APPENDIX V

$PM_{2.5}$ Particulate Bound Organic Compound Analysis

Appendix V

$PM_{2.5}$ Particulate Bound Organic Compound Analysis

I. Background/Rationale

A goal of the MATES III Study is to identify and quantify health risks associated with major known toxic air contaminants within the Basin over a two-year period. An important aspect of the MATES III Study was to identify and quantify diesel exhaust within collected $PM_{2.5}$ samples. To do this, the MATES III Technical Advisory Group suggested the analysis of particulate-bound organic compounds from MATES III $PM_{2.5}$ samples.

Diesel exhaust emissions are comprised of gaseous and particle phases. The gaseous phase contains typical combustion components which include carbon dioxide, nitrogen oxides, carbonyl compounds, and volatile hydrocarbons (Kirchstetter, 1999; Shah, 2005). Diesel particulate emissions occur primarily in the fine ($PM_{2.5}$) region that consist of organic (OC) and elemental carbon (EC) fractions along with trace amounts of inorganic compounds (Abu-Allaban, 2004; Lloyd, 2001). The OC fraction of diesel exhaust contains heavy hydrocarbons such as lubricating oils and PAHs with low volatility; the EC fraction is considered soot. Unfortunately, no physical property clearly distinguishes between the OC and EC fractions; therefore, measurements of OC-EC from particulate samples are defined by the method of analysis. Typical methods of analysis characterize OC from EC by thermal, optical or solvent- based properties (Moosmuller, 2001; Fermo, 2006). Solvent- based extraction techniques define organic carbon as the extractable mass within the solvent, and the carbon remaining on the filter is characterized as EC. Thermal methods (IMPROVE, NIOSH, TMO) are the most widely used for the analysis of EC and OC collected upon particulate samples. These methods utilize temperature changes within reducing and oxidizing atmospheres to distinguish between EC and OC. Optical-based techniques are typically real-time particle measurements based upon optical absorption and/or particle scattering. Each method does not yield directly comparable results (Chow, 2001).

The presence of high levels of EC within diesel exhaust is a unique property of this combustion source. The concentration of diesel exhaust during MATES II was estimated by applying a factor of 1.04 to the EC concentration measured for 24 hour PM_{10} filter samples. A factor of 1.04 was determined from diesel source profiles and fine particle samples collected upon PM_2 samples in 1982 (Gray, 1986). From this 1982 study it was determined an average of 67% of elemental carbon mass in the Los Angeles atmosphere comes from diesel engine exhaust and diesel exhaust has an average of 64% elemental carbon (67%/64% = 1.04) (MATES II Final Report, 2000). Applying a factor of 1.04 to measured EC concentrations may have underestimated the concentration of diesel exhaust for MATES II. The 1998 $PM_{2.5}$ emissions inventory suggested a factor of 1.39 might have been more appropriate (MATES II Final Report, 2000, pg 9-15).

Using elemental carbon measurements solely to determine diesel emissions does not provide information on contributions of EC from other sources or address how much organic carbon is associated with these sources. Other sources of elemental carbon may include automobile exhaust, meat charbroiling, biomass burning, coal burning, and fuel oil (ship emissions). Emissions from these sources are often seasonally dependent and may have different spatial emissions within the Basin (Magliano, 1999; Reinhart, 2006). For instance, during colder winter months an increase in residential wood burning would be expected (Jordan, 2006; Fine, 2004).

Determining sources of elemental and organic carbon may be done using particulate bound organic compounds and metals that act as tracers to identify and apportion contributing sources. This technique relies upon updated source profiles of major sources and reconciles sources using chemical mass balance. 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. (Christoforou, 2000; Fraser, 2002; Shah, 2004). Analyzing for organic compounds, metals and elemental carbon upon collected particulate samples in conjunction with source profiles can provide specific information to determine contributing sources. For instance, the analysis of levoglucosan provides a specific indicator of cellulose combustion from wood burning (McDonald, 2000; Fine, 2004). Several receptor source reconciliation studies have been conducted using particulate bound organics, metal, and elemental carbon analysis in conjunction with a chemical mass balance model (Watson, 1998; Schauer, 2000; Schauer, 2002; Zheng, 2002; Chow, 2007). Notably this source apportionment technique was applied to PM_{10} filter samples collected in 1995 as part of the Southern California Children's Health Study (Manchester-Neesvig, 2003).

II. Work Plan

From the MATES III Technical Advisory Group's recommendation, a work plan was established to analyze for particulate- bound organic compounds within the MATES III collected $PM_{2.5}$ filters samples. Through the SCAQMD's procurement procedure, a contract was awarded to Desert Research Institute (DRI) for the analysis of 75 particulate-bound organic compounds (Table-1). A contract laboratory was facilitated for this analysis due to highly specific standards and equipment needed. To provide sufficient quantities of organic material, monthly composite samples were made for each of the MATES III fixed sampling locations. Additional Wednesday and Sunday monthly composite samples were also analyzed for particulate-bound organics.

a. Sample Handling

The MATES III $PM_{2.5}$ samples were collected upon 47mm quartz, Teflon, and vinyl filters using a Met One SASS through four sampling channels for a 24-hour sample period every third day. The quartz filters were used for EC/OC analysis and for the analysis of particulate-bound organic compounds. Upon collection from the field, the $PM_{2.5}$ quartz samples are individually sealed within plastic bags, transferred to the laboratory in coolers, and stored under freezing temperatures. Storage of collected quartz filter samples under freezing conditions has been shown to maintain the integrity of the particulate-bound organics for an indefinite period (Schauer, 1996). Prior to the analysis of particulate- bound organics the quartz samples were analyzed for EC and OC using the IMPROVE method, which required the removal of two or three 5mm circular pieces of filter sample (Chow, 1993). During this analysis the filters are removed from the storage freezer and placed within a portable cooler. Upon completion of the EC/OC analysis, the filters were made into monthly station composites and sent to DRI for the analysis of particulate-bound organics. Samples were shipped under freezing conditions using a portable cooler with overnight delivery. Upon receipt by DRI, the samples were logged into the Laboratory Information Management System (LIMS). If the time span between sample login and extraction was greater than 24 hours, the samples were stored in a freezer.

b. Compositing Filter Samples

To obtain sufficient material needed for organic analyses, $PM_{2.5}$ filter samples collected at each of the monitoring sites were made into composite samples on a monthly basis. Composite samples were made after analysis had been completed for EC/OC. A composite sample was made by leaving each individual filter sealed in a plastic bag and placing the sealed filter within a labeled larger plastic bag with other samples from the appropriate month and sample location. Once a composite sample has been prepared, each individual filter was re-checked to ensure its proper location within the monthly composite. Filters within the composite were compared to ensure each filter had the same number of 5mm samples removed during EC/OC analysis. If needed, filters within the composite were adjusted by removing a 5mm punch from filters; therefore, all filters within the composite had identical punches removed. Each monthly composite sample is identified by sample location/month/year. For example, the monthly composite collected at Burbank in October 2005 is identified as BK10_2005. A list of composite samples analyzed for particulate-bound organic compounds is shown in Table-2.

An additional set of Wednesday/Sunday $PM_{2.5}$ filter samples were analyzed for particulate-bound organic compounds. During this sampling a four-channel PTEP sampler simultaneously collected three quartz and one Teflon $PM_{2.5}$ filter. The quartz filters were made into composites by location/month/day/year. For example, a composite consisting of samples collected on Sundays at Wilmington in October-2004 is identified as WL10S04. For a given month of sampling, each location has a separate set of composite samples based upon day of collection, one composite for Wednesday and one for Sunday. One difference between the Wednesday/Sunday composites with the monthly station composites was the use of a PTEP sampler instead of a Met One SASS.

c. Analysis

A description of the analysis of particulate-bound organic compounds conducted by DRI is described below:

For each composite sample, the quartz filters were extracted and analyzed together. Prior to extraction, a set of deuterated internal standards, as listed in Table-3, were added to each sample. The amount of internal standards added should correspond to the expected range of concentrations found in real samples and the final volume of extracts during analysis. Filters were extracted with ~170 mL dichloromethane (DCM) using the Dionex ASE (accelerated solvent extractor) for 15 min/cell at 1500 psi and 80°C followed by ~170 mL acetone extraction under the same conditions. Extracts were concentrated to ~1ml by rotary evaporation at 35 °C under gentle vacuum, and filtered through a 0.2 µm PTFE disposable filter (Whatman Pura disc^{TM} 25TF), rinsing the flask 3 times with 1 ml dichloromethane and acetone (50/50 by volume) each time. Filtrate was collected in a 4 mL amber glass vial for a total volume of ~4 mL.

Approximately 200 µl of acetonitrile was added at this time and the extract was split into two fractions. Each fraction was then concentrated under a gentle stream of ultra-high purity (UHP) nitrogen with hydrocarbon and water traps to 100 µL. The final extract volume is adjusted to 100 µL with acetonitrile.

One fraction was analyzed by the GC/MS method for PAH, hopanes/steranes, alkanes, and cycloalkanes, as described below. If necessary (in case of very dirty samples), the extracts were pre-cleaned by the solid-phase extraction technique, using Superclean LC-SI SPE cartridges (Supelco) with sequential elution with hexane, and hexane/benzene (1:1). The hexane fraction contains the non-polar aliphatic hydrocarbons (alkanes), and hopanes and steranes, and the hexane/benzene fraction contains the PAH. These two fractions were combined and concentrated to ~100 µL and analyzed by GC/MS technique. The second fraction was derivatized using a mixture of bis(trimethylsilyl)trifluoroacetamide and pyridine to convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids and diacids, cholesterol, methoxyphenols, and levoglucosan. The extract was reduced to a volume of 50 µL using a Pierce Reacti-Therm under a gentle stream of ultra-high purity (UHP) nitrogen with a water trap (Chrompack CP-Gas-Clean moisture filter 17971). Then, 50 µL of silylation grade pyridine and 150 µL of bis(trimethylsilyl)trifluoroacetamide was added slowly to each vial and immediately capped. The sample was then placed into thermal plates (custom made) containing individual vial wells with the temperature maintained at 70°C for three hours. The samples were then analyzed by GC/MS within 18 hours.

The extracts were analyzed by gas chromatography/mass spectrometry (GC/MS) using a Varian CP-3800 GC equipped with a CP8400 auto sampler and interfaced to a Varian Saturn 2000 Ion Trap (Batch 1 of samples) or Varian 4000 Ion Trap (all remaining Batches) operating in electron impact (EI) ionization mode. Injections (1 µL) were made in the split less mode onto a 30m long 5% phenylmethylsilicone fused-silica capillary column (DB-5ms, J&W Scientific or equivalent). Quantification of the individual compounds was obtained by selective ion storage (SIS) technique, monitoring the molecular and characteristic ions of each compound of interest and the corresponding deuterated internal standard ions. Since hopanes and steranes are usually present in very low concentrations in ambient $PM_{2.5}$ samples, a new Varian 1200 triple quadrupole gas chromatograph – mass spectrometer (GC/MS/MS) system was used for these compounds quantification. The superior selectivity and sensitivity of this instrument (in EI/MS SIM mode it reaches 50 fg/ µL with 10:1 S/N) allows for accurate analysis of compounds present in very low concentrations.

Calibration curves for the GC/MS quantification were made for the most abundant and characteristic ion peaks of the compounds of interest (Table-1) using the deuterated species most closely matched in volatility and retention characteristics as internal standards. For PAH, National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1647 (certified PAH) with the addition of deuterated internal standards and of those compounds not present in the SRM was used to make calibration solutions. For hopanes/steranes, the calibration mixture obtained from NIST and prepared by Chiron AS, Norway, was used. For alkanes and cycloalkanes, the calibration solutions are made from the authentic standards purchased from Aldrich, Accustandard, and Chiron AS. For polar compounds, a separate calibration mixture is prepared using the authentic compounds purchased from various sources (i.e. Aldrich Inc., Accustandard, Chiron AS, and others) and derivatized the same way as described above, just before the analysis. A six- to eight-level calibration is performed for each compound of interest and the calibration check (using median calibration standards) is run every 10 samples to check for accuracy of analyses. If the relative accuracy of measurement (defined as a percent difference from the standard value) is less than 20%, the instrument is recalibrated. Field blanks and media blanks were analyzed by the same method as actual samples. Approximately 10% of the extracts were run as duplicate analysis, to determine the replicate precision. Field blanks were extracted and analyzed using the same methods.

III. References

Abu-Allaban, Mahmoud, C. Rogers, and A. Gertler, A Quantitative Description of Vehicle Exhaust Particle Size Distributions in a Highway Tunnel, J. Air & Waste Manage. Assoc., 54, 360-366 (2004).

Chow, J., J. Watson, L. Pritchett, W. Pierson, C. Frazier, and R. Purcell, The DRI Thermal/Optical Reflectance Carbon Analysis System: Description, Evaluation and Application in U.S. Air Quality Studies, Atmos. Environ., 27A #8, 1185-1201 (1993).

Chow, J, J. Watson, D. Crow, D. Lowenthal, and T. Merrifield, Comparison of IMPROVE and NIOSH Carbon Measurements, Aeros. Sci. & Technol, 34 #1, 23-34(2001).

Chow, J., J. Watson, D. Lowenthal, L. Chen, B. Zielinska, L. Mazzoleni, and K. Magliano, Evaluation of Organic Markers for Chemical Mass Balance Source Apportionment at the Fresno Supersite, Atmos. Chem. Phys., 7, 1741-1754 (2007).

Christoforou, C., L. Salmon, M. Hannigan, P. Solomon, and G. Cass, Trends in Fine Particle Concentration and Chemical Composition in Southern California, J. Air & Waste Manage. Assoc., 50, 43-53 (2000).

Fermo, P., A. Piazzalunga, R. Vecchi, G. Valli, and M. Ceriani, A TGA/FT-IR Study for Measuring OC and EC in Aerosol Samples, Atmos. Chem. & Phys., 6, 225-266 (2006).

Fine, P., B. Chakrabarti, M. Krudysz, J. Schauer, and C. Sioutas, Diurnal Variations of Individual Organic Compound Constituents of Ultrafine and Accumulation Mode Particulate Matter in Los Angeles Basin, Environ. Sci. Technol., 38, 1296-1304 (2004).

Fraser, M. and K. Lakshmanan, Variation in composition of fine particulate emissions from heavy-duty diesel vehicles, J. Geophys. Res. 107 #D21, 8346-8352 (2002).

Gray, A., G. Cass, J. Huntzicker, E. Heyerdahl, and J. Rau, Characteristics of Atmospheric Organic and Elemental Carbon Particle Concentrations in Los Angeles, Environ. Sci. Technol., 20, 580-589 (1986).

Jordan, T, A. Seen, and G. Jacobsen, Levoglucosan as an Atmospheric Tracer for Woodsmoke, Atmos. Environ, 40, 5316-5321 (2006).

Kirchstetter, T, R. Harley, N. Kreisberg, M. Stolzenburg, and S. Hering, On-road Measurement of Fine Particle and Nitrogen Oxide Emissions from Light and Heavy Duty Motor Vehicles, Atmos. Environ., 33, 2955-2968 (1999).

Lloyd, A. and T. Cackette, Diesel Engines: Environmental Impact and Control, J. Air & Waste Manage. Assoc., 51, 809-847 (2001).

Magliano, K. V. Hughes, L. Chinkin, D. Coe, T. Haste, N. Kumar, F. Lurmann, Spatial and Temporal Variations in PM_{10} and $PM_{2.5}$ Source Contributions and Comparison to Emission During the 1995 Integrated Monitoring Study, Atmos. Environ., 33 #29, 4757-4773 (1999).

McDonald, J., B. Zielinska, E. Fujita, J. Sagebiel, J. Chow, and J. Watson, Fine Particle and Gaseous Emission Rates from Residential Wood Combustion, Environ. Sci. Technol., 34, 2080-2091 (2000).

Manchester-Neesvig, J, J. Schauer, and G. Cass, The Distribution of Particle-Phase Organic Compounds in the Atmosphere and Their Use for Source Apportionment during the Southern California Children's Health Study, J. Air & Waste Manage. Assoc., 53, 1065-1079 (1065).

Moosmuller, H., W. Arnott, C. Rogers, J. Bowen, J. Gillies, W. Pierson, J. Collins, T. Durbin, and J. Norbeck, Time-Resolved Characterization of Diesel Particulate Emissions. 2. Instruments for Elemental and Organic Carbon Measurements Environ. Sci. Technol., 35, 1935-1942 (2001).

Reinhart, L., E. Fujita, J. Chow, K. Magliano, and B. Zielinska, Spatial Distribution of $PM_{2.5}$ Associated Organic Compound in Central California, Atmos. Envir., 40 #2, 290-303 (2006).

Schauer, J., W. Rogge, L. Hildemann, M. Mazurek, and G. Cass, Source apportionment of airborne particulate matter using organic compounds as tracers, Atmos. Environ, 30, 3837-3855 (1996).

Schauer, J. and G. Cass, Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers, Environ. Sci. Technol., 34, 1821-1832 (2000).

Schauer, J., M. Fraser, G. Cass, and B. Simoneit, Source Reconciliation of Atmospheric Gas-Phase and Particle-Phase Pollutants during a Severe Photochemical Smog Episode, Environ. Sci. Technol., 36, 3806-3814 (2002).

Shah, S., T. Ogunyoku, J. Miller, and D. Cocker, On-Road Emission Rates of PAH and n-Alkane Compounds from Heavy-Duty Diesel Vehicles, Environ. Sci. Technol., 39, 5276-5284 (2005).

Watson, J., E. Fujita, J. Chow, B. Zielinska, L. Richards, W. Neff, and D. Dietrich, Northern Front Range Air Quality Study (NFRAQS) final report (1998).

Zheng, M., G. Cass, J. Schauer, and E. Edgerton, Source apportionment of $PM_{2.5}$ in the Southeastern United States Using Solvent-Extractable Organic Compounds as Tracers, Environ. Sci. Technol, 36, 2361-2371 (2002).

Table-1: Particulate Bound Organics Analyzed for in MATES III PM2.5 Monthly Composite Samples

Mnemonic	Compound Name	Mnemonic	Compound Name
Alkanes		**PAH**	
PHYTAN	Phytane	PYRENE	Pyrene
DOCOSA	Docosane	RETENE	Retene
DEC6YHX	Hexadecylcyclohexane	BGHIFL	Benzo(ghi)fluoranthene
TRICOSA	Tricosane	BAANTH	Benz(a)anthracene
DEC7YHX	Heptadecylcyclohexane	CHR_TR	Chrysene/Triphenylene
DEC8YHX	Octadecylcyclohexane	BBJKFL	Benzo(b+j+k)fluoranthene
TETCOS	Tetracosane	BEPYRN	BePyrene
PENCOS	Pentacosane	BAPYRN	BaPyrene
DEC9YHX	Nonadecylcyclohexane	IN123PYR	Indeno[123-cd]pyrene
HEXCOS	Hexacosane	DBAHACAN	Dibenzo(ah+ac)anthracene
CYHXEIC	Eicosylcyclohexane	PIC	Picene
HEPCOS	Heptacosane	BGHIPE	Benzo(ghi)perylene
CYHXHEN	Heneicosylcyclohexane	CORONE	Coronene
OCTCOS	Octacosane	**Polar Compounds**	
NONCOS	Nonacosane	guai	Guaiacol
HTRICONT	Hentriacontane	sucac	Succinic acid (d-c4)
TTRICONT	Tritriacontane	syri	Syringol
Hopanes/Steranes		guac	Glutaric acid (d-c5)
ster42	C27-20S5a(H),14a(H)-cholestane	hexdac	Hexanedioic (adipic) acid (d-c6)
ster43	C27-20R5a(H),14ß(H)-cholestane	cpinac	Cis-pinonic acid
ster44	C27-20S5a(H),14ß(H),17ß(H)-cholestane	fguai4	4-formyl-guaiacol (vanillin)
ster45+40	C27-20R5a(H),14a(H),17a(H)-cholestane&C29-20S13ß(H),17a(H)-diasterane	phthac	Phthalic acid
ster46	C28-20S5a(H),14a(H),17a(H)-ergostane	levg	Levoglucosan
ster47	C28-20R5a(H),14ß(H),17ß(H)-ergostane	syrald	Syringaldehyde
ster48	C28-20S5a(H),14ß(H),17ß(H)-ergostane	isphac	Isophthalic acid
ster49	C28-20R5a(H),14a(H),17a(H)-ergostane	azeac	Azelaic acid (d-c9)
ster50	C29-20S5a(H),14a(H),17a(H)-stigmastane	palol	Palmitoleic acid
ster51	C29-20R5a(H),14ß(H),17ß(H)-stigmastane	palac	Palmitic acid (c16)
ster52	C29-20S5a(H),14ß(H),17ß(H)-stigmastane	olac	Oleic acid
hop13	18a(H),21ß(H)-22,29,30-Trisnorneohopane	steac	Stearic acid (c18)
ster53	C29-20R5a(H),14a(H),17a(H)-stigmastane	isopim	Isopimaric acid
hop15	17a(H),21ß(H)-22,29,30-Trisnorhopane	dhabac	Dehydroabietic acid
hop17	17a(H),21ß(H)-30-Norhopane	abac	Abietic acid
hop19	17a(H),21ß(H)-Hopane	oxodeh7	7-oxodehydroabietic acid
hop20	17ß(H),21a(H)-hopane	chol	Cholesterol
hop21	22S-17a(H),21ß(H)-30-Homohopane	hop25	22R-17a(H),21ß(H)-30,31-Bishomohopane
hop22	22R-17a(H),21ß(H)-30-Homohopane	hop26	22S-17a(H),21ß(H)-30,31,32-Trisomohopane
hop23	17ß(H),21ß(H)-Hopane	hop27	22R-17a(H),21ß(H)-30,31,32-Trishomohopane
hop24	22S-17a(H),21ß(H)-30,31-Bishomohopane		

Table-2. List of Composite Samples

Station/Month/Year

Anaheim	Burbank	Compton	Fontana	Huntington Park	Los Angeles	Long Beach	Pico Rivera	Rubidoux	Wilmington
AN04_2004	BK04_2004	CT04_2004	FT04_2004	HP04_2004	LA04_2004	LB04_2004	PR04_2004	RB04_2004	*WL04_2004
AN05_2004	BK05_2004	CT05_2004	FT05_2004	HP05_2004	LA05_2004	LB05_2004	PR05_2004	RB05_2004	WL05_2004
AN06_2004	BK06_2004	CT06_2004	FT06_2004	HP06_2004	LA06_2004	LB06_2004	PR06_2004	RB06_2004	WL06_2004
AN07_2004	BK07_2004	CT07_2004	FT07_2004	HP07_2004	LA07_2004	LB07_2004	PR07_2004	RB07_2004	WL07_2004
AN08_2004	BK08_2004	CT08_2004	FT08_2004	HP08_2004	LA08_2004	LB08_2004	PR08_2004	RB08_2004	WL08_2004
AN09_2004	BK09_2004	CT09_2004	FT09_2004	HP09_2004	LA09_2004	LB09_2004	PR09_2004	RB09_2004	WL09_2004
AN10_2004	BK10_2004	CT10_2004	FT10_2004	HP10_2004	LA10_2004	LB10_2004	PR10_2004	RB10_2004	WL10_2004
AN11_2004	BK11_2004	CT11_2004	FT11_2004	HP11_2004	LA11_2004	LB11_2004	PR11_2004	RB11_2004	WL11_2004
AN12_2004	BK12_2004	CT12_2004	FT12_2004	HP12_2004	LA12_2004	LB12_2004	PR12_2004	RB12_2004	WL12_2004
AN01_2005	BK01_2005	CT01_2005	FT01_2005	HP01_2005	LA01_2005	LB01_2005	PR01_2005	RB01_2005	WL01_2005
AN02_2005	BK02_2005	CT02_2005	FT02_2005	HP02_2005	LA02_2005	LB02_2005	PR02_2005	RB02_2005	WL02_2005
AN03_2005	BK03_2005	CT03_2005	FT03_2005	HP03_2005	LA03_2005	LB03_2005	PR03_2005	RB03_2005	WL03_2005
AN04_2005	BK04_2005	CT04_2005	FT04_2005	HP04_2005	LA04_2005	LB04_2005	*PR04_2005	RB04_2005	WL04_2005
AN05_2005	BK05_2005	CT05_2005	FT05_2005	*HP05_2005	LA05_2005	LB05_2005	*PR05_2005	RB05_2005	WL05_2005
AN06_2005	BK06_2005	CT06_2005	FT06_2005	*HP06_2005	LA06_2005	LB06_2005	*PR06_2005	RB06_2005	WL06_2005
AN07_2005	BK07_2005	CT07_2005	FT07_2005	*HP07_2005	LA07_2005	LB07_2005	*PR07_2005	RB07_2005	WL07_2005
AN08_2005	BK08_2005	CT08_2005	FT08_2005	*HP08_2005	LA08_2005	LB08_2005	*PR08_2005	RB08_2005	WL08_2005
AN09_2005	BK09_2005	CT09_2005	FT09_2005	*HP09_2005	LA09_2005	LB09_2005	PR09_2005	RB09_2005	WL09_2005
AN10_2005	BK10_2005	CT10_2005	FT10_2005	*HP10_2005	LA10_2005	LB10_2005	PR10_2005	RB10_2005	WL10_2005
AN11_2005	BK11_2005	CT11_2005	FT11_2005	*HP11_2005	LA11_2005	*LB11_2005	*PR11_2005	RB11_2005	WL11_2005
AN12_2005	BK12_2005	CT12_2005	FT12_2005	*HP12_2005	LA12_2005	LB12_2005	*PR12_2005	RB12_2005	WL12_2005
AN01_2006	BK01_2006	CT01_2006	FT01_2006	*HP01_2006	LA01_2006	LB01_2006	PR01_2006	RB01_2006	WL01_2006
AN02_2006	BK02_2006	CT02_2006	FT02_2006	*HP02_2006	LA02_2006	LB02_2006	PR02_2006	RB02_2006	WL02_2006
AN03_2006	BK03_2006	CT03_2006	FT03_2006	*HP03_2006	LA03_2006	LB03_2006	PR03_2006	RB03_2006	WL03_2006
AN04_2006	BK04_2006	CT04_2006	FT04_2006	*HP04_2005	LA04_2006	LB04_2006	PR04_2006	RB04_2006	WL04_2006

(* Composite samples not analyzed for particulate bound organics)

Table-3. List of internal deuterated standards

PAH	Hopanes& Steranes	Alkanes	Polar Compounds
benz(a)anthracene-d_{12} chrysene-d_{12} benzo[k]fluoranthene-d_{12} benzo[e]pyrene-d_{12} benzo[a]pyrene-d_{12} benzo[g,h,i]perylene-d_{12} coronene-d_{12} pyrene-d_{10}	cholestane- d_6	eicosane-d_{42} octacosane-d_{58} tetracosane-d_{50} hexatriacontane-d_{74}	cholesterol-d_6 levoglucosan-u-$^{13}C_6$ oleic-d_2 acid benzoic-d_5 acid palmitic-d_{31} acid heptadecanoic-d_{33} acid succinic-d_4 acid phthalic -d_4 acid