources of elemental carbon within the South Coast Basin that will be taken into consideration are: diesel exhaust, automobile exhaust, meat charbroiling, road dust (includes tire wear particles, organometallic brake lining and fine paved road dust), wood smoke and ship emissions utilizing bunker fuel. From this list of sources, the most recently published source profiles were obtained and a preliminary list of organic compounds and elemental constituents was compiled. The preliminary list of organic compounds and constituents shown in table 1 are based upon uniqueness in relation to a source, considered to be conserved in transport from source to sample, and have low volatilities making them particulate bound.

Table 1: Preliminary list of organic compounds, elemental constituents and major primary sources.

Compound	Source	Reference
Alkanes		
n-docosane	Diesel, non-catalyst gasoline	1,9
n-tricosane	Diesel, non-catalyst gasoline	1,9
n-tetracosane	Diesel, non-catalyst gasoline	1,9
n-pentacosane	Diesel, non-catalyst gasoline	1,9
n-hexacosane	Diesel, non-catalyst gasoline	1,9
n-heptacosane	Diesel, non-catalyst gasoline	1,9
n-octacosane	Diesel, non-catalyst gasoline	1,9
n-nonacosane	Diesel, non-catalyst gasoline	1,9
hentriacontane	Road Dust	3,8
tritriacontane	Road Dust	3,8
Saturated Cycloalkanes		
Hexadecylcyclohexane	Diesel, non-catalyst gasoline	1,2
Heptadecylcyclohexane	Diesel, non-catalyst gasoline	1,2
Octadecylcyclohexane	Diesel, non-catalyst gasoline	1,2
Nonadecylcyclohexane	Diesel, non-catalyst gasoline	1,2
Hopanes		
17α(H),21ß(H)-29-Norhopane	Diesel, non-catalyst gasoline	1,2
17α(H),21ß(H)-Hopane	Diesel, non-catalyst gasoline	1,2
Aromatic hydrocarbons		
Benzo[*ghi*]fluoranthene	Diesel, non-catalyst gasoline	1,2,9
Benz[a]anthracene	Diesel, non-catalyst gasoline	1,2,9,10
Chrysene	Diesel, non-catalyst gasoline	1,2,9
Pyrene	Diesel, non-catalyst gasoline	1,2,9,10
Benzo[ghi]fluoranthene	Vehicle Exhaust	1,2,9,10
Benzo[ghi]perylene	Vehicle exhaust	9,10
Dibenz[a,h]anthracene	Vehicle exhaust	10
Cholesterol	Meat cooking	11
Oleic acid	Meat cooking	
Levoglucosan	Wood combustion	4,5
2,6-dimethoxyphenol	Hardwood combustion	4,5
2-methoxyphenol	Softwood combustion	4,5
Elemental Constituents		
Organic Carbon	Various	1,3,4,5,9
Elemental Carbon	Various	1,3,4,5,9,11
Si, Al	Road Dust	3
Vanadium	Fuel Oil (ship emissions)	6,7

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Work Plan

The MATES-III $PM_{2.5}$ samples are collected upon 47mm quartz and Teflon filters simultaneously within the same particulate sampler for a 24 hour duration every third day. Collected samples are stored within a freezer and only removed from the freezer for analysis. Teflon filters are used for the analysis of total particulate mass and metals. The $PM_{2.5}$ quartz filter is currently only used for the analysis of elemental carbon and organic carbon which requires the removal of a 5mm circular piece of sample from the quartz filter.

Analysis of particulate bound organic compounds is done using quartz filters. However it is crucial that collected samples are stored within a freezer. Freezing the samples prevents reactions between constituents within the sample and eliminates evaporation of organic compounds. In one instance, a study has analyzed organic compounds within filter samples collected ten years earlier; this was made possible by storage of the samples under freezing conditions (Schauer *et al*, 1996).

Compositing Filter Samples for Analysis of Organic Compounds:

Analysis of particulate bound organic compounds requires approximately 1 mg of organic matter. Typical 24hr $PM_{2.5}$ filter samples collected within the basin contain approximately 27 to 200 μg of organic carbon. Therefore, to obtain the minimum amount of organic material needed for analysis, it will be necessary to composite $PM_{2.5}$ samples. Monthly composite samples will be made from quartz filter samples collected at each of the ten fixed MATES-III sampling sites. This will result in a total of 120 composite filter samples analyzed for organic compounds. Each monthly composite filter sample will be compiled by placing an entire months worth of samples into a sealed glass jar from which the extraction of organic compounds will be made. Preparation of monthly composite filter samples will be done after the analysis of EC/OC.

Organic Speciation Analysis:

Extraction of organic compounds from particulate filters is performed using a sonicator with solutions of hexane and benzene/2-propanol. The extract then undergoes volume reduction, deuterated internal standards are added and organic acids are derivatized with diazomethane. Analyses of organic compounds are then identified using GC-MS and often are done using GC-MS-MS. Identification and quantification of the particulate bound organic compounds is aided by the addition of deuterated internal standards to the solution. Currently the South Coast A.Q.M.D Laboratory does not have dedicated instrumentation and deuterated standards needed for the analysis of particulate bound organic compounds. Two laboratories have been contacted that are capable of these measurements and estimated costs for each composited sample are approximately $1,400. The cost for sample includes a greater number of organic compounds than listed in Table 1. Analysis of 120 composite samples would therefore put the total analysis cost at approximately $168,000.

Chemical Mass Balance Modeling:

Source reconciliation upon collected data will be conducted using the EPA Chemical Mass Balance model (CMB 8.2) and current published source profiles. Source profiles utilized will need to be applicable to the Southern California Basin.

Estimated Time Line for Completion of Analysis and Modeling:

April, 2004   ----------   MATES-III Start

February, 2005   --------   Composite April 2004 samples for organic speciation after EC/OC
analysis is performed and checked.

March, 2005   -------   Compile April 2004 data and source profiles needed for modeling.
Begin CMB modeling upon April 2004 data. Composite May 2004
samples for organic speciation.

April-December, 2005 -- Proceed as in February, 2005 until analysis and modeling
is completed.

January, 2006   ----------   Draft report.

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