ABSTRACT

Title of Dissertation:	CHARACTERIZATION OF CARBONACEOUS AEROSOL: IMPROVED METHODS, SOURCES AND SIZE DISTRIBUTIONS
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A highly sensitive method was developed for measuring polycyclic aromatic hydrocarbons and nitro-substituted polycyclic aromatic hydrocarbons in ambient aerosol. Using large volume injection, this technique provided an order of magnitude increase in sensitivity compare to conventional injection techniques. This method facilitated the measurement of the first reported diurnal size distribution of NPAHs. Size resolved samples were collected using a Berner low-pressure impactor deployed at the Baltimore $PM_{2.5}$ Supersite in April 2002. Both classes of compounds were found predominantly on particles less than 0.49μm with similar size distributions among samples for most of the 12 hr periods. A linear relationship between compound geometric mass median aerodynamic diameter (GMMAD) and log sub-

cooled vapor pressures ($p_l°$) was observed for PAHs and NPAHs, respectively, during each sampling period. The inter-relationhips between the slopes and y-intercepts from the GMMAD/log vapor pressure correlations suggest the source of PAHs to the Baltimore atmosphere reside on particles with GMMADs equal to 0.18 μm, consistent with vehicle emissions.

Bulk organic aerosol was collected in Baltimore, MD during the spring, summer and winter of 2002-2003. Concentrations of *n*-alkanes, hopanes, polycyclic aromatic hydrocarbons (PAH), and nitro-substituted polycyclic aromatic hydrocarbons (NPAH) were measured in the gas and particle phase. The organic compounds varied little, with seasonal concentrations typical of North American urban atmospheres. Principal Components Analysis/Multiple Linear Regression (PCA/MLR) and Positive Matrix Factorization (PMF) were used to determine the sources of individual compound classes (PAHs, NPAHs, hopanes and alkanes) and total particulate carbon and $PM_{2.5}$ to the Baltimore atmosphere for during 2002-2003. PMF was used to determine the total carbon and $PM_{2.5}$ source estimates to the Baltimore atmosphere. The sources identified included tire wear/road dust, gasoline and diesel exhaust, oil combustion, biogenic, secondary organic aerosol, incineration, and coal explaining 64% of the variability in the total carbon and $PM_{2.5}$ concentrations.

CHARACTERIZATION OF CARBONACEOUS AEROSOL: IMPROVED

METHODS, SOURCES AND SIZE DISTRIBUTIONS

By

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Dissertation submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
2006

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DEDICATION

To my wife, Cindy, for everything that is life, love and happiness. I cherish every

moment with you.

To my family, Jim, Kate, Cori and Eric, I would like to thank you for keeping me grounded and showing me the important things in life. To my father, I will always cherish how you have always been there with a unique perspective on life, which we may not understand sometimes, but can all can benefit from when we figure it out. To my mother who inspired me to undertake this endeavor years ago.

And lastly, I would like to express my deepest gratitude to my wife, Cindy for being there for me, without you I would never have had the strength.

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Chapter 1

Executive Summary

1.1 Introduction

There is a significant relationship between atmospheric particulate matter and increased mortality in highly polluted areas (Dockery *et al.*, 1993). Organic carbon can contribute up to 60% of the ambient aerosol mass (Malm *et al.*, 2004). This fraction of ambient aerosol is composed of hundreds of compounds with a myriad of functionalities and molecular weights. Deconvoluting the organic matrix is essential to understanding the behavior and potential health effects of ambient particulate matter. Polar organic moieties can affect the hygroscopicity of ambient particulate matter (Novakov and Penner, 1993, Cruz and Pandis, 1997) and the cloud condensation properties of ambient aerosol. The total concentration of particulate matter has been implicated in increased mortality (EPA, 1996), and the organic fraction contains highly mutagenic compounds such as polycyclic aromatic hydrocarbons and nitro-substituted polycyclic aromatic hydrocarbons (Arey, 1988, IARC, 1989).

In recent years, air quality managers have focused on determining the sources of particulate matter due to potential health effects. Although sources of ambient particulate matter have been estimated using inorganic markers for decades (*e.g.*, Gordon, 1980), significant contributors such as gasoline combustion and biogenic emissions, can not be identified using elemental markers alone. Recent studies have

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attempted to resolve organic compounds representative of possible aerosol sources (Rogge *et al.*, 1993, 1997a, b, 1998). These profiles are then employed to unravel the contribution of each organic signature to the ambient organic aerosol concentration. The current methods rely on select organic profiles from a limited number of sources to drive mass balance receptor models (Schauer *et al.*, 1996, 2000), most of which have been developed for the Southern California region.

The introduction of new multivariate techniques, such as Positive Matrix Factorization, overcome the limited organic marker source techniques by employing literature-reported profiles to guide the identification of resolved sources. The multivariate model results are based on the sample to sample covariance of compound profiles specific to a receptor site. Both types of models are limited by the temporal resolution of previous sampling campaigns (usually 24 hrs), therefore better methods are needed to increase temporal resolution, hence our understanding of the sources of organic matter to the ambient atmosphere. In addition, select regions such as Baltimore, MD have limited organic aerosol composition data available. Therefore, implementing multivariate models with extensive chemical characterization, using highly sensitive methods will inevitably broaden our understanding of the behavior and sources of organic particulate matter.

1.2 Rational

In 2000 the United States Environmental Protection Agency awarded $22 million in grants for fine particle research to seven University Research Centers: University of California (Los Angeles, CA), Washington University (St. Louis, MO), University of Texas (Houston, TX), UCCSN/Desert Research Institute (Fresno, CA), State

University of New York (New York, NY), Carnegie Mellon University (Pittsburgh, PA) and University of Maryland (Baltimore, MD). The lead Primary Investigator for the Baltimore Supersite, John Ondov graciously allowed me to participate in three sampling intensives during the spring, summer and winter of 2002-2003. The objectives of the Baltimore Supersite were to; i) provide an extensive data suited for the current advanced factor analysis models, ii) provide information of the health effects of particles from different sources, iii) provide significant amount particulate matter that has been characterized for chemical species, iv) provide information on the sources and composition of organic aerosol in the Baltimore region, v) provide support for epidemiology studies related to particulate matter sources.

A variety of instrumentation was deployed at the Baltimore Supersite. A real-time single particle mass spectrometer (RSMS III) using laser ablation time-of-flight mass spectrometry captured periods where a burst of pure nitrate particles were observed in the 50-90 nm range attributed to condensation of ammonium nitrate (Tolocka *et al.*, 2004). Inorganic analysis of individual particles was also performed using this instrument (Lake *et al.*, 2004). Harrison *et al.* (2004) evaluated the compatibility of 10 min and 24 hr nitrate measurements. The size and formation process of nitrate was found to be dependent on the time-of-day (Park *et al.*, 2005). Advances in multivariate receptor models have been employed. Bulk particle parameters and elements measured on different timescales deconvoluted 9 sources of $PM_{2.5}$ to the Baltimore Atmosphere (Ogulie *et al.*, 2005). Size related compositional data has also been analyzed using Partial least Squares (PLS) and Positive Matrix

Factorization determining the source of PM2.5 to the Baltimore area (Ogulie *et al.*, 2006).

Previous characterizations of the ambient organic aerosol fraction in the Baltimore atmosphere are limited to select compound classes. Polycyclic aromatic hydrocarbons (PAHs) have been extensively studied by Offenberg and Baker (1999), Dachs and Eisenriech (2000) and Bamford *et al.* (1999). Bamford and Baker (2003) measured the winter and summer nitro-substituted PAHs in Baltimore and a suburban location approximately midway between Baltimore and Washington, DC. Elevated secondary formation of 2-nitrofluoranthene was observed during the summer and the dominant formation pathway was via the OH radical. The sources of PAHs to the Baltimore area as determined by Larsen and Baker (2003) consisted of gasoline and diesel combustion, wood combustion, oil and coal combustion.

The need for a better understanding of the organic fraction of Baltimore aerosol is outlined by the objectives of the Baltimore Supersite Program. The multitude of meteorological and air quality measurements at the site provide an excellent resource to evaluate changes in the organic composition with respect to sources and chemical processing. The coordinated studies at the Baltimore Supersite created an extensive dataset of ambient atmospheric gas and particle species that will be explored for years to come.

The overall goal of my dissertation was to improve our understanding of particulate organic matter in the atmosphere by developing more sensitive analytical methods to measure individual organic species to facilitate our understanding of the

sources and behavior of alkanes, hopanes, PAHs and NPAHs to the Baltimore atmosphere. Specifically, the main objectives of my thesis were to:

1. Develop a large-volume gas chromatography mass spectrometry method to determine the concentrations of PAHs and NPAHs on hourly timescales.

2. Characterize the seasonal variation in the PAH, NPAH, alkane and hopane concentrations in the Baltimore atmosphere.

3. Measure the first diurnal size distributions of NPAHs

4. Determine the sources of the carbonaceous aerosol to the Baltimore atmosphere using the multivariate receptor model Positive Matrix Factorization

1.3 Strategy

Three intensives were conducted at the Baltimore Supersite in the spring, summer and winter of 2002-2003. With the assistance from David Harrison and Patrick Pancras (University of Maryland Department of Chemistry and Biochemistry), I placed 2 Anderson Hi-Volume samplers on the roof of the sampling trailer. A Berner low-pressure impactor was acquired by Raymond Hoff of the University of Maryland Baltimore County from Environment Canada and placed on the roof during the spring and summer of 2002. The Maryland Department of the Environment (MDE) was an integral partner at the Baltimore Supersite, providing analysis of gases and VOCs. Walt Cooney (MDE) provided an automated VOC canister system that was deployed during the same times as the Hi-Volume samplers. These canisters were then analyzed for toxics (EPA Method TO-15) at the MDE laboratory in Baltimore, MD.

An Agilent 6890/5973 gas chromatograph/mass spectrometer (GC/MS) equipped with a Programmed Temperature Vaporization (PTV) injection port was employed to develop a highly sensitive method for determining PAHs and NPAHs. This instrument allowed for a larger fraction sample extract to be loaded onto the analytical system. Two methods were developed for PAHs and NPAHs, respectively, and evaluated using surrogate particulate matter, SRM 1649 and 1650, generously supplied by Dianne Poster, Michele Shantz and Steven Wise from the National Institutes of Standards and Technology.

This sensitive method was then employed to determine the first size resolved concentrations of NPAHs. The increased sensitivity of the method improved the temporal resolution of size resolved NPAH analysis from 42 days (Kawnaka *et al.*, 2004) to 12 hrs. Particle and gas phase samples were collected during the spring summer and winter 2002-2003 with the assistance of Travis Burrell (University of Maryland Center for Environmental Science). I was then able to measure 6 hr NPAH concentrations in the Baltimore, MD atmosphere previously limited to 24 hrs (Bamford and Baker, 2003).

The source contributions of PAHs, NPAHs, alkanes, and hopanes were determined using a new Windows-based version of Positive Matrix Factorization (PMF) and Principal Components Analysis/Multiple Linear Regression, where technical advice from Randy Larsen (St. Mary's College of Maryland) was essential. Philip Hopke (Clarkson University) supplied the authentication key allowing a comparison this version of PMF and the widely used PMF2. Air quality data, supplied by Patrick Pancras and John Ondov (University of Maryland, College Park),

was essential for discriminating possible sources of organics to the Baltimore

atmosphere. The total carbon and PM$_{2.5}$ measurements obtained was then used to

determine the source contribution of these parameters identified using PMF.

Chapter 2

Improved GC/MS Methods for Measuring Hourly PAH and Nitro-PAH Concentrations in Urban Particulate Matter

2.1 Introduction

Understanding the evolving chemical composition of atmospheric aerosol is critical to accurately assessing aerosol sources and their potential health effects. Polycyclic aromatic hydrocarbons (PAHs) and nitro-substituted polycyclic aromatic hydrocarbons (NPAHs) are two classes of compounds implicated in the mutagenicity of ambient air (Arey *et al.* 1988, IARC 1989, Gupta *et al.*, 1996). Formed from incomplete combustion, PAH profiles have also been utilized in source apportionment studies in urban areas (Venkataraman and Friedlander 1994, Harrison *et al.*, 1996, Simcik *et al.*, 1999, Larsen and Baker, 2003). NPAHs are either directly emitted from combustion sources (i.e. diesel, Paputa-Peck *et al.*, 1983) or formed through the oxidation of parent PAHs in the atmosphere (Arey, 1998 and references therein). NPAH isomers are source specific (combustion or oxidation) and therefore NPAH fingerprints may be useful to determine primary and secondary aerosol sources (Cecinato *et al.*, 1999).

The observed atmospheric distributions (gas/particle and isomeric) of PAHs and NPAHs depend strongly on the temporal scale of the measurement. Measured PAH and NPAH profiles at a receptor site result from the integration of many time variable sources. These profiles are influenced by changing wind direction, oxidant

concentration and source emission patterns (*i.e.* traffic) during the sampling period. The phase distribution (particle vs. gas) of these semi-volatile organics is governed by vapor pressure and hence temperature (Pankow, 1994). Therefore, changes in temperature during a sampling period may alter the observed gas and particle distributions during extended sampling times (Yamasaki *et al.*, 1982, Mader and Pankow, 2000). The collected particulate matter can be exposed to elevated levels of oxidants (ozone), concurrently sampled, degrading more labile constituents (Schauer *et al.*, 2003). Therefore, minimizing these sampling errors requires measuring PAH and NPAH concentrations on timescales relevant to temperature, wind direction and source type changes while minimizing exposure to oxidants.

In the literature PAH and NPAH samples are typically collected using a filter/polyurethane plug (PUF) configuration (EPA Method 625**,** Yamasaki *et al.*, 1982**,** Keller and Bidleman, 1984**,** Offenberg and Baker 1999, Marino *et al.*, 2000, Feildberg *et al,*. 2001, Bamford and Baker, 2003). Potential artifacts associated with this technique have been discussed in detail by Turpin *et al.* (2000). Arguably, the most debated artifact of the filter/PUF sampler is the magnitude and correction for ad/absorption of organic gases to the filter media (*i.e.* quartz fiber, glass fiber or Teflon). Others have employed a denuder/filter technique for PAHs (Gundel *et al.*, 1995**,** Kavouras *et al.* 1999, Peters *et al.*, 2000, Possanzini *et al.*, 2004) and NPAHs (Wilson *et al.*, 1995, Fan *et al.*, 1995) to minimize this artifact by scavenging gas phase organics via an annular denuder prior to the filter. This technique disturbs the gas/particle equilibrium during sampling, perhaps initiating particulate matter volatilization losses. These are collected on a second vapor sorbent after the filter. In

addition, entrainment of small particles in the denuder has been observed (Volckens and Leith, 2003), further skewing the measured distribution.

Sampling times for the aforementioned studies, as well as, the standard for monitoring campaigns (Integrated Atmospheric Deposition Network, IADN, Gatz *et al.*, 1994, Sweet *et al.*, 1996) are usually 24 hrs. To our knowledge, the greatest temporal resolution using standard analytical techniques for PAHs was 4 hours in Baltimore, MD (Dachs and Eisenreich, 2000) and Southern California (Fraser *et al.*, 1998) using hi-volume samplers operated at ~0.5 and 0.19 m^3/min, respectively. Dachs and Eisenreich (2000) evaluated the soot contribution to the PAH gas/particle partitioning coefficient (K_p) by modeling the evolving K_p over multiple days. Fraser *et al.* (1998) observed PAH degradation and enhanced NPAH formation downwind during a photochemical smog episode.

In Southern California Reisen *et al.* (2003) analyzed NPAHs by compositing 3.5 hr segments over 5 days using a hi-volume filter/PUF sampler (~0.6 m^3/min). Feildberg *et al.* (2001) reported selected 12 hr NPAH concentrations in Denmark using flow rates >1 m^3/min. The flow rates employed in these studies are on the upper edge of commercially available instruments (See Watson and Chow, 1992 for review). Typical denuder/filter designs have a much lower flow rate (usually 0.1 m^3/min or less, Gundel *et al.* 1995, Volkens and Leith, 2003, URG, Chapel Hill, NC).

The temporal resolution of these compounds in ambient air is limited by the detection limits of current analytical techniques. Either collecting more sample or increasing the analytical sensitivity is required to increase the detectability of PAHs and NPAHs in ambient air. Greater sampling flow rates and the corresponding larger

pressure drops may increase volatilization losses from the sampling substrate. In addition, the higher sample volumes and longer sampling times may increase the exposure of PAHs and NPAHs to oxidants. Increasing collection surface area to increase sampler flow rates without additional pressure drops may increase both gas ab/adsorption and the potential for greater matrix contamination. Therefore increasing sample volumes using the current sampling methodology is not a promising approach to improve PAH and NPAH detection.

While numerous sensitive high-performance liquid chromatography (HPLC) methods have been published for the determination of PAHs and NPAHs (MacCrehan *et al.*, 1988, Li and Westerholm, 1994, Lee, 1995, Bonfanti *et al.*, 1996), gas chromatography/mass spectrometry (GC/MS) is more commonly used due to greater separation efficiency of complex non-polar analytes. For GC analysis the final volume of the organic extracts is usually >100μL. Using the conventional inlets (hot splitless and cool on-column) only 2μL or less of extract is applied to the column. For semi-volatile compounds (i.e. PAHs and NPAHs) concentrating extracts below this volume may increase losses of the more volatile components. Therefore 98% of the analyte mass extracted is not introduced into the chromatographic system. With the advent of large volume injection (Vogt *et al.*, 1979), the widely used hot splitless injection technique can be modified to load a greater portion of an extract (from 2μL to 100s of μL). The use of large volume injection (specifically programmed temperature vaporization-large volume injection) has been increasing (see Engewald *et al.* 1999 for review). The commercial availability of the Programmed Temperature Vaporization (PTV) inlet has made this injector attractive for trace level analysis. The

performance of other large volume techniques, such as cool on-column injection with solvent venting (SVE-COC) may be quickly degraded by system fouling from complex sample extracts (see Grob and Tiedemann 1996 for review). Like the splitless injector, the PTV incorporates a glass sleeve that traps nonvolatile contaminants, keeping them from degrading the capillary column. Zrostlkova *et al.* (2001) reported greater chromatographic stability (peak shape and compound response) per number of plant extracts analyzed for a suite of pesticides using the PTV in solvent vent mode as compared to a pulsed splitless and cool on-column configuration.

The PTV can be configured to inject large volumes of liquid depending on the volume of the inlet liner (usually <250μL) or in sequential injections of smaller volumes. During the injection time, the cool inlet sleeve is purged to remove solvent. The initial injector temperature is set below the carrier solvent boiling point and optimized to retain (cold trapping) the compounds of interest. The solvent is then evacuated through the open split vent. Once the solvent is removed, the split valve is closed. Then the inlet is rapidly heated (up to 700°C/min) to a final temperature, desorbing analytes to the column. Typical conditions for optimizing the PTV injection parameters are outlined in the literature (Mol *et al.,* 1996, Engewald *et al.* 1999, Grob and Biedermann 1996).

Previously, this technique has been used to quantify numerous classes of compounds in a variety of matrices (See Teske and Engewald, 2002 for review). Norlock *et al.* (2002) evaluated the PTV for PAH analysis in air and sediment samples. Although this work was extensive using standards, sediment and ambient air

collected in Chicago, IL, matrix effects were not evaluated. In this study, we present optimized methods for PAH and NPAH quantification in ambient aerosol. These methods outline an efficient way to increase the analytical sensitivity and temporal resolution by utilizing a greater percentage of the extract (mass of analyte extracted) through large volume injection. Matrix effects are evaluated using Standard Reference Materials (National Institutes of Standards and Technology, Gaithersburg, MD) and an example of the benefits of increased temporal resolution is presented in our analysis of the diurnal size distribution of NPAHs in the Baltimore, MD atmosphere. The goal of this study is to develop an analytical method capable of pg/m^3 detection limits and a precision of 20% for measuring PAHs and NPAHs in ambient aerosol samples with one hour resolution.

2.2 Materials and Methods

2.2.1 *Standards*

The 42 PAHs used in this study were supplied by Ultra Scientific (North Kingstown, RI). Two deuterium labeled PAH solutions, internal and surrogate standards, were also made using neat standards from Ultra Scientific in hexane. Nitro-PAH standards were acquired from AccuStandard (New Haven, CT) in concentrated solutions (~100mg/mL in toluene) except for 2-nitrofluoranthene and 2-nitropyrene which were supplied by Chiron (Trondheim, Norway) and Chemsyn Science Laboratories (Lenexa, KS), respectively. The internal standard solution components (3-nitrofluoranthene-d_9, 6-nitrochrysene-d_{11}, 2-nitrofluorene-d_9 and 5-nitroacenaphthene-d_9) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). The surrogate solution components were acquired from C/D/N

Isotopes (Pointe-Claire, Quebec, Canada, nitronaphthalene-d_7) and Cambridge Isotope Laboratories, Inc. (9-nitroanthracene-d_9 and 1-nitropyrene-d_9).

2.2.2 *Standard Reference Materials and Ambient Particulate Matter*

Size resolved aerosol was collected at the Baltimore PM2.5 Supersite during April 2002. The Berner low-pressure impactor collected 5 particle size cuts (0.04-0.14, 0.14-0.49, 0.49-1.7, 1.7-6, 6-20μm) at 80Lpm. Non-greased foils ashed at 450°C for 4 hr and tared to 0.1μg prior to deployment. The particle laden foils were prepared in the same manner as the SRM outlined below.

Urban Dust and Diesel Particulate Matter Standard Reference Materials (SRM 1649a and SRM 1650a, respectively) were obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD). Microgram quantities were transferred to 20mL test tubes via tared foil (pre-rinsed with DCM) sonicated for 30 min in dichloromethane (DCM) and stored at -20°C for 48 hrs. Prior to adding DCM, PAH (naphthalene-d_8, fluorene-d_8, fluoranthene-d_{10}, perylene-d_{12}) and NPAH (1-nitronaphthalene-d_7, 9-nitroanthracene-d_9, and 1-nitropyrene-d_9) surrogates were added.

The PAH extracts were filtered, concentrated under N_2 (Turbovap II, Zymark, Hopkinton, MA) to ~200μL and analyzed. PAH internal standard containing acenaphthene-d_{10}, phenanthrene-d_{10}, benz[*a*]anthracene-d_{12}, benzo[*a*]pyrene-d_{12} and benzo[*g,h,i*]perylene-d_{12} were added to each sample just prior to analysis. Further purification was required for NPAHs using additional cleanup steps previously reported (Bamford *et al.*, 2003) with minor modifications. After PAH analysis, each

extract was eluted through an aminopropyl SPE cartridge (Sep-Pak, Waters, Milford, MA) using 40mL of a 20% DCM/hexane solution, concentrated under N_2 and exchanged to hexane. Normal phase LC was then employed for the final clean-up step using a 5μm, 9.6mm x 30cm Chromegabond amino/cyano column (ES Industries, West Berlin, NJ) using 20% DCM/hexane as the mobile phase. After concentration, NPAH internal standards were added just prior to analysis.

2.2.3   Instrumental Parameters

An Agilent (Palo Alto, CA) 6890/5973 gas chromatograph/mass spectrometer equipped with a standard split/splitless and a Programmed Temperature Vaporization (PTV, Gerstel, Mülheim an der Ruhr, Germany) inlet was employed in the analysis. The instrument was configured for electron ionization (EI) for PAH analysis with a source temperature of 230°C. Negative chemical ionization (NCI) using methane ionization gas (40ml/min) and a source temperature of 200°C was employed for NPAHs. The instrument was tuned to factory specifications and selective ion monitoring was used in both MS configurations. Molecular ions were used in PAH and NPAH quantification. A 0.25mm x 30m x 0.25μm DB-5ms (Agilent Technologies, Palo Alto, CA) capillary column was used in the PAH quantification. The initial oven temperature (40°C) was ramped to 280°C at 10°C/min, then ramped at 5°C/min to 310°C and held for 10 min. NPAHs were resolved using a 0.25mm x 30m x 0.25μm DB-17ms capillary column. The oven temperature program for NPAH analysis was 40°C (held 1.7 min) ramped to 150°C at 20°C/min, held for 10min, then

to 220°C at 10°C/min, held for 10 min and finally ramped to 310°C and held for 15 min.

For PAHs the hot splitless injector was configured for 2μL injections at 250°C. The oven was held at 40°C for 1.0 min. The PTV injector was configured for 10 injections of 5μL at 45°C held for 1.2 min then ramped to 250°C at 600°C/min holding the oven at 40°C for 1.6 min. During the injection process the inlet was held at 5psi with a purge flow of 50mL/min. For NPAH analysis the PTV was configured to perform ten 5μL injections venting at 100mL/min at 2 psi for 1.10 min. At 1.2 min the PTV was ramped at 600°C/min to 280°C.

2.3 Results

2.3.1   Reproducibility

PAHs

The reproducibility of the split/splitless and PTV injectors are shown in Table 2.1. For each injector, a standard containing 43 PAHs and 9 perdeuterated PAHs (5 internal standards and 4 surrogates), was used to test the reproducibility of each injector (N=7). A similar mass (~100pg) of each analyte was introduced into the chromatographic system. The mean percent relative standard deviation (%RSD) after normalizing the PAHs to their respective internal standards was 2.6% ranging 0.6 to 9.5% (fluorene-d_{10} and 3-methylcholanthrene, respectively). Using the PTV, naphthalene-d_8 exhibited the largest variability (13%) while the %RSD for acenaphthene was the lowest (0.4%). The variability of the low molecular weight

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Table 2.1 Injector precision; 2µL hot splitless (SL) and 50µL PTV in solvent vent mode.

	PAHs[a]	SL %RSD[c] norm	PTV %RSD norm		NPAHs[b]	PTV %RSD norm
I.S.[d]	acenaphthene-d_{10}			I.S.	5-nitroacenaphthene-d_9	
Surr[e]	naphthalene-d_8	3.5	13		1-nitronaphthalene	4.2
	naphthalene	3.2	11		2-nitronaphthalene	6.5
	Azulene	2.2	7.0		2-nitrobiphenyl	2.2
	2-methylnaphthalene	1.6	4.2		3-nitrobiphenyl	2.3
	1-methylnaphthalene	1.8	7.3		4-nitrobiphenyl	3.3
	acenapthylene	1.0	4.9		1,3-dinitronaphthalene	3.8
	Biphenyl	1.5	2.1		1,5-dinitronaphthalene	3.1
	Acenaphthene	0.9	0.4		5-nitroacenapthene	2.2
I.S.	phenanthrene-d_{10}			I.S.	2-nitrofluorene-d_9	
Surr	fluorene-d_{10}	0.6	3.3		2-nitrofluorene	1.3
	Fluorine	2.4	5.0		2,2'-dinitrobiphenyl	3.1
	phenanthrene	0.9	0.4		9-nitroanthracene	1.3
	anthracene	3.1	1.8		2-nitroanthracene	1.3
	1-methylfluorene	2.4	4.1		9-nitrophenanthrene	1.7
	4,5-methylenephenanthrene	3.0	2.0		3-nitrophenanthrene	4.7
	2-methylphenanthrene	2.4	2.2		4-nitrophenanthrene	1.5
	2-methylanthracene	5.9	3.9			
	1-methylanthracene	6.4	5.3	I.S.	3-nitrofluoranthene-d_9	
	1-methylphenanthrene	4.1	3.4		2-nitrofluoranthene	1.4
	9-methylanthracene	7.0	5.4		3-nitrofluoranthene	1.6
					1-nitropyrene	1.4
I.S.	benz[a]anthracene-d_{12}				2-nitropyrene	2.1
Surr	fluoranthene-d_{10}	4.4	10.2		2,7-dinitrofluorene	4.7
	Fluoranthene	5.5	11			
	Pyrene	4.4	9.8	I.S.	6-nitrochysene-d_{11}	
	9,10-dimethylanthracene	4.9	8.2		7-nitro[a]anthracene	1.4
	benzo[a]fluorene	3.7	7.6		6-nitrochysene	0.8
	benzo[b]fluorene	4.2	7.8		1,3-dinitropyrene	2.4
	benz[a]anthracene	0.7	1.8		1,6-dinitropyrene	1.4
	chrysene+triphenylene	4.5	9.2		9,10-dinitroanthracene	4.7
	napthacene	2.2	10		1,8-dinitropyrene	3.7
	3-methylcholanthrene	9.5	7.7		6-nitrobenzo[a]pyrene	6.5
					1-nitrobenzo[e]pyrene	1.5
I.S.	benzo[a]pyrene-d_{12}				3-nitrobenzo[e]pyrene	1.8
Surr	perylene-d_{12}	1.2	7.8		1-nitro- and 3-nitro-	
	benzo[b]fluoranthene	1.5	5.6		benzo[a]pyrene	5.5
	benzo[k]fluoranthene	4.1	5.2			
	benzo[a]pyrene	2.4	4.0			
	benzo[e]pyrene	3.7	3.3			
	Perylene	1.1	2.8			
	dimethylbenz[a]anthracene	2.4	6.1			
I.S.	benzo[g,h,i]perylene-d_{12}					
	indeno[1,2,3-c,d]pyrene	2.2	6.0			
	benzo[g,h,i]perylene	1.6	2.3			
	anthanthrene	2.3	6.8			
	dibenz[a,h+a,c]anthracene	2.2	4.6			
	Coronene	3.8	8.1			

a.100pg per analyte b.1000pg per analyte c. Relative standard deviation of internal standard normalized responses d. Internal standard e. Surrogate standard

PAHs were higher using the PTV whereas the largest %RSD using the splitless injector was found for the high molecular weight PAHs. Although internal standard normalization increased precision, significant variability was found for naphthalene-d_8 using the PTV. Due to the solvent venting during multiple injections, compounds with elevated vapor pressures may purge with the carrier solvent (Mol *et al.*, 1996**,** Bosboom *et al.*, 1996), resulting in greater variability for low molecular weight compounds. The elevated precision for internal standard normalized acenapthene is due to the use of acenaphthene-d_{10} as the internal standard for that window.

NPAHs

Recent studies utilize cool on-column injection for GC analysis of NPAHs (Bamford *et al.* 2003, Bamford and Baker, 2003) due to degradation artifacts using hot splitless injections. However, column degradation and contamination associated with loading large volumes of sample matrix limit the use of cool on-column injection for this application. For the NPAH evaluation, a standard solution containing 30 NPAHs and 4 perdeuterated NPAHs (~20 ng/mL) was employed. The injection volume was 50μL, introducing ~1ng of each NPAH into the chromatographic system. The %RSDs for NPAHs were similar to and often better than those of the PAHs (Table 2.1). The geometric mean %RSD for the normalized area counts was 2.4 %, ranging 0.8% (6-nitrochrysene) to 6.5% (2-nitronaphthalene and 6-nitrobenzo[a]pyrene), with no apparent trend with vapor pressure. The mass used in this analysis is approximately 1000 fold greater than the method detection

limits presented below. Therefore, the precision reported here is applicable to NPAH

analysis where concentrations are well above reporting limits.

2.3.2   Mass Transfer Efficiency

PAHs

The major advantage to the PTV is the ability to introduce a larger volume

(larger fraction) of sample onto the column, thus increasing sensitivity. We evaluated

the relative mass transfer efficiency of each PAHs from the injection port to the

column using the hot splitless and the PTV in solvent vent mode (Figure 2.1). If both

injectors transfer analytes equally, the ratio of the mean detector response from

injections of equal masses using the PTV and splitless (PTV/SL response) injectors

should equal one. The lighter PAHs (naphthalene to acenapthene) have ratios less

than one with naphthalene exhibiting a response ratio of 0.5. The response ratios are

greater than 1 for mid to high molecular weight PAHs (166 to 300 amu, fluorene and

coronene, respectively), with an apparent increase in the response ratio with

decreasing vapor pressure from fluorene to benzo[*b*]fluorene. For PAHs larger than

fluorene the injector response ratio (PTV/SL) is consistently 4 to 5.

The lighter PAHs naphthalene to acenaphthene (128 and 154, respectively)

are apparently better transferred using the splitless injector. The loss of low molecular

weight PAHs in the PTV is due to co-venting the more volatile PAHs with the solvent

(Mol *et al.*, 1996**,** Bosboom *et al.*, 1996). This also corresponds to the lower

precision observed for the low molecular weight PAHs. A splitless or possibly a large
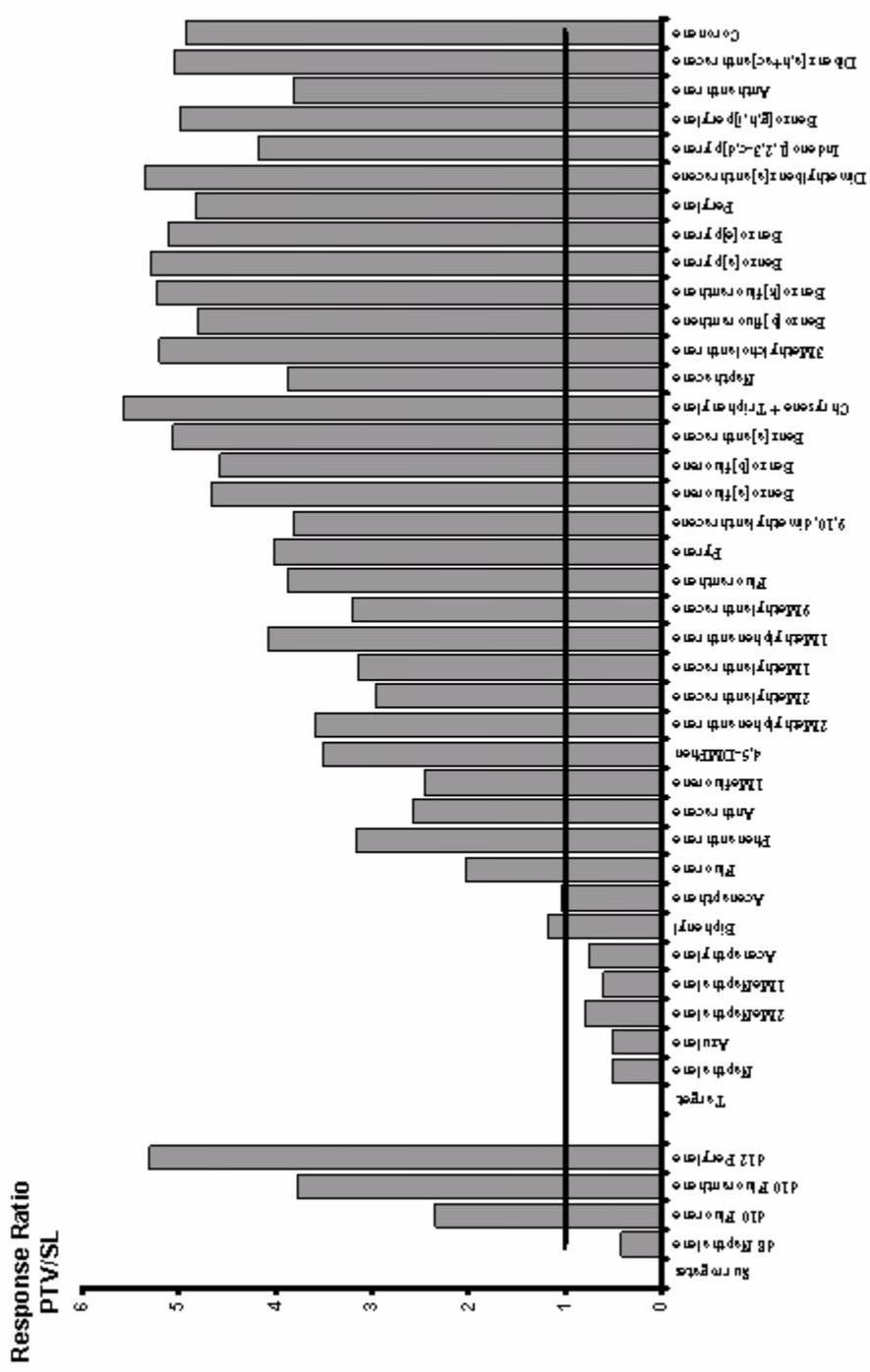
Figure 2.1 PAH 100pg response comparison; PTV (50µL injected), hot splitless (SL, 2µL injected).

volume cool on-column injection may remedy co-venting losses of lighter PAHs
(Bosboom *et al.*, 1996). PTV parameters such as the initial temperature and carrier
 (keeper) solvent may also be altered to compensate for volatiles losses (Mol *et al.*,
1996).

Particulate matter contains minimal concentrations of the lightest PAHs. The
increase in sensitivity using the PTV for PAHs with 4 rings or more
(benz[*a*]anthracene to coronene) can not be accounted for by the variability in
replicate runs. One explanation is the smaller volume of the PTV multi-baffled liner
compared to the single gooseneck splitless injector liner. The smaller liner volume
results in large carrier gas velocities. The smaller liner volume results in larger carrier
gas velocities, less active sites on the liner surface and less exposure to elevated
temperatures that may degrade analytes (Zrotlikova *et al.*, 2001), thus better transfer
of PAH mass to the chromatographic column. This problem may be easily solved
using a different liner in the splitless injector with a volume comparable to the PTV.
But possible degradation of high molecular weight PAHs may also be attributed to
thermal degradation in the hot splitless injector as observed for NPAHs (see below).

NPAHs

To evaluate the mass transfer efficiency of NPAHs using the PTV, 3 PTV
inlet heating configurations were tested; hot splitless (280°C), temperature
programmed splitless (initial temperature of 40°C, ramped 600°C/min to 280°C in
splitless mode), and solvent vent (initial temperature of 40°C, held 1.0 min, then 600
°C/min to 280°C at 2psi with a purge flow of 100mL/min). The initial oven time was

held for 1.06 min at 40°C for each injector configuration. A 2 μL injection volume was used for each mode to eliminate any solvent effects in the hot and programmed temperature splitless modes. The response for the hot splitless mode is consistently lower than the temperature programmed modes, indicating thermal degradation of NPAHs in the injection port (Figure 2.2). The dinitro-substituted PAHs are not detectable in the constant temperature mode (10 ng injected). This illustrates the degradation of more labile NPAHs in a constant temperature splitless injector. The programmed temperature solvent vent and splitless mode responses agree well. In the solvent vent and temperature programmed splitless modes, a similar replicate precision was observed for all NPAHs with no apparent co-venting of the lighter NPAHs (mononitronaphthalenes) in the solvent vent mode.

As described above, the PTV uses multiple injections to load larger sample volumes to the inlet while venting the solvent. Therefore to test the NPAH trapping efficiency, or losses of analytes, during the multiple injections the PTV was configured to inject 2 and 10μL (2 times 5μL each) of the NPAH standard containing ~10ng of each analyte. The area count ratio 10μL/2μL injections (Figure 2.3) exhibited no losses of NPAHs with respect to vent time. In fact, a greater relative sensitivity (10μL area counts/ 2μL area counts > 5) was achieved with the increased mass loadings using the 10μL injection. Therefore we conclude that there are no significant losses of NPAHs during the sequential injections.

2.3.3   *Evaluation of Method*

The advantages of using the PTV in solvent vent mode for PAHs and NPAH are two-fold. In addition to loading a larger fraction of the extract to the

Figure 2.2 NPAH mean area counts for solvent vent, hot splitless (SLC) and temperature programmed splitless (SLT).
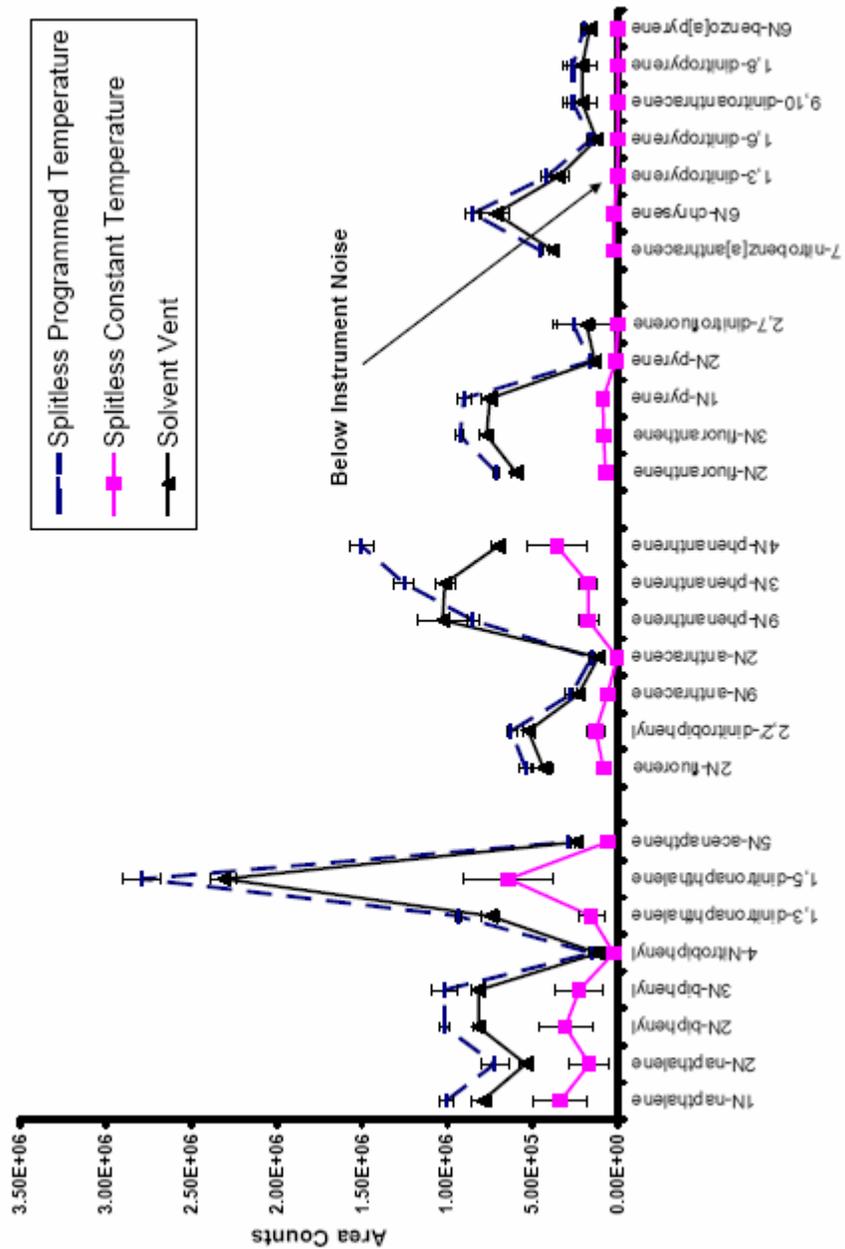
Figure 2.3 PTV solvent vent mode NPAH trapping efficiency for 2 and 10μL injections.
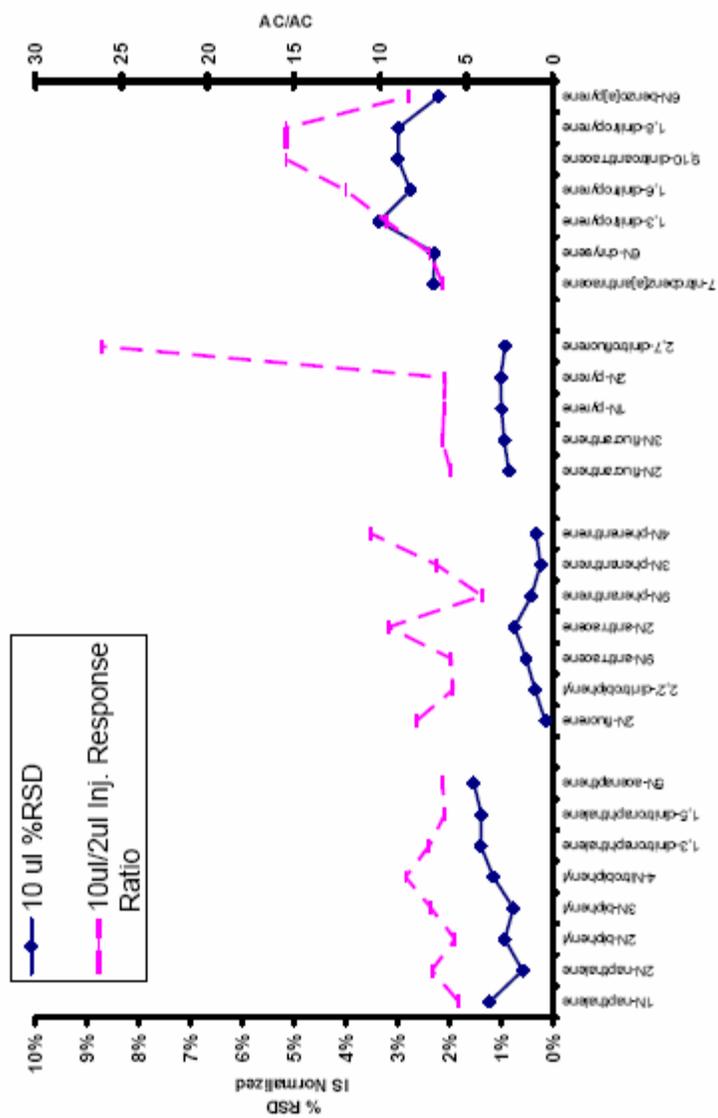
chromatographic system, the PTV in solvent vent mode apparently allows for a more efficient transfer of analyte mass to the GC as compared to the conventional hot splitless configuration. To test the applicability of this method for atmospheric particulate matter, a series of Standard Reference Materials (SRMs) were quantified for PAHs and NPAHs. Microgram quantities of Diesel Particulate Matter and Urban Dust (SRM 1650 and 1649a, respectively) were analyzed using standard extraction and purification techniques described above. Using these two SRMs as surrogate matrices, we can assess the potential use of the PTV to quantify PAHs and NPAHs in ambient particulate matter on hourly timescales or better.

PAHs

Triplicate analysis of SRM 1649 and 1650 (~80μg and 30μg, respectively) were performed (Table 2.2). The geometric mean %RSD of the analysis was 22% and 6.5% for 1649a and 1650, respectively. The Urban Dust SRM PAH concentrations (Certificate of Analysis 2001) were consistent with the certified values with the exception of the lightest PAHs quantified in this study. Fluoranthene, pyrene, benz[*a*]anthracene, benzo[*b*]- and benzo[*k*]fluoranthene, benzo[*e*]pyrene, perylene, indeno[1,2,3-*c,d*]pyrene, benzo[*g,h,i*]perylene were within 1 to 2 standard deviations (from this study) of the certified values. Phenanthrene, anthracene, 2-methylphenanthrene, 1-methylphenanthrene and fluorene were consistently 5 to 10-fold above reported values, of which the latter three are not certified concentrations. All of these compounds were quantified using the same internal standard (phenanthrene-d_{10}), suggesting possible matrix interference.

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Table 2.2 PAH SRM comparison using the PTV

	1650 certified	1650[a] this study	1649 certified	1649[b] this study
fluorene			*0.23(0.05)	8.3(1.3)
phenanthrene	68.4(8.5)	120[c](24)[d]	4.14(0.37)	20(4.0)
anthracene	*1.5(0.06)	11(3.1)	0.432(0.082)	2.4(0.54)
2-methylphenanthrene	*70(4)	108(17)	*0.73(0.12)	11(2.5)
1-methylphenanthrene	*34(7)	48(10)	*0.37(0.04)	4.3(0.7)
fluoranthene	49.9(2.7)	48(16)	6.45(0.18)	5.6(0.7)
pyrene	47.5(2.7)	46(2.9)	5.29(0.25)	5.3(1.2)
benz[a]anthracene	6.33(0.77)	7.3(0.3)	2.208(0.073)	2.0(0.5)
chrysene+triphenylene	26	15(0.8)	4.406	2.4(0.4)
benzo[b]fluoranthene	8.81(0.60)	7.0(0.2)	6.45(0.64)	5.0(0.7)
benzo[k]fluoranthene	2.64(0.31)	4.1(0.4)	1.913(0.031)	2.3(0.5)
benzo[a]pyrene	1.33(0.35)	3.6(0.04)	2.509(0.087)	1.7(0.3)
benzo[e]pyrene	7.44(0.53)	42(5.5)	3.09(0.19)	6.6(2.2)
perylene	0.16(0.04)	2.8(0.6)	0.646(0.075)	0.54(0.3)
indeno[1,2,3-c,d]pyrene	5.62(0.53)	6.8(0.2)	3.18(0.72)	4.8(0.9)
benzo[g,h,i]perylene	6.5(0.94)	5.0(0.2)	4.01(0.91)	3.7(0.6)
coronene	*2(0.1)	1.8(0.3)	NR[e]	3.4(0.2)

a.Approximately 80µg extracted and analyzed, b. Approximately 30µg extracted and analyzed, c. Geometric mean µg/g (N=3), d. 1 Standard deviation
e.Not reported, * Not certified reference value

The Diesel Particulate Matter SRM (Certificate of Analysis 2000) results for PAHs were more consistent, exhibiting a geometric mean %RSD of 6.5%. Similar to SRM 1649, the most volatile PAHs (phenanthrene, anthracene, 1-methylphenanthrene and 2-methylphenanthene) were 1.4 to 7.6-fold above reported values, with phenanthrene as the only certified concentration. Fluoranthene, pyrene, benz[*a*]anthracene, indeno[1,2,3-*cd*]pyrene, benzo[*g,h,i*]perylene and coronene were all within 1 to 2 standard deviations of reported values. The PAHs with molecular weight of 252 were greater than two standard deviations above reported values. Benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and benzo[a]pyrene were 1.2, 1.5 and 2.7 fold above certified values. Benzo[e]pyrene and perylene were 5 and 17 fold, respectively, above certified values. For the majority of PAHs the certification process of this SRM employs GC/MS and liquid chromatography with fluorescence detection (LC-FL). The latter 2 certified values did not include a LC-FL method. Therefore, injection port related matrix affects may be causing the greater discrepancy in these 2 compounds which are more pronounced in the Diesel SRM than the Urban Dust SRM.

The SRM values from this study agreed well with certified values for the majority of PAHs analyzed. The explanation for the elevated recoveries of the lightest PAHs in SRM 1649 is unclear at this time. Therefore the current method is not recommended for the lightest PAHs in ambient particulate matter.

NPAHs

NPAH concentrations in the SRMs are orders of magnitude lower than PAHs (Bamford *et al.* 2003). To ensure the detectability of these compounds while retaining low particle mass, larger SRM masses (compared to the PAH analysis) were extracted (500μg and 200μg, respectively). These masses are considerably less than the 50 to 100mg extracted by Bamford *et al.* (2003) analyzed using cool on-column (2μL) injection. The geometric mean of the %RSDs for the triplicate analysis was 9.8% and 14% for 1650 and 1649, respectively. Poor reproducibility was found for 2-nitrofluorene (95 %RSD) due to low concentration in SRM 1649a (very close to the analytical detection limits). This high uncertainty is consistent with the below detection values reported by Bamford *et al.* (2003). Unlike the PAH results, there was no vapor pressure specific trend in NPAH recoveries. This is most likely due to the lower vapor pressures of nitro-substituted PAHs relative to parent the PAHs. With the exception of 9-nitroanthracene, our results for both SRMs were consistently below values previously reported (Bamford *et al.* 2003). The lower concentrations found in this study may be due to matrix-induced thermal degradation of the NPAHs during the thermal desorption step or to incomplete extraction. Values previously reported below detection limits were quantifiable using this method (2-nitrobiphenyl and 2-nitrofluorene for 1649 and 1-nitrobenzo[*e*]pyrene for 1650).

The dinitropyrenes were not detected in the SRMs (Table 2.3). During our analysis, we found these compounds to be very sensitive to matrix-induced degradation in the inlet. The relative response of the dinitropyrenes decreased dramatically (>2-fold) in the standard solution quantified after the above mentioned

Table 2.3 NPAH SRM comparison using PTV

	1650 Bamford *et al.*, 2003b	1650[a] This study	1649 Bamford et al	1649[b] This study
1-nitronaphthalene	86.4	56[c](21)[d]	6.8	8.4(1.6)
2-nitronaphthalene	238	116(2.9)	10	12(1.7)
2-nitrobiphenyl	15.3	6.8(0.6)	<5	2.5(1.4)
3-nitrobiphenyl	58.1	35(6.0)	3.6	4.7(1.0)
4-nitrobiphenyl		78(16)		5.5(3.5)
1,3-dinitronaphthalene				
1,5-dinitronaphthalene				
5-nitroacenapthene	37	46(5.5)	3.1	4.2(3.1)
2-nitrofluorene	46.2	44(3.3)	<2	2.6(3.4)
2,2'-dinitrobiphenyl				
9-nitroanthracene	6080	13000(350)	35.9	70(11)
2-nitroanthracene		1400(50)		14(2.8)
9-nitrophenanthrene	510	320(21)	1.7	2.1(0.6)
3-nitrophenanthrene	4350	2040(79)	0.47	1.6(N=1[e])
4-nitrophenanthrene				
2-nitrofluoranthene	201	230(9.0)	282	190(16)
3-nitrofluoranthene	65.2	54(3.8)	4.5	1.9(0.15)
1-nitropyrene	18330	16000(1200)	71.5	40(3.6)
2-nitropyrene			24.4	7.0(0.1)
2,7-dinitrofluorene				
7-nitro[*a*]anthracene	995	390(48)	35.1	15(2.0)
6-nitrochysene	44.4	36(3.4)	4.4	2.5(0.6)
1,3-dinitropyrene				
1,6-dinitropyrene				
9,10-dinitroanthracene				
1,8-dinitropyrene				
6-nitrobenzo[*a*]pyrene	1442	970(300)		
1-nitrobenzo[*e*]pyrene	<10	13		
3-nitrobenzo[*e*]pyrene	89	70(N=1)		
1-nitro- and 3-nitro-benzo[*a*]pyrene				

a.Approximately 200μg extracted. See text for specifics, b. Approximately 500μg extracted c.Geometric mean ng/g (N=3) d.1 standard deviation (N=3), e. Above detection limits in 1 sample

SRMs (N=6). Therefore we conclude the dinitropyrenes are not reliably quantified in SRMs and ambient aerosols using the current instrumental setup.

2.4 Method Implications

The goal of this study is to develop an analytical method for trace level analysis of PAHs and NPAHs suited for hourly quantification of PAHs and NPAHs. The maximum mass of SRM employed was 500μg. Assuming a particulate matter concentration of 50 μg/m^3 of Urban Dust SRM, this corresponds to approximately 10 m^3 of air sampled. A collection rate of 0.5m^3/min would achieve this mass of particulate material in 20 minutes. Therefore, the sampling time intervals can be on the order of minutes rather than hours or days.

Instrumental detection limits (IDLs) were developed from foil blanks concurrently analyzed with the SRMs (Table 2.4). These values correspond to the instrument noise multiplied by 3 for each compound. This represents the lower limit of detection of PAHs and NPAHs. The IDLs for NPAHs are consistently 1 to 2 orders of magnitude below PAHs. Due to the ubiquitous nature of PAHs, method detection limits (MDLs) are usually determined from the greater of the instrument noise and/or contamination. Bamford *et al.* (1999) reported a minimum detection limit for PAHs of 1 pg/m^3 using 12 hr (0.5 m^3/min flow) corresponding to a minimum detection mass of ~400 pg. A similar value can be calculated from the flow and method detection limits presented by Halsall *et al.* (1997) in their study of PAHs in the Artic (Dunai) atmosphere. Larger monitoring programs such as the IADN report similar detection (1 – 9 pg/m^3 for ~600m^3 sampled) limits for PAHs using GC/MS analysis.

Table 2.4 Instrumental detection limits for PAHs and NPAHs

PAHs	IDL (pg)[a]	NPAHs	IDL (pg)
naphthalene	9.8	1-nitronaphthalene	0.51
azulene	23	2-nitronaphthalene	0.79
2-methylnaphthalene	2.7	2-nitrobiphenyl	0.57
1-methylnaphthalene	9.6	3-nitrobiphenyl	0.26
acenapthylene	7.6	4-nitrobiphenyl	2.4
biphenyl	1.8	1,3-dinitronaphthalene	0.57
acenaphthene	4.4	1,5-dinitronaphthalene	0.23
		5-nitroacenapthene	0.71
fluorene	7.4		
phenanthrene	40	2-nitrofluorene	0.15
anthracene	24	2,2'-dinitrobiphenyl	0.27
1-methylfluorene	9.2	9-nitroanthracene	0.88
4,5-methylenephenanthrene	10	2-nitroanthracene	1.0
2-methylphenanthrene	12	9-nitrophenanthrene	0.19
2-methylanthracene	19	3-nitrophenanthrene	0.11
1-methylanthracene	25	4-nitrophenanthrene	0.13
1-methylphenanthrene	20		
9-methylanthracene	22	2-nitrofluoranthene	0.27
		3-nitrofluoranthene	0.16
fluoranthene	25	1-nitropyrene	0.17
pyrene	11	2-nitropyrene	1.8
9,10-dimethylanthracene	33	2,7-dinitrofluorene	0.16
benzo[a]fluorene	6.0		
benzo[b]fluorene	26	7-nitro[a]anthracene	0.30
benz[a]anthracene	5.0	6-nitrochysene	0.09
chrysene+triphenylene	2.3	1,3-dinitropyrene	0.53
napthacene	24	1,6-dinitropyrene	2.85
3-methylcholanthrene	12	9,10-dinitroanthracene	2.1
		1,8-dinitropyrene	1.7
benzo[b]fluoranthene	11	6-nitrobenzo[a]pyrene	0.65
benzo[k]fluoranthene	7.7	1-nitrobenzo[e]pyrene	1.1
benzo[a]pyrene	8.2	3-nitrobenzo[e]pyrene	1.8
benzo[e]pyrene	28	1-nitro- and 3-nitro-	
perylene	3.3	benzo[a]pyrene	12
dimethylbenz[a]anthracene	30		
indeno[1,2,3-c,d]pyrene	5.4		
benzo[g,h,i]perylene	1.7		
anthanthrene	1.5		
diben[a,h+a,c]anthracene	0.44		
coronene	4.4		

a. 3 times the instrument noise

Using similar IDL calculations to this study (3xs the noise) others have found NPAH detection limits orders of magnitude above those presented in Table 2.4. Bonfanti *et al.* (1996) found IDLs ranging 1pg to 700pg for 1-nitropyrene and 2-nitrobiphenyl, respectively, using particle beam liquid chromatography-mass spectrometry in NCI mode. Jinhui *et al.* (2001) employed a derivatization technique to increase their NPAH sensitivity using a GC-electron capture detector as opposed to GC/MS (30 and 150pg, respectively). This method utilized a hot splitless injector possibly contributing to the high (compared to this study) IDLs reported. Fieldberg *et al.* (2001) used a temperature programmed injector and ion trap GC/NCI for NPAH analysis in Denmark. The IDLs for 9-nitroanthracene (35pg), 2-nitrofluoranthene (20pg), 3-nitrofluoranthene (22), 1-nitropyrene (24pg) and 2-nitropyrene (22pg) are also orders of magnitude above the method presented here. Bamford *et al.* (2003) developed method detection limits using 3 times the blank values using cool on-column injection GC/NCI. From the mean volume ($1400m^3$) collected and the method detection limit range (0.001 to 0.12 pg/m^3) we can estimate an IDL (including possible interferences) ranging 1.4 to 170 pg. This is still 5 to 10 times above the majority of the NPAH IDLs presented here.

From the IDLs presented in this study, an upper limit of the temporal resolution of PAHs and NPAHs has been calculated for a variety of samplers (Table 2.5). For this conservative comparison, a method detection limit was calculated as 10x the IDL for benzo[*a*]pyrene and 1-nitropyrene. Mean July 2003 concentrations in Baltimore, MD from Bamford and Baker (2003) were chosen as representative

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Table 2.5 Lower limit of sampling times using conventional instruments and PTV-GC/MS

| | MDL[a] (pg) | Typical Concentration[b] (pg/m³) | Sampling times (minutes) | | | |
			Hi-vol (0.5m³/min)	Denuder (0.05m³/min)	Impactors[c] (0.08 m³/min)	Personal[d] sampler (5Lpm)
1-nitropyrene	1.7	8	0.42	4.2	2.6	42
benzo[a]pyrene	80	80	0.20	2.0	1.3	20

a. Method detection limit from this study. b. Mean summer concentration Bamford and Baker., 2003, c. This study, d. Personal sampler, TSI Incorporated, Shoreview, MN

ambient concentrations. The lower limit of sampling frequency for 1-nitropyrene ranges 0.4 min (hi-vol) to 42 min for a personal sampler. The sampling time required for detecting benzo[*a*]pyrene is approximately half that of 1-nitropyrene.

This method has been recently employed to measure 12 hr NPAH size distributions in Baltimore, MD using a Berner low-pressure impactor with a flow of 80 Lpm (Crimmins and Baker in preparation). Figure 2.4 depicts a mean size distribution of 1-nitropyrene and 2-nitrofluoranthene for two consecutive day and night samples collected in April 2002. For all samples 2-nitrofluoranthene and 1-nitropyrene were above detection limits (0.34 and 0.10 pg/m^3) in the four smallest size cuts of the impactor (<6.0μm). The concentration in the accumulation mode (0.14 – 0.49μm) was greater than 2 orders of magnitude above the MDLs accounting for the largest particle mass (~500μg) and concentration of 2-nitrofluoranthene (48 – 77 pg/m^3). A similar trend was found for 1-nitropyrene with the exception of one night sample where the stage 3 (0.49 – 1.7μm) concentration was greatest (13 pg/m^3). During the day approximately 83% of the total 2-nitrofluranthene concentration was associated with the greatest particle surface area (*i.e.* accumulation mode, 0.14 – 0.49μm) whereas 1-nitropyrene was more evenly distributed among the smallest 3 particle size classes collected. To our knowledge this is the first reported size distribution of NPAH on time scales less than day. Using this method we were able to quantify NPAHs consistently from <300μg (extracted per stage) of ambient particulate matter mass.
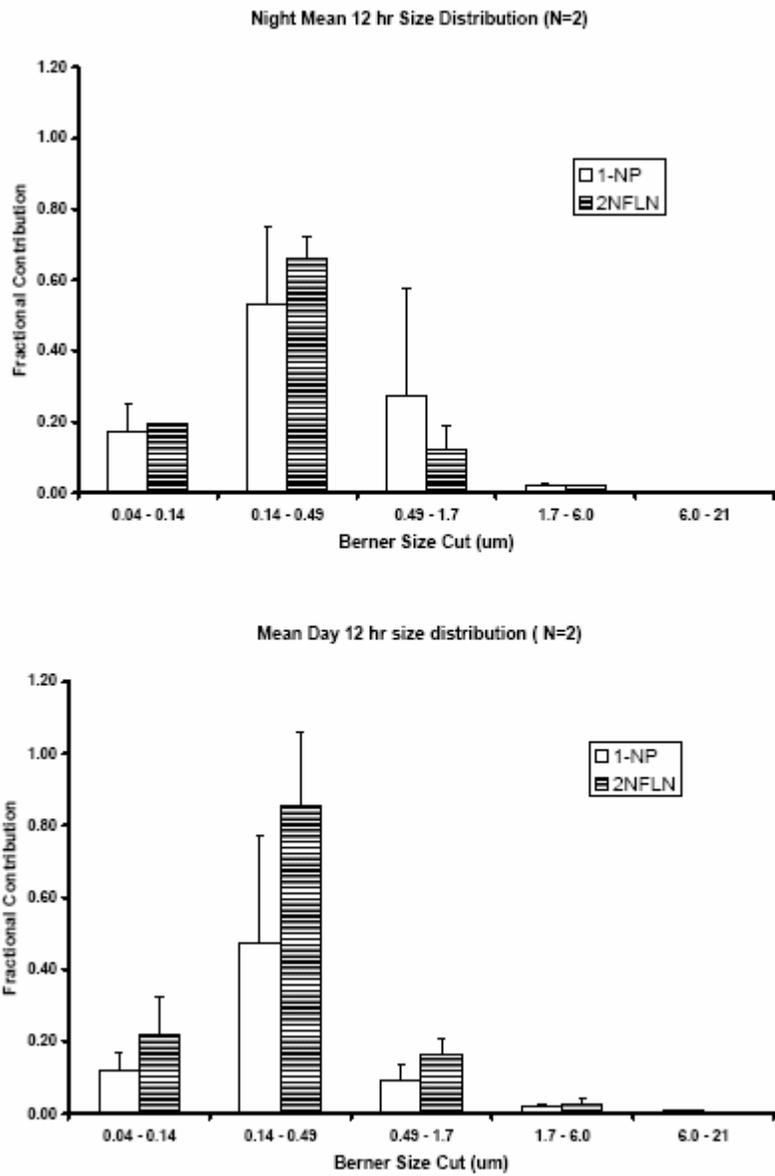
Figure 2.4 Mean size distribution of 1-nitropyrene and 2-nitrofluoranthene April 2002.

2.5 Conclusions

Enhanced temporal resolution of air toxics such as PAHs and NPAHs is critical to understanding their sources and behavior in the ambient atmosphere. We present a large volume injection technique for the quantification of both classes of compounds. The programmed temperature vaporization large-volume injection techniques have similar precision as the standard hot splitless injection, while enhancing the sensitivity per mass injected up to 5-fold for PAHs. The methods were verified using microgram quantities of Standard Reference Materials. The dinitro-substituted PAHs were not quantifiable using this technique, possibly due to matrix-induced degradation.

The significance of the increased analytical sensitivity (temporal resolution) is demonstrated by the diurnal NPAH size distribution presented here. Using this method we were able to present the first reported diurnal NPAH size distribution in ambient particulate matter. Further application of this injection technique will undoubtedly increase our knowledge and certainty (lower artifacts) of the phase distribution, sources, photochemistry and inevitably the real-time health effects associated with PAH and NPAHs in the ambient atmosphere. From the detection limits presented in this study commercially available sampling equipment may be employed to better elucidate PAH and NPAH behavior on timescales of minutes.

In a broader sense, this technique provides a gentler sample introduction technique able to efficiently and consistently increase the method sensitivity of these compounds by orders of magnitude using commercially available sampling equipment. This increased sensitivity corresponds to greater temporal resolution,

hence, minimizes potential artifacts associated with extended sampling times. In the future, this injection technique should be further evaluated for other non-polar and polar organic tracers analyzed by GC. Encompassing these tracers along with PAHs and NPAHs will undoubtedly broaden our understanding particulate organic carbon sources, photochemistry and potential health effects.

Chapter 3:

Charaterization of Alkanes, PAHs, Nitro-PAHs and Hopanes in the Baltimore Atmosphere: Seasonal Trends and Source Profiles

3.1 Introduction

Ambient aerosol is a mixture of organic and inorganic constituents. The organic fraction, which may contribute up to 60% of the mass (Malm *et al.*, 2004), is composed of hundreds of compounds with a variety of functional groups (Rogge *et al.*, 1993a). Polycyclic aromatic hydrocarbons (PAHs) and nitro-substituted polycyclic aromatic hydrocarbons (NPAHs) contribute to a small fraction of the overall particulate matter mass but have been implicated in the increased mutagenicity of specific aerosol types (Arey *et al.*, 1988, Gupta *et al.*, 1996, IARC 1989).

Previous studies in Baltimore, MD have examined the aerosol PAH distribution and the effect of this urban center on the deposition of contaminants to the Chesapeake Bay (Offenberg and Baker, 1999). PAHs have also been employed as chemical tracers where diesel was found to be significant source to the Baltimore atmosphere (Larsen and Baker, 2003). Recently, Bamford and Baker (2003) reported the first concentrations and seasonal distribution of NPAHs in the mid-Atlantic region identifying the dominant NPAH formation pathways (primary vs. secondary) in the Baltimore urban center and at a suburban site midway between Baltimore and Washington DC.

N-Alkanes are ubiquitous in ambient air, having biogenic, petroleum, and biomass and fossil fuel combustion sources. Characteristic *n*-alkane profiles have been observed in source studies and are useful for determining the relative contribution of biomass and fossil fuel contribution of ambient aerosol (Simoneit and Mazurek, 1982, Simoneit, 1984, Simoneit *t al.*, 1988, Simoneit, 1989, Rogge *et al.*, 1993a, Oros and Simoneit, 2000, Hayes *et al.*, 2002). Hopanoid compounds are extensively used to determine the age of fossil fuels (Nytoft *et al.*, 2000, Price *et al.*, 1994). These compounds are formed by bacteria on geologic timescales as organic matter is converted from plant matter to coal and petroleum (Oros and Simoneit, 2000). These compounds are also found in aerosol emitted from fossil fuel combustion (Rogge *et al.*, 1993e, Rogge *et al.*, 1997b), roofing tar (Rogge *et al.*, 1997a) and in road dust (Rogge *et al.*,1993d).

NPAHs are highly mutagenic and have isomer specific sources (Arey, 1998). Unlike PAHs that are primarily formed via incomplete combustion, NPAHs can also be formed by gas phase reactions in the atmosphere (Arey *et al.*, 1986, Pitts, 1987). The dominant isomer in ambient aerosol is usually 2-nitrofluoranthene, which can be formed *via* OH radical mediated nitrate substitution during the day or direct addition *via* nitrate radical at night (Arey, 1998). 1-nitropyrene has not been observed in chamber studies (Arey, 1998), but is one of the dominant NPAH isomer in diesel exhaust. Therefore, the isomeric composition of NPAHs are indicators of primary and secondary sources as well as the mutagenicity potential of ambient aerosol.

The objective of this study is to present the seasonal distribution of alkanes, PAH, NPAHs and hopanes at the Baltimore Supersite during the 2002 -2003 spring,

summer and winter intensives. The results are combined with collocated gas (NO, NO$_2$, O$_3$) and bulk particle phase (organic carbon, OC and elemental carbon, EC), and volatile organic compound (VOCs) concentrations to provide insight into possible sources to and formation pathways (NPAHs) in the Baltimore atmosphere.

3.2 Sampling

The sampling site is described by Harrision *et al.* (2004) and Ogulei *et al.* (2005) and is briefly summarized here. Aerosol samples were collected at the Baltimore PM$_{2.5}$ Supersite during the spring (April), summer (July-August) and winter (January-February) of 2002-2003. Samples were collected ~6 m above the asphalt parking lot. The sampling site was flanked to the west (~100 m) by a Maryland Transit Authority bus depot. A four lane access road separated the site and bus depot spanning south to northwest of the site. A major highway Interstate (I895) is positioned to the east (~100 m). The interstate is elevated (~6 m) passing through the Baltimore Harbor Tunnel approximately 2 km south of site. An onramp to the interstate is located between the site and I895 (~10 m) with limited traffic.

Aerosol samples were collected using a modified Anderson Hi-Volume sampler consisting of a glass fiber filter (GFF) followed by a polyurethane foam (PUF) plug for particulate and gas phase organics, respectively (Bamford and Baker, 2003, Offenberg and Baker, 1999). Sampling times ranged from approximately 6 to 24 hr at a flow rate of ~0.5 m^3 min^{-1}. Prior to deployment, the filters were ashed at 450°C for >4 hrs in individual foil pouches. The PUF were precleaned by Soxhlet extraction with petroleum ether for 24 hrs, dried and stored in ashed glass jars fitted

with Teflon lined caps. After deployment, the filters and PUF were returned to their respective containers and stored in the dark at -20°C until analysis.

In addition to the semi-volatile compounds, a series of bulk particulate matter parameters (elemental carbon, organic carbon, nitrate and $PM_{2.5}$ mass) were measured during the spring and summer and gas phase parameters (CO, NO, NO_2, and ozone) were measured during the spring, summer and winter intensives (Park *et al.*, 2005a, b, Harrison *et al.*, 2004). Some of these constituents were measured on different timescales (10 min – 1hr) therefore, a time integrated average was calculated, coinciding with the semi-volatile organics collections (6 to 24 hr). Volatile organic compounds (VOCs) were also measured using SUMA canisters concurrently collected with semivolatiles and analyzed via EPA method TO-15 by the Maryland Department of the Environment during the spring, summer and winter.

3.3 Methods

All PAHs used in this study were supplied by Ultra Scientific (North Kingstown, RI) with the exception of 2- and 4-methyldibenzothiophene, cyclopenta[*c,d*]pyrene and 4-methylchrysene which were supplied by Accustandard (New Haven, CT). Two deuterium labeled PAH solutions, internal and surrogate standards, were made from neat standards (Ultra Scientific) in hexane. Nitro-PAH standards were acquired from AccuStandard (New Haven, CT) in concentrated solutions (~100 mg mL^{-1} in toluene) except for 2-nitrofluoranthene and 2-nitropyrene, which were supplied by Chiron (Trondheim, Norway) and Chemsyn Science Laboratories (Lenexa, KS), respectively. The internal standard solution components

(3-nitrofluoranthene-d_9, 6-nitrochrysene-d_{11}, 2-nitrofluorene-d_9 and 5-nitroacenaphthene-d_9) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). The surrogate solution components were acquired from C/D/N Isotopes (Pointe-Claire, Quebec, Canada, nitronaphthalene-d_7) and Cambridge Isotope Laboratories, Inc. (9-nitroanthracene-d_9 and 1-nitropyrene-d_9). The series of 9 hopane standards were obtained from Chiron and a series of even n-alkanes (C_{10} – C_{36}) with the addition of C_{17} and C_{29} were provided by Ultra Scientific. Most odd carbon chain alkanes were identified by using the midpoint retention time between the adjacent even chain alkanes. Odd alkanes were quantified using the mean response factor of the adjacent even carbon alkanes.

The particle phase (GFF) and gas phase (PUF) were separately Soxhlet extracted with dichloromethane (DCM) and petroleum ether, respectively for 24 hrs (Bamford and Baker, 2003, Offenberg and Baker 1999). A series of PAH (naphthalene-d_8, fluorene-d_{10}, fluoranthene-d_{10}, perylene-d_{12}) and NPAH (1-nitronaphthalene-d_7, 9-nitroanthracene-d_9, and 1-nitropyrene-d_9) surrogates were added each sample prior to extraction. Extracts were then concentrated by rotary evaporation to ~20 mL and quantitatively transferred to 200 mL tubes, then further concentrated under a gentle stream of N_2 (Turbovap II, Zymark, Hopkinton, MA) to a final volume of 1 mL and transferred to 2 mL vials. A series of perdeuterated PAHs (benz[a]anthracene-d_{12}, benzo[a]pyrene-d_{12} and benzo[g,h,i]perylene-d_{12}) were then added as internal standards and PAHs, alkanes and hopanes were analyzed without further purification. PAHs, alkanes and hopanes were quantified using an Agilent 6890/5973 gas chromatograph/mass spectrometer (GC/MS) with electron ionization

(EI) in selective ion mode (SIM). Samples were eluted through a 0.25mm x 30m x 0.25μm DB-5ms (Agilent Technologies, Palo Alto, CA) capillary column equipped with a hot splitless injector at 250°C. The oven was held at 50°C for 0.60 min and ramped 10°C/min to 310°C and held for 10 min.

The extracts were transferred to 4 mL vials and quantitatively subsampled (~1/2). The subsamples were further purified by elution through an aminopropyl SPE cartridge (Sep-Pak, Waters, Milford, MA) with a 20% DCM/hexane solution, concentration under N_2 and exchange to 100% hexane with a final volume of ~0.25 mL (Bamford *et al*., 2003). Normal phase LC was then employed for the final clean-up step using a 5 μm, 9.6 mm x 30 cm Chromegabond amino/cyano column (ES Industries, West Berlin, NJ). The mobile phase was 20% DCM/hexane at a flow rate of 5 mL min^{-1}. Two fractions were collected, separating the mono- and dinitro-PAHs. The purified extracts were then exchanged to 100% hexane to a final volume of ~200μL. NPAH internal standards (3-nitrofluoranthene-d_9, 6-nitrochrysene-d_{11}, 2-nitrofluorene-d_9 and 5-nitroacenaphthene-d_9) were then added just prior to analysis.

The NPAH analysis was performed as described in Crimmins and Baker (2006). The 6890/5973 GC/MS was configured for negative chemical ionization (methane reagent gas) in SIM mode. NPAHs were resolved using a 0.25mm x 30m x 0.25μm DB-17ms capillary column. The oven temperature program for NPAH analysis was 40°C (held 1.7 min) ramped to 150°C at 20°C min^{-1}, held for 10 min, then to 220°C at 10°C min^{-1}, held for 10 min and finally ramped to 310°C and held for 15 min. Sample introduction (50 μL) was performed using a programmed temperature vaporization (PTV) injector in solvent vent mode. The injector was

configured to introduce 50 μL of sample using a series of ten 5 μL injections at 45°C held for 1.5 min then ramped at 600°C min^{-1} to 280°C.

3.4 Quality Assurance

PAHs: The mean PAH surrogate recoveries (naphthalene-d_8, fluorene-d_{10}, fluoranthene-d_{10} and perylene-d_{12}) for the PUF samples were 60.1% ± 15.1, 113% ± 52, 138% ± 43 and 97% ± 20 whereas filter surrogate recoveries were 35% ± 15, 125% ± 27, 80% ± 9, 92% ± 6.7. A series of field and laboratory blanks were processed concurrent with samples to assess possible contamination. Field blank masses ranged from 1.9 to 5.8 ng (naphthalene and 1,8-dimethylnaphthalene, respectively) in the filters and 5.4 to 7.6 ng (1-methylnaphthalene and naphthalene, respectively) in the PUF. The field blank values for each matrix were consistently higher than laboratory blanks for all compound classes, therefore field blank values are used to develop method detection limits (MDL) for each compound. Applying a mean volume of 600 m^3 to 3 times the field blank masses result in MDLs of 9.5 to 29 pg m^{-3} and 27 to 38 pg m^{-3} for filters and PUF, respectively.

Alkanes and Hopanes: Due to the low vapor pressure of the hopanes analyzed in this study, only particulate phase concentrations were determined. The hopane and alkane extraction efficiency was monitored with the PAH surrogates. Hopane field blanks ranged from 1.2 to 26 ng for 17β(H),21β(H)-hopane and 17α(H),21β(H)-30-norhopane, resulting in MDLs ranging 6.0 to 130 pg m^{-3}. Alkane filter and gas phase MDLs ranged from 9 (C_{17}) to 58 (C_{24}) pg m^{-3} and 36 (C_{19}) to 6700 (C_{21}) pg m^{-3}, respectively.

NPAHs: Lower recoveries were found for the NPAH surrogates 1-nitronaphthalene-d_7, 1-nitroanthracene-d_9 and 1-nitropyrene-d_9 (36% $\pm$ 20, 45% $\pm$ 16, 44% $\pm$ 17, respectively) with more sample to sample variability. This is due to the increased purification and concentration steps required for this analysis. Therefore, NPAH concentrations were surrogate corrected using a relationship between surrogate recovery and retention time. The NPAH MDLs (3x's blank) for the PUF and filter ranged 9.0 to 420 fg m^{-3} (6-nitrochrysene and 1-nitronaphthalene) and 5.8 to 50 fg m^{-3} (3-nitrofluoranthene and 2-nitroanthracene), respectively.

Procedural Recovery: A series of matrix spikes (filter and PUF) were analyzed to assess the analytical accuracy of the extraction methods. Hopanes, PAHs, and NPAHs were added to PUF and GFF substrates in triplicate prior to extraction and processed using the methods described above. The n-alkane standard consisted of even chain number n-alkanes (C_{10}-C_{36}), C_{17} and C_{29}. The filter spike recoveries were consistently above 80%, 75% and 65% for PAHs, hopanes and NPAHs, respectively. Apparent contamination was observed in the n-alkane spikes accounting for elevated recoveries of (>200%) for C_{24}, C_{26}, C_{28}, C_{29}, C_{30}. C_{12} and C_{22} were recovered with 81 and 130% efficiency. This contamination was not observed in the PUF spikes therefore, we conclude that this contamination was not representative of the dataset.

PUF spike alkane recoveries were more consistent than the filters ranging 65% (C_{17}) to 130% (C_{10}) with the majority of values above 90%. PUF PAH and NPAH recoveries exhibited a lower recovery (<40%) of the lightest compounds (C1-, C2-naphthalene, biphenyl and nitronaphthalenes, methylnitronaphthalenes and nitrobiphenyls) due to volatilization losses during extract concentration. The mid to

high molecular weight PAH and NPAH recoveries were usually greater than 80%. The lower vapor pressure NPAHs also exhibited better recoveries but, were consistently below PAH values (52% to 81%), similar to surrogate values discussed above.

The sampler was fitted with a second PUF plug downstream of the sampling train to assess collection efficiency during the spring and summer (N=3). Significant quantities (<50%) of the lightest PAH (molecular weight < fluorene) and alkane (< C_{20}) mass was found on the second PUF decreasing with increasing molecular weight. Therefore, the concentrations reported here are lower estimates of actual concentrations. The total alkane and PAH concentrations presented below have been separated into 2 groups, low molecular weight and mid to high molecular weight totals.

3.5 Results

The seasonal distribution of gases and bulk particle parameters are summarized in Table 3.1. Further details and a complete discussion of these air quality parameters are presented elsewhere (Park *et al.*, 2005a, b, Harrison *et al.*, 2004). PM$_{2.5}$, elemental carbon (EC), organic carbon (OC), nitrate (NO$_3^-$) and semivolatile organic concentrations were concurrently measured during the spring and summer only. OC, EC and PM$_{2.5}$ concentrations were similar among seasons. PM$_{2.5}$ concentration (geometric mean[geometric standard deviation]) increased from spring (13[1.5] μg m^{-3}) to summer (19[1.9] μg m^{-3}), whereas NO$_3^-$ concentrations were lower during the summer (0.6[2.0] μg m^{-3}) compared to spring (1.8[1.8] μg m^{-3}).

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Table 3.1 Air Quality Parameters, Baltimore Supersite

	Spring 2002		Summer 2002		Winter 2003	
	Mean[1]	GSD[2]	Mean	GSD[2]	Mean	GSD[2]
Ozone (ppb)	7.5	1.5	31	1.7	6.7	2.1
CO (ppm)	0.55	1.5	0.28	1.32	0.52	1.5
NO (ppb)	22	2.4	9.5	1.8	54	1.9
NO_2 (ppb)	24	1.4	25	1.4	35	1.2
EC (ug m^{-1})	0.5	2.1	0.5	2.1		
OC (ug m^{-1})	3.0	1.8	3.3	1.8		
NO_3^- (ug m^{-1})	1.8	1.8	0.8	2.0		
$PM_{2.5}$ (ug m^{-1})	13	1.5	19	1.9		

[1] Geometric mean,
[2] Geometric standard deviation

Ozone concentrations were higher in the summer (31[1.7] ppb), consistent with increased photochemical activity, while the NO concentrations were higher during the winter intensive (54[1.9] ppb), suggesting increased high temperature combustion or decreased mixing. Summer CO (0.26[1.3] ppm) concentrations were not significantly different than spring (0.55[1.5] ppm) and winter (0.52[1.5] ppm) periods.

The bulk particle and gas phase parameters were inter-correlated ($p<0.005$) with the following exceptions (Table 3.2). OC was only significantly correlated with CO, NO_2, NO_3^- and EC. Ozone was negatively correlated with NO. $PM_{2.5}$ mass was less related to CO ($p<0.01$) concentrations compared to NO_2 ($P < 0.001$). The relationship between EC and OC suggests that the organic fraction of the ambient aerosol may be dominated by combustion sources. NO is emitted in larger quantities during diesel combustion due to a lean air/fuel ratio with a lower fraction of OC to EC compared to gasoline combustion (Schauer *et al.*, 1999, 2002). At this site, OC and CO were correlated, whereas OC and NO were not, suggesting that the OC mass at this site is not significantly influenced by NO sources.

Of the non-halogenated VOCs (1,3-butadiene, cyclohexane, heptane, benzene, toluene, *m*- and *p*-xylene, *o*-xylene, 1-ethyl-4-methylbenzene, 1,3,5-trimethylbenzene, and 1,2,4-trimethylbenzene), only 1,3-butadiene exhibited a seasonal difference. Lower 1,3-butadiene concentrations in the summer (55[1.8] ppb) compared to spring (98[1.8] ppb) and winter (112[1.6] ppb), are likely due to photochemical degradation. Photochemical degradation may also explain the higher benzene concentration variability during the summer period. The low seasonal

Table 3.2 Air Quality Pearson Correlation Coefficients

	Ozone	CO	NO	NO_2	EC	OC	NO_3^-	$PM_{2.5}$	Temp	Wind Speed
Ozone		-0.55[1]	-0.50				-0.45	0.64	0.61	
CO	-0.55		0.79	0.48	0.62	0.36[2]	0.59			
NO	-0.50	0.79		0.59	0.62	0.38	0.44		-0.40	-0.32
NO_2		0.48	0.59		0.64	0.56		0.43		-0.51
NO_x	-0.44	0.78	0.98	0.72	0.69	0.44	0.41		-0.38	-0.38
EC		0.62	0.62	0.64		0.52			0.43	
OC		0.38	0.38	0.56	0.52			0.66	0.56	
NO3-	-0.45	0.59	0.44						-0.30	
pm2.5	0.64			0.43		0.66			0.59	
PM 10		0.45	0.42	0.51	0.50	0.61		0.55	0.34	-0.31
Temp	0.61		-0.40		0.43	0.56	-0.30	0.59		
Wind speed 1			-0.32	-0.51						

[1] Bold values p < 0.005. [2] p < 0.05

variation for the majority of VOCs suggests a relatively constant local source to the site.

A significant (p<0.005) correlation was found among the majority of non-halogenated VOCs (Figure 3.1). Benzene was less correlated (p<0.01) with the other VOCs. The majority of VOCs were significantly (p<0.005) correlated with NO, NO_2, EC and OC (except, cyclohexane and heptane, p<0.02). Benzene was not significantly correlated with these parameters (p > 0.1). The non-halogenated VOCs have numerous sources including, gasoline and diesel combustion, fugitive gasoline and diesel emissions, coatings, and solvents (Schauer *et al.*, 1999, Watson *et al.*, 2001 Schauer *et al.*, 2002). The alkybenzene concentrations did not track the ambient temperature therefore volatilization from road surfaces or refueling stations appears to be a minimal source of these compounds to the site. The correlation of these compounds with the combustion parameters (NO, CO, EC) and a lack of seasonal variation or temperature dependence indicate a traffic related source of these species.

Alkanes: The *n*-alkane concentration, sum of particulate (filter) and gas (PUF) phases, (Table 3.3 $C_{20} - C_{35}$) exhibited no seasonal difference during the spring, summer and winter intensives (91[1.7], 110[1.5], 91[1.4] ng m^{-3}, respectively). When the lighter homologues ($C_{15} - C_{19}$) are included in the total alkane concentration (Figure 3.2), the winter concentration (230 ng m^{-3}) is approximately 2-fold greater than the spring and summer (120 ng m^{-3}). No backup PUF was analyzed for the winter period (described above) therefore, the PUF collection efficiency at winter temperatures (< 5 °C) period is unknown. The latter seasonal difference in the lightest
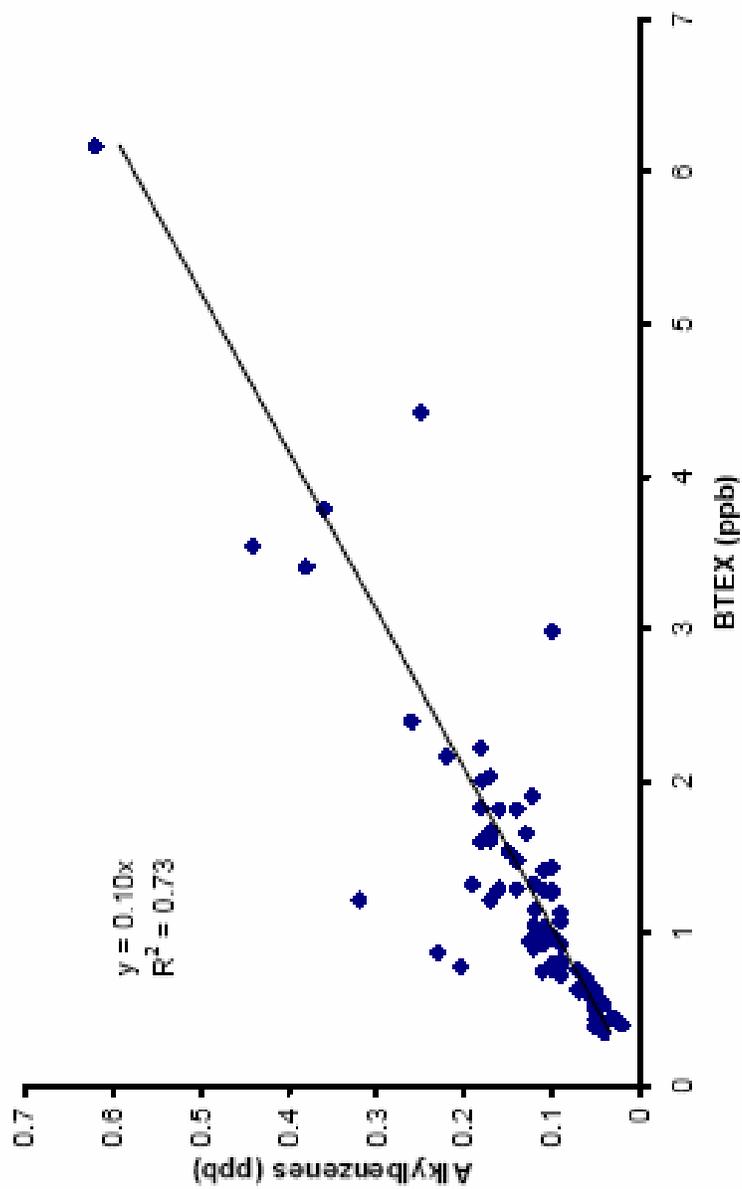
Figure 3.1 Sum alkybenzenes (1-ethyl-4-methylbenzene + 1,3,5-Trimethylbenzene + 1,2,4-trimethylbenzene) vs. BTEX (benzene + toluene + ethylbenzene+ xylenes)

y = 0.10x
$R^2 = 0.73$

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Table 3.3 Alkane Seasonal Mean Concentrations

	Spring 2002		Summer 2002		Winter 2003	
	Mean[1]	GSD[2]	Mean	GSD	Mean	GSD
C_{15}	1.1	2.0	0.61	2.1	17	1.7
C_{16}	2.9	2.5	1.5	1.9	34	1.6
C_{17}	2.1	5.0	0.64	5.8	38	1.5
C_{18}	5.3	3.0	3.8	2.2	27	1.6
C_{19}	8.2	2.9	5.6	1.8	19	1.5
C_{20}	9.9	2.9	11	2.0	16	1.7
C_{21}	5.0	5.2	3.8	5.9	8.0	1.6
C_{22}	7.1	2.4	13	1.6	11	1.6
C_{23}	7.0	2.5	12	1.6	6.7	1.4
C_{24}	5.0	2.1	8.1	1.7	6.2	1.7
C_{25}	6.7	2.0	8.4	1.5	5.9	1.4
C_{26}	3.6	2.0	3.9	1.8	4.1	1.8
C_{27}	4.7	1.9	6.3	1.5	3.1	1.4
C_{28}	2.8	1.8	2.4	1.8	3.4	1.6
C_{29}	5.3	1.6	7.5	2.0	4.4	1.3
C_{30}	2.6	1.5	2.1	1.6	2.6	1.5
C_{31}	4.4	1.6	5.6	1.7	3.1	1.4
C_{32}	2.0	1.5	1.6	1.6	1.7	1.5
C_{33}	2.8	1.6	2.5	1.8	2.1	1.3
C_{34}	3.7	1.6	3.3	1.6	4.4	1.4
C_{35}	3.8	1.5	2.9	2.2	4.4	1.5
Total alkane (C_{20}-C_{36})	91	1.7	110	1.5	91	1.4
CPI_{total} (C_{12}-C_{35})	1.2	1.3	1.1	1.4	0.99	1.2
$CPI_{biogenic}$ (C_{26}-C_{36})	1.4	1.3	1.9	1.8	1.1	1.3

[1] Geometric mean, ng m^{-3}
[2] Geometric standard deviation

Figure 3.2 Timeseries summary of total alkanes, hopanes, PAHs and NPAHs during 2002-2003.
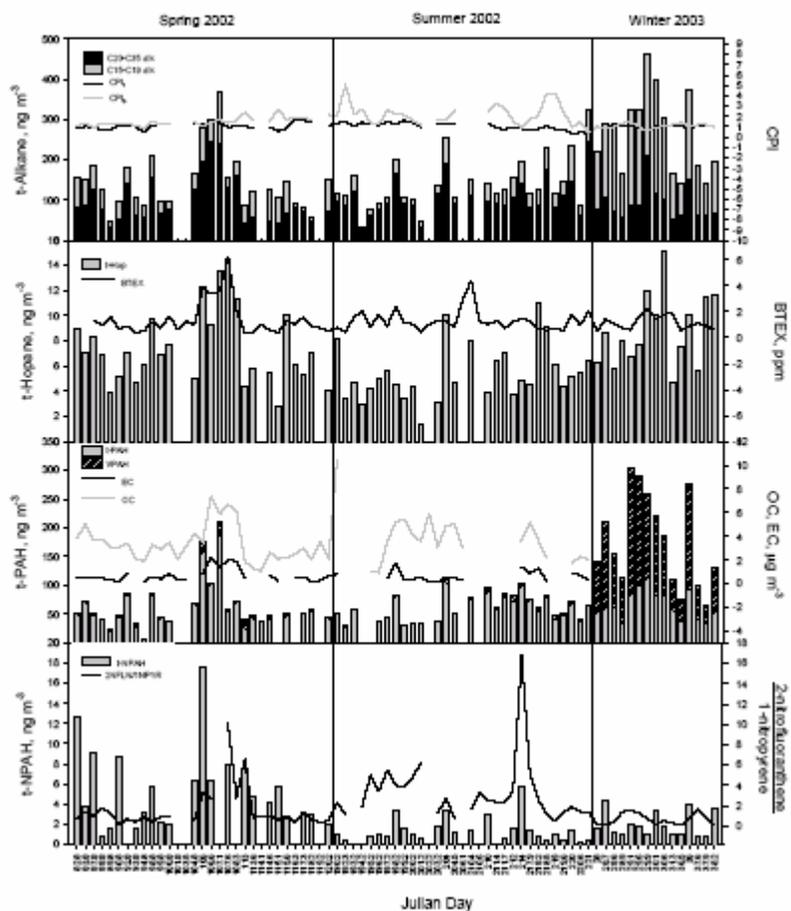
alkanes suggests increased fossil fuel combustion during the winter months, consistent with elevated NO concentrations and NPAH distribution (see below) during this period. Due to the possible increased collection efficiency of the PUF during the colder months, this interpretation must be viewed with caution.

Fraser *et al.* (1997) found similar alkane concentrations (e.g. mean *n*-pentacosane of 6.4 ng m^{-3}) using a filter/PUF sampler during a Los Angeles photochemical smog event in 1993 (Table 3.4). As part of the Southeast Aerosol Research and Characterization (SEARCH) air monitoring network, Zheng *et al.* (2002) measured n-triacontane concentrations on PM$_{2.5}$ in 4 southeastern urban sites (Atlanta, GA, Birmingham, AL, Gulfport, MS and Pensacola, FL). The authors reported values ~1/2 or less the mean Baltimore concentrations. Triacontane concentrations in Baltimore are similar to urban Houston, TX values (Fraser *et al.*, 2002). Winter 1995-1996 n-triacontane concentrations measured in California's San Joaquin Valley (Fresno and Bakersfield) during a pollution episode were approximately twice the Baltimore levels (Schauer and Cass, 2000). Baltimore and Denver, CO, gas + particle pentacosane concentrations are within a factor of 2 (Foreman and Bidleman, 1990). C$_{28}$ concentrations reported along the Niagera River in January 1983 (0.7 ng m^{-3}, gas + particle, Hoff and Chan, 1987) were well below Baltimore concentrations.

Southeastern rural alkane concentrations from the SEARCH project and Galveston Island, TX (Zheng *et al.*, 2002, Fraser *et al.*, 2002) were an order of magnitude below Baltimore values. Rural/remote concentrations measured in the Northern Highlands State Forest, WI, 200 km away from Green Bay (7 ng m^{-3}, total

Table 3.4 PAH, Hopane and Alkane Concentration Comparison[a]

	Matrix	C25	C26	C27	C28	C29	C30	C31	17α(H), 21β(H)-hopane	Fluoranthene	Pyrene	Benzo[a]pyrene	Indeno(1,2,3-cd)pyrene	Benzo[ghi]perylene	Refs
Urban															
Baltimore, MD															
Spring	G and P	6.7	3.6	4.7	2.8	5.3	2.8	1.9	5.4	4.1	0.17	0.23	0.2		This Study
Summer	G and P	8.4	3.3	6.3	2.4	7.5	2.1	1.5	8.1	4.7	0.12	0.2	0.22		This Study
Winter	G and P	5.5	4.1	3.1	3.4	4.4	2.6	2.3	3.7	3.6	0.43	0.89	0.79		This Study
Southern California, 1996	G and P	6.3	4.3	3	1.4	2.6	1	0.50	9.6	7.3			0.8		Fraser et al., 1997, 1998
N. Birmingham, AL	PM2.5	2.1	2.0	1.9	1.2	2.8	1.1	0.50	0.48	0.58	3.2	1.6	2.2		Zheng et al., 2002
Jefferson St, GA	PM2.5	4	2.9	2.8	1.4	2.4	0.87	0.56	0.12	0.12	0.36	0.36	0.58		Zheng et al., 2002
Gulfport MS	PM2.5	0.24	0.34	0.54	0.28	0.63	0.16	0.12	0.03	0.04	0.1	0.08	0.13		Zheng et al., 2002
Pensacola, FL	PM2.5	0.49	0.56	0.91	0.62	1.2	0.57	0.23	0.03	0.04	0.12	0.18	0.41		Zheng et al., 2002
Houston, TX	PM2.5	2.6	2.6	2.1	1.9	3.4	2	0.24	0.03	0.21	NR	0.4	0.4		Fraser et al., 2002
Fresno, CA	PM2.5	29	21	20	10	37	6.4	~2	1.4	1.9	5.1	5.5	7.7		Schauer and Cass, 2000
Denver, CO	G and P	4.4	12	4.3	3.2	9	5.1	NR	15	24	NR	NR	4.2		Fraser and Eldeman, 1999
Bakersfield, CA	PM2.5	16	12	11	6	24	4.6	NR	0.78	0.75	NR	2.6	4.1		Schauer and Cass, 2001
Chicago, IL	G and P	NR	NR	NR	NR	NR	NR	NR	~15	~10	3	2	2		Simcik et al., 1999
Rural/Suburban															
Charlestown, MD	G and P	NR	NR	NR	NR	NR	NR	NR	0.3	0.2	0.01	0.01	0.01		Offenberg and Baker, 1999
Centerville, AL	PM2.5	0.58	0.47	0.63	0.35	1.3	0.29	0.01	0.05	0.04	0.1	0.06	0.07		Zheng et al., 2002
Yorkville, GA	PM2.5	0.29	0.4	0.54	0.34	0.66	0.29	0.05	0.04	0.03	0.05	0.04	0.05		Zheng et al., 2002
Oak Grove, MS	PM2.5	0.19	0.4	0.56	0.34	1.2	0.26	0.01	0.03	0.02	0.1	0.04	0.04		Zheng et al., 2002
Galveston Is, TX	PM2.5	0.35	0.42	1.5	0.86	0.27	0.32	0.02	0.03	0.03	NR	0.01	0.01		Fraser et al., 2002
Kenn Wildlife Refuge	PM2.5	2.6	1.6	NR	NR	6	NR	NR	0.06	0.08	NR	NR	NR		Schauer and Cass, 2002
Niagara River, NY	G and P	NR	NR	NR	0.08	NR	NR	NR	5.1	3.2	0.4	NR	0.53		Hoff and Chan, 1997

[a] Concentrations in ng m^{-3}

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C_{11}-C_{32}, Doskey and Andren, 1986), Kern Wildlife Refuge south central San Joaquin Valley, CA (C_{28} ~1 ng m^{-3}, Schauer and Cass, 2000), Seney National Wildlife Refuge in Northern Michigan (C_{28} < 2 ng m^{-3}, Sheesley *et al.*, 2004) as much as 14 - fold below values reported for Baltimore.

The Carbon Preference Index (CPI), defined as $\sum$odd carbon alkane concentration / $\sum$even carbon alkane concentration, has been employed to discriminate aerosol sources (Simoneit, 1984, 1989). An odd carbon predominance of alkanes or elevated CPIs have been found in regions dominated by biogenic sources (Simoneit and Mazurek, 1982, Simoneit, 1984, Simoneit *et al.*, 1988), source studies of biomass combustion (Oros and Simoneit, 1999, Hays *et al.*, 2002, Rogge *et al.*, 1998), and direct leaf wax extraction (Simoneit and Mazurek, 1982, Rogge *et al.,* 1993b). Fossil fuel aerosol CPIs are closer to 1 with no apparent carbon preference (Simoneit, 1984, Oros and Simoneit, 2000). Fossil fuel particle phase emissions are dominated by alkanes shorter than C_{25}, whereas plant wax emissions are larger than C_{25} (Simoneit, 1989). Therefore, the CPI of the biogenic (CPI$_{biogenic}$) and fossil fuel (CPI$_{fossil}$) ranges can be calculated independently (C_{26} –C_{34} and C_{12} –C_{25}, respectively) to better represent alkane sources. For example, at 4 southern California urban sites, Fraser *et al.* (1997) observed an odd carbon predominance for the heavier alkanes (C_{28} – C_{35}) and Hildemann *et al.* (1996), using biogenic alkane source profiles (C_{27} – C_{33}), calculated 0.2 - 1.0 µg m^{-3} of the fine aerosol in the Los Angeles atmosphere could be attributed to urban vegetation.

The daily CPIs are shown in Figure 3.2. Since volatilization is governed by vapor pressure, CPIs should reflect the relative profile (odd to even) without bias

from PUF breakthrough. The spring, summer and winter geometric mean CPI_{fossil} values were similar (1.2[1.3], 1.1[1.4] and 1.0[1.2], respectively). $CPI_{biogenic}$ values in the spring (1.4 [1.4]) and summer (1.9[1.8]) were larger than those in the winter (1.1[1.3]). Winter CPI_{fossil} and $CPI_{biogenic}$ values of 1 suggest foliar fuels (wood combustion) are not a significant source of alkanes during the winter period. The elevated summer $CPI_{biogenic}$ values are consistent with an increased biogenic input during that period. Simoneit (1989) notes particulate matter CPI_{fossil} and $CPI_{biogenic}$ values range 0.9 to 2 and 2 to 13, respectively in rural areas of the western United States, while the ranges in urban atmospheres are 0.9 to 1.3 (CPI_{fossil}) and 2 to 3.3 ($CPI_{biogenic}$), well within values observed for Baltimore.

During the spring and summer periods the alkane with the maximum concentration (C_{max}) was usually C_{20} or C_{21}. But 3 of 24 and 4 of 26 samples in the spring and summer, respectively, had a C_{max} at C_{29} then C_{31} (Figure 3.3). $CPI_{biogenic}$s were also greater than 2 for these periods, suggesting an increased biogenic influence (Rogge 1993a, Simoneit *et al.* 2000). The total alkane concentrations (>C_{20}) were not significantly different compared to other periods where C_{29} and C_{31} were less predominant. The biogenic alkane periods were associated with winds from the NNE to NNW away from the urban center and adjacent interstates. C_{20} had the highest concentration during the winter and CPIs (CPI_{fossil} and $CPI_{biogenic}$) were close to 1, supporting the fossil fuel predominance during this period.

Select odd alkanes (C_{21}, C_{23}, C_{25}) from the petroleum-dominated alkane region (<C_{27}, see above) covaried with EC and OC. The non-halogenated VOCs (except benzene) covaried with C_{21}-C_{27}, C_{30} and C_{32}. Gasoline vehicle (catalyst

Figure 3.3 Typical (a) and biogenic influenced (b) alkane profiles at the Baltimore.
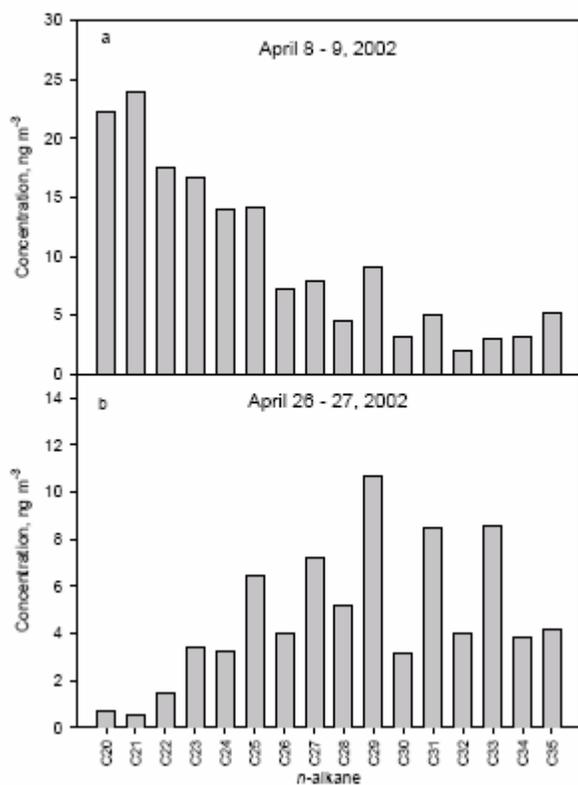
equipped) particulate matter emissions have elevated concentrations of pentacosane (Rogge *et al.*, 1993e). Schauer *et al.* (2002) found elevated of n-tricosane and n-pentacosane in gasoline combustion relative their adjacent even carbon homologues, not observed in medium duty diesel emissions (Schauer *et al.*, 1999, Rogge *et al.*, 1993e). In addition, elevated levels of benzene, toluene and alkyl benzenes have been observed in gasoline exhaust (compared to diesel, Schauer *et al.*, 1999, 2002). Pentacosane is also the dominant alkane measured in vehicle brake linings (Rogge *et al.,* 1993d). Elevated levels of *n*-tricosane have also been observed in pine wood fireplace combustion relative to adjacent even homologues (Schauer *et al.*, 2001). A slight even predominance in this carbon range has been observed in hot asphalt fumes (Rogge *et al.*, 1997a). Even though alkanes have discrete biogenic vs. fossil fuel profiles, distinguishing specific source types using alkanes alone is limited.

In Baltimore, alkane concentrations usually increased from $C_{32} - C_{35}$. This is consistent with tire wear from the adjacent highway (Rogge *et al.*, 1993d). In addition, the two highest molecular weight alkanes (C_{34} and C_{35}) covaried with traffic markers NO, EC and alkylbenzenes. This is expected as tire wear particles should covary with traffic intensity. In addition, an even carbon predominance was observed during 1, 2, and 1 sampling periods during the spring summer and winter, respectively. Previously, this profile has been observed in plastics and plastic incineration (Simoneit *et al.*, 2005). This profile occurred at night when the winds were from the north. This may be due to plastic incineration or possibly several industrial facilites specializing in plastic extruding, shapes, pipe and resins located to the northwest of the city.

Table 3.5 Hopane Seasonal Distribution

	Spring 2002		Summer 2002		Winter 2003	
	Mean[1]	GSD[2]	Mean	GSD	Mean	GSD
17α(H), 22,29,30-trisnorhopane	0.50	1.5	0.35	1.8	0.66	1.4
17α(H), 21β(H)-30-norhopane	1.9	1.5	1.3	1.5	2.4	1.4
17β(H), 21α(H)-30-norhopane +	0.35	1.6	0.32	1.5	0.45	1.7
17α(H), 21α(H)-30-norhopane						
17α(H), 21β(H)-hopane	1.9	1.5	1.5	1.8	2.3	1.5
17β(H), 21α(H)-hopane	0.22	1.6	0.20	1.5	0.25	1.7
17α(H), 21β(H)-22S-homohopane	1.0	1.5	0.76	1.5	1.2	1.3
17α(H), 21β(H)-22R-homohopane	0.82	1.5	0.62	1.5	1.0	1.3
Total hopane	6.8	1.5	5.0	1.5	8.3	1.4

[1] Geometric mean, ng m^{-3}
[2] Geometric standard deviation

Hopanes: The sum of the 7 particle phase hopanes measured in this study (Table 3.5) were similar during the spring (6.8[1.5] ng m^{-3}) and summer (5.0[1.5] ng m^{-3}) and winter (8.3[1.4] ng m^{-3}). The seasonal mean 17α(H),21β(H)-hopane concentrations were within the range reported in Los Angeles (0.93 ng m^{-3}, Fraser *et al.*, 1997, Table 3.4). And were two times greater than those in North Birmingham, AL and Atlanta, GA (0.6 ng m^{-3}, Zheng *et al.*, 2002). Hopane levels in rural areas from the same study were usually a factor of 100 below values observed in Baltimore. The 17α(H),21β(H)-hopane concentrations in Fresno, California (~2 ng m^{-3}, Schauer and Cass, 2000) were similar to Baltimore concentrations observed during the spring and summer and winter. 17α(H),21β(H)-hopane concentrations in Baltimore were approximately ten times less than values reported in industrial and suburban sites in Houston, TX (Fraser *et al.*, (2002). Background levels of 17α(H),21β(H)-hopane observed in the northern Michigan Seney Wildlife Refuge (<0.3 ng m^{-3}, Sheesley *et al.*, 2004), Galveston Island, TX (0.02 ng m^{-3}, Fraser *et al.*, 2002), Big Bend National Park, TX (<0.01 ng m^{-3}, Brown *et al.*, 2002) are significantly less than Baltimore concentrations.

The highest hopane concentrations observed, mainly during the evening-night samples, did not vary systematically with wind speed or direction. The dominant hopanes were 17α(H),21β(H)-30-norhopane and 17α(H),21β(H)-hopane in all samples. The patterns did not vary with total hopanoid concentration, suggesting a constant source or sources at the site, with dilution (boundary layer mixing) controlling concentrations. 17α(H),21β(H)-hopane is the dominant isomer in gasoline and diesel vehicle emissions (Rogge *et al.*, 1993e). Oros and Simoneit (2000) found a

ratio of ~1 for 17α(H), β(H)-hopane to 17β(H),17α(H)-hopane in bituminous coal combustion compared to a mean value of 8.6 ± 1.4 (mean $\pm$ SD) in this study. Distillate No. 2 Fuel oil emissions measured by Rogge *et al.*, (1997) had a ratio of ~5 for 17α(H), 21β(H)-hopane and 22*R*-17α(H), 21β(H)-30-homohopane compared 2.4 ± 0.4 found in Baltimore. From these source studies it appears that distillate fuel and coal combustion are not the dominant sources of the hopanes in the Baltimore particulate matter.

The sum of the seven hopanes analyzed in this study was positively related ($p < 0.005$) to NO and EC and negatively related to ozone and CO. Lower significance levels were found for OC and NO_3^- ($p=0.03$ and 0.009, respectively). Non-halogenated VOCs (except cyclohexane and benzene) were also significantly with all hopanes measured in this study except 17α(H)22,29,30-trisnorhopane and 17α(H),21β(H)-30-norhopane + 17β(H),21α(H)-30-norhopane. The former hopanoid was correlated with styrene, whereas the latter compounds were correlated with toluene and styrene. Cass (1998) suggests the styrene/butadiene copolymer is a good tracer for tire wear as it is the major component of synthetic tire tread. The relationship between styrene and the select hopanes may be due to degassing of styrene via tire wear. The hopane correlations are similar to the heaviest alkanes, also supporting a traffic influence. Similar hopane profiles have been observed for gasoline and diesel vehicle emissions due to the co-emission of crankcase oil during vehicle operation (Rogge 1993e). The positive relationship between hopanes, C_{34}, C_{35} and, NO, EC and VOCs is also consistent with vehicle traffic.

Table 3.6 PAH Seasonal Distribution

	Spring 2002		Summer 2002		Winter 2003	
	Mean[1]	GSD[2]	Mean	GSD	Mean	GSD
Naphthalene	0.56	2.7	0.31	2.6	13	1.8
2-Methylnaphthalene	0.79	2.8	0.42	2.7	18	1.8
Azulene	0.01	2.7	0.005	2.0	0.06	2.2
1-Methylnaphthalene	0.33	2.8	0.18	2.9	7.4	1.9
Biphenyl	0.21	2.7	0.13	2.8	4.9	1.7
2,7-Dimethylnaphthalene	0.47	2.5	0.29	2.6	10	1.9
1,3-Dimethylnaphthalene	0.49	2.6	0.30	2.5	11	2.0
1,6-Dimethylnaphthalene	0.28	2.8	0.18	2.5	6.2	1.9
1,4-Dimethylnaphthalene	0.17	3.0	0.11	3.0	3.4	1.9
1,5-Dimethylnaphthalene	0.11	2.4	0.05	2.1	1.2	1.9
Acenapthylene	0.17	2.9	0.10	2.7	6.2	1.9
1,2-Dimethylnapthalene	0.13	2.2	0.08	2.4	2.4	1.9
Acenapthene	0.37	3.3	0.43	3.1	2.5	1.7
2,3,5-Trimethylnapthalene	0.63	3.0	0.30	3.4	8.3	1.7
Fluorene	1.7	3.3	1.4	3.6	8.2	1.6
1-Methylfuorene	0.98	2.6	0.52	3.1	3.2	1.6
Dibenzothiophene	1.3	2.2	1.1	2.9	1.6	1.6
Phenanthrene	14	2.5	15	3.3	18	1.5
Anthracene	0.70	2.4	0.74	2.2	0.99	2.0
2-Methyldibenzothiophene	1.1	2.3	0.87	2.9	1.6	1.6
4-Methyldibenzothiophene	0.77	2.2	0.68	2.7	1.1	1.6
2-Methylphenanthrene	3.2	2.3	2.9	2.7	4.6	1.5
2-Methylanthracene	0.10	3.5	0.13	2.0	0.14	3.0
4,5-Methylenephenanthrene	0.69	2.3	0.88	2.8	0.95	1.4
1-Methylanthracene	1.6	2.5	1.4	2.7	2.2	1.5
1-Methylphenanthrene	1.3	2.6	1.3	2.8	2.0	1.5
9-Methylanthracene	0.05	1.7	0.02	2.1	0.04	1.8
9,10-Dimethylanthracene	1.1	2.4	0.84	2.9	0.92	1.6
Fluoranthene	5.4	2.2	8.1	2.6	3.7	1.3
3,6-Dimethylphenanthrene	0.23	2.5	0.04	4.9	0.16	3.7
Pyrene	4.1	2.0	4.7	2.4	3.6	1.4
Benzo[a]fluorene	0.18	1.8	0.15	1.9	0.32	1.5
Retene	0.22	2.0	0.20	2.0	0.35	2.0
Benzo[b]fluorene	0.16	1.7	0.15	2.0	0.27	1.5
Cyclopenta[c,d]pyrene	0.04	5.2	0.01	2.0	0.01	3.1
Benz[a]anthracene	0.15	2.2	0.13	2.0	0.55	1.8
Chrysene+Triphenylene	0.35	2.2	0.32	1.6	0.82	1.4
Napthacene	0.03	2.9	0.02	1.9	0.06	1.8
4-Methylchrysene	0.03	2.1	0.02	1.8	0.05	1.5
Benzo[b]fluoranthene	0.29	3.0	0.21	1.9	0.83	1.3
Benzo[k]fluoranthene	0.17	2.5	0.11	2.2	0.57	1.4
Dimethylbenz[a]anthracene	0.02	1.7	0.01	1.7	0.03	1.6
Benzo[e]pyrene	0.17	2.3	0.12	2.0	0.43	1.3
Benzo[a]pyrene	0.18	1.8	0.12	2.1	0.48	1.9
Perylene	0.03	1.7	0.02	2.0	0.08	1.7
Indeno[1,2,3-c,d]pyrene	0.23	1.6	0.20	1.7	0.89	1.4
Dibenz[a,h+ac]anthracene	0.02	1.7	0.02	1.9	0.06	1.4
Benzo[g,h,i]perylene	0.20	1.7	0.22	1.6	0.79	1.4
Anthanthrene	0.02	1.8	0.03	1.8	0.11	1.9
Coronene	0.10	1.7	0.12	1.3	0.34	1.6
Total PAH	58	1.6	58	1.5	160	0.83
Total PAH (Fluorene on)[3]	51	1.7	53	1.5	61	0.75

[1] Geometric Mean, ng m^{-3}
[2] 95% Confidence Interval
[3] See Text

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PAHs: The total PAH (filter + PUF, Table 3.6) concentrations (molecular weight $\geq$ fluorene) were similar during the spring, summer and winter (51[1.7], 53[1.5] and 61[0.75] ng m^{-3}, respectively). Greater volatile PAH (VPAHs) concentrations were observed during the winter (Figure 3.2). Significant breakthrough of these compounds was observed during the spring and summer suggesting increased levels are possibly due to better collection efficiency of these compounds on the PUF during colder temperature periods. Similar to the alkanes, increased NO concentrations and the NPAH profiles (see below) observed during the winter period support a greater influence of high temperature combustion.

Individual PAH concentrations were consistent with previous Baltimore measurements (Dachs and Eisenreich, 2000, Offenberg and Baker 1999, Bamford *et al.*, 2003, Table 3.4) and concentrations reported along the Niagara River (Hoff and Chan, 1987). Pyrene concentrations measured in Chicago, IL (10 ng m^{-3}, Simicik *et al.*, 1997), Denver, CO (24 ng m^{-3}, Foreman and Bidleman, 1990) and Los Angeles, CA during a photochemical smog episode (Fraser *et al.*, 1998) were 2 to > 4 - fold above values reported here. A more recent study in Los Angeles found benzo[*g,h,i*]perylene concentrations similar to those in Baltimore (Fine *et al.*, 2004). Baltimore, MD seasonal mean concentrations of PAHs are within the range of concentrations reported for southeast urban areas (Atlanta, GA, N. Birmingham, AL, Gulfport, MS, and Pensacola, FL, Zheng *et al.*, 2002), Houston, TX (Fraser *et al.*, 2002) and New Brunswick and Sandy Hook NJ (Gigliotti *et al.*, 2000).

Rural PAH concentrations are typically an order of magnitude lower than Baltimore values. Offenberg and Baker (1999) found pyrene concentrations on the

rural eastern shore of the Chesapeake Bay (Chestertown, MD) approximately an order of magnitude lower than reported here. Background values in Texas (Galveston Island, Fraser *et al.*, 2002), and rural areas in the southeast (Centerville, AL, Oak Grove, MS, and Yorkville, GA, Zheng *et al.*, 2002), northern Michigan (Kern Wildlife Refuge, Sheesley *et al.*, 2004), San Joaquin Valley, CA (Schauer and Cass, 2000) were more than an order of magnitude below Baltimore concentrations.

In the spring and summer intensives, the greatest concentration of PAHs (> 150 ng m^{-3}) was often associated with elevated EC concentrations (1.5 – 2.0 μg m^{-3}, Figure 3.2) and light winds (< 1.5 m s^{-1}) with no uniform direction, indicating the influence of local sources and reduced mixing. The lower concentration periods (< 30 ng m^{-3}) were associated with wind speeds greater than 3 m/s from the NNE to NNW. The elevated wind speeds and directional dependence (away from urban center) suggest the site is less influenced by local sources during the low concentration periods, which often coincided with a biogenic alkane profile in aerosols.

The total PAH concentration was significantly (p<0.005) related to NO, NO$_2$ and PM 2.5 (p=0.007). Total PAHs were also related to CO, EC, OC and ozone (negative) with a lower significance (p=0.03, 0.006, 0.05, and 0.02, respectively, Table 3.7). A stronger relationship between PAHs and NO (compared to CO) suggests diesel may contribute a significant concentration of the total PAH concentration at the site. As expected, total PAHs and OC covary (p < 0.022), with combustion sources contributing to the particulate matter organic carbon.

Among individual PAHs, alkylphenanthrenes and alkylanthracenes, fluoranthene, pyrene and cyclopenta[*c,d*]pyrene were significantly (p<0.005)

Table 3.7 PAH Pearson Correlation Coefficients

	Ozone	CO	NO	NO$_2$	EC	OC	NO$_3$-	PM$_{2.5}$	Temp	Wind Speed
Naphthalene	-0.33[1]		**0.52**[2]	0.46					-0.71	-0.42
2-Methylnaphthalene	-0.33		0.62	0.46					-0.70	-0.42
Azulene	-0.28		0.47	0.48	0.40				-0.61	-0.47
1-Methylnaphthalene	-0.33		0.61	0.46					-0.69	-0.42
Biphenyl	-0.34		0.64	0.60					-0.72	-0.44
2,7-Dimethylnaphthalene	-0.32		0.48	0.46					-0.69	-0.42
1,3-Dimethylnaphthalene	-0.32		0.48	0.46					-0.69	-0.42
1,6-Dimethylnaphthalene	-0.32		0.48	0.46					-0.69	-0.42
1,4-Dimethylnaphthalene	-0.33		0.60	0.46					-0.68	-0.42
1,5-Dimethylnaphthalene	-0.35		0.63	0.43					-0.69	-0.40
Acenapthylene	-0.34		0.61	0.46					-0.68	-0.42
1,2-Dimethylnapthalene	-0.33		0.61	0.46					-0.70	-0.42
Acenapthene	-0.28		0.38	0.39					-0.48	-0.41
2,3,5-Trimethylnapthalene	-0.37		0.65	0.46					-0.72	-0.43
Fluorene	-0.33		0.40	0.38					-0.49	-0.40
1-Methylfluorene	-0.41	0.31	0.48	0.44					-0.65	-0.41
Dibenzothiophene										
Phenanthrene										
Anthracene										
2-Methyldibenzothiophene	-0.32	0.33	0.35	0.38					-0.26	-0.28
4-Methyldibenzothiophene	-0.27	0.32	0.35	0.42	0.40	0.33				-0.28
2-Methylphenanthrene		0.34	0.38	0.61	0.50	0.42				-0.35
2-Methylanthracene										
4,5-Methylenephenanthrene				0.38	0.58	0.44				
1-Methylanthracene	-0.26	0.38	0.40	0.48	0.53	0.44				-0.33
1-Methylphenanthrene		0.36	0.41	0.63	0.52	0.45				-0.34
9-Methylanthracene	-0.40	0.61	0.33		0.59	0.43				
9,10-Dimethylanthracene		0.33		0.34	0.42	0.41				
Fluoranthene	0.32				0.67	0.80		0.41	0.68	
3,6-Dimethylphenanthrene	-0.33	0.38					0.46		-0.27	
Pyrene		0.29		0.28	0.70	0.68			0.43	
Benzo[a]fluorene	-0.35	0.37	0.48	0.62	0.47	0.37			-0.34	
Retene		0.40	0.65	0.43	0.66	0.63				
Benzo[b]fluorene	-0.29	0.29	0.39	0.48	0.43	0.36			-0.28	
Cyclopenta[c,d]pyrene		0.36			0.33		0.31			
Benz[a]anthracene	-0.39	0.28	0.68	0.47	0.39				-0.60	-0.31
Chrysene+Triphenylene	-0.42	0.48	0.63	0.61	0.48	0.43			-0.44	
Napthacene										
4-Methylchrysene	-0.44	0.40	0.62	0.34	0.36				-0.38	
Benzo[b]fluoranthene	-0.62	0.47	0.70	0.61	0.42	0.37	0.27		-0.60	-0.26
Benzo[k]fluoranthene	-0.47	0.37	0.65	0.61	0.37	0.32			-0.67	-0.31
Dimethylbenz[a]anthracene	-0.40	0.40	0.66	0.36		0.36			-0.44	
Benzo[e]pyrene	-0.60	0.48	0.70	0.61	0.44	0.38			-0.59	-0.27
Benzo[a]pyrene	-0.39	0.27	0.63	0.42					-0.54	-0.30
Perylene	-0.40	0.30	0.64	0.40	0.35				-0.48	
3-Methylcholanthrene					0.71	0.42				
Indeno[1,2,3-c,d]pyrene	-0.41		0.61	0.60					-0.69	-0.35
Dibenz[a,h+ac]anthracene	-0.32		0.48	0.39					-0.59	
Benzo[g,h,i]perylene	-0.39	0.28	0.65	0.63	0.35	0.33			-0.66	-0.39
Anthanthrene			0.43	0.40			-0.33		-0.57	-0.32
Coronene	-0.34	0.27	0.64	0.66	0.57	0.40			-0.57	-0.45
Total (pg/m3)	-0.30	0.28	0.60	0.62	0.44	0.30			-0.51	-0.45

[1] p < 0.05, [2] Bold values p < 0.005

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correlated with the majority of non-halogenated VOCs. Cyclopenta[*c,d*]pyrene, which has been suggested as a unique tracer for gasoline combustion (Daisey *et al.*, 1986), is correlated with CO and EC at a slightly lower significance level (p = 0.02 and 0.05, respectively). This may be due to the reactivity of this PAH to photochemical degradation ($t_{1/2}$ = 6 – 96 min, Atkinson and Arey, 1994). The total alkyphenanthrene (3-, 9-, 1-, 2-methylphenanthrene and 4,5-dimethylphenanthrene) to phenanthrene ratio is lower for gasoline (0.7) compared to diesel (>3) combustion (Nielson, 1996, Limm *et al.*, 1999). In this study only 1- and 2-methylphenanthrene and 4, 5-dimethylphenanthrene were quantified. The concentration of these compounds relative to phenanthrene is 0.36 (geometric mean). If diesel is the dominant source of these compounds, the sum of 3- and 9-methylphenanthrene must be 10 fold greater than the total alkylphenanthrenes analyzed in this study, which is not likely. Combined with the VOC data it appears that the alkyphenanthrenes may have a gasoline engine source.

In contrast, the benzofluorenes, benzofluoranthenes, benz[*a*]anthracene were significantly correlated with NO and EC. A relatively poor correlation between these compounds and non-halogenated VOCs was also observed. Alkylbenzene emissions from gasoline combustion are much greater than diesel (Schauer *et al.*, 1999, 2002), therefore a poor relationship with VOCs suggests a diesel combustion source of these PAHs.

NPAH: t-NPAH concentrations (filter + PUF, Table 3.8) were not significantly different during the spring (2.8[2.1] ng m^{-3}), summer (0.88[2.1] ng m^{-3}) and winter (1.3[1.9] ng m^{-3}). NPAHs of differing sources (primary vs. secondary) did not follow

Table 3.8 NPAH Seasonal Distribution

	Spring 2002		Summer 2002		Winter 2003	
	Mean[1]	GSD[2]	Mean	GSD[2]	Mean	GSD[2]
1-nitronaphthalene	640	3.7	100	4.1	440	2.0
2-nitronaphthalene	410	3.1	85	3.5	250	1.8
2-nitrobiphenyl	53	3.7	8.8	4.2	16	1.9
3-nitrobiphenyl	54	4.5	9.2	3.8	25	1.9
4-nitrobiphenyl	37	4.1	16	3.5	52	2.4
3-nitrodibenzofuran	18	3.1	10	2.2	4.7	2.2
1,3-dinitronaphthalene	2.0	2.5	1.5	2.4	0.51	1.9
1,5-dinitronaphthalene	0.7	2.9	1.0	3.5	0.17	1.8
5-nitroacenaphthene	43	5.0	54	4.5	7.8	2.8
2-nitrofluorene	21	4.3	3.3	3.0	6.7	3.0
2,2'-dinitrobiphenyl	11	2.9	5.4	2.4	39	3.4
9-nitroanthracene	240	2.6	220	3.1	83	2.4
9-nitrophenanthrene	50	2.8	20	2.5	21	2.3
3-nitrophenanthrene	24	3.0	17	2.4	12	2.6
4-nitrophenanthrene	3.0	3.2	4.7	2.7	2.0	2.5
2-nitrofluoranthene	74	2.9	57	2.5	69	2.3
3-nitrofluoranthene	5.8	8.0	0.6	2.2	2.0	2.6
1-nitropyrene	74	2.1	23	2.1	150	2.4
2-nitropyrene	11	5.4	1.6	2.2	6.2	2.1
2,7-dinitrofluorene	3.5	2.9	1.9	2.4	3.3	2.5
7-nitrobenz[a]anthracene	9.4	3.3	3.6	1.9	17	3.5
6N-chrysene	8.3	9.5	0.2	1.9	1.6	2.1
Total NPAH (ng m⁻³)	2.8	2.1	0.88	2.1	1.3	1.9
2NFLN/1NPY	1.1	2.18	2.5	2.1	0.45	2.7

[1] Geometric mean, pg m⁻³
[2] Geometric standard deviation

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the t-NPAH seasonal trends. For example, 1-nitropyrene is the dominant NPAH found in diesel exhaust (Bamford *et al.*, 2003, Zielinska *et al.*, 2004). The winter (150[2.4] pg m^{-3}) concentrations were significantly greater than the summer (23[2.1]pg m^{-3}). Spring (74 [2.1] pg m^{-3}) concentrations were not significantly different than the winter or summer. The dominant particle bound secondary NPAH found in the ambient atmosphere is usually 2-nitrofluoranthene and Baltimore concentrations were similar during the spring (74[2.9] pg m^{-3}), summer (57[2.5] ng m^{-3}) and winter (70[2.3] pg m^{-3}).

Similar to Bamford and Baker (2003) and Reisen and Arey (2005), NPAH concentrations were a factor of 5 to 1000 below parent PAHs for the phenanthrenes, fluoranthenes and pyrenes. In contrast, the nitro-substituted biphenyls, 9-nitroanthracene and 5-nitroacenaphthene concentrations were up to 6 fold greater than parent PAH levels. The latter may be due to the lower collection efficiency mentioned above for the lightest PAHs compared. Concentrations of 1-nitropyrene were 2 to 5 times greater than those in measured at a different downtown Baltimore site in 2001 (Bamford and Baker, 2003). The differences in the 1-nitropyrene concentrations may be due to the proximity of the current site to an interstate and bus depot. Summer and winter 2-nitrofluoranthene concentrations in the 2001 study were similar to values observed here. The winter mean concentrations of 1-nitropyrene (150 pg m^{-3}) and 2-nitrofluoranthene (69 pg m^{-3}) are similar to the mean concentration of three winter samples (Feb. 1998) reported by Fieldberg *et al.* (2001) for a heavy traffic area in Copenhagen, Denmark. The spring 1-nitropyrene concentration range at this site (80 – 360 pg m^{-3}, April, 1998, N=5) was up to 4 fold above the mean spring concentration

presented here. Dimashki *et al.* (2000) observed concentrations of 1-nitropyrene (90 pg m^{-3}) and 2-nitrofluoranthene (221 pg m^{-3}) in Birmingham, UK, also within the range reported here. Summer and winter 1-nitropyrene concentrations were consistent with those in Athens, Greece (20 and 180 pg m^{-3}, respectively), whereas the Baltimore spring concentrations are 3 times higher than the mean value reported by Marino *et al.* (2000). Increased winter concentrations of 2-nitrofluoranthene, reported for Athens, were not observed in Baltimore.

Due to the site location and elevated 1-nitropyrene concentrations, diesel exhaust is most likely a significant contributor of NPAHs. The ratio of 2-nitrofluranthene/1-nitropyrene has been used to determine the primary vs. secondary contribution of NPAHs to the ambient atmosphere. Typically values less than 5 indicate the occurrence of primary sources whereas values greater than 5 indicate secondary sources (Ciccioli *et* al., 1996). The time series of 2-nitrofluoranthene to 1-nitropyrene is plotted in Figure 3.2 with seasonal mean ($\pm$ 1 standard deviation) values of 1.0 $\pm$ 0.8, 2.5 $\pm$ 1.1, and 0.45 $\pm$ 0.28 for spring, summer and winter, respectively (Table 3.8), confirming the high primary (diesel) NPAH influence at this site. Bamford and Baker (2003) found statistically higher values ($p < 0.05$) in July compared to January in downtown Baltimore. Values less than 1 have been reported for a high traffic area in Copenhagen, Denmark (Feildberg *et al.*, 2001). Mean spring, summer and winter values reported for urban residential areas in Athens, Greece (2.3, 2.0 and 2.8, respectively, Marino *et al.*, 2000) were similar to Baltimore summer concentrations with elevated values during the spring and winter. The 2-nitrofluoranthene/1-nitropyrene ratios illustrate the high primary (diesel) contribution

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to the NPAH distribution to Baltimore $PM_{2.5}$ Supersite, with a greater influence of secondary reactions in the summer months due to increased greater photochemical activity.

Although the 2-nitroflouranthene/ 1-nitropyrene ratios suggest primary sources dominate the NPAH distribution at the site, the ratio of 2-nitrofluoranthene to 2-nitropyrene provides insight into the formation mechanism of the secondary NPAHs. The 2-nitrofluoranthene isomer has primarily two formation pathways (OH and NO_3), whereas 2-nitropyrene is solely formed via OH attack (Arey *et al.*, 1986, Atkinson *et al.*, 1990). The ratio of these two secondary isomers provides evidence of the seasonal dependence of the formation pathway. Gas phase PAHs only react with the NO_3 at night due the efficient removal of this oxidant by photolysis. Figure 3.4 shows the ratio of 2-nitrofluoranthene/ 2-nitropyrene for the spring, summer and winter samples. Ratios of 10 and 100 denote the OH and NO_3 radical formation pathways, respectively (Zielinska *et al.*, 1989a, b, Feilberg *et al.*, 2001). During the spring and winter, the 2-nitrofluoranthene/2-nitropyrene ratios (2NFLN/2NPYR) are usually 10 or less and ranged 1.6 – 33 and 6 – 24, respectively. Typical NO/NO_2 and O_3 levels were > 0.5 and < 20 ppb, respectively. During the summer period the NO/NO_2 concentrations were lower corresponding to an increase of the 2NFLN/2NPYR ratio and increased O_3 concentrations. An inverse relationship between the 2NFLN/2NPYR and NO/NO_2 ratios is apparent for the summer samples. The 2NFLN/2NPYR ratio is less sensitive to O_3 concentrations. This is likely due to the scavenging of NO_3 radicals by NO ($NO + NO_3 \rightarrow 2NO_2$). The sensitivity between these two ratios may serve as a predictive tool for determining the dominant oxidant

Figure 3.4 Spring, summer and winter 2-nitroflouranthene/2-nitropyrene ratio, NO/NO₂ concentration at the Baltimore Supersite 2002-2003. Samples collected during the day and night are signified by ° and *, respectively, with the remainder sampled 24 hrs.
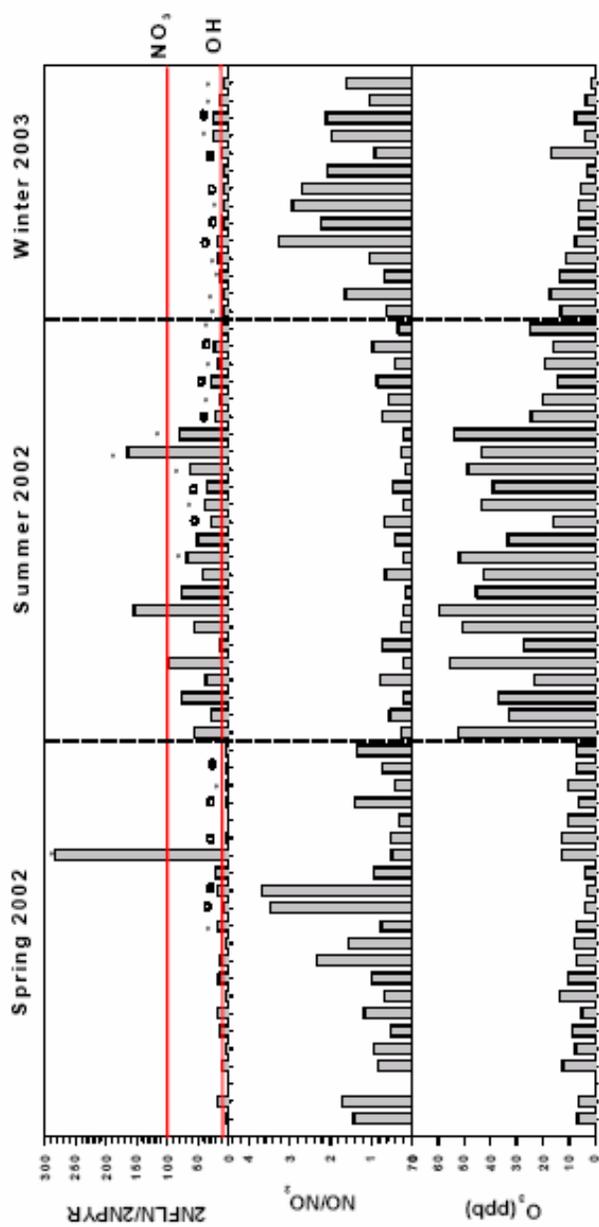
responsible for secondary organics in the urban atmosphere. From Figure 3.4 we see that NO_3 reactions usually dominate when the ratio between NO and NO_2 is <0.2. Therefore, during periods where NO/NO_2 is less than 0.2, secondary products from reaction involving NO_3 may dominate the night time chemistry.

Bamford and Baker (2003) observed a similar seasonal trend in 2001 for Baltimore. The current 2NFLN/2NPYR maxima (2NFLN/2NPYR = 160) for the summer period was greater than reported in 2001 (2NFLN/2NPYR = 60). These levels are also greater than other studies reported for residential Athens, Greece (~2, Marino *et al.*, 2000), urban and vehicular influenced Copenhagen, Denmark (2 – 18, Feildberg *et al.*, 2001). Values reported for Claremont, CA during a smog episode (Zielinska *et al.*, 1989a) are within the range of the summer 2NFLN/2NPYR maxima observed in Baltimore, MD.

The following equation has been employed to quantify the fractional contribution of OH vs. NO_3 initiated NPAH formation Feilberg *et al.* (2001);

$$\alpha_{OH} = (R_{obs} - R_N)/(R_{OH} - R_N) \tag{1}$$

where α_{OH} corresponds to the relative contribution of the OH pathway, R_{obs} is the observed 2NFLN/2NPYR ratio, R_N and R_{OH} are the ratio of 2NFLN/2NPYR from the NO_3 and OH pathway, respectively. R_N and R_{OH} are constants. R_{OH} is taken from chamber and modeling studies (Atkinson and Arey, 1994, Fan *et al.*, 1995, Kamens *et al.*, 1994) and is set to 10. R_N is assigned a value of 100 although this may be as much as 1000 (Feilberg *et al.*, 2001). When this equation ($R_N = 100$) is applied to the

current dataset $\geq$ 90% of the spring and winter 2-ntrofluoranthene concentrations are due to the OH reaction pathway. A larger contribution from NO_3 was observed during the summer (Figure 3.4). The NO_3 mechanism was responsible for > 75% of the 2-nitrofluoranthene concentrations in 3 out of 31 samples collected during the summer. This is consistent with previous results from Baltimore (Bamford and Baker, 2003) where as much as 55% of the 2NFLN during a given period was attributed to the NO_3 radical formation process during July 2001 (Bamford and Baker, 2003). Overall the dominant mechanism for 2-nitrofluoranthene formation employs OH while NO_3 can be a significant during select summer periods.

Among individual NPAH isomers, 1-nitropyrene (Table 3.9) was significantly correlated (p<0.005) with NO similar to Fieldberg *et al*, (2001) at a road side station in Copenhagen, Denmark. Bamford and Baker (2003) did not observe this relationship in a suburban area between Baltimore, MD and Washington, DC, postulating alternate sources of NO to that region. A lower correlation between 1-nitropyrene and EC (p=0.2) suggests diesel is not the dominant source of EC to the site. Ogulei *et al.* (2005) found that spark ignited vehicle emissions contributed 5 times the aerosol mass (compared to diesel) to this site during their multivariate source apportionment using inorganic species. This is consistent with the poor 1-nitropyrene and EC relationship. Although NO is emitted in smaller quantities in gasoline combustion (compared to diesel engines), the relationship between NO and 1-nitropyrene suggests diesel emissions (1-nitropyrene and NO) are a significant contributor (but not necessarily OC and EC) or covary with PM2.5 during the spring and summer.

Table 3.9 NPAH Pearson Correlation Coefficients

	Ozone	CO	NO	NO$_2$	EC	OC	NO$_3^-$	PM$_{2.5}$	Temp	Wind Speed
1N-napthalene	-0.32†						0.30			
2N-napthalene	-0.38‡	0.34					0.44			
2N-biphenyl	-0.33	0.29					0.28			
3N-biphenyl	-0.28	0.63	0.68		0.54	0.29	0.33			
4-Nitrobiphenyl	-0.28						0.49			
3N-dibenzofuran							0.40			
1,3-dinitronaphthalene		0.51	0.65	0.42	0.63	0.41			0.37	
1,5-dinitronaphthalene	0.48			0.31		0.41		0.35	0.62	
5N-acenapthene					0.48				0.44	
2N-fluorene	-0.33									
2,2'-dinitrobiphenyl	-0.27		0.31						-0.42	-0.28
9N-anthracene					0.41				0.42	
9N-phenanthrene							0.27			
3N-phenanthrene		0.38	0.33		0.63					
4N-phenanthrene					0.68	0.37			0.42	
2N-fluoranthene		0.48	0.41	0.48	0.62	0.32				-0.27
3N-fluoranthene	-0.28									
1N-pyrene	-0.43	0.39	0.38	0.31	0.39				-0.68	-0.27
2N-pyrene	-0.38		0.25		0.36					
2,7-dinitrofluorene			0.31							
7-nitrobenz[a]anthracene	-0.30	0.27		0.28			0.38		-0.42	-0.40
6N-chrysene				-0.29					0.51	0.29
2NFLN/1NPY	0.46			0.26	0.45			0.35		

† p < 0.05, ‡ Bold values p < 0.005

The dominant secondary NPAH, 2-nitrofluoranthene, was positively

correlated with NO and EC. This may due to the covariance of combustion products

and secondary organic aerosol. 2-nitropyrene was correlated with NO and EC, and 2-

nitrofluoranthene was significantly correlated with fluoranthene suggesting a NPAH

formation dependence on PAH concentrations (Fieldberg *et al.*, 2001). Bamford and

Baker (2003) observed a similar relationship with between 2-nitropyrene and NO at

the suburban site, but not 2-nitrofluoranthene.

Cyclohexane, heptane and alkybenzenes were significantly correlated

($p<0.005$) with 3-nitrobiphenyl, 3-nitrodibenzofuran, 5-nitroacenaphthene, 9-

nitroanthracene, 3- and 4-nitrophenanthrene, and 2-nitrofluoranthene. All of these

NPAHs can be formed via gas phase reactions (Arey, 1988). The significant

relationship between the secondary NPAHs and VOCs suggests that the amount of

secondary organics formed in the Baltimore area are directly linked to anthropogenic

(vs. biogenic) emissions. In other words, the significant correlation between the

secondary NPAHs and traffic markers illustrates the connection between gasoline

combustion emissions and oxidized products (secondary organic aerosol). While 1-

nitropyrene emissions may be dominated by diesel combustion, gasoline emissions

initiate the atmospheric conditions necessary for secondary NPAH formation. In the

Baltimore atmosphere, this corresponds to non-diesel emissions indirectly enhancing

the toxicity of the urban aerosol by promoting secondary NPAH formation.

3.5.1   *Semivolatile Organics Profiles*

Individual sample periods illustrate the different sources or chemistry

occurring at the Baltimore PM2.5 Supersite. Overall, the alkanes provide the greatest

variability for distinguishing primary sources impacting the site. The hopane and PAH profiles did not dramatically differ from day to day suggesting similar sources of these compounds to the site. The following section provides examples of contrasting profiles observed at the Baltimore indicative of different source strengths. The April 23 day alkane profile (Figure 3.5) shows elevated concentrations of C_{29} and C_{31}, typical of biogenic sources along with the increasing concentration of from C_{32} to C_{35} indicative of tire wear (Rogge *et al.*, 1993d). In addition, elevated concentrations of C_{25} relative to C_{24} and C_{26} indicate gasoline and diesel combustion sources (Rogge *et al.*, 1993e). Road dust is a repository leaf/grass debris, vehicle exhaust and abrasive emissions (tire wear), therefore the combination of these individual profiles is expected**.** The 2N-fluoranthene to 1-nitropyrene ratio (0.8) is consistent with a primary aerosol sources (Figure 3.6). This day is a typical set of profiles observed at the Baltimore Supersite.

The April 26 alkane profile (Figure 3.5) does not contain the tire wear profile intermixed with the biogenic profile. An odd carbon predominance is observed from C_{22} to C_{35} with a C_{max} at C_{29}. The PAH concentrations and profiles are similar among these two periods (April 23 and 26) suggesting the dominant source of PAHs and alkanes are not linked. Lower concentrations of NPAHs are observed but the profiles are similar. The ratio of 2-nitrofluoranthene to 1-nitropyrene is also similar (1.6, Figure 3.6) suggesting a primary sources of NPAHs.

The August 1, night sampling period was characterized by elevated 2-nitrofluoranthene concentrations relative to 1-nitropyrene (Figure 3.6, 1.1 and 0.06 ng m^{-3}, respectively) indicating high secondary NPAH production. The ratio of 2-
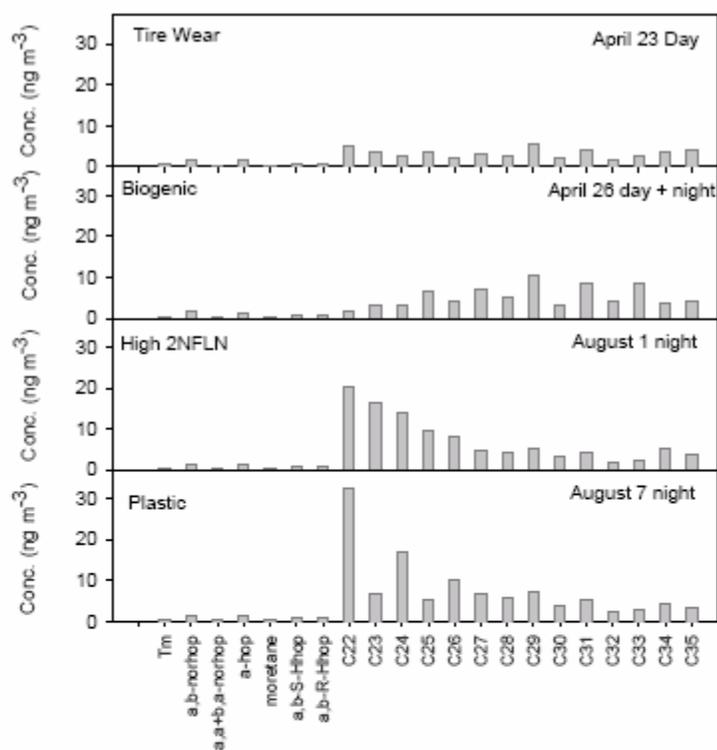
Figure 3.5 Spring and summer 2002 profile plots for C_{22} to C_{35} alkanes and hopane series $17\alpha(H),22,29,30$-trisnorhopane (Tm), $17\alpha(H)$, $21\beta(H)$-30-norhopane (a,b-norhop), $17\beta(H),21\alpha(H)$-30-norhopane+$17\alpha(H),21\alpha(H)$-30-norhopane (a,a+b,a-norhop), $17\alpha(H),21\beta(H)$-hopane (a-hop), $17\beta(H)$, $21\alpha(H)$-hopane (moretane), $17\alpha(H),21\beta(H)$-22S-homohopane (a,b-S-Hhop) and $17\alpha(H),21\beta(H)$-22R-homohopane (a,b-R-Hhop).

Figure 3.6 Spring and summer NPAH profile plots.
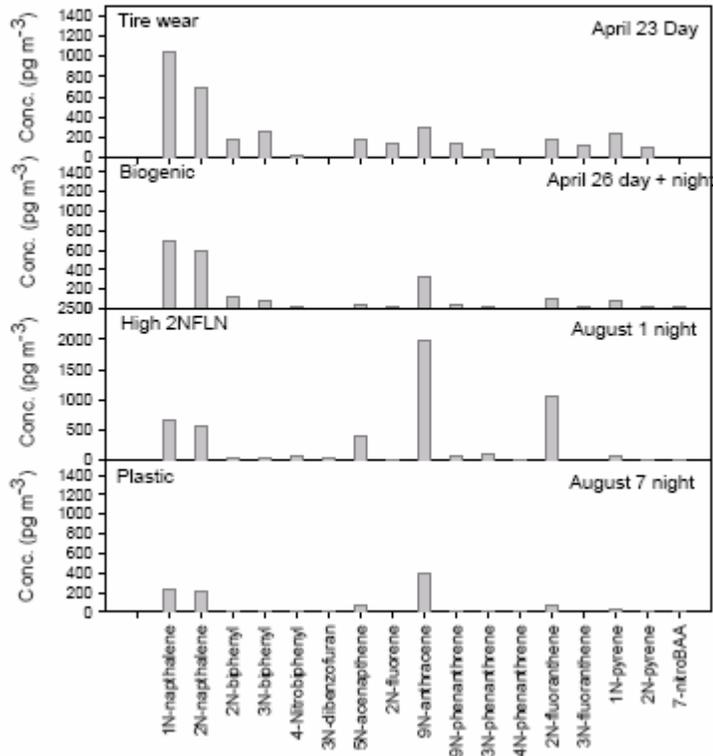
nitrofluoranthene to 2-nitropyrene (160) suggests the dominant NPAH formation pathway is via the NO_3 radical (see above). This period was also characterized by an elevated 9-nitroanthracene concentration. 9-nitroanthrcene has diesel sources (Paputa-Peck, *et al.*, 1983, Ciccicioli *et al.*, 1989, Arey, 1998, Bamford *et al.*, 2003) and can be formed via heterogeous reactions (Pitts *et al.*, 1978, Arey *et al.* 1989). The increased NO_3 chemistry suggests heterogeneous reactions are responsible for the elevated 9-nitroanthracene concentrations. The alkane profile was typical anthropogenic with a decreasing concentration from C_{22} to C_{28} and a slight biogenic source signature apparent with elevated C_{29} and C_{31} concentrations. The PAH profiles are similar to previous periods with the exception of decreased concentrations of cyclopenta[*c,d*]pyrene. This is most likely due to degradation of this reactive PAH due to increased oxidant concentrations during this period.

The August 7 night period (Figures 3.5 and 3.6) exhibited a distinct even carbon predominance from C_{22} to C_{27} ($CPI_f = 0.5$) in the alkane profile consistent with plastic incineration (Simoneit *et al*. 2005). Increased levels of C_{29} and C_{31} relative to adjacent alkanes show a mixed biogenic source also contributing the profile. The PAH profile from open burning of plastic bags, roadside litter and landfill trash from Chile consists of elevated benzofluoranthenes relative to benzo[*g,h,*i]perylene (~4), but the combustion emissions of US plastic bags did not contain detectable levels of these PAHs (Simoneit *et al.*, 2005). The observed ratio in Baltimore, MD during this period was 1.4, suggesting plastic incineration (using Chilean profiles) is not the dominant source of PAHs during this period. The ratio of 2-nitropyrene to 1-nitropyrene (1.9) signifies low photochemical production during

this period relative to primary emissions, similar to the previous selected periods. The above profiles represent the typical differences among days and compound classes observed in Baltimore. Although the alkanes appeared to contain the greatest variability, subtle difference in the PAH and hopane profiles may be elucidated using multivariate receptor models.

3.6 Conclusions

During the spring summer and winter of 2002-2003 a series of nonpolar organic compounds were collected at the Baltimore PM2.5 Supersite to evaluate the seasonal composition changes of the aerosol organic fraction. The total alkane, PAH and hopane concentrations were not significantly different among seasons suggesting local sources. Concentrations at the Baltimore Supersite were within the range of previous urban studies and up to an order of magnitude above rural values. Various alkane source profiles were observed during the ambient sampling including; tire wear, biogenic emissions, plastic incineration and vehicle exhaust. Primary sources dominated the NPAH distribution at the site with 2-nitrofluoranthene/1-nitropyrene concentrations typically less than 5. A greater proportion of secondary NPAHs were found during the spring and summer whereas 1-nitropyrene (and NO) concentrations were greater during the winter periods due to increased fossil fuel combustion. In addition, the formation of secondary NPAHs is dominated by the OH radical during the spring and winter, whereas night time NO_3 reactions are a significant contributor (as much as 100%) to the summer 2-nitrofluoranthene concentrations. The fraction of OH initiated secondary NPAH formation is more sensitive to the NO/NO_2 ratio than ozone illustrating the effect of NO in scavenging the NO_3 radical. A strong

correlation between secondary NPAHs and VOCs during the three seasons suggests the oxidative potential or gas phase oxidants involved in the formation of secondary NPAHs are related combustion emissions. Although gasoline combustion is not the major source of NPAHs, oxidant precursors (*i.e.* VOCs) are directly related to the formation of secondary NPAHs.

Using multiple species from primary and secondary sources, this study provides the framework for future studies using these non-polar organic constituents as tracers for organic matter. In addition, the NPAH distribution provides information on the amount (relative to primary emissions) and mechanism (OH vs. NO_3) of secondary organic aerosol formation typical for a Mid-Atlantic urban area.

Chapter 4:

Diurnal Size Distributions of Polycyclic Aromatic Hydrocarbons and Nitro-substituted Polycyclic Aromatic Hydrocarbons in the Baltimore, MD Atmosphere

4.1 Introduction

Size and composition influence the fate of organic particulate matter in the ambient atmosphere. Organics make up 20% to 60% of the aerosol mass (Malm *et al.*, 2004) and this fraction may be an important contributor to cloud condensation nuclei (CCN) in remote regions (Novakov and Penner, 1993) but may suppress rain in highly polluted regions (Ramanathan *et al.*, 2001). An increasing amount of evidence links ambient particulate matter concentrations to increased mortality (Dockery *et al.*, 1993, Pope, 2000). Particle size determines the penetrating efficiency of particulate matter (Phalen *et al.*, 1991, Tsuda *et al.*, 2002) and the removal mechanisms from the ambient atmosphere (Slinn and Slinn, 1980, Sehmel, 1980, Poster and Baker, 1996a, b, Seinfeld and Pandis, 1998). Polycyclic aromatic hydrocarbons (PAHs) and nitro-substituted polycyclic aromatic hydrocarbons (NPAHs) constitute a relatively small portion of the organic fraction but are implicated in its increased mutagenicity (Arey *et al.* 1988, Gupta *et al.*, 1996, IARC 1989). Formed concurrently with black carbon during incomplete combustion, PAHs are often associated with elemental carbon (EC) or soot and their size distribution may reflect the source and aging of primary ambient particulate matter (van Vaeck and van Cauwenberghe, 1985, Venkataraman *et al.*, 1994, Offenberg and Baker, 1999, Schnelle *et al.*, 2001).

NPAHs have primary and secondary sources to the ambient atmosphere. Certain NPAH isomers have been detected in fossil fuel combustion whereas others are formed in the gas phase (reactions with OH and N_2O_5 radical, Arey, 1998) and/or through heterogeneous reactions (Fan *et al.*, 1996) in ambient air. Although some isomers can be formed by more than one pathway, certain NPAH isomers are source type specific. For example, 1-nitropyrene is a dominant NPAH found in diesel exhaust, while 2-nitropyrene is formed via OH mediated gas phase reaction (see Arey, 1998 for review). Therefore, the relative abundance of individual congeners indicates sources (primary vs. secondary) of NPAHs.

The size distribution of PAHs has been previous reported in urban, suburban, forested and over water atmospheres (van Vaeck and van Cauwenberghe, 1985, Aceves *et al.*, 1993, Venkataraman *et al.* 1994, Poster *et. al.*, 1996, Allen *et al.*, 1996, 1997, Miguel *et al.*, 1998, Offenberg and Baker, 1999, Schelle-Kreis *et al.* 2001, Sanderson and Farant, 2005, Kawanda *et al.*, 2005). Offenberg and Baker (1999) measured the PAH size distribution in Chicago, IL and over Lake Michigan. The geometric median diameter of indeno[1,2,3-*cd*]pyrene decreased from 2.6 μm to 0.73 μm from the Chicago to Lake Michigan sites under northwest winds, due to deposition of larger particles during over-water transport. Poster *et al.* (1995) found that PAHs occurred on particles less than 1μm in Egbert, ON and Chicago, IL. In Boston MA, greater than 85% of the indeno[1,2,3-*cd*]pyrene mass was associated with particles less than 1.9 μm (Allen *et al.*, 1996). Vehicle emissions have found EC and PAH mass median diameters less than 0.2 μm (Venkataraman *et al.*, 1994), while road dust PAH size distributions are much greater (>100 μm, Yang *et al.*,

1999). Venkataraman *et al.* (2002) reported mass median aerodynamic diameters of ~0.5 μm, > 0.7 μm and > 0.8 μm for PAHs emitted during wood, dung-cake, and biofuel briquette combustion, respectively. Other PAH size distribution measurements have included fly ash (>40 - <105 μm Arditsoglou *et al.*, 2004) and residential coal combustion (~0.35 μm, Chen *et al.*, 2004).

The concentrations of NPAHs in the ambient atmosphere are orders of magnitude below those of PAHs. To our knowledge, the only size resolved NPAH results are from Kawanaka *et al.* (2004), who reported the size distribution of 2-nitrofluoranthene in Tokyo, Japan from a 42 day composite of weekly samples using a cascade impactor. They found 72% of the 2-nitrofluoranthene mass was concentrated on particles with diameters less than 0.68 μm. Fine and coarse aerosol NPAHs have been presented by Cecinato *et al.* (1999) over successive 12 hr periods in Rome. The largest concentrations were found on the fine fraction (0.01-2.5 μm) with a lower, but significant contribution in the coarse mode (2.5 μm-10 μm).

The size distribution of individual compounds in the ambient atmosphere depends on their vapor pressure. Lighter PAHs are associated with larger particles compared to non-volatile PAHs (Allen *et al.*, 1996, Offenberg and Baker, 1999, Poster *et al.*, 1995) with either an increase in the overall PAH size distribution with distance from sources (Schnelle *et al.*, 2001, van Vaeck and van Cauwenberghe, 1985) due to aging or a decrease due to dry deposition of larger particle associated PAHs via transport (Offenberg and Baker, 1999). In their modeling study, Venkataraman *et al.* (1999) proposed that volatilization rates of lighter PAHs from the nuclei mode (direct emissions) are enhanced due to the Kelvin effect, followed by

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adsorption of these compounds to accumulation mode particles. Approximately 68% of the variability observed in the PAH gas particle partitioning coefficient in Chicago, IL ambient air was explained by incorporating compound vapor pressure, particle size and organic carbon content (Offenberg and Baker, 2002). Significant correlations were also observed between the PAH geometric median diameter and PAH vapor pressure.

We have recently developed a large-volume injection method that increases our analytical sensitivity orders of magnitude, allowing for the determination of PAH and NPAH size distributions on 12 hr timescales using a Berner low pressure impactor (Crimmins and Baker, 2006a). Adding to our understanding of the seasonal bulk aerosol organic distribution in Baltimore, MD (Crimmins and Baker, 2006b), the objective of this study was to characterize the diurnal size distributions of PAHs and NPAHs in the Baltimore, MD atmosphere. These results are the first size-resolved comparison of PAHs and primary and secondary NPAHs, providing insight into the behavior of these two classes of compounds with respect to particle size and sources in the Baltimore, MD atmosphere.

4.2 Methods

4.2.1 Sampling

Size resolved 12 hr ambient aerosol samples were collected between April 15 - 18 and April 22 - 25, 2002 at the Baltimore PM2.5 Supersite, Baltimore, MD. The site description has been previously reported by Harrision *et al.* (2004) and Ogulei *et al.* (2005) and is briefly summarized here. Aerosol samples were collected at the

Baltimore PM2.5 Supersite ~6 m above the asphalt parking lot. The sampling site is flanked to the west (~100 m) by a Maryland Transit Authority bus depot. A four lane access road separates the site and bus depot, spanning south to northwest of the site. A major highway interstate (I895) is positioned to the east (~100 m). The interstate is elevated (~6 m) passing through the Baltimore Harbor Tunnel approximately 2 km south of site. An on ramp to the interstate is located between the site and I895 (~10 m) with limited traffic.

Particulate matter was collected using a Berner low-pressure impactor operated for 12 hr at 80 Lpm (Poster *et al*., 1995). Day and night samples were collected approximately 7 am - 7 pm, and 7 pm -7 am EST, respectively. The impactor consists of 5 stages (0.04 - 0.14, 0.14 - 0.49, 0.49 - 1.7, 1.7 - 6 and 6 - 21μm) where particles are collected on non-greased aluminum foils, previously ashed at 450°C for 4 hrs and sealed in individual foil pouches. Prior to deployment, each foil was tared (0.1μg) using a Mettler (UM T-2) microbalance. Particle loaded foils were returned to their respective foil pouches and immediately frozen at -20°C upon returning to the laboratory.

4.2.2   Analysis

Prior to analysis each foil was placed in a desiccator (24 hr) and reweighed. The foil was quantitatively subsampled (cut in half) just prior to extraction. The foil subsample extraction and processing has been previously described (Crimmins and Baker, 2006a). Briefly, each foil was loaded in a 20 mL test tube previously ashed at 450 °C for 4 hrs. A series of PAH (fluoranthene-d_{10}, perylene-d_{12}) and NPAH (1-

nitronaphthalene-d_7, 9-nitroanthracene-d_9, and 1-nitropyrene-d_9) surrogates were added each tube. Dichloromethane (DCM) was added, the tubes were sealed with Teflon lined screw caps and the samples were sonicated for 30 min. Each tube was then placed in the freezer (-20°C) for 48 hrs. Extracts were filtered, exchanged to hexane and concentrated under a gentle stream of N_2 (Turbovap II, Zymark, Hopkinton, MA) to 500μL. A series of perdeuterated PAHs (benz[*a*]anthracene-d_{12}, benzo[*a*]pyrene-d_{12} and benzo[*g,h,i*]perylene-d_{12}) were then added as internal standards just prior to PAH analysis.

PAHs were quantified using an Agilent 6890/5973 gas chromatograph/mass spectrometer (GC/MS) with electron ionization (EI) in selective ion mode (SIM). A programmed temperature vaporization (PTV, Gerstel, Mülheim an der Ruhr, Germany) injector was configured for 25μL pulsed splitless injection (Crimmins *et al.*, 2004) Extracts were then eluted through a 0.25mm x 30m x 0.25μm DB-5ms (Agilent Technologies, Palo Alto, CA) capillary column.

After PAH analysis, the extracts were further purified using an aminopropyl SPE cartridge (Sep-Pak, Waters, Milford, MA) then concentrated under N_2 and exchanged to hexane (Bamford *et al.*, 2003). Normal phase LC was then employed for the final clean-up step using a 5μm, 9.6 mm x 30 cm Chromegabond amino/cyano column (ES Industries, West Berlin, NJ). The purified extracts were concentrated to ~200μL and NPAH internal standards (3-nitrofluoranthene-d_9, 6-nitrochrysene-d_{11}, 2-nitrofluorene-d_9 and 5-nitroacenaphthene-d_9) were added just prior to analysis. The instrumental parameters for NPAH quantification have been previously presented (Crimmins and Baker, 2006a). The GC/MS was configured for negative chemical

ionization (methane) in SIM mode. The PTV was set in solvent vent mode

introducing 50μL of each extract to a 0.25mm x 30m x 0.25μm DB-17ms capillary

column.

4.2.3   Quality Assurance

Method detection limits (MDLs) were developed using field and laboratory foil

blanks. MDLs were defined as 3 times the greater of the instrument noise or mean

blank mass. The PAH and NPAH MDLs ranged 2 to 20 pg/m^3 and 0.02 to 0.8 pg/m^3

(benzo[a]anthracene, fluoranthene and 2-nitrofluorene and 2-nitroanthracene,

respectively) for 30m^3 of air. Mean PAH surrogate recoveries were $100 \pm 9.7\%$

(fluoranthene-d_{10}) and $98 \pm 6.4\%$ (perylene-d_{12}). NPAH surrogate recoveries were

slightly lower $55 \pm 11\%$, 77 ± 9.3, and $70 \pm 9.1\%$ for 1-nitronaphthalene-d$_7$, 9-

nitroanthracene-d$_9$, and 1-nitropyrene-d$_9$, respectively. No systematic trends were

observed across samples therefore, no surrogate corrections were performed on the

concentrations presented here.

The sampling efficiency of the Berner low-pressure impactor has been

previously evaluated for PAHs (Poster *et al.*, 1996). Adsorption artifacts were

assessed by passing gas phase deuterated PAHs (fluorene-d_{10}, anthracene-d_{10},

fluoranthene-d_{12} and chrysene-d_{12}) over clean foils, organic film coated foils, and

foils pre-loaded with particulate matter. Chrysene-d_{12} on the particulate matter loaded

foils was the only PAH detected above MDLs at levels ~1% of the gas phase

concentration. Volatilization losses were assessed by drawing PAH-free air through

the impactor at 20°C loaded with National Institutes of Standards and Technology

(NIST) Ambient Particulate Matter Standard Reference Material (SRM 1649). For

PAHs with vapor pressures below fluoranthene, less than 15% of the PAH mass was

lost in the smallest stage (greatest pressure drop). Therefore, our analysis includes

PAHs and NPAHs with vapor pressures equal to or less than fluoranthene and 5-

nitroacenaphthalene (Poster *et al.*, 1996).

4.2 Results

4.2.3 Concentration and Size Distributions

The total PAH particle concentration (sum of 5 stages) ranged from 0.51 to 3.1 ng/m^3

and the total NPAH concentration ranged from 0.014 to 0.31 ng/m^3 with a significant

correlation (p<0.01) between the total PAH and NPAH concentrations.

Benzo[*g,h,i*]perylene (180 $\pm$ 69 pg/m^3), indeno[1,2,3-*c,d*]pyrene (160 $\pm$ 57 pg/m^3),

fluoranthene (130 $\pm$ 63 pg/m^3), benzo[*b*]fluoranthene (140 $\pm$ 44 pg/m^3), and pyrene

(120 $\pm$ 56 pg/m^3) had the highest mean concentrations (Table 4.1, geometric mean $\pm$

95% confidence interval). The greatest NPAH (Table 4.2) concentrations were found

for 9-nitroanthracene (43 $\pm$ 38 pg/m^3), 2-nitrofluoranthene (16 $\pm$ 30 pg/m^3) and 1-

nitropyrene (11 $\pm$ 7 pg/m^3). Previously Bamford and Baker (2003) found summer

benzo[*e*]pyrene (55 - 170 pg/m^3) and 1-nitropyrene concentrations (3.0 – 16 pg/ m^3)

similar to this study (32 - 177 pg/m^3 and 2.9 – 57 pg/ m^3, respectively).

Benzo[*g,h,i*]perylene and 1-nitropyrene concentrations in Rome (bulk aerosol, 5.0

and 0.12 ng/ m^3, respectively, Cecinato *et al.*, 1999) were an order of magnitude

higher than values from Baltimore. Concentrations of 1-nitropyrene (20 pg/m^3) and

indeno[1,23-*cd*]pyrene (60 pg/m^3) in Athens are consistent with Baltimore values,

Table 4.1 PAH Geometric mass median diameter (GMMAD)

	GMMAD (μm)[a]	σ_g[b]	4/23 Day GMMAD (μm)	σ_g	Concentration (pg/m³) Mean[c] (95%CI)[d]
Fluoranthene	0.56(0.40)[e]	2.18(0.87)	3.04	3.92	130 (63)
Pyrene	0.49(0.10)	2.07(0.76)	0.98	4.03	120 (56)
Benzo[a]fluorene	0.55(0.19)	1.78(0.27)			12 (7)
Benzo[b]fluorene	0.43(0.10)	1.54(0.30)			11 (6)
Benz[a]anthracene	0.49(0.13)	2.10(0.76)	1.03	4.1	58(25)
Cyclopenta[c,d]pyrene	0.37(0.04)	1.50(0.17)			56(60)
Chrysene+Triphenylene	0.46(0.09)	2.01(0.63)	0.82	3.66	94(35)
Benzo[b]fluoranthene	0.44(0.09)	1.93(0.64)	0.83	3.47	140(44)
Benzo[k]fluoranthene	0.40(0.09)	1.62(0.40)	1.21	1.67	89(31)
Benzo[e]pyrene	0.43(0.09)	1.95(0.75)	0.77	3.92	96(31)
Benzo[a]pyrene	0.42(0.12)	1.65(0.51)			93(36)
Indeno[1,2,3-c,d]pyrene	0.41(0.10)	1.74(0.71)	0.73	3.71	160(57)
Benzo[g,h,i]perylene	0.37(0.07)	1.67(0.41)	0.51	2.50	180(69)
Anthanthrene	0.35(0.02)	1.42(0.13)			14(13)
Dibenz[a,h+a,c]anthracene	0.34(0.03)	1.24(0.13)			11(8)
Coronene	0.35(0.03)	1.49(0.18)			57(27)
Mass	0.93(0.13)	2.55(0.41)	1.38	3.06	18(7)[f]

a. geometric median diameter (μm, Equation 1) b. geometric standard deviation (Equation 2) c. geometric mean concentration (Σall stages, pg/m³)d. 95% confidence interval e. 1 standard deviation f. μg/m³

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Table 4.2 NPAH Geometric mass median diameter (GMMAD) summary

	GMMAD (μm)[a]	σ_g[b]	4/24 Night GMMAD (μm)	σ_g	4/25 Day GMMAD (μm)	σ_g	Concentration (pg/m³) Mean[c] (95%CI)[d]
5-nitroacenaphthene	0.55(N=1)	2.36(N=1)					0.36(0.2)
2-nitrofluorene	0.48(0.20[b])	1.60(0.21)	1.73	2.06			0.15(0.14)
9-nitroanthracene	0.43(0.08)	1.70(0.28)	1.04	1.54	1.55	1.48	43(38)
9-nitrophenanthrene	0.42(0.05)	1.63(0.21)	1.10	1.36			0.73(0.95)
3-nitrophenanthrene	0.40(0.05)	1.49(0.08)	1.12	1.60			1.2(0.9)
4-nitrophenanthrene	0.42(0.07)	1.64(0.20)			1.37	1.54	0.40(0.21)
2-nitrofluoranthene	0.34(0.02)	1.41(0.09)			1.18	1.40	16(30)
3-nitrofluoranthene	0.31(0.03)	1.40(0.07)	1.05	1.65	1.22	1.56	0.23(0.12)
1-nitropyrene	0.37(0.09)	1.66(0.35)	0.92	1.23		1.56	11(7)
2-nitropyrene	0.36(0.09)	1.47(0.35)					2.5(2.5)
7-benz[a]anthracene	0.34(0.05)	1.40(0.09)	1.01	1.24	1.14	2.13	1.7(1.4)
Mass	0.96(0.20)	2.58(0.45)	1.06	2.49	0.92	2.2	18(7)[f]

a. geometric median diameter (μm, Equation 1) b. geometric standard deviation (Equation 2) c. geometric mean concentration (Σall stages, pg/m³)d. 95% confidence interval e. 1 standard deviation f. μg/m³

while 2-nitrofluoranthene is approximately a factor of four above those reported here (Marino *et al.*, 2000).

Figure 4.1 and 4.2 illustrate the mean fractional size distributions of PAHs and NPAHs, respectively. These plots only include samples where the concentration of each analyte was above MDLs for 3 or more stages. For stages below detection limits, MDL values were used in the calculation. During this period, $75 \pm 10\%$ and $67 \pm 8.0\%$ of the PAH and NPAH mass, respectively, was associated with particles <0.49μm. Tunnel studies have observed 62% to 80% of the PAH mass associated with particles <0.12μm (Venkatarraman *et al.*, 1994, Miguel *et al.*, 1998). Schelle-Kreis *et al.* (2001) observed 40% of PAH mass associated with particles <0.13μm collected next to a busy road in Germany and increased size distributions (0.26 – 0.9μm) with winds away from the roadway. PAHs were associated with particles less than 1.4 μm in Egbert, Ontario and Chicago, IL (Poster *et al.*, 1996). Chen *et al.* (2004) observed 56% to 76% of the PAH mass (phenanthrene and benzo[*e*]pyrene, respectively) associated with particles <0.49μm in residential coal emissions in China. Alves *et al.* (2000) observed unimodal (~1μm or 0.15μm peak), and a bimodal (0.15μm and 2μm peaks) size distribution of PAHs in an *Abies boressi* forest in central Greece.

4.2.4   Size Statistics

The geometric mass median aerodynamic diameter (GMMAD) and geometric standard deviation (σ_g) were calculated for each PAH and NPAH using equation 1 and 2, respectively (Hinds, 1982), for compounds above MDLs on 3 or more stages.

Figure 4.1 Mean PAH size distribution. Error bars denote 1 standard deviation.

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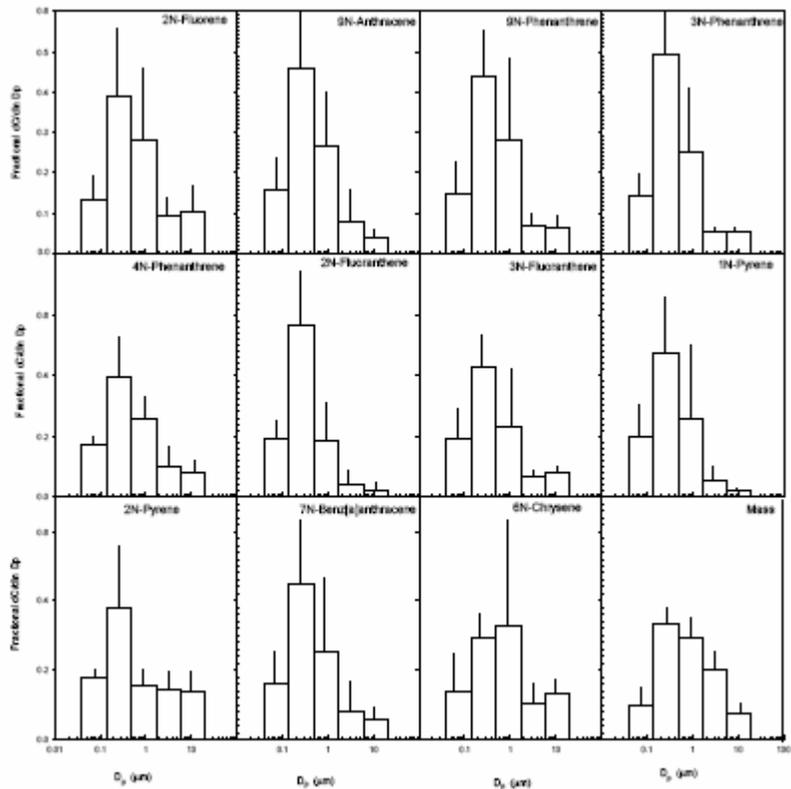
Figure 4.2 Mean NPAH size distribution. Error bars denote 1 standard deviation.

$$\ln (\text{GMMAD}) = 1/M \sum m_i \ \ln d_i \qquad\qquad \text{Equation (1)}$$

$$\ln^2 (\sigma_g) = 1/M \sum [m_i (\ln d_i - \ln \text{GMMAD})^2] \qquad\qquad \text{Equation (2)}$$

where m_i is the compound mass on stage i, M is the total compound mass on all stages ($\sum m_i$), and d_i is the particle midpoint diameter for each stage. A sensitivity analysis of GMMAD and σ_g was performed using a uniform and log normal random distribution. Input values were 2.7, 7.5, 3.5, 1.8 and 0.45 ng for stages 1 – 5, respectively, representing a realistic PAH mass distribution observed in Baltimore. A 20% error was applied to each stage. The cumulative variance (sample size 200) of the GMMAD was 9.1% and 5.4% for the normal and uniform error distribution, respectively. Sigma (σ_g) varied 4.5% and 7.6%, respectively in response to a 20% applied error. The smallest stage (0.04 – 0.14μm) dominated the variability in the GMMAD and the second to smallest stage (0.14 – 0.49μm) had the greatest affect on sigma. In addition, if the first stage is allowed to randomly vary by $\pm$ 50% using the "seed" PAH size distribution (described above), the percent difference in the minimum and maximum GMMAD and sigma is <30%. The error analysis suggests GMMAD differences >30% among samples are larger than variation due to sampling or analytical errors, even as high as 50%.

The mean PAH GMMAD (Table 4.1) for all the samples (excluding 4/22 night) in this study ranged from 0.37 ± 0.04 μm (cyclopenta[1,2,3-c,d]pyrene) to 0.6 $\pm$ 0.4 μm (fluoranthene). Corresponding σ_g values ranged from 1.2 ± 0.3

(dibenz[*ah+ac*]anthracene) to 2.2 $\pm$ 0.87 (fluoranthene) with no apparent dependence on GMMAD. The PAH GMMADs for the sample collected during the 4/23 day period were considerably larger, with a GMMAD ranging from 0.51μm (benzo[*g,h,i*]perylene) to 3.0 μm (fluoranthene). The PAH size distribution was broader during this time as sigma ranged from 1.67 (benzo[*k*]fluoranthene) to 4.03 (pyrene). The elevated wind speeds (> 4 m/s) from the northwest, away from the urban center, during this period combined with the increased GMMADs suggests non-local sources (Van Vaeck and Cauwenbergh, 1985, Schnelle-Kreis *et al.*, 2001). But further inspection of the particle chemistry (see below) revealed road dust is the most probable cause of the increased PAH GMMAD for this period consistent with the proximity of the site and traffic sources.

The mean NPAH GMMADs (Table 4.2) were similar for all samples except 4/24 night to 4/25 night, ranging 0.31 $\pm$ 0.03 μm (3-nitrofluoranthene) to 0.48 $\pm$ 0.2 μm (2-nitrofluorene). Unlike the PAHs, there was no increase in the GMMAD during the 4/22 night sample. A significant increase (~2-fold) in the NPAH GMMAD was observed during the 4/24 night – 4/25 night. The elevated NPAH GMMAD straddled a rain event that began during the last 2 hrs of the 4/24 night sample and continued until ~noon 4/25. Although the NPAHs were associated with larger particles during this time, no increase in PAH GMMAD or NPAH σ_g was observed.

The PAH GMMADs from this study are consistent with values reported for roadside (Pierce and Katz, 1975, Yang *et al.*, 1999, Aceves and Grimalt, 1993, Schnelle-Kreis *et al.*, 2001) and residential coal (Chen *et al.*, 2004 in China) emissions. Venkataraman *et al.* (1994) reported PAH mass median diameters <0.2μm

in the Caldecott tunnel in southern California. In a later study from that location, PAHs were associated with larger particles (0.12 – 2 μm, Miguel *et al.*, 1998). The size difference was attributed to increased heavy duty diesel source during the latter sampling period. PAH mass median aerodynamic diameters (MMAD) from biomass combustion are somewhat larger (>0.5μm Venkataraman *et al.*, 2002). Sandersan and Farrant (2005) found PAH GMMADs of ~0.5μm in aerosol collected near an aluminum smelter in Quebec, Cananda. Chicago PAH GMMADs reported by Offenberg and Baker (1999) were more than 5 times larger than those in Baltimore. Kawanaka *et al.* (2004) found 72% of the 2-nitrofluoranthene mass was associated with particles <0.68μm. Cecinato *et al.*, (1999) found significant quantities of 1-nitropyrene on fine and coarse particulate matter during separate sampling times, while 2-nitrofluoranthene was primarily associated with fine particles. The 1-nitropyrene and 2-nitrofluoranthene mass on Baltimore particulate matter was primarily associated with the fine fraction (size cuts <2.5μm).

Interestingly, the PAH and NPAH size distributions are similar even though NPAHs have both primary and secondary sources. The mass of particle bound semivolatile organics depends on the ab/adsorptive capacity of the particulate matter and its surface area (Pankow, 1987). Similarities in the PAH and NPAH size distributions, regardless of source (primary vs. secondary) indicate the gas/particle partitioning rather than sources govern their size distribution. The partitioning behavior of a compound is, in part, a function of its sub-cooled liquid vapor pressure. Therefore, the redistribution of a compound with respect to size may be a function of this physical property. In the next section the relationship between compound vapor

pressure and GMMAD is examined as it relates to sources and processes governing

the size distribution of PAHs and NPAHs.

4.4.3 Vapor Pressure/GMMAD Correlations

The available literature suggests that there is no particle size/vapor pressure

dependence for PAHs in combustion emissions (Venkataraman *et al.* 1994, 2000). In

contrast, ambient measurements have shown that the size distribution of PAHs is not

constant with respect to vapor pressure. Unimodal and bimodal distributions (Poster

et al., 1995, Allen *et al.*, 1996, Offenberg *et al*., 1999, Miguel *et al.*, 1998, 2004)

have been explained by different sources and the redistribution of PAHs with respect

to particle size. During PAH redistribution, PAHs shift to larger particles due to

cyclic volatization/condensation from primary emissions (enriched in PAHs) to

ambient aerosol until sorptive equilibrium is reached. The extent of this process is

driven by the physical (surface area) and chemical properties of the emission and

ambient particulate matter (Pankow, 1987). The lightest PAHs are usually associated

with larger particles due to greater gas phase concentrations initiating shorter

equilibrium times (Allen *et al.*, 1996).

In the Chicago, IL atmosphere Offenberg and Baker (1999) observed a linear

relationship between GMMAD and the log sub-cooled liquid vapor pressure ($p_l°$) for

unsubstituted PAHs. From the general equation GMMAD $= m_g$ log $p_l° + b_g$, the y-

intercept (b_g) of the equation refers to a reference state equal to the GMMAD for a

compound with $p_l° = 1$ Pa. The slope of the line (m_g) represents the change in particle

size for a group of compounds with respect to vapor pressure (for a given sampling

time). In our study, the PAH GMMADs and log $p_l°$s (derived from Offenberg, 1998, and Bamford, 2003) were also significantly correlated ($p < 0.001$, Figure 4.3). The PAH GMMAD/vapor pressure dependence was not significantly different for 7 of the 11 samples where $m_g = 0.028 \pm 0.0068$ μm Pa^{-1} and $b_g = 0.55 \pm 0.035$ μm (mean $\pm$ 1 standard deviation) representing a typical size/vapor pressure relationship for the site. The April 24 day relationship had a smallest slope and y-intercept (GMMAD = 0.019 $p_l°$ + 0.40) whereas the April 23 day period had an greatest slope and y-intercept (GMMAD = 0.094 log $p_l°$ + 1.35). A similar linear relationship was found for the NPAHs in all but 3 samples (Figure 4.3). Independent regressions (PAH and NPAH, respectively) exist for samples collected during the rain event (4/24 night and 4/25 day) and the period associated with the increased PAH (relative to NPAH) GMMADs (4/17 pm-4/18 pm day).

The correlations presented above were qualified by determining the minimum amount of sampling/measurement error needed to explain the observed slopes. Using the equation from the 4/24 day sampling period (GMMAD = 0.019 log $p_l°$ + 0.39, R^2 = 0.47), two scenarios were tested using the range of compound log sub-cooled liquid vapor pressures (-7.57 to -2.88 Pa) employed in this study. From this equation the size distribution would span 0.25 to 0.34 μm (heaviest to lightest). The first case is volatilization from the smallest impactor stage (which has the greatest pressure drop). The measured GMMAD must be 0.09 μm (lightest – heaviest GMMAD) above the "real" size distribution, if the low vapor pressure PAH GMMAD is held constant. This represents a 28% difference or GMMAD error. From the error analysis above

Figure 4.3 GMMAD vs. sub-cooled liquid vapor pressure for NPAHs (●) and PAHs (○)
during the spring 2002 sampling intervals.
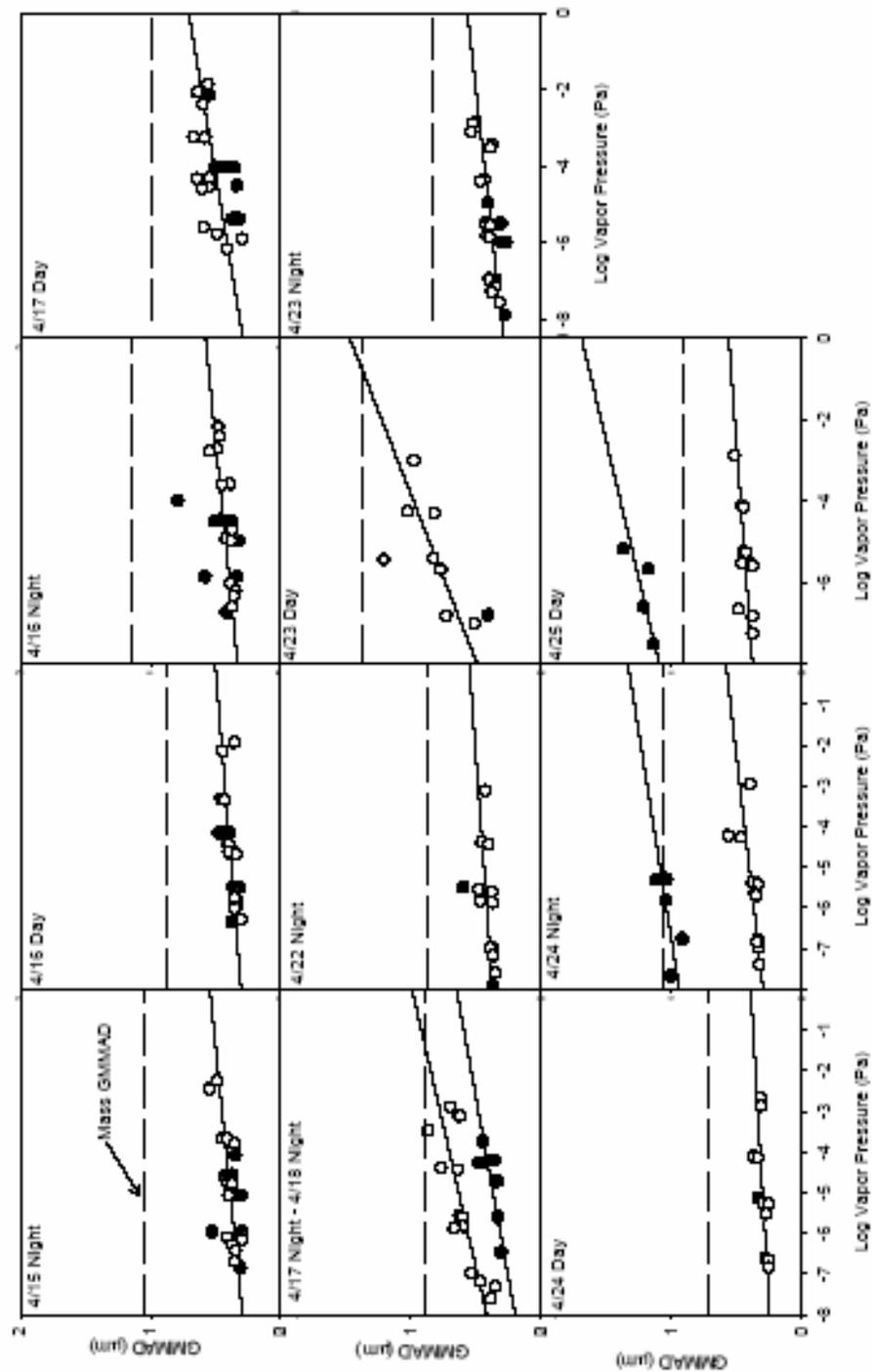
this would represent a ~50% measurement/sampling error, well above the <20% difference between the Berner and Hi-Vol concentrations discussed above.

If larger particles bounce to smaller stages, a lower GMMAD will result for the heaviest PAHs. If there is no volatilization of the lightest PAHs, the GMMAD for the largest PAHs would have ~36% error. Again from the error analysis this corresponds to ~70% measurement error, well above that observed in this study. Therefore, while particle bounce and volatilization can not be discounted, these errors do not explain the observed GMMAD/vapor pressure relationships. In addition, there is no trend in the detectable levels of PAHs per stage with respect to vapor pressure, negating possible artifacts in the GMMAD calculation itself. When the method detection limits were inserted into the GMMAD calculation for values below detection limits, similar slopes were found suggesting the relationship between GMMAD and vapor is not an artifact of PAH detection limits with respect to vapor pressure.

Further inspection of the particle chemistry using collocated hi-vol measurements (Crimmins and Baker, 2006b) helped explain at least one of the PAH size shifts. The April 23 day sample showed an increased slope relative to the previous period (4/22 night) which exhibited a typical GMMAD/vapor pressure relationship. During the transition from 4/22 night to 4/23 day no discernable PAH profile changes were observed. The PAH and mass size distributions shifted to larger particles. A look at the particle chemistry provides insight into the possible cause (source vs. redistribution) of the PAH size differences. The total concentration (gas + particle) of semivolatile (pyrene) and non-volatile (benzo[*g,h,i*]perylene) PAHs from

collocated hi-vol measurements were not significantly different (61 and 82 pg m^{-3}, and 57 and 62 pg m^{-3}, respectively, Crimmins and Baker, 2006b). But, the alkane profile (Figure 4.4, C_{30} to C_{35}) shifted from a typical biogenic signature (4/22 night) to a tire wear pattern (Rogge *et al.*, 1993) during the April 23 day period. Although the PAH size distribution of tire debris is not known, it is likely associated with road dust which resides on super-micron particles (Yang *et al.*, 1999). Therefore the increase in the GMMAD vs. log $p_l°$ slope during this period (4/23 day) is probably due to an influx of larger particles from the adjacent highway consistent with measured wind speeds greater than 4 m/s. From this we conclude that the shift in the PAH size distribution is mainly due to changes in sources (road dust/tire debris) and not redistribution. The other cases where the GMMAD vs. log vapor pressure line differs from the typical relationship are not as easily interpreted, but are most likely a combination of source shifts and PAH redistribution.

Outliers in indivdual GMMAD, $p_l°$ regressions were also observed during the 4/24 night sample, as 2-nitrofluorene and fluoranthene were significantly above the 95% confidence interval of the regression line. These compounds have similar vapor pressures and 2-nitrofluorene has been detected in diesel exhaust (Arey, 1998). The individual slopes of the NPAH and PAH regressions were not significantly different when both compounds were included ($m_g = 0.15$ and 0.14, respectively) or removed ($m_g = 0.05$ and 0.04, respectively). This suggests similar factors affecting the size distribution of these two compounds. The elevated GMMADs were associated with an increase in the mass GMMAD (0.72 to 1.06μm) and 10-fold increase in 1-nitropyrene concentration, not reflected in the PAH concentrations from 4/24 day to

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Figure 4.4 Alkane profile shift from April 22 night to April 23 day measured using an Andersen Hi-Vol
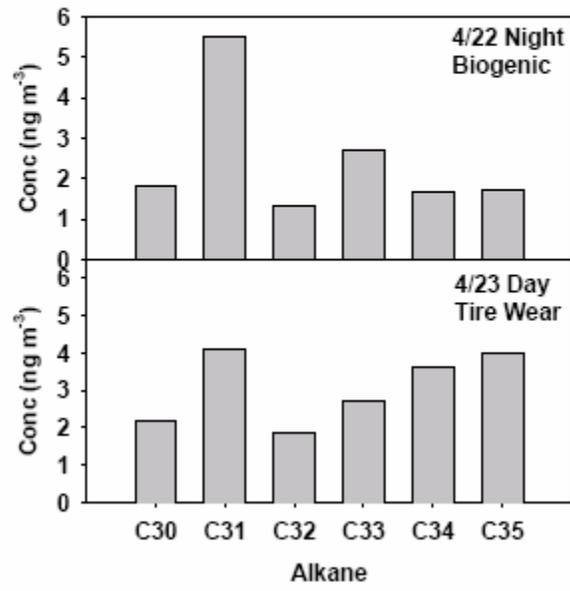
4/24 night. 1-nitropyrene is the dominant NPAH found in diesel exhaust therefore the elevated mass, fluoranthene and 2-nitrofluorene size distributions may be associated with a diesel plume or source that covaries with 1-nitropyrene.

A rain event occurred during the last two hrs of the 4/24 night sample until early afternoon 4/25 day. The increased slope (4/25 day) suggests that the PAHs and NPAHs are associated with different particle populations during this period. The NPAH size distribution during 4/24 night time was similar to the particle mass GMMAD and increased to above the mass GMMAD during 4/25 day. It is unlikely that the elevated NPAH GMMADs are due to aged aerosol as the PAH size distribution was similar to other locally (dry) influenced periods. At this point it is unclear why the PAH and NPAH size distributions differ during the rain event. Further studies are needed to investigate this observation.

The slopes (m_g) of the Baltimore correlations (GMMAD = m_g log $p_l°$ + b_g) were significantly lower than those reported by Offenberg and Baker (1999) for urban ($m_g = 0.44$) and rural samples ($m_g = 0.39$). The authors suggest that the slope of this equation will decrease with aging as the PAH size dependence reaches equilibrium. Due to the proximity of this site and combustion sources (traffic and industry) the more likely explanation for the shallow size/vapor pressure dependence, is the dominance of primary emissions.

The slopes (m_g) and y-intercept (b_g) of the GMMAD/vapor pressure dependencies for PAHs are plotted in Figure 4.5. The relationship between these 2 parameters suggests a common size/vapor pressure dependence. In this study the regression ($b_h = m_h \, m_g + b_g$) is significant (p<0.05, $R^2 = 0.99$) with a slope ($m_h = 12$),

Figure 4.5 Intercepts (b_g) vs. slopes (m_g) for PAHs derived from GMMAD vs. log $p_l°$ plots in Figure 4.4. Point "A" denotes the mean of 7 samples not significantly different (see text).
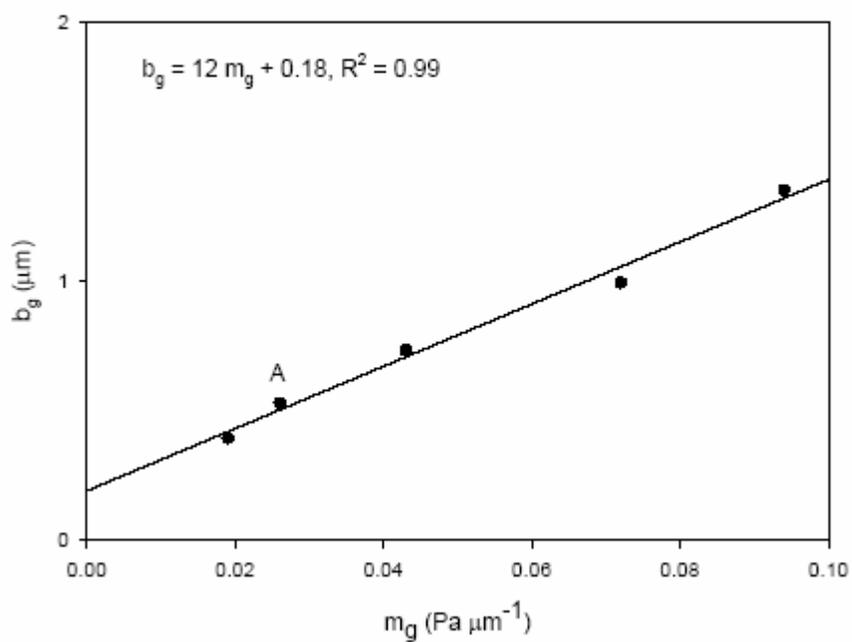
similar to Offenberg and Baker (1999, $m_h = 9.55$). The urban GMMAD/vapor

pressure dependence (b_g and m_g) reported by Offenberg and Baker (1999) for

Chicago, IL were up to 10-fold greater than those found in this study, but the

similarity of m_h from Chicago and this study suggests the relationship between these

two parameters is not location dependent.

The slope of this intercorrelation (m_h) is related to the redistribution of PAHs

with respect to vapor pressure. Although the physical meaning of this dependence is

still unclear, it may be related to the different equilibrium times associated with the

size dependent partitioning of PAHs. Specifically, PAH size distributions are

predictable regardless of aerosol composition or source (see below). The y-intercept

of this plot (b_h) corresponds to the GMMAD of PAHs when the slope (m_g) of the

GMMAD/vapor pressure dependence is low (~ 0). In other words, a constant PAH

GMMAD regardless of vapor pressure. Assuming the affinity for a given class of

compounds (PAHs) is the same with respect to particle size, b_h may represent the

equilibrium GMMAD. But due to the location of this site and the low vapor pressures

of heavier PAHs, reaching this size dependent equilibrium is not likely. Therefore, b_h

represents the PAH size distribution of one or a combination of the emission sources.

In our study, a b_h value of 0.18 μm is consistent with vehicle PAH size

distributions from tunnel and roadside measurements (Venkataraman *et al.*, 1994,

Yang *et al.*, 2005, Schnelle-Kreis *et al.*, 2001). This agrees with high vehicle

influence at the current sampling site. A previous source apportionment study in the

southern region of Baltimore City found vehicle emissions were a significant source

of PAHs to downtown Baltimore (~25%, Larsen and Baker, 2003). Offenberg and

Baker (1999) found a b_h value of 0.61μm for the Chicago/Lake Michigan region. This is above the value determined for Baltimore. But, a GMMAD range of 0.48 – 0.6 μm for coal combustion was observed by Sandersan and Farrant (2005) and MMD of ~0.6 μm was reported for an area dominated by fossil fuel combustion from domestic heating by Van Vaeck and Van Cauwenbergh (1985). These values are similar to the b_h value observed in Chicago/Lake Michigan aerosol. An aerosol source apportionment study for the Chicago, IL area, concurrent with the Offenberg and Baker (1999) study, found the dominant source of PAHs was coal (48%) followed by natural gas (26%) combustion (Simicik *et al.*, 1999). Therefore, b_h values are consistent with source study size distributions. Moreover, this type of analysis may provide insight into dominant the source of PAHs in a region regardless of the age and dilution. PAHs and EC are coemitted on similar size particles during combustion (Venkataraman *et al.,* 1994, 2002). If the intercept (b_h) from the PAH/vapor pressure slopes and y-intercept intercorrelation represents the size of the dominant combustion source, the intercept may represent the ambient size distribution of elemental carbon Baltimore, MD.

4.4 Conclusions

Diurnal PAH and NPAH size distributions were measured in the Baltimore atmosphere in April, 2002. Similar PAH and NPAH size distributions were observed for the majority of samples. The NPAH (but not PAH) size distributions increased during a rain event suggesting different sources or physical properties of PAH and NPAH containing particles. The PAH and NPAH and GMMADs correlated with their respective log sub-cooled liquid vapor pressures regardless of compound class and

source suggesting gas/particle partitioning dictates the size distribution. Utilizing the slopes (m_g) and y-intercepts (b_g) from the size/vapor pressure correlations, the dominant source of PAHs and possibly EC may be determined for the ambient atmosphere regardless of aging.

Chapter 5

Estimating the Sources of Carbonaceous Particulate Matter in the Baltimore Atmosphere Using Organic Markers and Positive Matrix Factorization

5.1 Introduction

The sources of atmospheric particulate matter are of great interest to air quality managers and governmental agencies due to the detrimental health affects of elevated ambient particulate matter (Pope III, 1996). Individual organic compounds can be used as fingerprints (organic markers) of individual sources. Several studies have employed organic markers with the Chemical Mass Balance approach (CMB, Zheng *et al.*, 2002, Schauer *et al.*, 1996, 2000), but the success of this technique relies on prior knowledge of the sources and profiles associated with each source-type affecting a receptor site. To date, only a few organic source characterizations have been performed in the Baltimore, MD area. The majority of source studies have been performed in the western United States (Rogge *et al.*, 1993a,b, 1997a, b, 1998, Schauer *et al.*, 1999a, b, 2001, 2002a, b). Extrapolating published profiles between regions may introduce unknown error into this type of model. The mass balance approach is predicated on the assumption that profiles are conserved from emission source to receptor site, and reactivity may limit the utility of organic compounds as source markers. In addition, a significant amount of organic aerosol results from secondary production, not captured using the mass balance approach.

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Multivariate techniques do not constrain the number and profiles of possible sources. Unlike CMB, literature profiles are used to identify potential sources, not drive the model results. One multivariate method, Principal Components Analysis, has been used to determine the source of polycylic aromatic hydrocarbons (PAHs) in aerosol (Simcik *et al.*, 1999, Harrison *et al.*, 1996, Larsen and Baker, 2003). The use of PCA with multiple compound classes assumes a constant measurement error among species. For multiple classes of compounds this is not likely due to systematic differences in sample preparation and instrumental analysis. In addition, PCA often results in negative source contributions, which are physically not interpretable.

Positive Matrix Factorization (PMF) is an alternative multivariate technique that overcomes the physically meaningless negative source loadings generated by PCA. This technique also enables the application of sample and species specific error estimates, providing a more realistic weighting of the potential marker compounds (Paatero and Tapper, 1994). This technique has been used primarily for inorganic and bulk particulate matter species (Polissar *et al.*, 1999, 2001, Huang *et al.*, 2001, Ogulei *et al.*, 2005, Kim *et al.* 2005). Recently Larsen and Baker (2003) compared PMF and PCA to estimate the sources of PAHs to the Baltimore, MD atmosphere. Interestingly, the profiles and general temporal trends generated from PCA and PMF were similar. However, PMF was the only model able to resolve vehicular PAH source into gasoline and diesel exhaust.

Recently, a Windows based version of Positive Matrix Factorization was released by EPA (EPA PMF 1.1). This program is currently in the beta testing form, but provides additional features to increase the productivity and ease of using PMF.

The algorithm is based on the multiple-linear engine variant of PMF (Paatero, 1999).

The data preparation and error calculations (see below) are similar to previous

versions (PMF-2), but editing the compound list and adjusting error estimates can be

performed without altering input files, speeding the analysis. The semi-volatile

organic compounds measured at the Baltimore $PM_{2.5}$ Supersite during the spring,

summer and winter of 2002-2003 (Chapter 3) provide an excellent dataset to evaluate

this new version of PMF for broad application to organic source apportionment

studies.

The objectives of this study were to determine the sources of alkanes, PAHs,

hopanes and NPAHs to the Baltimore atmosphere using PCA and PMF. The

Windows based version of Positive Matrix Factorization (EPA PMF 1.1) was then

employed to determine the sources of carbonaceous aerosol and $PM_{2.5}$ to the

Baltimore, MD atmosphere using alkanes, PAHs, hopanes and nitro-substituted

PAHs. This study expands on earlier work by Larsen and Baker (2003) in the

Baltimore, MD atmosphere while providing the first multivariate derived organic and

$PM_{2.5}$ source contributions to this region using organic markers.

5.2 Methods

The site description and collection parameters have been previously described in

Harrison *et al.* (2004), Ogulei *et al.* (2005) and Chapter 3 and will be briefly

discussed here. The gaseous and particulate phase hopanes, PAHs, NPAHs and

alkanes employed in this study were collected at the Baltimore Supersite during the

spring, summer and winter of 2002-2003. The site was located in an urban setting east

of downtown Baltimore. The sampling apparatus was approximately 6m above an asphalt parking lot adjacent to a major interstate (I895) and bus maintenance facility. Two tunnels (Harbor and Fort McHenry) are positioned approximately 2km south of the site.

Gas and particle phase organics were collected using a modified Andersen hi-volume sampler was fitted with an ashed (450°C) glass fiber filter followed by a precleaned polyurethane plug (PUF) to collected particulate and gas phase organics (Chapter 3). Sampling times were 6, 12 or 24 hrs. Samples collected on different timescales were treated as discrete snapshots of ambient aerosol profiles at the site and no attempt was made to average analyte concentrations collected on different timescales. The underlying assumption to this method is that samples on shorter timescales may provide seed profiles that may be masked by samples collected on longer timescales (*i.e.* 24 hrs). The concentration summary and seasonal distribution is discussed elsewhere (Chapter 3). In addition to the semi-volatile compounds, gas phase parameters (CO, NO, NO_x, and ozone) were measured during the spring, summer and winter intensives (Park *et al.*, 2005a, b, Harrison *et al.*, 2004). Some of these constituents were measured on different timescales (10 min – 1hr) therefore, a time integrated average was calculated, coinciding with the semi-volatile organics collections (6 to 24 hr). For the organic compounds presented, PMF and PCA were performed on the combined gas and particle phase concentrations.

5.3 Model Description

5.3.1 PCA

Principal Components analysis attempts to explain the total variance in a sample matrix with a minimum number of orthogonal factors. For this analysis, raw data (concentrations) were converted into z-score format (standard deviation units away from the mean) using the following equation:

$$Z = (x - x_m) / \sigma$$

where Z is the standardized normal deviate, x is the measured concentration, x_m is the mean concentration of the species and σ is the standard deviation of x in the sample population. SPSS statistical software was employed for this analysis, extracting factors with eigenvalues greater than 1.

The subsequent multiple linear regression analysis from extracted factors was performed in accordance with Larsen and Baker (2003). Briefly, the factor scores were regressed against the z-scores of the total concentration of specified analytes in the PCA analysis using the following equation;

$$Z_T = \Sigma\ B_i FS_i + r$$

where Z_T is the standardized normal deviate of total concentration of the input compounds for a sampling period, B_i is the regression coefficient associated with factor score i (FS_i), and r is the y-intercept of the resulting equation. This regression was performed using SPSS software in a stepwise fashion eliminating those factors

that fall below the default significance value of 0.10 during the addition of new

factors into the regression. The mean percent contribution of each factor was

calculated by normalizing B_i to the total B ($B_i/\Sigma B_i$). The daily source contribution is

calculated by the following equation;

daily contribution of source i = mean Σ(analyte concentration) x ($B_i/\Sigma B_i$) + $B_i\sigma_A FS_i$

where σ_A is the standard deviation of total concentration of analytes among sampling

periods.

5.3.2   PMF

PMF solves the following equation with positive constraints;

$$X_{ij} = \Sigma\, f_{ki}\, g_{kj} + e_{ij}$$

where X_{ij} if the concentration of species j during period i, f_{ki} is the fraction of factor k

that is species j and g_{ki} is the source contribution of factor k during period j, e_{ij} is the

model generated error of species j during period i (residuals). This equation is solved

by minimizing the sum of squares represented by;

$$Q = (e_{ij}/s_{ij})^2$$

where s_{ij} is the input error associated with species j during period i. The program is

set to run in robust mode (Paatero, 1997), which downweights outliers generated

during the iteration process. For the aerosol organics data, concentrations below

detection limits were replaced by ½ the MDL prior to using PMF. The error estimates

were calculated using a variant of the equation employed by Brinkman *et al.* (2006);

$$S{ij} = \{ [(\alpha_{fi} X_{fij})^2 + (\beta_{fi} DL_{fi})^2] * \sigma_{fi} + [(\alpha_{pi} X_{pij})2 + (\beta_{pi} DL_{pi})^2]* \sigma_{pi} \}$$

where S_{ij} is the error associated with compound i in sample j and σ_{fi} and σ_{pi} are the

fraction of analyte in the particle and gas (PUF) phase, respectively for each sample.

The uncertainty coefficients (fraction) for the detection limit (β) and measurements

(α), α_{pi}, α_{fi} and β_{pi} and β_{fi}, were calculated for each analyte in the PUF and filter,

respectively. These values were determined from the percent relative standard

deviation of the blanks (β) and surrogate values (α). The detection limits (DL) were

determined from the method detection limits for each phase using three times the

greater of the blank or instrumental detection limit. X_{fij} and X_{pij} are the concentrations

of compound j in sample i in the particle and gas phases, respectively. For values

below the method detection limit the calculated error was multiplied by a factor of 10.

Error estimates for the gas data were determined as 10% of the measure values.

Values below detection limits were replaced with half the minimum measured values

with respective error values were multiplied by 10.

The current version of Positive Matrix Factorization (EPA PMF 1.1) allows

for an additional percent uncertainty to be applied to the entire analyte list. The Q

value was loosely used as a guide for correct model fit. Minimum Q are equal to the

number of analytes times the number of samples minus the number of factors (*e.g.* the

model explained error is equal to the input error). Due to elevated Q values during the analysis (> 5 fold theoretical) an additional 2% error (scaled to concentration) was added to the estimates calculated above allowing for more realistic calculated Q values. Upon the initial runs, it was determined that the error estimates for the alkanes were too high resulting in a low explained variance (R^2) in the dataset. This was most likely due to elevated blank levels in our laboratory (Chapter 3). Therefore, the calculated error values for the alkanes were reduced by ½, resulting in a better fit of the model to our data. The majority of the R^2 values were > 0.7 (Table 5.1 and 5.2) for the optimized number of factors presented below.

5.4 Results

A previous study in the Baltimore atmosphere utilized PMF and PCA to determine sources of PAHs (Larsen and Baker, 2003). That study found PMF distinguished a greater number of PAH sources. Expanding on that work, PCA and PMF were employed to determine the sources of alkanes, hopanes, PAHs and NPAHs to the Baltimore atmosphere. The following sections compare the results using PMF and PCA to determine the individual compound class sources. Unlike PCA, the order in which the PMF factors are presented is not related to their relative significance.

5.4.1   Alkanes

PMF: PMF resolved 6 factors (Alkane PMF Factors 1 – 6) for the alkanes and hopanes Figure 5.1. Alkane PMF Factor 1 showed an odd carbon preference for the alkanes with C_{29} as the dominant alkane. C_{29} is usually the dominant alkane in biogenic emissions from leaf waxes (Rogge *et al.*, 1993). The carbon preference

Table 5.1 Individual Compound Class EPA PMF 1.1 Model Fit

Alkanes + Hopanes	R^2
17α(H), 22,29,30-trisnorhopane	0.98
17α(H), 21β(H)-30-norhopane	0.99
17β(H), 21α(H)-30-norhopane + 17α(H), 21α(H)-30-norhopane	0.93
17α(H), 21β(H)-hopane	0.99
17β(H), 21α(H)-hopane	0.96
17α(H), 21β(H)-22S-homohopane	0.98
17α(H), 21β(H)-22R-homohopane	0.98
C_{22}	0.85
C_{23}	0.96
C_{24}	0.97
C_{25}	0.94
C_{26}	0.94
C_{27}	0.84
C_{28}	0.96
C_{29}	0.97
C_{30}	0.97
C_{31}	0.98
C_{32}	0.94
C_{33}	0.79
C_{34}	0.93
C_{35}	0.94

NPAHs	R^2
1N-napthalene	0.16
2N-napthalene	0.31
2N-biphenyl	0.75
3N-biphenyl	0.25
4-Nitrobiphenyl	0.53
3N-dibenzofuran	0.38
5N-acenapthene	0.52
2N-fluorene	0.93
9N-anthracene	0.74
9N-phenanthrene	0.61
3N-phenanthrene	0.89
4N-phenanthrene	0.8
2N-fluoranthene	0.72
3N-fluoranthene	0.99
1N-pyrene	0.41
2N-pyrene	0.84

PAHs	R^2
Naphthalene	0.91
2-Methylnaphthalene	0.93
1-Methylnaphthalene	0.93
1,3-Dimethylnaphthalene	0.94
1,6-Dimethylnaphthalene	0.93
Acenaphylene	0.92
1,2-Dimethylnapthalene	0.96
Acenapthene	0.82
Fluorene	0.77
1-Methylfluorene	0.87
Dibenzothiophene	0.9
Phenanthrene	0.89
Anthracene	0.18
2-Methyldibenzothiophene	0.87
4-Methyldibenzothiophene	0.84
2-Methylphenanthrene	0.86
4,5-Methylenephenanthrene	0.78
1-Methylanthracene	0.84
1-Methylphenanthrene	0.84
9,10-Dimethylanthracene	0.75
Fluoranthene	0.5
Pyrene	0.55
3,6-Dimethylphenanthrene	0.96
Benzo[a]fluorene	0.78
Retene	0.44
Benzo[b]fluorene	0.83
Benz[a]anthracene	0.98
Chrysene+Triphenylene	0.91
4-Methylchrysene	0.92
Benzo[b]fluoranthene	0.98
Benzo[k]fluoranthene	0.98
Dimethylbenz[a]anthracene	0.82
Benzo[e]pyrene	0.99
Benzo[a]pyrene	0.99
Perylene	0.98
Indeno[1,2,3-c,d]pyrene	0.98
Dibenz[a,h+ac]anthracene	0.92
Benzo[g,h,i]perylene	0.98
Anthanthrene	0.98
Coronene	0.95

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Table 5.2 Combined Compound Class EPA PMF 1.1 Model Fit

Alkanes + Hopanes	R^2		PAHs	R^2
17α(H), 22,29,30-trisnorhopane	0.98		Naphthalene	0.81
17α(H), 21β(H)-30-norhopane	0.98		2-Methylnaphthalene	0.81
17β(H), 21α(H)-30-norhopane + 17α(H),				
21α(H)-30-norhopane	0.92		1-Methylnaphthalene	0.81
17α(H), 21β(H)-hopane	0.99		1,3-Dimethylnaphthalene	0.80
17β(H), 21α(H)-hopane	0.95		1,6-Dimethylnaphthalene	0.80
17α(H), 21β(H)-22S-homohopane	0.97		Acenapthylene	0.95
17α(H), 21β(H)-22R-homohopane	0.97		1,2-Dimethylnapthalene	0.83
C_{22}	0.65		Acenapthene	0.67
C_{23}	0.91		Fluorene	0.66
C_{24}	0.94		1-Methylfluorene	0.77
C_{25}	0.9		Dibenzothiophene	0.48
C_{26}	0.95		Phenanthrene	0.38
C_{27}	0.76		Anthracene	0.16
C_{28}	0.96		2-Methyldibenzothiophene	0.65
C_{29}	0.88		4-Methyldibenzothiophene	0.68
C_{30}	0.97		2-Methylphenanthrene	0.70
C_{31}	0.96		4,5-Methylenephenanthrene	0.62
C_{32}	0.92		1-Methylanthracene	0.73
C_{33}	0.72		1-Methylphenanthrene	0.73
C_{34}	0.93		9,10-Dimethylanthracene	0.58
C_{35}	0.67		Fluoranthene	0.84
			Pyrene	0.85
NPAHs			3,6-Dimethylphenanthrene	0.84
2N-fluoranthene	0.09		Benzo[a]fluorene	0.86
1N-pyrene	0.29		Retene	0.50
			Benzo[b]fluorene	0.82
Gases			Benz[a]anthracene	0.97
Ozone	0.88		Chrysene+Triphenylene	0.93
CO	0.59		4-Methylchrysene	0.87
NO	0.84		Benzo[b]fluoranthene	0.96
Nox	0.77		Benzo[k]fluoranthene	0.97
			Dimethylbenz[a]anthracene	0.79
			Benzo[e]pyrene	0.96
			Benzo[a]pyrene	0.97
			Perylene	0.97
			Indeno[1,2,3-c,d]pyrene	0.97
			Dibenz[a,h+ac]anthracene	0.92
			Benzo[g,h,i]perylene	0.94
			Anthanthrene	0.96
			Coronene	0.90

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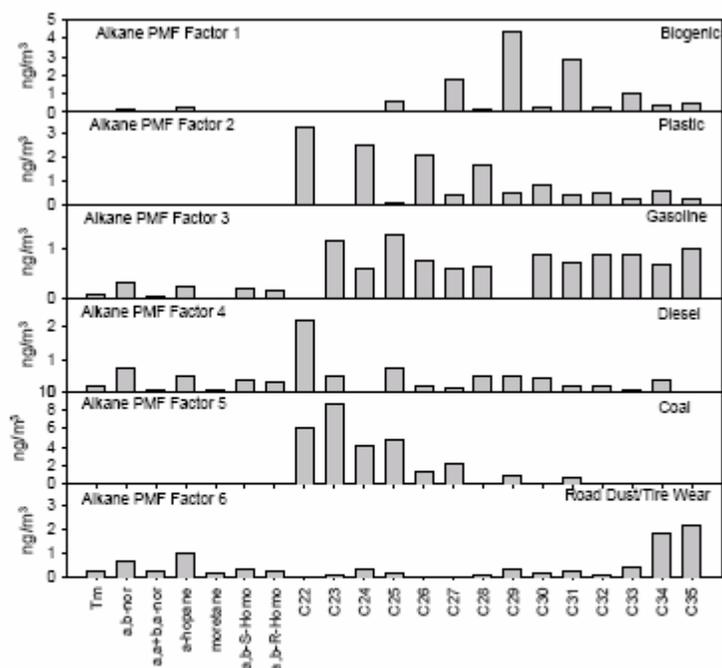
Figure 5.1 PMF profiles generated for $C_{22} - C_{35}$ alkanes and $17\alpha(H)$, 22,29,30-trisnorhopane (TM), $17\alpha(H)$, $21\beta(H)$-30-norhopane (a,b-nor), $17\beta(H)$, $21\alpha(H)$-30-norhopane + $17\alpha(H)$, $21\alpha(H)$-30-norhopane (a,a+b,b-nor), $17\alpha(H)$, $21\beta(H)$-hopane (a-hopane), $17\beta(H)$, $21\alpha(H)$-hopane (moretane), $17\alpha(H)$, $21\beta(H)$-22S-homohopane (a,b-S-Homo), $17\alpha(H)$, $21\beta(H)$-22R-homohopane (a,b-R-Homo).

index (CPI = sum odd alkane concentration/ sum even alkane concentration) for C_{26} – C_{35} for this profile was 9, consistent with biogenic emissions in rural areas (2 – 13, Simoneit, 1989). The contribution of this factor to total alkane and hopane concentrations is also greater during the summer (Figure 5.2) period.

In contrast, Alkane PMF Factor 2 was heavily loaded in the even alkanes with a maximum concentration at C_{24}. No seasonal trend was apparent and the time series plots show select days where this source is impacting the site. A recent study by Simoneit *et al.* (2005) found plastic extracts and plastic combustion particulate matter displayed this unusual alkane profile. Industrial sources of the plastic source can not be ruled out, therefore this factor is genericly denoted plastic.

Alkane PMF Factors 3 and 4 displayed similar alkane and hopane profiles. Both factors have elevated concentrations of C_{25}, consistent with vehicle emissions (Schauer *et al.*, 1999, 2002). In addition, the hopane profiles are typical of vehicle exhaust. Factor 4 has a greater concentration of hopanes relative to factor 3, suggesting diesel and gasoline emissions, respectively. But, this designation does not agree with the PMF analyses using PAHs and the dataset as a whole (see below).

Alkane PMF Factor 5 has an odd carbon preference from C_{28} - C_{33}, but elevated concentrations of alkanes $<C_{27}$ indicate a fossil fuel source. Elevated contributions of this source to the alkane and hopane concentrations occur during the spring and summer periods suggesting a seasonal source. The ratio of 17α(H), 21β(H)-30-norhopane to 17β(H), 21α(H)-hopane (1.6) is similar to bituminous coal (~1, Oros and Simoneit, 2000). The similar temporal contribution of a coal PAH source (see below) support designating this factor as coal.
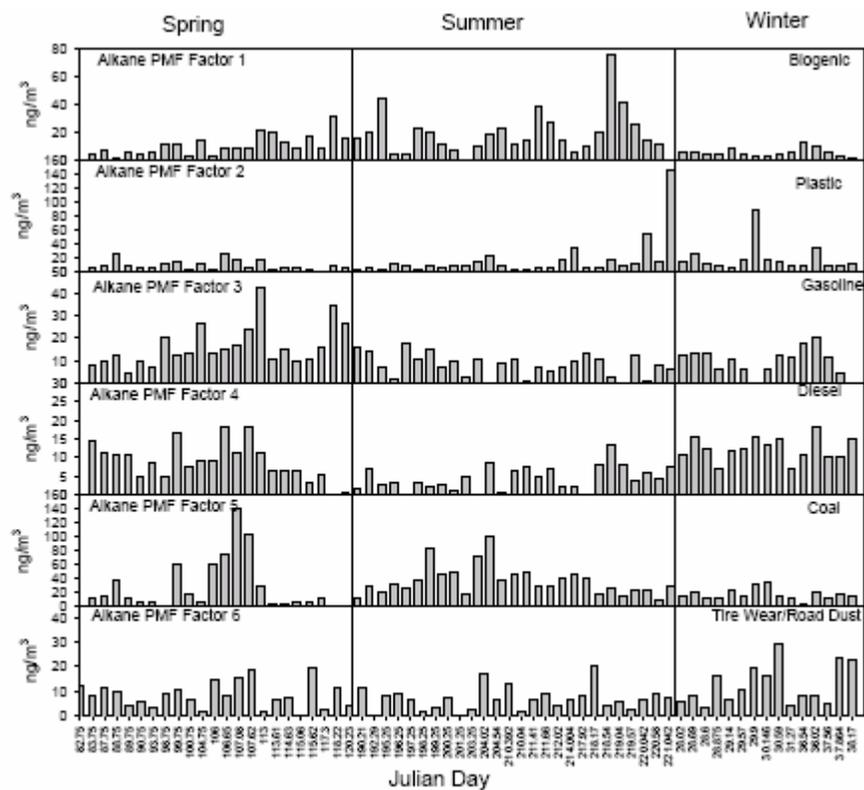
Figure 5.2 Alk PMF alkane + hopane sampling period source contributions.

Alkane PMF Factor 6 exhibited the highest concentrations of hopanes of the resolved factors. The alkanes showed an increase in the concentration from C_{32} to C_{35} consistent with tire wear (Rogge *et al.*, 1993). In addition, a slight odd carbon preference for C_{29} and C_{31} is evident, indicating a biogenic influence. This factor also exhibits no seasonal dependence, suggesting a constant source to the site. Since the road surface is a repository for vehicle and vegetative debris, road dust would have a mixed biogenic/anthropogenic/petrogenic source profile explaining the hopanes (crank case oil, Schauer *et al.*, 1999, 2002), biogenic (leaf litter, grass clippings), and tire wear profiles. Therefore this source is identified as tire wear/road debris.

PCA: PCA only resolved 4 factors (Figure 5.3, Alkane PCA Factors 1 – 4). The profiles of these factors were similar to those identified by EPA PMF. Alkane PCA Factor 1 explained 38% of the variance and was heavily weighted in C_{34} and C_{35} and the hopanes measured in this study consistent with road dust. The temporal profile of this factor (Figure 5.4) is similar to the Alkane PMF analysis with no seasonal trend. Alkane PCA Factor 2 was weighted in the even alkanes, and Alkane PCA Factor 3 exhibited the characteristic odd carbon alkane weighting indicative of plastic and plant waxes accounting for 24% and 15% of the variance, respectively. Both of these factor track well with the Alkane PMF results. The highest weighting in Factor 4 (15% variance) was in the $C_{22} – C_{27}$ alkanes. The elevated weighting for C_{25} is similar to PMF Alkane PCA Factor 4 indicating a vehicular signature. But the time series source contribution of Alkane PCA Factor 4 is more similar to the coal factor identified using PMF (Alkane PMF Factor 5). Therefore, this factor was either
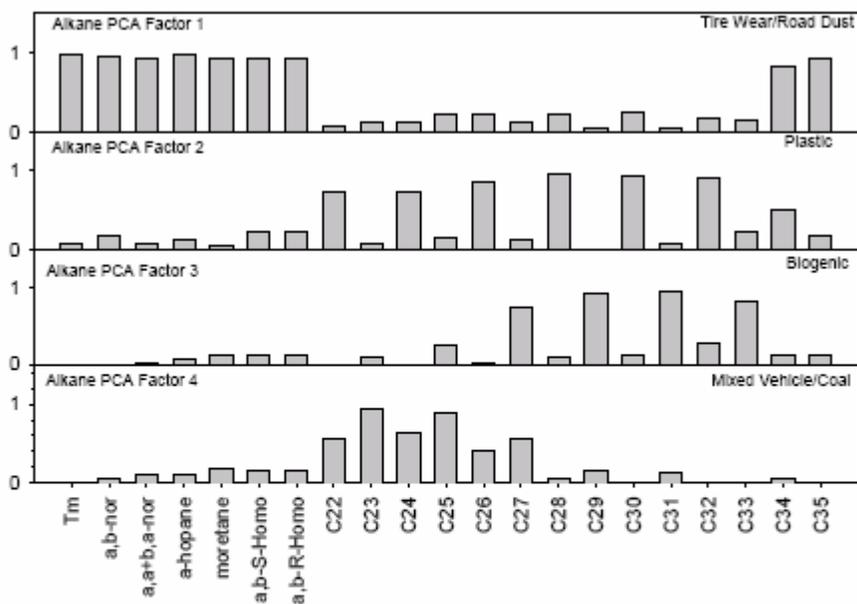
Figure 5.3 PCA profiles generated for $C_{22} - C_{35}$ alkanes and $17\alpha(H)$, $22,29,30$-trisnorhopane (TM), $17\alpha(H)$, $21\beta(H)$-30-norhopane (a,b-nor), $17\beta(H)$, $21\alpha(H)$-30-norhopane + $17\alpha(H)$, $21\alpha(H)$-30-norhopane (a,a+b,b-nor), $17\alpha(H)$, $21\beta(H)$-hopane (a-hopane), $17\beta(H)$, $21\alpha(H)$-hopane (moretane), $17\alpha(H)$, $21\beta(H)$-22S-homohopane (a,b-S-Homo), $17\alpha(H)$, $21\beta(H)$-22R-homohopane (a,b-R-Homo). Varimax rotation applied to component matrix.
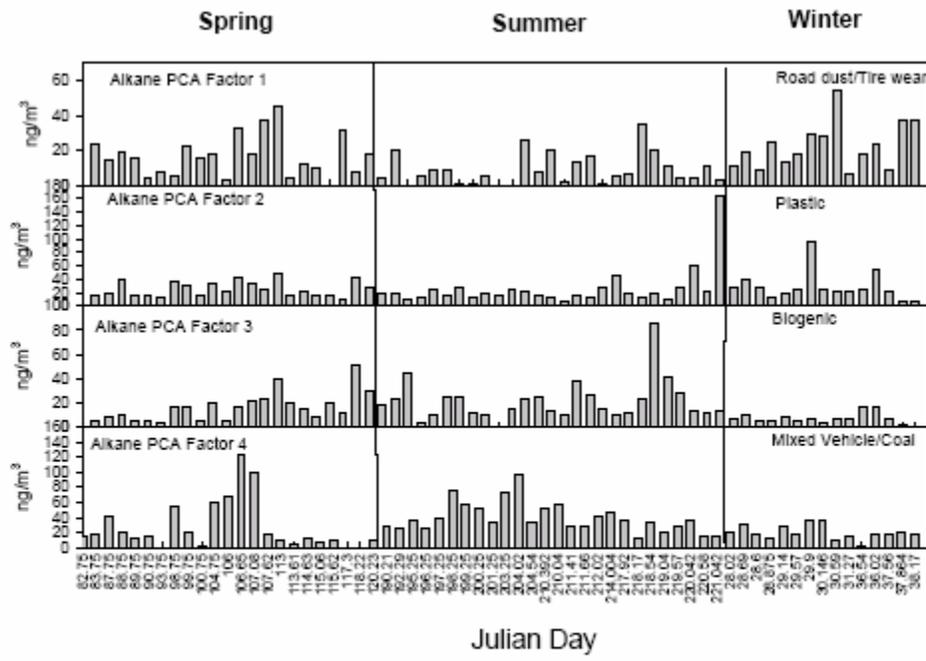
Figure 5.4 Alk PCA time series source contribution of hopanes and alkanes to the Baltimore atmosphere

misidentified by the profiles alone or most likely, PCA was unable to distinguish between the coal and vehicle sources of these compounds. The source contribution from the coal factor in the PAH PMF analysis is > 5-fold the gasoline or diesel values. Therefore, the mixed source identified by PCA is dominated by the loadings from coal compared to vehicles. Therefore, this is assigned a mixed source.

5.4.2   PAHs

PMF: For the PAH PMF the number of factors and source profiles agree well with those previously reported for the Baltimore atmosphere (Larsen and Baker, 2003). PAH PMF Factors 1 and 2 have similar profiles (Figure 5.5), with elevated concentrations of coronene, benzo[*g,h,i*]perylene and indeno[1,2,3-*cd*]pyrene, suggesting a vehicular source (Harrison *et al.*, 1996). Similar to Larsen and Baker (2003), elevated benzo[*b*]-and benzo[*k*]fluoranthene were used to distinguish diesel (PAH PMF Factor 1) from gasoline (PAH PMF Factor 2) combustion for these two factors. Phenanthrene, fluoranthene and pyrene emission rates from diesel exhaust are approximately an order of magnitude above those from gasoline engines (Schauer *et al.*, 1999, 2002), also consistent with the current profiles and source assignments. A greater contribution of gasoline compared to diesel exhaust emissions was observed in the winter compared to spring (Figure 5.6).

PAH PMF Factor 3 was enriched in retene, methylanthracenes and methylphenanthrenes and phenanthrene. This profile is consistent with the Baltimore wood combustion profile identified by Larsen and Baker (2003). This factor exhibited
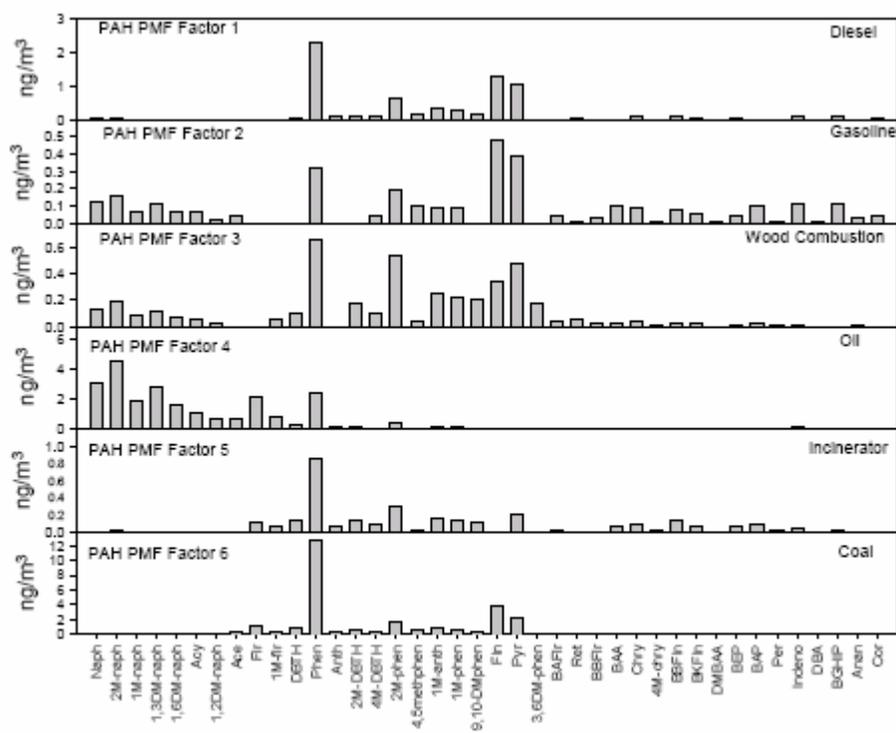
Figure 5.5 PAH PMF source profiles
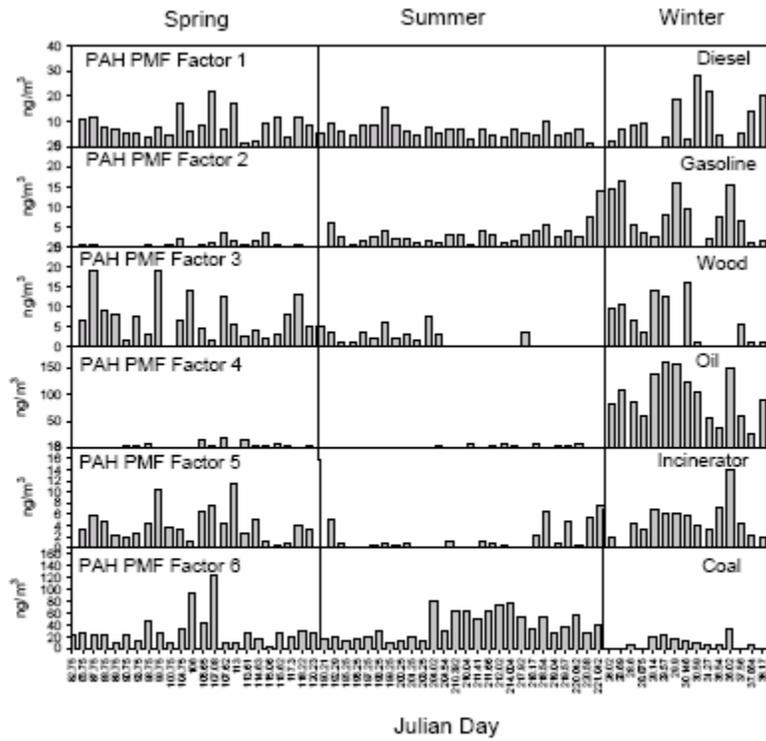
Figure 5.6 PAH PMF source contribution

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elevated concentrations in the spring and winter. The contribution of Factor 4 to the PAH concentrations was primarily during the winter. This factor was heavily loaded with the lightest PAHs including naphthalene, methyl- and dimethylnaphthalenes. In addition, the concentrations of the heaviest PAHs were also observed (indeno[1,2,3-cd]pyerne, benzo[*g,h,i*]perylene and coronene) consistent with an oil source profile previously identified. Residential oil furnaces are common throughout Baltimore city, and the seasonal dependence of this source profile supports home heating oil as the source of this factor.

PAH PMF Factor 5 has elevated loadings of phenanthrene, 2-methylphenanthrene and pyrene (not fluoranthene). The elevated pyrene concentration relative to fluorathene may indicate an incinerator source (Harrison *et al.*, 1996). Elevated contributions from this source during the spring and winter may be due to the influence of meteorological parameters such as mixing height.

PAH PMF Factor 6 is heavily weighted in fluoranthene, pyrene, phenanthrene, anthracene and fluorene with elevated concentrations during the summer sampling periods. A similar source profile and temporal distribution was observed by Larsen and Baker (2003) for the PAH coal source. Elevated concentrations of this factor are found during the summer season, possibly due to increased energy demand during the warmer periods (*i.e.*, electricity demand for air conditioning). The contribution of this coal source tracks well with the seasonal contribution Alkane PMF Factor 5 indicating that the fossil fuel source identified by the alkane profile is most likely a coal combustion profile.
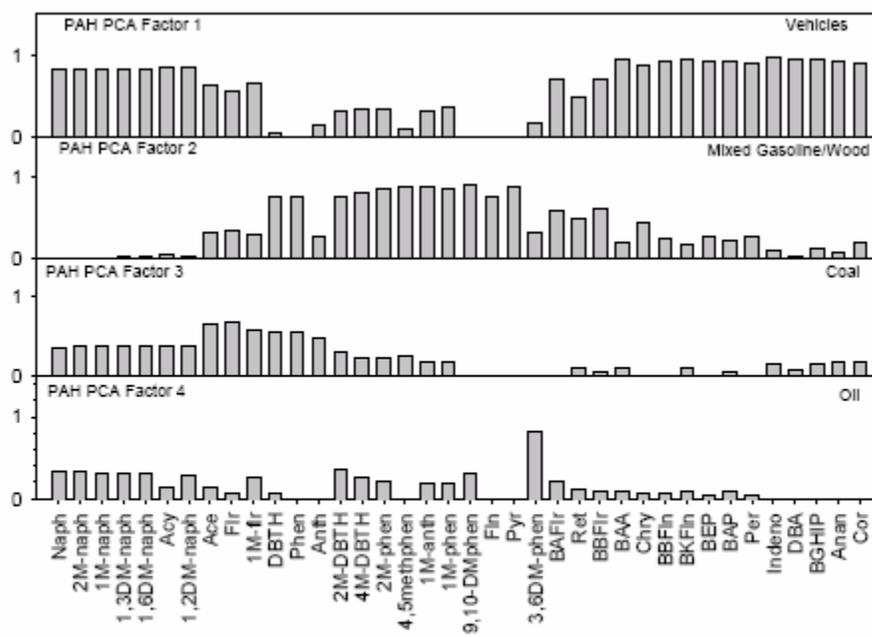
Figure 5.7 PAH PCA profile

PCA: PCA only resolved 4 factors, similar to the previous Baltimore study, explaining 48%, 25%, 10% and 6% of the total variance in the PAH concentrations. PAH PCA Factor 1 (Figure 5.7) was heavily weighted in the lightest (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and heaviest PAHs (benzofluorenes to coronene) measured at the site, consistent with vehicle emissions. The temporal source contribution (Figure 5.8) is consistent with the PAH PMF results if the gasoline and diesel are combined. PAH PCA Factor 2 was initially deemed wood combustion due to the elevated retene, methylphenanthrenes, anthracenes and fluoranthene and pyrene. But when the alkanes were added to the PCA analysis (see below) this factor may also be a gasoline combustion source. PAH PCA Factors 3 and 4 are identified as fossil fuel sources. The elevated loadings of phenanthrene and anthracene in Factor 3 relative to 4 suggested that this is coal while Factor 4 is oil due to elevated napththalene, and methyl- and dimethyl derivatives. The temporal source contribution PAH PCA Factor 3 (coal) is consistent with the PAH PMF results discussed above. The PAH PCA oil source did not track the PAH PMF oil source well. This is possibly due to the elevated concentrations of this source during the winter months.

5.4.3   NPAHs

PMF: The underlying premise of multivariate models is the composition of organic aerosol is a linear combination of individual sources that are conserved from source to receptor site. Although NPAHs have primary and secondary sources, evaluating this class of compounds may provide insight into the possible sources (primary and
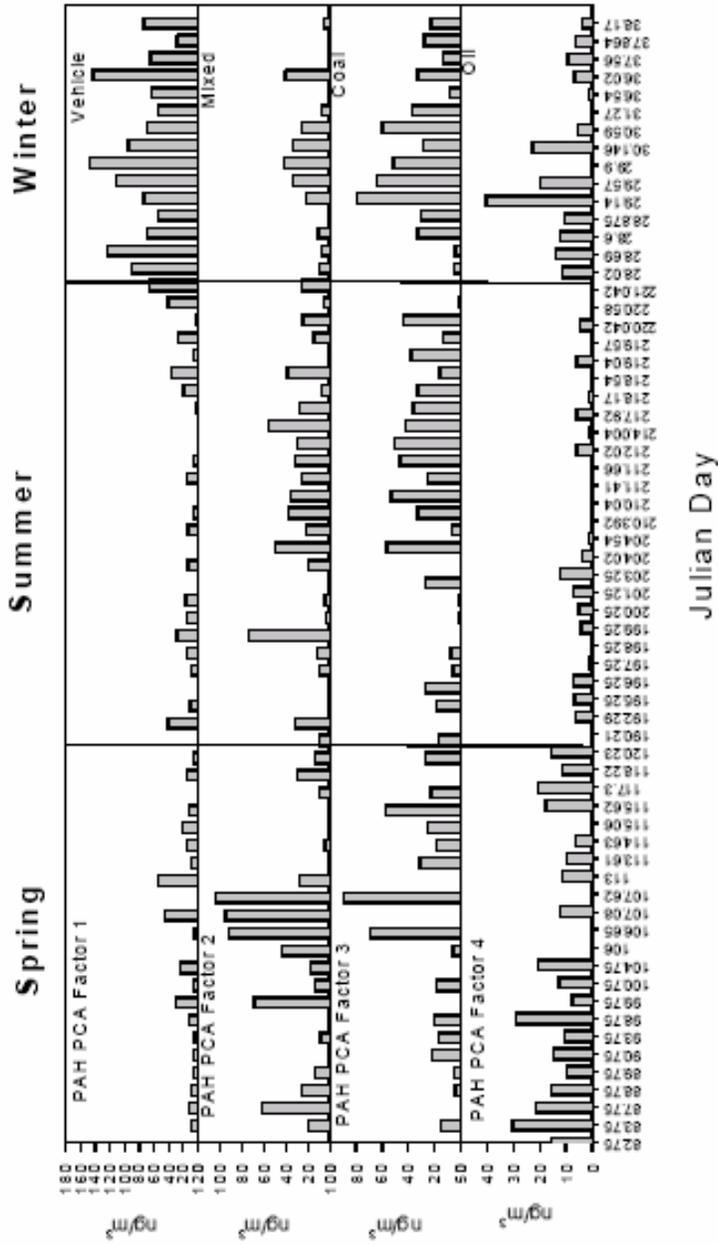
Figure 5.8 PAH PCA source contributions
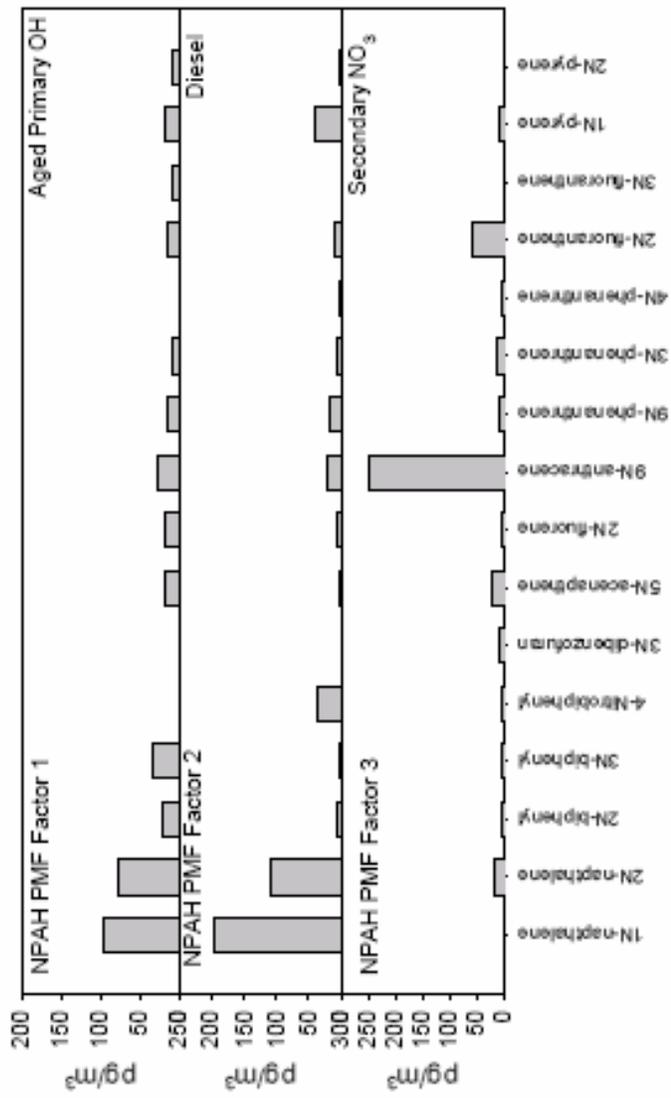
Figure 5.9 NPAH PMF source profiles

secondary) to the ambient atmosphere. Three factors were resolved by PMF in this study (Figure 5.9). NPAH PMF Factor 1 contains both primary and secondary NPAHs. The 2-nitrofluoranthene/1-nitropyrene ratio of this factor (0.85) suggests a primary source even though this factor is significantly loaded with 2-nitropyrene and 3-nitrobiphenyl, which are formed solely from the OH mediated mechanism (Arey *et al.*, 1986, Atkinson *et al.*, 1990). The presence of primary and secondary NPAHs may indicate that this source is a mixed air mass possibly from long range transport. This factor is significant during select spring periods (Figure 5.10) especially during the day time samples. Therefore this factor is denoted as aged primary aerosol.

NPAH PMF Factor 2 is heavily loaded with primary NPAHs (1-nitropyrene, 1- and 2-nitronaphthalene) which have been detected in diesel exhaust (Bamford *et al.*, 2003, Zielinska *et al.*, 2004). This profile is found predominantly in the spring and winter samples similar to the diesel source profiles determined in the PAH and alkane analysis. The temporal distribution of the NPAH diesel source does not track well with the diesel PAH and alkane source contributions. Like PAHs, NPAH isomers have numerous primary sources in addition to secondary production (Arey, 1998). Primary source studies incorporating more than a select few of these compounds are scarce. Therefore, using this marker as a definitive diesel marker needs further exploration through intensive source aerosol characterizations.

The third factor identified (NPAH PMF Factor 3) is heavily weighted in 9-nitroanthracene, 5-nitroacenaphthene and 2-nitrofluoranthene, suggesting a secondary source profile. The ratio of 2-nitrofluoranthene/2-nitropyrene is 140, consistent with an elevated NO_3 radical activity. This source has an increased contribution during the
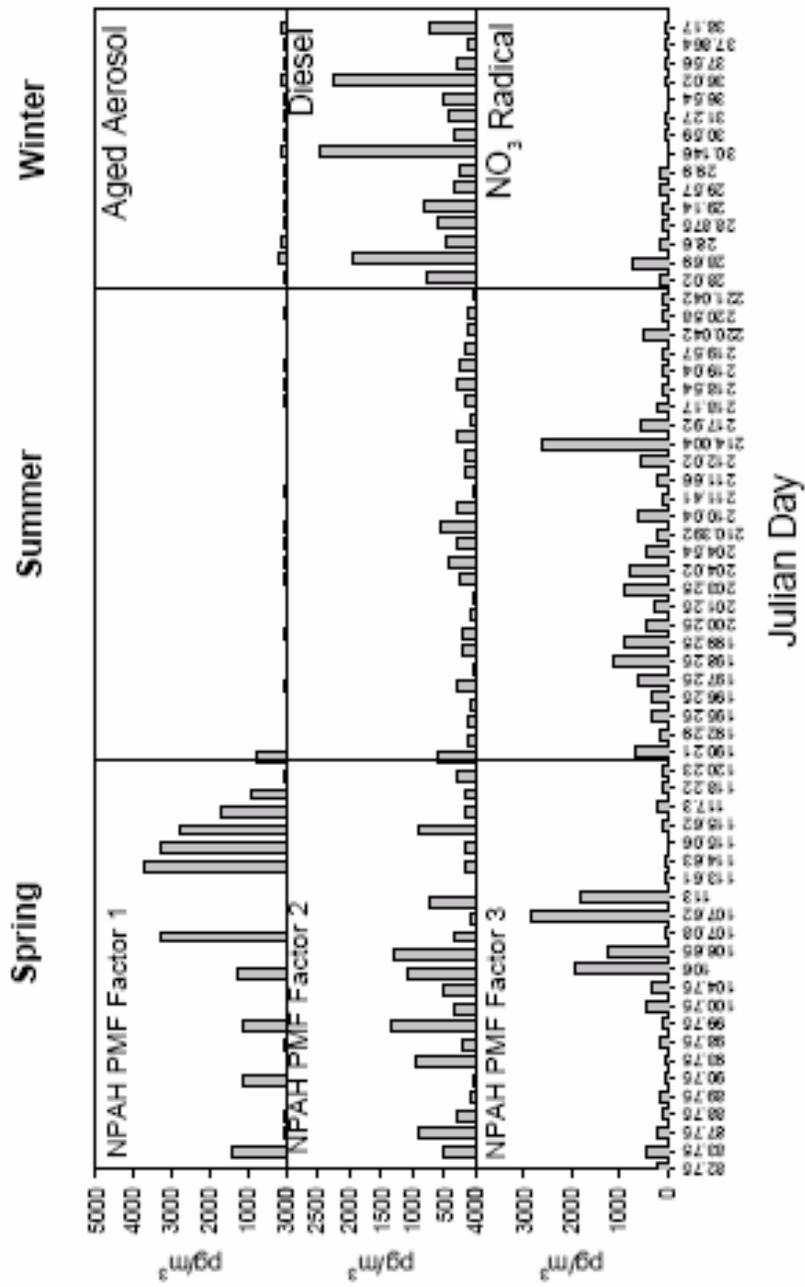
Figure 5.10 NPAH PMF source contributions

summer samples consistent with previous results (Chapter 3). In addition, elevated loadings of this factor are observed during the night samples, when NO_3 is not photolyzed. Therefore, this factor is denoted as NO_3 radical secondary organic aerosol (SOA).

PCA: PCA resolved 4 factors for the NPAHs explaining 29%, 29%, 19% and 8.6% of the variance (Figure 5.11). The first factor (NPAH PCA Factor 1) was heavily weighted in 4-nitrophenanthrene, 5-nitroacenapthene, and 2-nitrofluoranthene, the latter of which is the dominant secondary NPAH isomer in the ambient atmosphere. 3-nitrobiphenyl is also enriched in this factor and is believed to be formed via an OH radical initiated pathway (Arey, 1998). Therefore this factor is a secondary NPAH source, possibly OH initiated. This factor exhibited contribution spikes during 2 consecutive day (12 hr) sample periods during the spring (Figure 5.12), consistent with daytime OH radical chemistry. NPAH PCA Factor 2 is heavily weighted in primary NPAHs 3-nitrofluoranthene, 2-nitrofluorene, 2-nitrobiphenyl and the secondary isomer 2-nitropyrene. The mixture of these isomers may indicate an aged primary source of this factor. This factor is a significant contributor to the total NPAH concentration during the spring. NPAH PCA Factor 3 is dominated by the nitronaphthalene isomers, 3-nitrodibenzofuran and 4-nitrobiphenyl. All of these compounds (except 3-nitrobenzofuran, for which no source information was found) have combustion sources. Zeilinska *et al*. (2004) found that gasoline exhaust contains small amounts of the low molecular weight NPAHs, this profile may be identified as gasoline exhaust. The last factor (NPAH PCA Factor 4) is heavily weighted in 1-
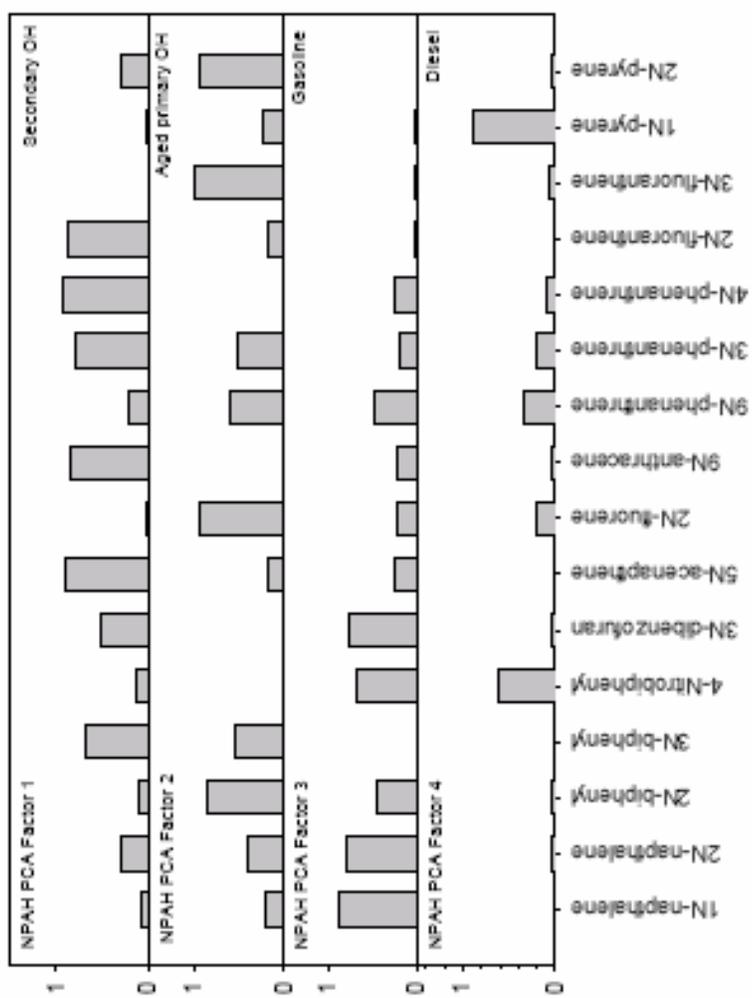
Figure 5.11 PCA profiles for NPAHs. Component matrix with Varimax rotation
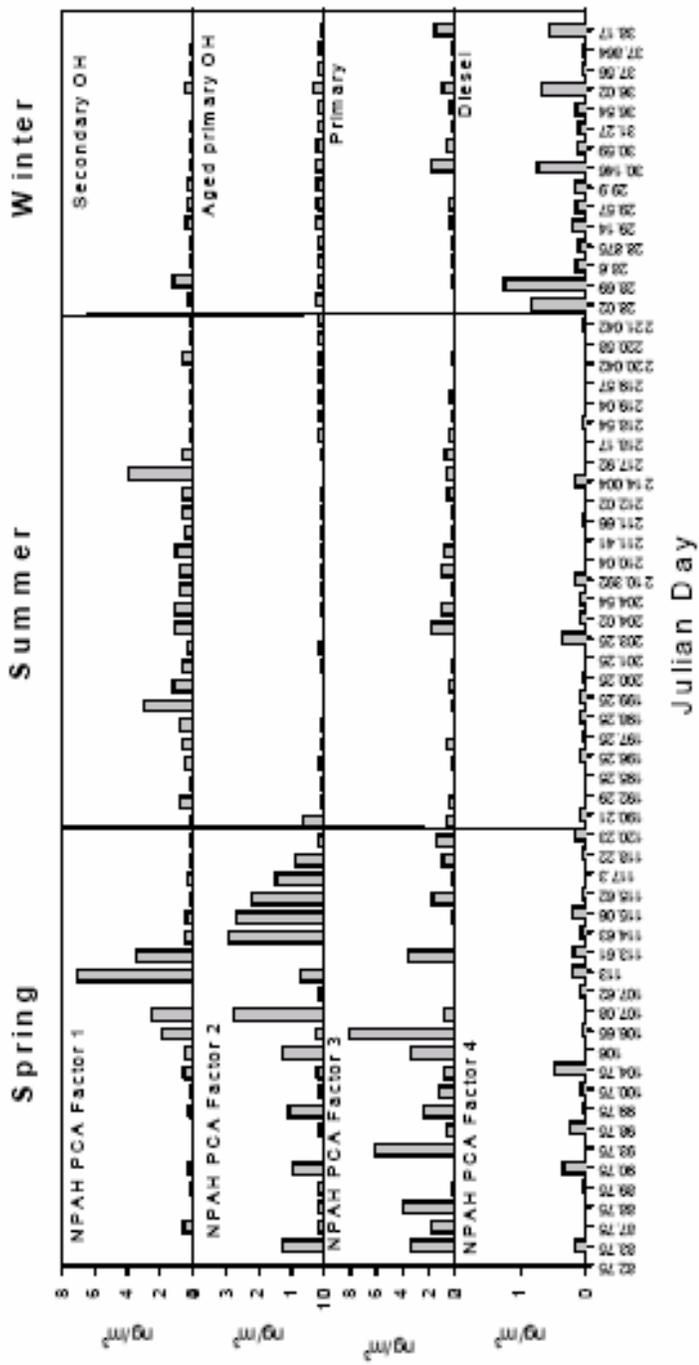
Figure 5.12 NPAH PCA sampling period source contribution

nitropyrene and 4-nitrobiphenyl suggesting a diesel source (Arey, 1998). The temporal source contribution agrees well with the NPAH PMF Factor 2 (diesel).

5.4.4   Combined Compound Classes

PMF consistently resolved a greater number of sources compared to PCA for the compound classes analyzed. Although similar profiles were obtained for the majority of cases, the output of PMF in concentration units allows for direct comparison of individual compounds within a source, aiding identification. This is illustrated by Alkane PCA Factor 4. A fossil fuel factor was generated by PCA which could have been easily misidentified from the component matrix alone, whereas the Alkane PMF results was able to correctly identify this factor using the ratio of $17\alpha(H)$, $21\beta(H)$-30-norhopane to $17\beta(H)$, $21\alpha(H)$-hopane. Although this is a limitation of PCA, increasing the number and diversity of analytes may solve this short coming. In the next section, compound classes are combined and analyzed using PCA and PMF accounting for a greater number of potential markers. This analysis allows for a direct comparison of the different multivariate techniques and the affect of additional analytes of multiple classes on the resolving power of PMF and PCA.

PMF: The alkanes, PAHs and hopanes, 1-nitropyrene, 2-nitrofluoranthene, NO, NO_x ozone and CO were used as input parameters to EPA PMF 1.1 to compare the use of multiple compound classes and gas phase species to individual organic compound class results presented above. The model parameters were similar to those employed for the individual class analysis. This species compilation resolved 9 sources to the Baltimore atmosphere (All Data PMF Factors 1 – 9). All Data PMF Factor 1 was

Figure 5.13a All Data PMF Results PAH source profiles
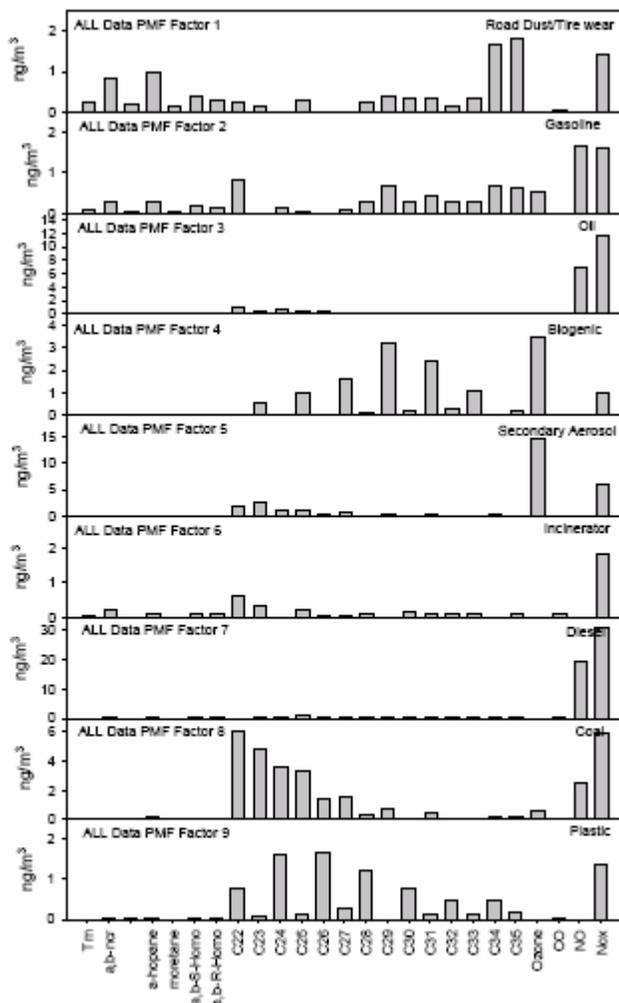
Figure 5.13b All Data PMF source profiles. Ozone, NO and NO$_x$ in ppb, while CO is in ppm.

heavily weighted in C_{34} and C_{35}, and exhibited the greatest concentration of hopanes of all of the factors. From the previous alkane + hopane analysis this source is identified as a tire wear/road dust source (Figure 5.13).

All Data PMF Factors 2 and 7 appear to be vehicular emissions. Both factors are heavily weighted in coronene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene. The concentrations of NO and NO_x are lower in All Data PMF Factor 2 compared to 7. 1-nitropyrene was associated with All Data PMF Factor 7 and not 2 and a significant (>0) contribution of the lightest PAHs was also present. From these observations and the correlation analysis presented in Chapter 3, All Data PMF Factor 7 is assigned a diesel source, whereas All Data PMF Factor 2 is denoted gasoline emissions. The elevated benzofluoranthenes, used to distinguish gasoline from diesel in the PAH analysis alone were not evident when multiple classes of compounds were used as input parameters. Therefore, these compounds may have limited value in distinguishing these two sources when multiple classes of compounds are used.

All Data PMF Factor 3 is heavily loaded in the lightest PAHs, a slight even alkane carbon preference and a decreasing alkane concentration with increased molecular weight from C_{22} to C_{30} suggesting a petrogenic source. The PAH profile is consistent with oil combustion. Significant quantities of CO, NO and NO_x were also associated with this factor which was primarily observed during the winter (Figure 5.14). Therefore this factor was assigned an oil source, most likely from domestic home heating.
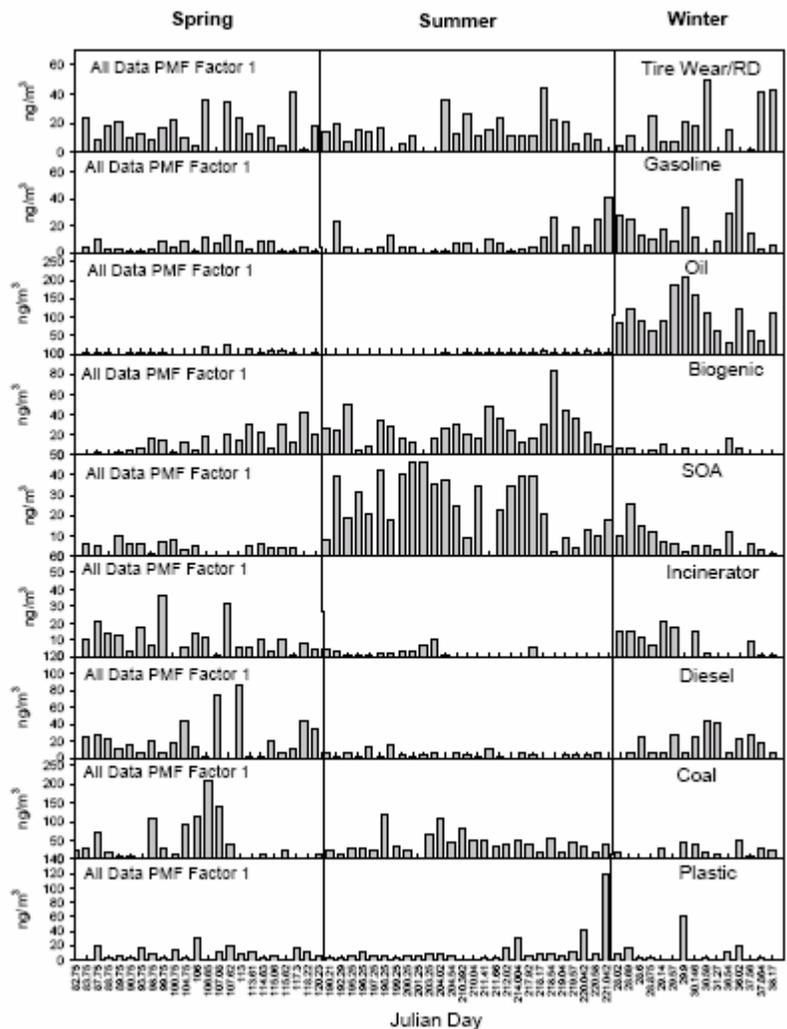
Figure 5.14 All Data PMF daily contribution

All Data PMF Factor 4 was identified as biogenic from the strong odd carbon preference in the alkane profile with a maximum concentration at C_{29} and was associated with increased levels of ozone. Interestingly, this factor also contained elevated concentrations of phenanthrene, fluoranthene and pyrene. This may be due to the covariance of biogenic emissions with long range transport of combustion emissions to the Baltimore region. The temporal source contribution was well correlated ($R^2 = 0.89$) with the biogenic source identified using alkanes only with the greatest concentrations during the spring and summer periods.

All Data PMF Factor 5 exhibited the greatest ozone concentration and a slight odd carbon predominance, decreasing in concentration from C_{22} to C_{32}. The greatest concentration of 2-nitrofluoranthene and elevated concentrations of fluroanthene and pyrene are also apparent. High ozone and fluoranthene, pyrene and 2-nitrofluoranthene were associated with this profile, representative of fossil fuel initiated secondary organic aerosol formation. NO_x was elevated for this factor, whereas the NO concentration was not greater than 0 ng/m^3, indicative of high photochemical conversion of primary NO to NO_2, consistent with a secondary organic aerosol factor.

All Data PMF Factor 6 exhibited elevated concentrations of pyrene relative to fluoranthene, significant levels of phenanthrene, and was the major contributor to 3,6-dimethylphenanthrene. No carbon preference was observed in the alkane profile and the ratio of 2-nitrofluoranthene/1-nitropyrene was 0.4, consistent with primary NPAH formation (Ciccioli *et* al., 1996). The elevated levels of phenanthrene and pyrene (relative to fluoranthene) have been reported for incinerator sources (see above),

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therefore this factor is denoted as the incineration source for the combined organic analysis. Elevated concentrations of this factor were observed during the spring and winter months similar to the incinerator source identified by the PAHs alone.

All Data PMF Factor 8 had the highest concentrations of phenanthrene, fluoranthene, pyrene and decreasing alkane concentrations with molecular weight ($C_{22} - C_{28}$) and elevated NO and NO_x concentrations. A significant concentration of ozone and a greater secondary NPAH contribution (2-nitrofluoranthene/1-nitropyrene = 7) compared to the factor 3 (oil) suggests aged aerosol. From the PAH profiles we assigned this as a coal combustion profile. The aged component of this profile may indicate that this source is not local, most likely from electricity generation *via* coal fired power plants. Although the alkane source contribution for this factor was better correlated than the PAHs (R^2 = 0.83 and 0.20, respectively) peak contributions of this factor are similar among the three analyses.

The last factor (All Data PMF Factor 9) was identified from the unique even alkane carbon preference and low PAH concentrations characteristic of plastic incineration (Simoneit *et al.*, 2005). The temporal source contribution was well correlated with the alkane only analysis (R^2 = 0.90). The soft wood combustion source identified using PAHs was not resolved when all of the compounds were added to the PMF analysis. This may be due to the low contribution of this source to the Baltimore area for these sampling periods compared to the other sources resolved when alkanes and NPAHs were added to the input matrix. This also may illustrate the loss of statistical power from the increase in the number of analytes compared to samples in the analysis (Brinkman *et al.*, 2005).

PCA: The PCA results when PAHs, alkanes, hopanes, 1-nitropyrene, 2-nitrofluoranthene, NO, CO, O3, and NOx were combined as an input matrix differ from the All Data PMF results, but are consistent with the individual compound class PCA (Figure 5.15). The explained variance for the 8 significant factors was 31, 15, 14, 8, 6, 5, 5, 2 and 3 percent, respectively. All Data PCA Factor 1 contains the greatest loadings in the lightest and heaviest PAHs and, NO and NO_x. This profile is consistent with the PAH PCA vehicle profile. Compared to the All Data PMF results this appears to be a combination of the oil and diesel signature as the greatest contribution is found during the winter (Figure 5.16).

All Data PCA Factor 2 (15% variance) contains the elevated retene and alkyl phenanthrenes and anthracenes identified as wood combustion in the PAH PCA. But the elevated contributions from the lightest alkanes especially C_{25} relative to C_{24} and C_{26} indicating a gasoline profile. The grouping of these compounds is consistent with the gasoline source previously identified using correlation analysis (Chapter 3). But as discussed above the temporal profile is more consistent with the coal source identified using PMF (PAH PMF Factor 6). Therefore a definitive assignment is not possible.

All Data PCA Factors 3 and 4 are easily identified as road dust and plastic, respectively due to their characteristic alkane profiles discussed above. All Data PCA Factor 6 (5.2 % variance) was heavily weighted in the odd carbon alkanes denoting a biogenic source. These sources track well with the All Data PMF results affirming their source designation.

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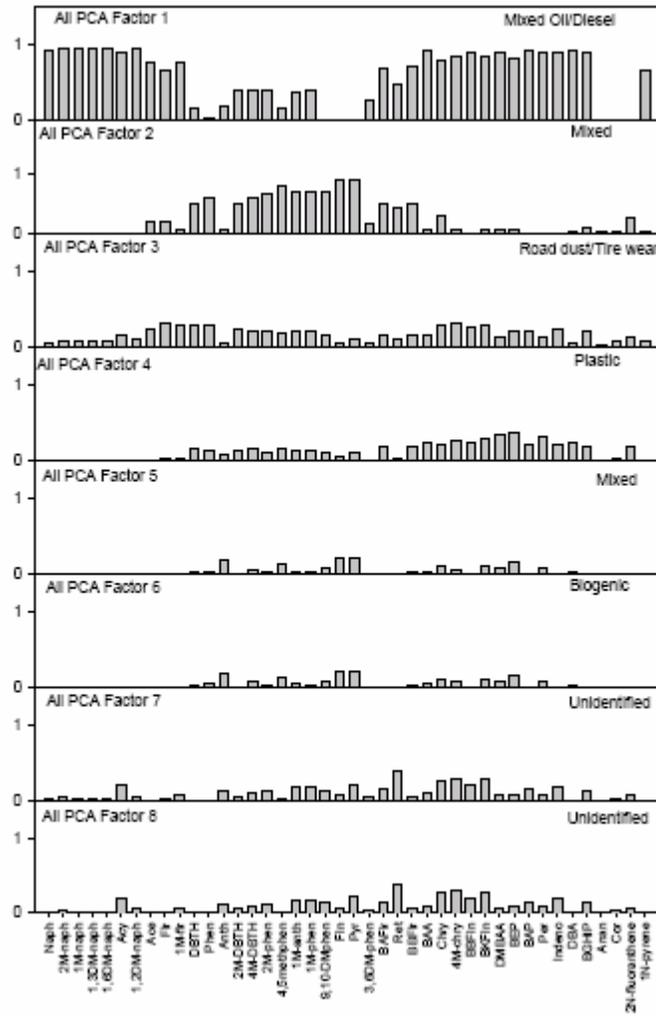
Figure 5.15a All Data PCA PAH and NPAH source profiles
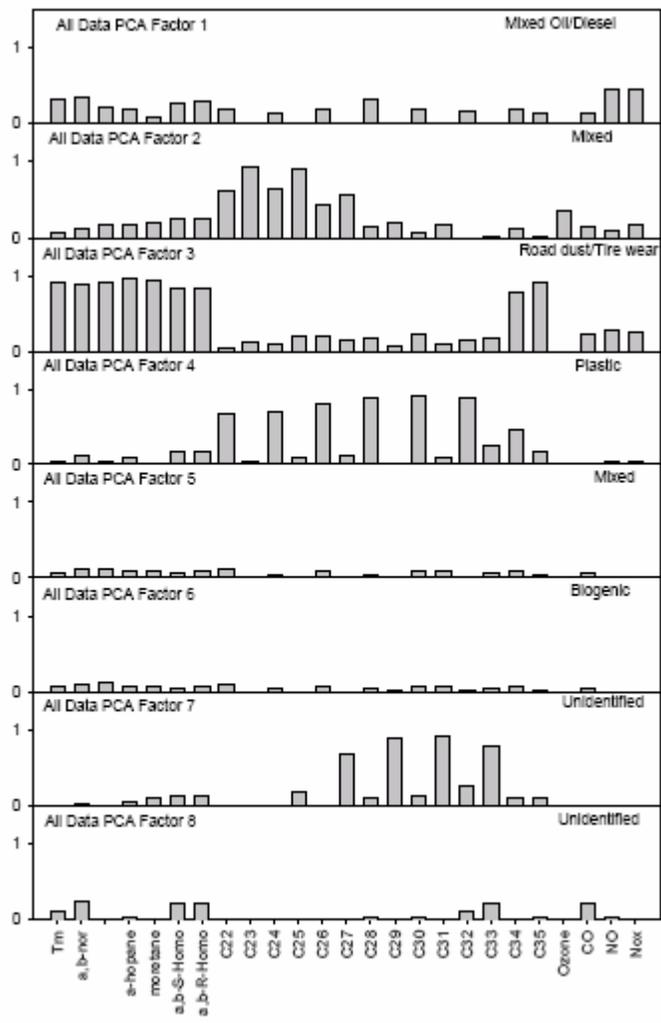
Figure 5.15b All Data PCA alkane, hopane and gas profiles
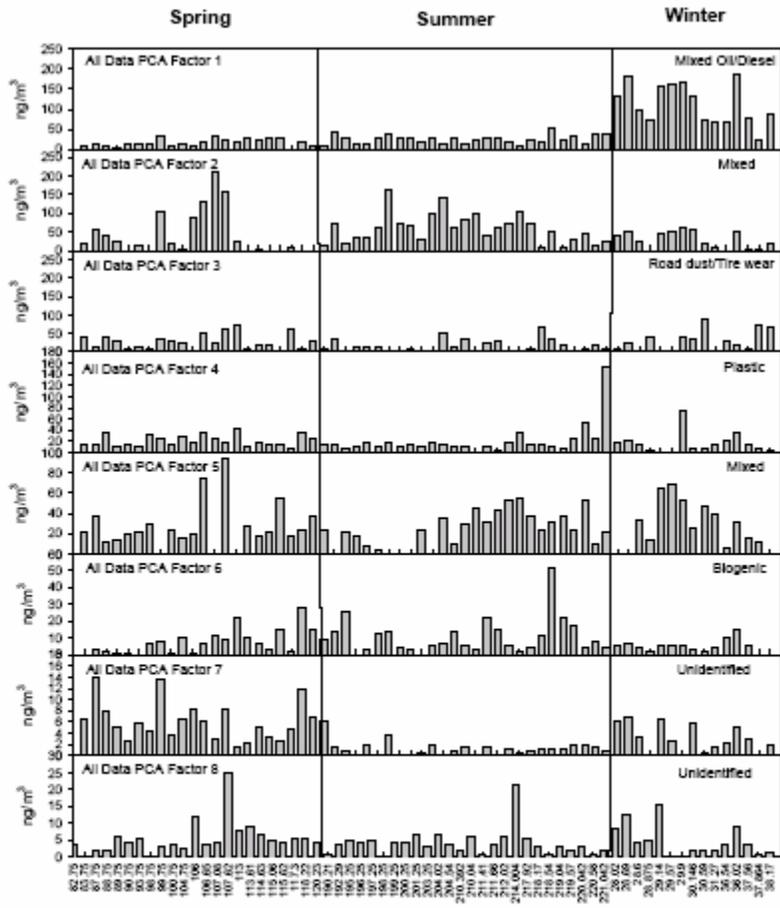
Figure 5.16 All Data PCA daily contribution.

All Data PCA Factor 5 was weighted with phenanthrene, anthracene and fluorene and initially assigned a coal source. Again, the temporal source contribution does not track with the All Data PMF results. ALL Data PCA Factors 7 and 8 were not assigned sources due to the ambiguous weighting of the analytes. All Data PCA

Factor 7 had the highest weighting in methyldibenzothiophenes and methylanthracenes and methylphenanthrenes while All Data PCA Factor 8 was heavily weighted in 2-nitrofluoranthene. This may indicate a secondary organic aerosol factor, but the low ozone weighting does not support this. The temporal source contribution agreed well with the NO_3 radical designation from the NPAH PMF analysis (NPAH Factor 3) during the spring and summer.

5.5 Discussion

Similar to the previous analysis using PAHs in the Baltimore atmosphere, PCA and PMF produce similar source profiles and contributions when individual compound classes are analyzed. PMF consistently resolved more factors than PCA for the individual compound class analysis. For the alkane + hopanes and PAHs, PCA was unable to distinguish gasoline and diesel sources.

A drastic difference was observed when multiple classes of compounds were simultaneously analyzed with PCA and PMF. Both models generated replicate profiles and contributions sources that relied on distinct alkane profiles (biogenic, plastic, and road dust). In the All Data analysis, sources that relied on PAH profiles did not agree well among PCA and PMF. One of the benefits of using PMF is the ability to introduce analyte specific error into the model. It is unlikely that the errors

Table 5.3 Source identification parameters for PMF and PCA from individual compound class analysis

Analytes	Factor	Description	Assigned Source
Alkanes + Hopanes			
PMF	1	odd carbon predominance, elevated C_{29}	Biogenic
	2	even carbon predominance, elevated C_{24}	Plastic
	3	Elevated C_{25}	Gasoline Exhaust
	4	Elevated C_{25} and hopanes relative to Factor 3	Diesel Exhaust
	5	Elevated concentrations of alkane<C27, $17\alpha(H)$, $21\beta(H)$-hopane/$17\beta(H),21\alpha(H)$-hopane = 1.6	Coal
	6	Greatest concentrations of hopanes, increase in concentration from $C_{32} - C_{33}$	Tire wear/road dust
PCA	1	Heavily weighted in C_{24} and C_{25} and hopanes	Tire wear/road dust
	2	Elevated even carbon alkane weighting	Plastic
	3	Elevated odd carbon weighting	Biogenic
	4	Elevated weighting of C_{25}, time series similar to coal factor in PMF	Mixed vehicle/coal
PAHs			
PMF	1	Elevated levels of coronene, benzo[g,h,i]perylene, indeno[c,d]pyrene, elevated phenanthrene, fluoranthene, pyrene relative to Factor 2	Diesel Exhaust
	2	Elevated levels of coronene, benzo[g,h,i]perylene, indeno[c,d]pyrene	Gasoline Exhaust
	3	Elevated retene, methylanthracenes, methylphenanthrenes	Wood Combustion
	4	Naphthalene, methyl- and dimethylnaphthalenes, indeno[c,d]pyrene, coronene, benzo[g,h,i]perylene	Oil
	5	Phenanthrene, 2-methylphenanthrene, pyrene	Incinerator
	6	Fluoranthene, pyrene, phenanthrene, anthracene and fluorene	Coal
PCA	1	Naphthalene, methyl-and dimethylnaphthalenes, benzofluorenes to coronene, temporal contribution similar to PAH PMF Factor 1 + 2	Vehicles
	2	Methylphenanthrenes, retene, methylanthracenes, fluoranthene, pyrene	Mixed Gasoline exhaust/wood
	3	Phenanthrene, anthracene	Coal
	4	Naphthalene, methyl- and dimethylnaphthalene	Oil
NPAH			
PMF	1	1- and 2-nitronaphthalene, 2-nitrofluoranthene/1-nitropyrene = 0.85, 2-nitropyrene	Aged primary OH
	2	1-nitropyrene, 1-and 2-nitronaphthalene	Diesel
	3	9-nitroanthracene, 5-nitroacenaphthene, 2-nitrofluoranthene/2-nitropyrene = 140	Secondary NO_3
PCA	1	4-nitrophenanthrene, 5-nitroacenaphthene, 2-nitrofluoranthene, 3-nitrobiphenyl	Secondary OH
	2	3-nitrofluoranthene, 2-nitrofluorene, 2-nitrobiphenyl, 2-nitropyrene	Aged primary OH
	3	Nitronaphthalenes, 3-nitrobenzofuran, 4-nitrobiphenyl	Primary Gasoline exhaust
	4	1-nitropyrene, 4-nitrobiphenyl	Diesel

Table 5.4 Source identification parameters for PMF and PCA from combined compound class analysis

Analytes	Factor	Description	Assigned Source
All Data			
PMF	1	C_{34} and C_{35}, heavily weighted in hopanes,	Tire wear/Road Dust
	2	High NO and NO_x, coronene, benzo[g,h,i]perylene, inden[c,d]pyrene,	Gasoline
	3	Methyl and dimethylnaphthalenes, fluorine, phenanthrene, coronene, benzo[g,h,i]perylene, inden[c,d]pyrene, winter dominated	Oil
	4	Odd carbon predominance, C_{29} highest concentration	Biogenic
	5	Ozone, decreasing alkane concentration from C_{22} to C_{32}, highest 2-nitrofluoranthene concentration	Secondary Aerosol
	6	Pyrene (no fluoranthene), phenanthrene	Incinerator
	7	1-nitropyrene, coronene, benzo[g,h,i]perylene, inden[c,d]pyrene, fluoranthene and pyrene relative to All Data Factor 2	Diesel
	8	Phenanthrene, fluoranthene, pyrene, decreasing alkane concentrations from C22 – C28, ozone	Coal
	9	Even alkane predominance	Plastic
PCA	1	Lightest and heaviest PAHs, NO, NO_x, High winter contribution	Mixed Oil/Diesel
	2	Retene, alkylphenanthrenes, alkylanthracenes, Elevated C2 relative to C_{34} and C_{35}, PAH profile similar to gasoline profile via correlation analysis (Chapter 3)	Mixed
	3	C_{34} and C_{35}, elevated hopanes	Road dust/Tire wear
	4	Even carbon alkane predominance	Plastic
	5	Phenanthrene, anthracene, fluorine, temporal does not agree with All Data PMF coal source	Mixed
	6	Odd carbon alkane predominance	Biogenic
	7	Methyldibenzothiophenes, methylphenanthrenes and methylanthracenes	Unidentified
	8	2-nitrofluoranthene, 1-nitropyrene	Unidentified

associated with different classes of compounds are equal, which is assumed by PCA. Therefore the unique error associated with each input variable may skew the results when multiple classes of compounds are used (See Tables 5.3 and 5.4 for summary). This may explain the discrepancies between PCA and PMF in the All Data PCA and All Data PMF results. In addition, correctly identifying the factors is probably the most difficult part of multivariate source apportionment. The output of PMF is in concentration units, which can be used to evaluate the relative concentration of potential markers within a factor. Although the compounds driving the variability in a prescribed factor may be determined using PCA, the relative concentration of individual compounds can not be directly evaluated within a factor. This is illustrated in the two factors from the All Data PCA that were not identifiable (All Data Factors 7 and 8). Therefore in the following sections the PMF results are used to calculate the seasonal contribution of the identified sources to individual compound class, total carbon and $PM_{2.5}$ concentrations measured in Baltimore.

5.5.1 *Seasonal Source Contributions of PAHs, NPAHs, Alkanes and Hopanes*

The seasonal distribution of alkanes, hopanes, PAHs and NPAHs were calculated using the individual class PMF results. The superior resolving ability provides a better estimate of the sources and source contributions (described above) compared to PCA. Therefore, the seasonal source contributions using PCA/MLR are not presented. The mean spring, summer and winter percent contribution of alkanes and hopanes using PCA and PMF are shown in Figure 5.17. In the PMF results, the diesel and gasoline contribution of these compounds decreases in the summer,
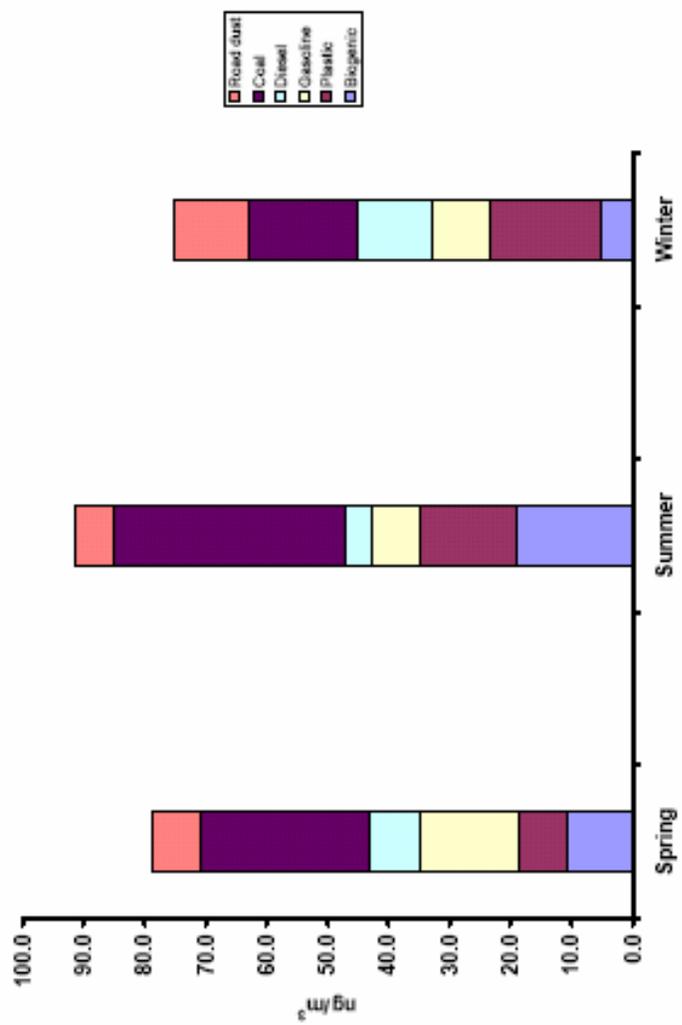
Figure 5.17 Mean seasonal contribution of alkane and hopane sources identified using PMF to the Baltimore atmosphere

whereas the coal and biogenic fraction increases during the summer. The contribution of gasoline exhaust is about two fold greater than diesel in the spring and summer. In contrast, the winter period exhibited a larger diesel contribution relative to gasoline. In the spring the dominant sources of organics are coal and gasoline exhaust (24%).

The coal source appears to dominate the contribution of alkanes and hopane during the summer period accounting for 42% of the alkane and hopane concentration. During the winter, alkane and hopane concentrations were evenly impacted by all the sources identified, with the exception of the biogenic source.

The dominant source of PAHs during the spring and summer was coal (Figure 5.18), accounting for ~50% and 70% of the PAH concentration, respectively. The winter PAHs were dominated by oil combustion, accounting for 72% of the observed concentrations. Gasoline was the dominant vehicle source of alkanes in all seasons with the greatest difference during the spring. The largest contribution of PAHs from the soft wood combustion source was observed during the spring.

The mean concentration of the PMF resolved NPAH sources in the spring were similar (Figure 5.19). The aged primary source concentration was greater during the spring compared to summer and winter. The secondary NO_3 source was the highest contributor to the total NPAH concentration during the summer (65%) followed by the diesel source (33%). The abundance of this source during the summer is consistent with previous results (Chapter 3), where an elevated ratio of 2-nitrofluoranthene/2-nitropyrene indicated greater secondary production of NPAHs *via* the NO_3 pathway. The winter period was dominated by the diesel NPAH source,

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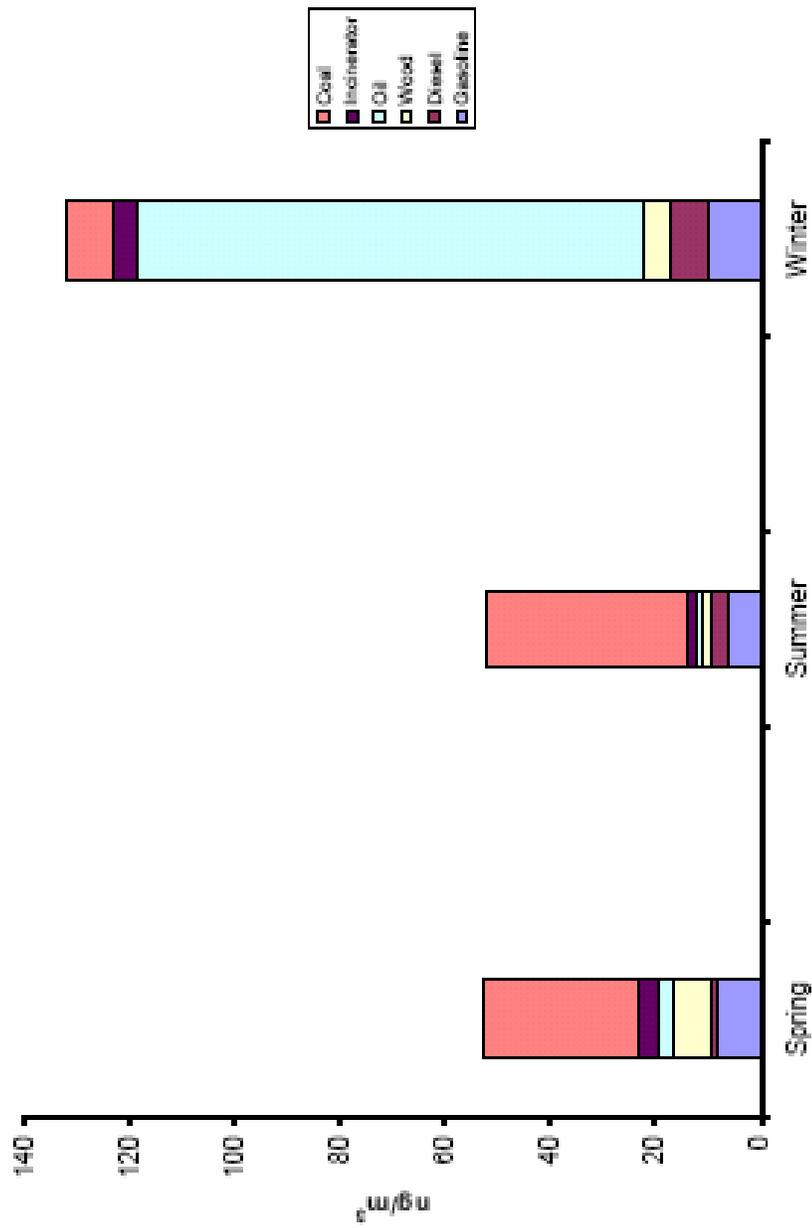
Figure 5.18 Mean seasonal contribution of PAH sources identified using PMF to the Baltimore atmosphere.
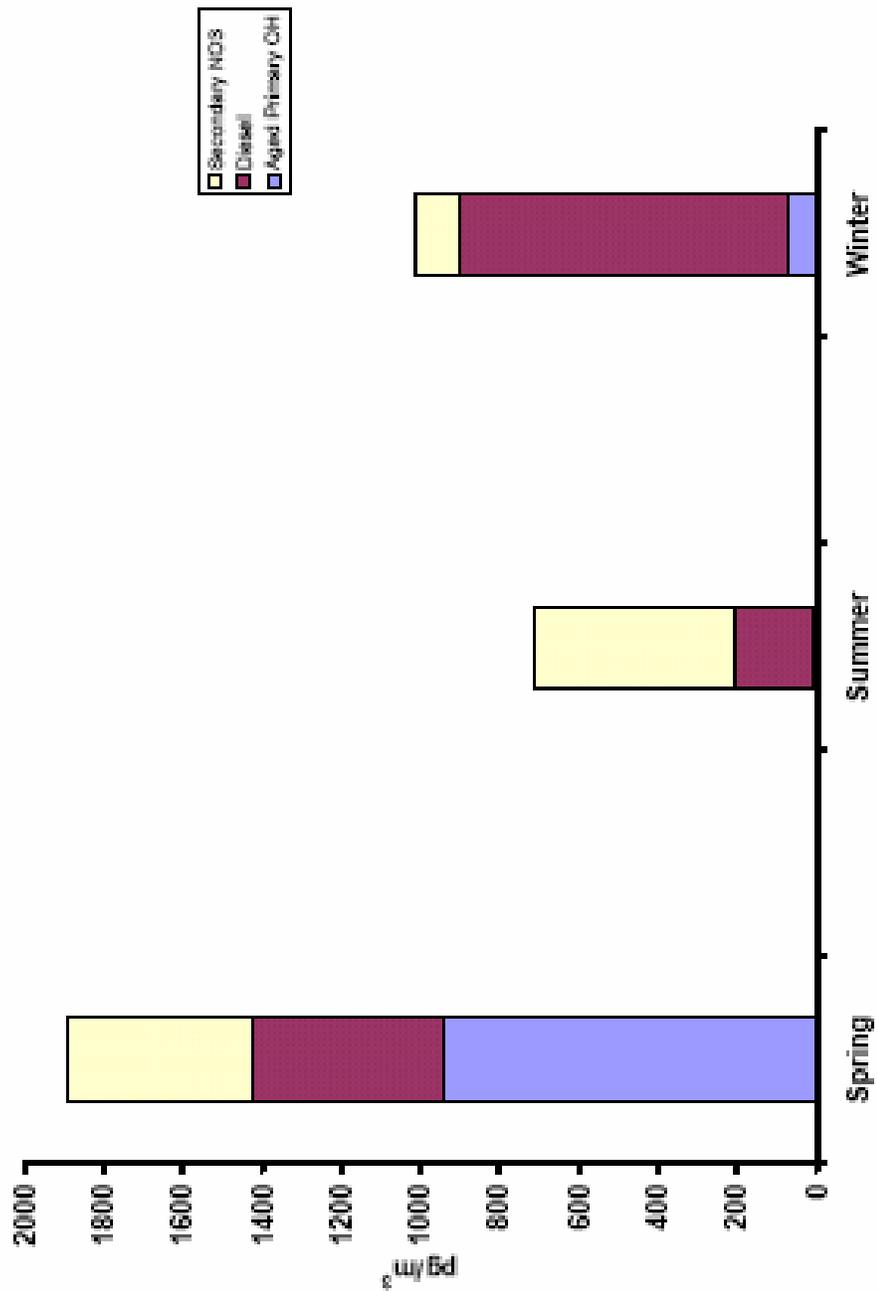
Figure 5.19 Mean seasonal contribution of NPAH sources identified using PMF to the Baltimore atmosphere

accounting for 80% of the observed concentration of total NPAHs in the Baltimore atmosphere.

5.5.2 Total Carbon and PM2.5 Source Estimates

The source contributions resolved from PMF were regressed against total carbon (TC, elemental + organic carbon) measured at the site. The mean sourcecontribution using these markers only applies for the spring and summer 2002 due to missing TC data during the winter. Also, the TC was measured on particles with diameters less than 2.5μm whereas the organics data was measured on total suspended particulate matter. The nine factors identified explained 64% of the variance in TC. The largest contributor to the total carbon mass is the anthropogenic secondary factor (24%) followed by diesel (20%) and gasoline (16%) combustion (Figure 5.20). The road dust/tire wear, incinerator and coal factor account for 10, 12 and 4% of the total carbon. The fraction of TC from the oil source was not significantly greater than 0 during the spring and summer consistent with the temporal source contributions (Figure 5.14). A negative contribution to TC was found for the plastic source. This negative concentration is not physically possible, but theoretically this indicates the decrease in the TC concentration when this source is present. Therefore, this factor was removed from the regression equation.

A similar analysis was performed for the measured $PM_{2.5}$ at the site explained 64% of the temporal variance in $PM_{2.5}$. Only spring and summer $PM_{2.5}$ was available for the regression analysis. Organic tracers do not resolve inorganic sources such as secondary sulfate, nitrate and sea salt. Therefore, this analysis does not attempt a full
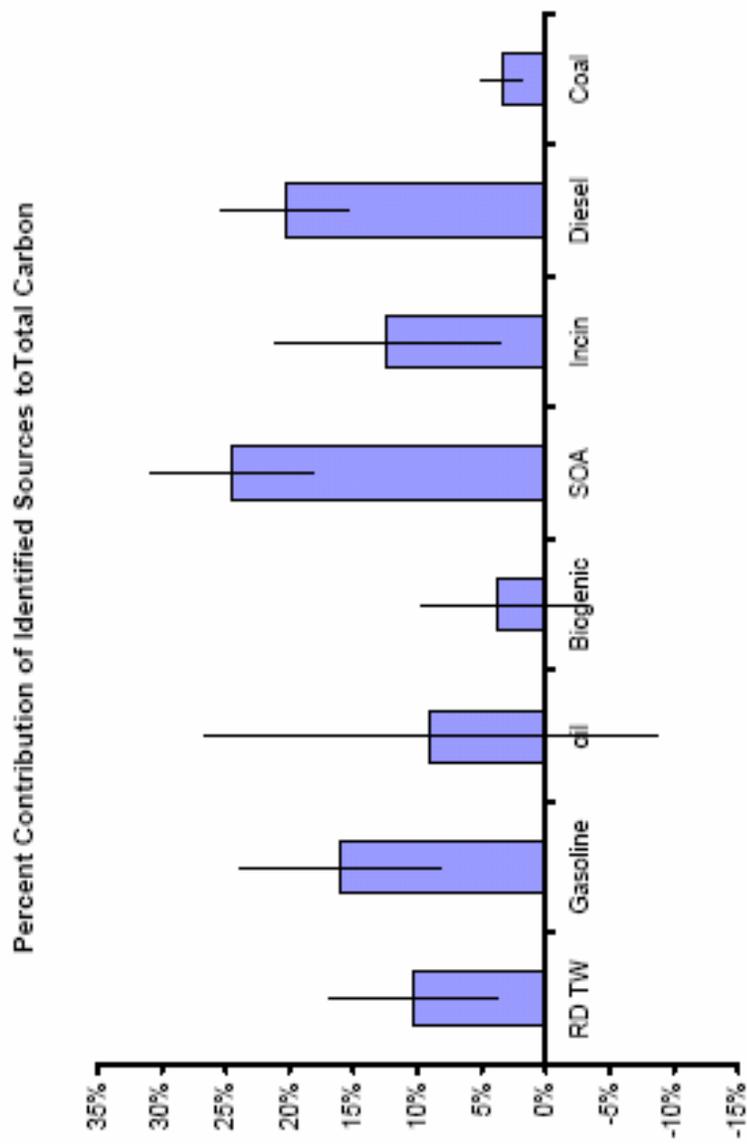
Figure 5.20 The estimated source contributions to total carbon measured in Baltimore during the spring and summer 2002. Error bars represent the standard error of the regression analysis (see text).
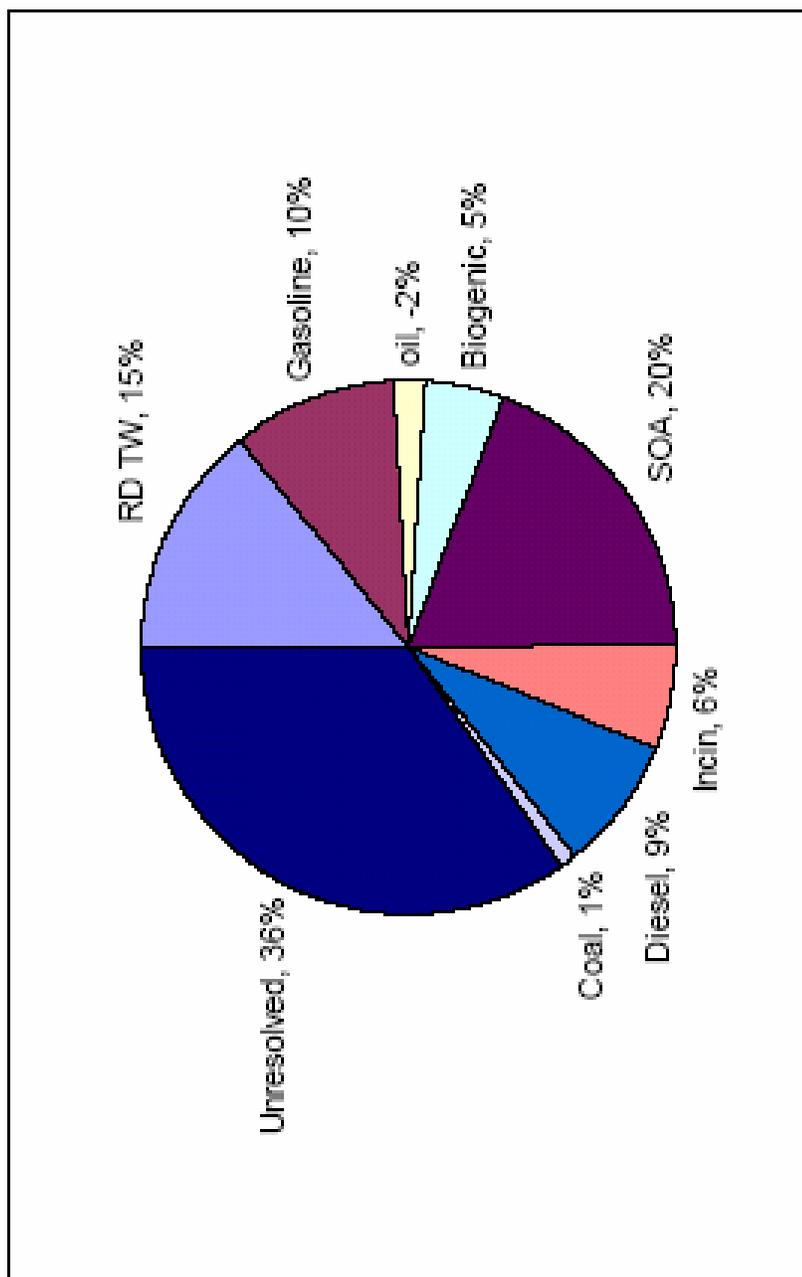
Figure 5.21 The estimated source contributions of PM2.5 to the Baltimore atmosphere during the spring and summer using PMF. See text for description.

PM$_{2.5}$ mass closure. Using the organics sources, anthropogenic secondary organic aerosol contributed the greatest PM$_{2.5}$ concentration (31%, Figure 5.21). This is similar to the percent contribution of secondary sulfate (23%) and nitrate (23%) observed by Ogulei *et al.* (2005) for the Baltimore Supersite using inorganic markers. The sum of the vehicle emissions (diesel + gasoline) from Ogulie *et al.* (27%) is similar to our results (30%). In our study diesel and gasoline account for similar contributions to the PM$_{2.5}$ mass (13 and 16 %, respectively) whereas the previous study found that gasoline emissions (26%) dominated the vehicular signature. The discrepancy between these two studies illustrates the difficulty in differentiating gasoline and diesel sources to the ambient atmosphere. The coal (2 and 3%) and incinerator (10 and 9%) contributions agree very well between this study and Ogulei *et al.* (2005), respectively. The oil source from this study was a significant source of PM$_{2.5}$ for the spring and summer. This is not unexpected as this source is predominantly found in the winter.

5.6 Conclusions

PMF and PCA were used to determine the sources of alkanes, PAHs, hopanes and NPAHs to the Baltimore, MD. PMF source profiles and contributions identified by individual compound classes were similar to those resolved when all of the species were included. PCA consistently resolved fewer sources than PMF with less certainty in the source identification. The loss of statistical power using PMF was evident as the number of species increased, as the wood source identified in the PAH only runs was not resolved when hopanes, alkanes, NPAHs and gases were added to the input matrix.

Combining these compound classes explained 64% total carbon and PM2.5 concentration. The identified total carbon and PM2.5 sources in Baltimore were road dust (10% and 23%), gasoline combustion (16% and 16%), oil (9% and 0%), biogenic (3.8% and 7.6%), secondary organic aerosol (24% and 31%), incinerator (12% and 10%), diesel (20% and 13%), and coal (3.5% and 1.7%). The results from this study provide the first total carbon and PM2.5 estimates to the Baltimore atmosphere using organic tracers in a multivariate receptor model. In addition, the ability of the EPA PMF 1.1 to generate this solution without the need for manual rotational manipulations suggests that this program is suitable for wider applications in the aerosol community.

Chapter 6

Summary of Results

6.1 Chapter 2

Two methods were developed to quantify polycyclic aromatic hydrocarbons (PAHs) and nitro-substituted polycyclic aromatic hydrocarbons (NPAH), respectively, using large-volume injection gas chromatography/mass spectrometry (GC/MS). Both methods (PAH and NPAH, respectively) employed a programmed temperature vaporization injector (PTV) in solvent vent mode, optimized using standard solutions. For the PAH method, the precision of the PTV was comparable to hot splitless injection, exhibiting a percent relative standard deviation (%RSD) consistently below 8% for 100 pg injections. Compound %RSDs for the NPAH method were consistently below 5% using the PTV. Microgram quantities (30 – 500μg) of particulate matter Standard Reference Materials (SRM 1649 and 1650, National Institutes of Standards and Technology) were analyzed to simulate PAH and NPAH quantification on small quantities of aerosol mass. The method detection limits from this study suggest PAHs and NPAHs can be easily quantified using low volume samplers (> 5 Lpm) on hourly timescales under in typical urban atmospheres. In addition, this technique enabled the quantification 12 hr NPAH size distributions in the Baltimore, MD atmosphere.

6.2 Chapter 3

Organic aerosol was collected in Baltimore, MD during the spring, summer and winter of 2002-2003. Concentrations of n-alkanes, hopanes, polycyclic aromatic hydrocarbons (PAH), and nitro-substituted polycyclic aromatic hydrocarbons (NPAH) were measured in the gas and particle phase to determine the composition and seasonal variability of organic aerosol. The organic compounds varied little with time, with seasonal concentrations typical of North American urban atmospheres. Elevated concentrations of 1-nitropyrene, a potential diesel exhaust marker, were observed in the winter intensive. The mean 2-nitrofluoranthene concentrations were consistent among seasons with greater variability in the spring and summer. Each of the compound classes were correlated with collocated gas (NO, NO_2, CO and ozone) and bulk particulate phase (EC, OC, nitrate and PM2.5 mass) measurements as well as non-halogenated volatile organic compounds (VOCs). The intercorrelation among species resolved several traffic related source profiles, including a tire wear-like alkane profile consisting of elevated hopanes and C_{34} and C_{35} alkanes. Other profiles were possibly from gasoline, diesel and biogenic sources. In addition, correlations between 1-nitropyrene and NO support diesel as the dominant source of this NPAH isomer to the Baltimore atmosphere. OH was found to be the dominant formation pathway of 2-nitrofluoranthene production during the spring and winter, while the NO_3 radical was responsible for > 90% of the 2-nitrofluoranthene production during select summer periods. Secondary NPAHs also covaried with primary VOCs, indicating secondary organic aerosol formed at this site is driven by oxidants with anthropogenic rather than biogenic precursors.

6.3 Chapter 4

Diurnal size distributions of polycyclic aromatic hydrocarbons (PAHs) and nitro-substituted polycylic aromatic hydrocarbons (NPAHs) provide insight into the dynamics of primary (PAHs and NPAHs) and secondary (NPAHs) toxics to the ambient atmosphere. Size resolved samples were collected using a Berner low-pressure impactor deployed at the Baltimore PM2.5 Supersite in April 2002. Both classes of compounds (PAHs and NPAHs) were found predominantly on particles less than 0.49μm with similar size distributions among samples for most of the 12 hr periods. A linear relationship between compound geometric mass median aerodynamic diameter (GMMAD) and log sub-cooled vapor pressures ($p_l°$) was observed for PAHs and NPAHs, respectively, during each sampling period. For the majority of samples, PAHs and NPAH correlations were not significantly different. The slope and y-intercepts from the GMMAD/log vapor pressure correlations suggest the source of PAHs to the Baltimore atmosphere reside on particles with GMMADs equal to 0.18 μm. This particle size is consistent with vehicle emission source studies and the location of the sampling site.

6.4 Chapter 5

Principal Component Analysis/Multiple Linear Regression (PCA/MLR) and Positive Matrix Factorization (PMF) were employed to determine the sources and contribution of alkanes, hopane, PAHs and NPAHs to the Baltimore atmosphere during the spring, summer and winter 2002-2003. Using these two methods, parallel analysis of these compound classes illustrate the greater resolving ability of PMF compared to PCA. Although similar sources were determined using both techniques, PMF usually

resolved a greater number of identifiable sources. PAH sources to the Baltimore atmosphere included vehicle, oil combustion, coal combustion and wood combustion. Alkane + hopane sources included leaf waxes, plastic incineration, gasoline and diesel exhaust, coal combustion and road dust. PMF was able separate the vehicle factor into diesel and gasoline for alkane +hopane and PAH analysis compared to PCA/MLR. PCA/MLR and PMF resolved 4 and 3 sources, respectively, of NPAHs to the Baltimore atmosphere consisting of diesel, nitrate radical secondary, aged primary and a possible gasoline source. The individual compound classes were also analyzed together in PMF. The resulting profiles and temporal contributions agreed well with the sources identified using individual classes. The results from this analysis were regressed against total carbon (TC) and PM2.5 measured during the spring and summer. The 9 sources (% contribution) of TC resolved using PMF were anthropogenic secondary organics (24%), diesel (20%), gasoline (16%), road dust (10%), incinerator (12%) and coal (4%) explaining 64% of the variance. Similarly, the mean PM2.5 source contribution of these factors was 31% (anthropogenic secondary factor), 13% (diesel), 16% (gasoline), 2% (coal), 10% (incinerator).

6.5 Implications

The implications of this body of work are as follows;

1) The large volume injection method developed in Chapter 2 has proven successful with PAHs and NPAHs. This method could be easily extrapolated to other analytes identified as organic source markers. The power of multivariate models depends on profile variability from sample to sample. Greater temporal resolution in ambient aerosol sampling campaigns will

provide concentration data on timescales similar to the sources and processes (chemical, meteorological) affecting the organic composition.

2) The covariance of secondary NPAHs with primary emissions in the Baltimore suggests the oxidation potential of the Baltimore atmosphere may be driven by anthropogenic (as opposed to biogenic) sources. Therefore, human exposure to mutagenic organic species such as NPAHs is driven by primary (possibly gasoline exhaust) emission precursors.

3) This study was the first to measure the diurnal size distribution NPAHs in the ambient atmosphere. For the spring of 2002, the size distributions of PAHs and NPAHs were similar. Since the penetrating efficiency of particulate matter is governed by size, the exposure to NPAHs in the ambient atmosphere will be similar to their parent mutagens PAHs.

4) The vapor pressure/size dependence of PAHs in the Baltimore atmosphere may indicate the source particle size of the dominant PAH emissions. Using this information in conjunction with organic source markers may provide a better understanding of the sources and behavior of PAHs in the ambient atmosphere.

5) This study was the first study to determine the sources of total carbon and PM2.5 to the Baltimore, MD region using organic markers. From this analysis the largest contribution to the carbon and PM2.5 appear to be secondary products. These results suggest greater attention must be to secondary organic precursors to control the carbonaceous aerosol.

Appendix A

Gas and Particle Concentrations of Alkanes, PAHs, NPAHs and Hopanes

Sample ID	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 8	MT 9	MT 10	MT 11	MT 12	MT 13	MT 16
Start Date	032302	032402	032802	032902	033002	033102	040202	040302	040402	040802	040902	041002	041402
Start Time	1906	1914	1920	2016	1809	1936	1927	1924	1930	1720	1835	1905	1555
Stop Date	032402	032502	032902	033002	033102	040102	040302	040402	040502	040902	041002	041102	041502
Stop Time	1800	1740	1901	1706	1802	1750	1758	1813	325	1808	1823	1826	1802
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
C10	<BG	0.30	0.07	<BG	0.30	<BG	<BG	<BG	<BG	0.07	0.08	<BG	<BG
C11	0.25	0.48	0.34	0.38	0.10	0.06	0.10	0.09	0.11	0.11	0.10	<BG	0.10
C12	0.11	0.10	0.05	0.04	0.04	0.04	<BG	0.05	0.09	0.03	0.02	<BG	0.02
C13	1.65	1.31	0.47	0.06	0.04	0.17	0.09	0.29	0.61	0.04	0.44	0.02	0.04
C14	0.15	0.24	0.19	0.18	0.14	0.12	0.20	0.13	0.15	0.17	0.16	0.03	0.12
C15	0.19	0.17	0.09	0.16	0.04	0.14	0.17	0.16	0.20	0.07	0.09	0.03	0.04
C16	0.53	0.62	0.35	16.15	0.14	0.21	0.21	0.29	0.47	0.16	0.20	0.06	0.52
C17	0.46	0.27	0.20	0.17	0.11	0.20	0.24	0.36	0.42	0.16	0.22	0.05	0.15
C18	0.17	0.26	0.24	0.18	0.06	0.12	0.15	0.18	0.49	0.21	0.06	0.08	0.03
C19	0.64	0.48	0.39	0.18	0.18	0.29	0.41	0.64	0.75	0.31	0.27	0.28	0.17
C20	0.74	0.84	0.47	0.31	0.37	0.45	0.70	0.77	1.51	0.55	0.44	0.45	0.25
C21	1.44	1.09	0.98	0.51	0.53	0.67	1.08	0.97	1.65	0.96	0.61	0.67	0.36
C22	2.80	2.07	1.98	0.65	0.86	0.89	1.20	1.79	3.82	1.13	0.80	0.93	0.37
C23	3.38	3.27	5.10	1.07	1.45	1.10	2.12	1.69	2.67	2.30	1.40	2.42	1.00
C24	3.17	3.21	6.96	1.53	1.91	1.32	4.54	2.42	5.51	3.73	1.71	3.04	1.50
C25	5.00	4.78	9.68	2.61	2.80	2.51	9.07	3.47	3.99	7.79	3.53	4.98	4.45
C26	2.69	2.68	9.17	2.60	1.52	1.36	6.31	2.50	4.57	5.25	1.73	2.72	2.53
C27	1.91	2.76	7.84	3.42	1.64	1.72	7.58	3.16	2.72	6.99	2.79	3.50	5.52
C28	3.01	2.40	5.16	1.95	1.57	1.87	4.22	3.27	4.64	4.46	1.48	2.37	1.46
C29	3.13	3.96	4.83	4.35	2.00	2.75	7.39	4.63	3.67	8.68	2.45	4.43	3.44
C30	1.77	1.96	3.61	1.67	1.27	1.14	2.84	3.90	3.87	2.96	1.67	3.01	1.47
C31	2.64	3.42	2.80	2.12	2.18	1.98	3.79	4.04	2.99	4.56	2.42	4.36	2.77
C32	1.26	1.42	1.80	1.20	1.09	0.95	1.93	2.91	2.48	1.87	1.47	2.06	1.54
C33	2.06	2.06	2.37	1.39	1.25	1.33	2.53	2.90	2.02	2.78	2.00	2.95	1.55
C34	4.49	3.13	5.74	3.33	1.91	2.28	4.41	3.02	3.19	2.93	3.65	4.35	1.50
C35	4.02	3.47	5.41	3.20	2.15	2.24	5.00	2.88	3.71	5.16	3.69	4.60	1.81
C36	0.51	0.87	0.68	0.82	0.70	0.91	1.60	1.41	1.65	1.53	0.92	1.99	0.61

Sample ID	MT 17	MT 18	MT 19	MT 20	MT 21	MT 22	MT 23	MT 25	MT 26	MT 27	MT 28	MT 29	MT 30	MT 32
Start Date	041502	041602	041602	041702	041702	042202	042302	042402	042402	042502	042502	042602	042702	042902
Start Time	1834	0846	1957	0855	1856	1833	0834	0913	1926	0855	1840	1905	1710	1734
Stop Date	041602	041602	041702	041702	041802	042302	042302	042402	042502	042502	042602	042702	042802	043002
Stop Time	742	1854	735	1759	1745	808	1839	1933	800	1814	1843	1700	1645	1704
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
C10	<BG	<BG	<BG	<BG	<BG	<BG	0.19	0.20	ND	<BG	0.11	0.28	<BG	0.13
C11	0.29	0.57	0.38	0.51	0.19	0.11	<BG	0.23	0.16	0.11	0.10	0.19	0.15	0.14
C12	0.10	0.07	0.16	0.10	0.32	0.04	<BG	<BG	0.08	0.07	0.05	0.09	0.05	<BG
C13	0.87	0.29	1.40	0.40	0.05	0.52	0.17	0.09	ND	0.10	0.49	1.27	0.05	0.29
C14	0.18	0.52	0.22	0.65	0.19	0.09	0.29	0.25	ND	0.23	0.20	0.37	0.10	0.18
C15	0.07	0.20	0.11	0.37	0.07	0.11	0.22	0.57	0.04	0.09	0.19	0.11	0.03	0.17
C16	0.35	2.12	0.50	7.09	0.29	0.14	0.38	0.77	17.47	0.11	0.60	1.05	0.12	0.27
C17	0.58	0.56	0.63	0.80	0.15	0.27	0.33	0.56	0.10	0.14	0.38	0.22	0.10	0.36
C18	0.45	0.38	0.39	0.67	0.17	0.19	0.31	0.38	0.05	0.14	0.13	0.24	0.15	0.15
C19	0.98	0.50	0.80	0.83	0.28	0.47	0.42	0.47	0.15	0.21	0.47	0.33	0.19	0.36
C20	1.95	0.56	1.36	0.81	0.51	0.87	0.60	0.72	0.29	0.35	0.43	0.26	0.31	0.43
C21	3.20	1.08	2.85	1.41	0.79	1.32	0.99	1.15	0.48	0.49	0.79	0.50	0.36	0.58
C22	3.74	0.77	2.69	1.41	0.83	1.40	1.40	1.74	0.64	0.55	1.18	0.77	0.37	0.78
C23	6.54	3.47	6.48	4.56	2.01	1.69	1.82	2.31	1.26	1.36	3.05	2.56	1.16	1.67
C24	5.93	3.48	4.22	5.14	2.71	1.39	1.90	2.43	1.06	1.58	3.24	2.24	1.50	1.52
C25	9.93	7.11	9.74	9.92	5.17	3.33	3.40	3.78	2.25	3.27	6.41	5.13	3.46	3.32
C26	9.18	3.15	4.16	5.54	2.70	2.19	2.08	2.10	1.78	1.32	3.25	2.32	1.60	1.45
C27	7.07	10.73	15.81	10.98	7.88	3.82	3.11	3.08	2.97	2.49	6.15	5.05	2.09	3.12
C28	4.26	3.42	3.43	3.87	2.52	1.87	2.61	1.44	0.88	1.16	3.25	2.35	1.06	1.33
C29	5.91	10.13	6.34	7.91	6.31	7.12	5.55	3.61	5.06	4.06	10.98	7.71	3.44	5.18
C30	3.68	3.13	3.64	4.39	2.93	1.80	2.20	1.70	1.16	1.46	2.96	2.00	1.37	1.55
C31	5.30	6.34	6.52	7.37	5.74	5.50	4.10	2.92	4.47	3.48	9.55	7.03	3.53	4.56
C32	1.96	2.55	2.39	3.28	2.33	1.35	1.88	1.13	0.80	1.56	2.17	1.80	0.65	1.56
C33	3.09	3.23	3.50	4.48	3.32	2.68	2.71	1.86	2.84	2.30	4.77	4.15	2.57	3.26
C34	6.43	5.29	7.02	9.72	6.15	1.67	3.62	3.38	1.09	5.68	4.31	3.87	4.60	2.64
C35	6.13	3.97	5.94	8.94	5.91	1.73	3.98	3.21	1.70	6.81	3.23	4.20	5.35	2.81
C36	1.98	1.56	2.63	3.56	2.42	1.16	1.45	1.04	0.51	0.25	0.94	1.24	0.87	0.96

Sample ID	MT 33	MT 34	MT 35	MT 36	MT 37	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43	MT 45	MT 46
Start Date	070902	071002	071102	071202	071302	071402	071502	071602	071702	071802	071902	072102	072202
Start Time	1705	1845	1915	1835	1923	1921	1903	1850	1905	1853	1935	1819	1832
Stop Date	071002	071102	071202	071302	071402	071502	071602	071702	071802	071902	072002	072202	072302
Stop Time	1745	1805	1720	1820	1811	1757	1754	1801	1804	1850	1828	1740	727
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
C10	0.17	0.12	<BG	0.16	0.09	<BG	0.19	<BG	0.22	<BG	ND	0.16	0.40
C11	0.04	0.06	0.09	0.09	0.06	0.04	0.12	0.07	0.08	0.04	0.06	0.04	<BG
C12	0.89	0.38	0.20	0.85	0.20	0.11	1.36	0.18	0.29	0.15	0.72	0.40	1.64
C13	0.13	0.06	0.07	0.09	0.07	0.05	0.13	0.04	0.16	0.10	0.10	0.14	0.15
C14	0.15	0.30	0.44	0.25	0.21	0.10	0.36	0.25	0.13	0.24	0.26	0.29	0.44
C15	0.02	0.05	0.03	0.26	<BG	0.05	0.05	0.09	0.09	0.06	0.09	0.07	0.08
C16	0.20	0.14	0.16	0.15	0.10	0.07	0.25	0.21	0.21	0.27	0.20	0.25	0.37
C17	0.11	0.17	0.17	0.12	0.06	0.08	0.14	0.25	0.08	0.08	0.16	0.09	0.21
C18	0.27	0.17	0.11	0.10	0.02	0.04	0.04	0.17	0.38	0.06	0.04	0.39	0.56
C19	0.16	0.18	0.21	0.13	0.06	0.11	0.14	0.20	0.10	0.10	0.09	0.14	0.25
C20	0.26	0.15	0.30	0.18	0.09	0.20	0.20	0.26	0.17	0.19	0.14	0.24	0.42
C21	0.31	0.27	0.34	0.20	0.09	0.18	0.25	0.34	0.16	0.19	0.13	0.25	0.43
C22	0.41	0.37	0.41	0.25	0.10	0.23	0.37	0.42	0.21	0.23	0.18	0.32	0.59
C23	0.79	1.01	0.91	0.53	0.22	0.44	0.85	0.83	0.48	0.52	0.47	0.66	1.39
C24	1.45	1.17	1.77	1.04	0.59	1.03	1.43	1.61	1.12	1.21	0.82	1.00	1.82
C25	2.96	5.20	4.35	2.66	0.89	1.54	3.53	3.68	1.68	1.32	1.75	2.65	4.59
C26	1.50	1.48	2.64	1.77	0.56	1.08	1.71	1.91	0.97	0.94	1.04	1.67	2.36
C27	3.97	10.83	8.06	5.19	1.85	1.94	5.66	6.79	2.90	2.16	4.10	4.78	7.48
C28	2.24	1.95	2.92	1.60	0.70	1.62	1.90	2.14	1.27	0.93	1.04	2.17	3.35
C29	8.58	16.55	8.78	5.98	2.29	2.87	8.96	9.69	5.23	4.19	0.72	6.59	11.82
C30	2.16	1.61	2.26	1.14	0.65	1.96	1.92	2.18	1.29	1.39	1.11	1.65	2.25
C31	7.01	10.58	6.87	4.00	1.71	3.20	6.86	7.38	3.98	3.37	1.31	4.64	6.83
C32	1.96	1.43	2.41	0.71	0.48	1.73	1.56	1.96	0.99	1.21	1.03	1.32	1.37
C33	3.38	3.71	3.16	1.70	0.93	2.62	3.37	3.22	2.20	2.02	0.23	2.18	3.06
C34	4.79	1.95	2.22	1.79	2.51	4.18	2.79	2.27	1.56	3.13	1.06	2.30	5.92
C35	4.64	2.20	3.08	2.10	2.31	3.85	3.49	3.03	2.15	3.18	0.10	2.60	5.69
C36	1.58	1.16	1.46	0.53	0.51	1.56	1.35	1.09	1.11	1.17	0.62	0.86	0.95

Sample ID	MT 47	MT 49	MT 51	MT 52	MT 53	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63
Start Date	072302	072902	072902	073002	073002	073002	080102	080502	080602	080602	080602	080702	080702	080802	080802
Start Time	734	620	1854	650	1250	1824	1759	1900	100	700	1900	745	1900	800	1900
Stop Date	072402	072902	073002	073002	073002	073102	080202	080602	080602	080602	080702	080702	080802	080802	080902
Stop Time	800	1124	605	1245	1814	750	807	100	700	1900	746	1900	754	1900	803
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
C10	0.12	<BG	0.35	0.31	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C11	0.07	<BG	0.12	0.19	0.28	0.07	0.12	<BG	<BG	0.18	<BG	0.14	0.13	0.08	0.12
C12	0.67	0.16	0.43	0.32	<BG	0.22	1.20	<BG	<BG	0.28	<BG	0.26	0.32	0.18	0.14
C13	0.11	<BG	0.15	<BG	<BG	0.39	0.39	0.06	0.10	0.11	0.04	0.11	0.91	0.03	0.59
C14	0.06	0.26	0.36	0.33	0.20	0.44	0.36	<BG	0.07	0.19	0.07	0.13	0.34	0.17	0.12
C15	0.05	0.14	0.13	0.13	0.11	0.10	0.08	<BG	<BG	0.18	0.06	0.12	0.04	0.08	0.08
C16	0.11	0.33	0.15	0.24	0.14	0.19	0.26	0.16	0.10	0.32	1.09	0.23	0.19	0.12	0.20
C17	0.15	0.25	0.14	0.21	0.17	0.22	0.29	0.13	0.13	0.34	0.14	0.24	0.38	0.16	0.19
C18	0.41	0.37	0.18	0.05	0.06	0.14	0.22	0.19	0.09	0.30	0.18	0.22	0.18	0.13	0.04
C19	0.13	0.20	0.19	0.18	0.17	0.16	0.22	0.16	0.16	0.45	0.20	0.35	0.27	0.24	0.39
C20	0.27	0.32	0.38	0.24	0.17	0.46	0.41	0.23	0.27	0.71	0.33	0.97	0.98	0.52	0.48
C21	0.28	0.35	0.39	0.26	0.39	0.31	0.37	0.32	0.38	0.78	0.48	0.48	0.64	0.37	0.63
C22	0.44	0.36	0.42	0.34	0.37	1.04	1.43	0.49	0.72	1.60	0.91	1.63	4.00	1.20	1.27
C23	0.96	0.65	0.94	0.70	0.87	1.12	1.70	0.81	1.03	2.54	1.40	1.42	1.45	0.90	2.02
C24	1.66	1.58	1.31	1.36	1.38	2.80	5.96	1.39	2.01	3.55	1.83	2.86	8.58	2.27	8.57
C25	3.30	2.36	2.17	3.22	3.39	2.76	3.57	2.38	3.49	10.21	4.77	4.87	4.03	2.30	4.54
C26	2.09	1.24	1.07	1.45	2.63	3.57	5.38	1.95	2.21	3.97	1.93	2.86	8.98	2.34	18.24
C27	5.71	3.32	3.32	6.63	5.41	4.64	3.69	3.54	5.01	20.78	10.10	8.70	6.77	3.17	4.84
C28	1.91	1.29	0.84	2.13	2.09	2.74	4.45	1.40	2.53	4.40	2.22	2.17	5.90	2.48	15.35
C29	10.37	7.57	5.71	15.78	12.00	6.77	5.36	5.32	9.46	33.63	17.90	11.16	7.43	5.03	6.40
C30	1.68	1.77	0.90	2.21	1.81	2.12	3.36	1.73	2.65	3.20	1.83	2.63	3.86	2.17	11.57
C31	6.69	5.03	4.18	9.84	7.52	5.29	4.45	4.16	6.91	18.59	10.12	7.62	5.40	4.14	6.05
C32	1.34	1.42	0.62	1.83	1.38	1.65	2.01	1.53	1.94	2.48	1.23	1.89	2.48	1.58	7.67
C33	3.01	2.86	1.88	4.05	3.08	2.22	2.38	2.33	3.22	5.84	3.25	3.03	2.59	2.01	3.32
C34	3.92	4.31	2.26	3.73	3.55	2.67	5.05	3.06	6.42	5.39	3.27	3.36	4.09	3.73	8.69
C35	4.09	4.09	0.86	3.47	4.11	2.36	3.48	3.52	7.71	4.70	3.07	3.03	3.16	3.75	4.47
C36	1.30	1.38	0.66	1.70	1.17	0.88	1.44	1.16	1.82	1.73	0.93	1.42	1.70	1.21	4.57

Sample ID	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
Start Date	012703	012803	012803	012803	012903	012903	012903	013003	013003	013003	020503	020503	020603	020603	020703
Start Time	1830	1230	820	1800	30	745	1837	30	810	1830	700	1825	735	1745	110
Stop Date	012803	012803	012803	012903	012903	012903	013003	013003	013003	013103	020503	020603	020603	020703	020703
Stop Time	802	800	1734	30	630	1831	30	630	1830	1830	1820	735	1740	110	710
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
C10	0.27	0.65	<BG	<BG	<BG	<BG	<BG	<BG	0.20	<BG	<BG	0.28	0.21	<BG	<BG
C11	0.22	0.47	0.13	0.24	0.41	0.23	0.67	0.37	0.16	0.13	0.09	0.97	0.16	<BG	<BG
C12	0.52	0.13	0.09	0.16	0.20	0.67	0.28	0.41	0.16	0.07	0.25	0.13	0.47	0.34	<BG
C13	0.28	0.49	0.16	0.25	0.92	<BG	0.15	0.06	0.04	0.04	0.03	0.17	0.08	0.14	0.04
C14	0.36	0.78	0.13	0.16	0.11	0.11	0.38	0.24	0.18	0.18	0.10	0.20	0.10	0.08	0.09
C15	1.55	2.81	0.47	0.72	0.36	1.71	2.04	0.93	0.27	1.32	0.51	2.68	0.44	0.11	0.09
C16	3.48	7.09	0.74	1.05	1.21	0.64	2.57	1.58	0.40	0.36	0.91	2.24	0.47	0.16	0.17
C17	6.19	11.49	1.27	2.14	1.89	0.92	2.87	2.47	0.48	0.38	1.63	5.01	0.60	0.30	0.36
C18	11.43	18.32	3.50	4.00	3.91	2.36	3.90	5.65	1.10	0.67	3.08	9.38	1.38	0.63	0.93
C19	13.17	16.21	9.97	7.85	7.12	3.22	6.79	10.99	3.15	1.93	5.05	14.33	3.76	0.94	2.65
C20	13.72	16.63	14.04	7.39	10.79	9.42	23.81	15.75	7.08	4.01	7.73	26.46	7.08	1.65	6.23
C21	9.21	10.39	10.52	5.07	10.70	7.72	10.87	15.17	8.72	4.47	5.78	16.87	6.58	2.81	7.67
C22	9.17	11.11	7.72	4.28	9.47	10.83	34.74	12.99	8.97	5.59	4.72	19.69	5.78	4.02	6.88
C23	6.35	8.42	5.48	3.87	7.42	5.94	10.34	9.80	6.98	4.82	3.55	9.75	4.07	4.83	5.34
C24	6.11	9.28	4.40	3.14	5.39	6.32	25.10	7.09	5.69	3.99	3.07	11.05	3.40	4.45	3.73
C25	6.90	10.81	5.44	4.06	5.92	4.19	9.65	9.04	7.24	3.86	3.96	8.78	4.37	5.27	4.52
C26	4.07	8.16	2.94	2.20	2.68	3.33	17.17	4.58	6.37	2.89	2.45	6.93	2.30	3.06	4.03
C27	3.50	5.86	2.31	2.25	2.76	2.24	5.37	4.01	3.32	2.35	3.00	5.21	2.39	2.76	1.74
C28	3.51	5.51	2.90	2.08	1.88	3.94	11.02	4.35	3.65	1.80	2.79	6.74	2.62	2.55	2.39
C29	4.11	5.44	3.50	3.36	4.79	3.98	6.77	3.90	4.61	3.31	6.28	7.38	3.94	3.63	3.06
C30	2.23	3.38	2.74	1.87	1.90	2.28	7.52	2.44	2.86	1.86	2.90	4.70	2.02	1.91	1.88
C31	2.79	3.37	2.53	2.62	4.15	2.63	4.91	2.86	3.64	2.59	4.56	5.47	2.82	2.29	1.70
C32	1.87	2.17	1.86	1.14	1.37	1.47	4.06	1.54	2.34	1.49	2.26	3.64	1.57	1.08	0.79
C33	2.03	2.43	1.74	1.73	2.01	1.99	3.00	1.98	2.51	1.64	2.79	3.40	1.80	1.69	1.42
C34	3.55	4.96	2.75	4.59	3.34	3.45	7.49	5.50	9.13	2.52	4.19	5.71	2.87	5.43	5.33
C35	3.07	3.94	2.26	5.83	3.43	3.78	6.36	4.95	11.08	2.94	3.98	5.10	2.66	6.67	6.08
C36	1.43	1.33	1.10	1.06	0.60	0.97	2.90	1.23	1.60	0.83	1.73	1.72	1.23	0.75	ND

Sample ID	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 8	MT 9	MT 10	MT 11	MT 12	MT 13	MT 16	MT 17
Start Date	032302	032402	032802	032902	033002	033102	040202	040302	040402	040802	040902	041002	041402	041502
Start Time	1906	1914	1920	2016	1809	1936	1927	1924	1930	1720	1835	1905	1555	1834
Stop Date	032402	032502	032902	033002	033102	040102	040302	040402	040502	040902	041002	041102	041502	041602
Stop Time	1800	1740	1901	1706	1802	1750	1758	1813	325	1808	1823	1826	1802	742
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
C10	0.55	0.08	0.53	ND	0.03	ND	0.10	0.25	0.22	ND	ND	0.05	ND	0.33
C11	39.95	10.66	27.33	4.71	0.64	0.47	2.02	12.88	25.10	0.95	<BG	0.22	<BG	2.81
C12	20.52	7.43	13.97	5.12	<BG	<BG	0.79	0.63	14.78	0.68	<BG	<BG	<BG	1.81
C13	1.00	<BG	1.51	<BG	<BG	<BG	1.39	<BG	<BG	1.41	<BG	<BG	<BG	<BG
C14	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C15	0.75	0.66	0.85	0.62	0.36	0.90	0.94	1.27	0.55	1.37	0.47	0.30	0.44	4.01
C16	1.40	1.21	1.74	1.10	0.74	1.79	1.87	2.69	1.31	2.57	1.01	0.61	0.82	10.52
C17	3.56	2.86	2.17	2.23	<BG	4.10	3.86	5.01	2.90	4.74	2.03	<BG	<BG	7.39
C18	13.30	6.70	7.56	3.56	2.10	7.24	5.07	8.60	5.42	7.49	2.94	1.54	3.25	14.94
C19	26.94	20.04	17.12	8.06	3.58	11.77	7.49	10.48	5.38	12.44	6.22	4.59	6.98	19.11
C20	22.09	21.93	19.81	15.76	5.18	11.62	14.03	9.67	6.22	21.67	10.08	8.31	21.12	22.97
C21	14.37	16.32	14.87	14.47	<BG	9.40	15.87	6.11	<BG	22.92	11.37	7.91	27.32	27.45
C22	5.50	8.02	11.31	9.75	2.33	5.23	13.06	3.52	2.03	16.31	7.41	4.82	18.08	14.95
C23	1.67	3.05	7.62	4.63	1.46	2.49	13.45	1.54	0.44	14.36	4.90	2.72	16.39	19.13
C24	0.45	0.85	3.64	2.08	0.73	1.01	9.95	0.54	0.31	10.17	2.17	1.22	7.46	8.64
C25	<BG	0.41	1.55	1.34	0.36	0.68	5.40	<BG	0.27	6.43	1.78	1.13	6.40	8.43
C26	<BG	<BG	0.43	<BG	<BG	<BG	1.98	<BG	<BG	1.97	0.50	0.97	2.00	3.62
C27	<BG	<BG	<BG	<BG	0.29	<BG	1.18	<BG	0.29	0.83	<BG	1.25	1.07	2.27
C28	<BG	<BG	<BG	<BG	<BG	<BG	0.88	<BG	<BG	<BG	<BG	1.27	0.33	2.12
C29	<BG	<BG	<BG	<BG	<BG	<BG	0.87	<BG	<BG	0.41	<BG	1.35	<BG	1.54
C30	<BG	<BG	0.08	<BG	0.17	0.28	0.69	<BG	0.19	0.26	<BG	1.24	0.22	1.02
C31	<BG	<BG	0.10	0.14	0.20	0.32	1.05	<BG	0.17	0.48	<BG	1.37	0.21	0.93
C32	0.05	<BG	<BG	<BG	0.10	0.10	0.48	<BG	0.09	0.14	ND	0.73	0.05	0.47
C33	<BG	<BG	<BG	0.03	0.05	0.11	0.36	<BG	0.06	0.18	ND	0.39	ND	0.32
C34	0.03	0.01	0.05	0.03	0.03	0.02	0.19	0.02	0.01	0.30	ND	0.16	ND	0.08
C35	<BG	<BG	<BG	<BG	<BG	<BG	0.07	<BG	<BG	<BG	ND	0.08	ND	ND
C36	0.10	0.07	0.03	<BG	<BG	0.06	0.47	ND	0.03	0.03	ND	0.03	ND	ND

Sample ID	MT 18	MT 19	MT 20	MT 21	MT 22	MT 23	MT 24	MT 25	MT 26	MT 27	MT 28	MT 29	MT 30	MT 31	MT 32
Start Date	041602	041602	041702	041702	042202	042302	042302	042402	042402	042502	042502	042602	042702	042802	042902
Start Time	0846	1957	0855	1856	1833	0834	1942	0913	1926	0855	1840	1905	1710	1655	1734
Stop Date	041602	041702	041702	041802	042302	042302	042402	042402	042502	042502	042602	042702	042802	042902	043002
Stop Time	1854	735	1759	1745	808	1839	807	1933	800	1814	1843	1700	1645	1720	1704
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
C10	ND	0.26	0.11	0.04	0.09	ND	0.42	ND	1.47	1.88	0.22	ND	0.22	0.21	0.63
C11	ND	2.93	<BG	25.00	1.45	ND	2.29	ND	ND	ND	0.25	ND	0.25	0.24	ND
C12	<BG	2.31	<BG	35.81	1.55	<BG	2.11	<BG	1.71	ND	<BG	ND	<BG	<BG	ND
C13	<BG	2.47	<BG	2.31	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C14	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C15	1.03	5.47	<BG	1.66	2.46	1.40	7.35	1.73	2.46	1.51	0.52	0.59	0.53	0.51	1.34
C16	1.84	9.72	0.85	2.84	6.44	3.31	17.88	3.84	5.41	3.16	0.63	0.72	0.64	0.62	2.91
C17	3.41	10.48	<BG	2.59	8.84	6.96	25.18	11.60	7.37	7.36	<BG	<BG	<BG	<BG	6.51
C18	6.12	24.01	1.87	5.29	7.46	14.10	19.56	21.18	9.37	18.09	0.32	0.36	0.32	0.31	17.24
C19	9.80	32.25	3.29	6.67	6.10	17.61	13.95	20.11	8.95	21.24	0.36	0.41	0.36	0.35	21.86
C20	19.90	35.58	5.24	9.82	4.08	13.75	7.47	12.89	7.36	17.65	0.41	0.47	0.42	0.40	18.27
C21	42.08	41.73	<BG	22.23	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	12.15
C22	30.99	21.50	8.08	18.35	1.32	3.67	1.50	2.65	2.94	7.22	0.60	0.69	0.61	0.59	5.90
C23	39.79	32.76	9.33	30.07	1.27	1.59	0.68	1.17	2.11	4.53	0.73	0.84	0.74	0.72	3.67
C24	18.85	12.04	3.90	9.37	0.42	0.51	0.22	0.40	0.85	2.39	0.91	1.04	0.93	0.89	1.47
C25	18.79	10.76	3.43	12.97	0.41	<BG	<BG	<BG	0.78	1.42	1.14	1.30	1.16	1.12	0.71
C26	7.13	3.46	2.08	3.02	<BG	<BG	<BG	<BG	<BG	<BG	1.48	1.70	1.50	1.45	<BG
C27	4.16	1.63	2.45	2.18	<BG	<BG	<BG	<BG	<BG	<BG	1.87	2.14	1.90	2.66	<BG
C28	0.93	<BG	2.36	<BG	<BG	<BG	<BG	<BG	<BG	<BG	2.49	2.85	2.52	ND	<BG
C29	<BG	<BG	2.47	<BG	<BG	<BG	<BG	<BG	<BG	<BG	2.59	2.96	2.63	2.53	<BG
C30	ND	0.30	2.02	0.07	<BG	<BG	<BG	<BG	0.64	0.71	0.99	1.13	1.00	0.97	0.32
C31	0.27	0.64	1.70	<BG	<BG	ND	<BG	0.23	0.88	1.54	1.28	1.47	1.30	1.84	0.68
C32	0.10	0.12	1.06	ND	ND	ND	0.07	ND	0.44	0.47	1.93	2.20	1.95	ND	0.23
C33	ND	0.23	0.71	ND	<BG	ND	ND	ND	0.46	ND	3.84	4.38	3.89	ND	ND
C34	ND	0.12	0.20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C35	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C36	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample ID	MT 33	MT 34	MT 35	MT 36	MT 37	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43	MT 45	MT 46	MT 47
Start Date	070902	071002	071102	071202	071302	071402	071502	071602	071702	071802	071902	072102	072202	072302
Start Time	1705	1845	1915	1835	1923	1921	1903	1850	1905	1853	1935	1819	1832	734
Stop Date	071002	071102	071202	071302	071402	071502	071602	071702	071802	071902	072002	072202	072302	072402
Stop Time	1745	1805	1720	1820	1811	1757	1754	1801	1804	1850	1828	1740	727	800
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
C10	ND	ND	0.07	0.00	ND	0.12	0.11	ND	ND	0.30	0.22	0.02	ND	0.04
C11	<BG	<BG	<BG	0.00	<BG	<BG	ND	<BG	ND	<BG	0.26	ND	<BG	<BG
C12	<BG	<BG	<BG	0.00	<BG	ND	<BG	<BG	<BG	ND	0.80	<BG	ND	ND
C13	<BG	<BG	<BG	0.00	<BG	<BG	<BG	<BG	ND	ND	<BG	ND	<BG	ND
C14	<BG	<BG	<BG	0.00	<BG	<BG	<BG	<BG	ND	ND	<BG	ND	ND	ND
C15	0.37	0.29	0.63	0.00	0.35	0.31	0.26	0.42	ND	0.54	0.30	0.47	1.84	0.40
C16	0.63	0.71	1.15	0.00	0.50	0.53	0.41	0.87	0.51	0.74	0.40	0.58	3.05	0.69
C17	<BG	1.56	2.26	0.00	<BG	<BG	<BG	1.75	<BG	<BG	<BG	<BG	5.66	1.39
C18	2.14	1.86	3.22	0.00	1.49	1.20	1.10	2.46	1.76	1.10	1.28	2.06	8.85	1.23
C19	4.07	4.27	8.44	0.00	2.50	2.78	2.72	6.61	2.51	1.93	2.21	2.86	12.89	2.23
C20	6.87	6.99	17.92	0.00	6.31	6.65	4.60	15.56	4.38	4.08	3.99	5.26	20.25	3.79
C21	11.84	8.06	18.25	0.00	9.29	10.67	9.01	26.36	9.93	8.75	<BG	11.43	20.49	8.38
C22	10.45	5.38	15.47	0.00	8.08	10.21	9.79	23.99	11.21	11.50	5.05	15.40	18.61	9.40
C23	12.51	5.71	10.70	0.00	8.74	9.16	14.48	22.72	19.17	17.01	7.21	18.46	26.32	10.01
C24	5.33	2.26	6.92	0.00	5.61	5.84	5.34	12.90	7.42	8.00	2.66	12.45	18.13	5.78
C25	5.02	2.35	3.41	0.00	5.77	5.63	5.68	13.26	9.84	9.07	2.91	14.74	20.09	5.65
C26	1.40	0.43	1.48	0.00	2.73	2.23	1.38	4.13	2.37	3.20	0.84	4.22	7.84	1.55
C27	1.22	0.51	0.53	0.00	2.07	1.51	1.07	2.98	2.40	3.08	0.75	3.35	4.42	1.15
C28	<BG	<BG	<BG	0.00	1.06	0.44	<BG	0.70	0.57	0.80	<BG	0.85	1.23	<BG
C29	<BG	<BG	<BG	0.00	0.67	<BG	<BG	0.47	0.40	0.86	<BG	0.70	0.68	0.48
C30	0.08	<BG	<BG	0.00	0.55	0.10	<BG	ND	0.08	0.29	0.07	0.10	0.14	<BG
C31	0.13	0.26	0.20	0.00	0.53	ND	ND	ND	0.14	0.28	ND	<BG	0.18	0.18
C32	ND	ND	ND	0.00	0.18	ND	ND	ND	ND	ND	ND	0.06	ND	<BG
C33	ND	ND	ND	0.00	0.14	ND	ND	ND	ND	ND	ND	ND	ND	ND
C34	ND	ND	ND	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C35	ND	ND	ND	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C36	ND	ND	ND	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample ID	MT 49	MT 50	MT 51	MT 52	MT 53	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63
Start Date	072902	072902	072902	073002	073002	073002	080102	080502	080602	080602	080602	080702	080702	080802	080802
Start Time	620	1206	1854	650	1250	1824	1759	1900	100	700	1900	745	1900	800	1900
Stop Date	072902	072902	073002	073002	073002	073102	080202	080602	080602	080602	080702	080702	080802	080802	080902
Stop Time	1124	1758	605	1245	1814	750	807	100	700	1900	746	1900	754	1900	803
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
C10	ND	0.50	0.27	ND	ND	0.08	ND	0.18	0.13	0.07	0.06	0.08	0.10	ND	ND
C11	<BG	<BG	<BG	ND	<BG	<BG	<BG	ND	ND	<BG	<BG	ND	ND	ND	ND
C12	<BG	<BG	<BG	<BG	<BG	<BG	ND	ND	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C13	<BG	<BG	<BG	<BG	<BG	<BG	ND	ND	<BG	<BG	<BG	<BG	<BG	<BG	ND
C14	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C15	0.81	0.70	1.88	<BG	0.77	0.94	0.84	1.03	1.34	0.64	0.89	0.60	1.33	0.36	0.73
C16	1.56	1.44	3.75	1.06	1.58	3.30	1.59	2.08	3.49	1.86	2.23	2.49	4.83	1.22	1.68
C17	<BG	<BG	5.70	<BG	<BG	4.30	3.13	<BG	5.76	3.69	3.99	<BG	6.30	<BG	3.65
C18	5.66	4.30	6.82	2.88	6.18	9.60	9.56	4.51	9.06	6.91	5.60	5.58	20.32	2.96	8.43
C19	9.11	7.37	8.76	5.16	9.29	9.28	10.03	7.67	7.32	13.18	6.49	6.20	10.48	3.78	10.57
C20	19.07	14.67	12.83	9.49	13.89	15.71	24.01	14.11	11.11	20.27	9.11	14.46	37.71	9.84	44.81
C21	<BG	<BG	14.20	<BG	<BG	11.52	17.20	<BG	<BG	13.88	<BG	13.84	<BG	<BG	15.06
C22	16.25	12.92	11.89	9.53	9.10	11.76	18.86	11.53	8.73	12.19	6.59	14.30	28.34	9.30	46.11
C23	19.65	13.10	18.19	10.64	9.31	13.33	14.57	11.59	7.51	5.91	3.32	6.45	5.40	4.58	8.68
C24	9.60	7.19	6.67	4.51	4.41	6.21	7.80	5.99	3.73	3.49	1.98	3.94	8.25	2.70	23.98
C25	8.76	7.78	7.52	4.69	4.15	5.34	6.10	5.72	2.67	1.67	0.86	1.35	0.98	1.13	2.82
C26	2.02	3.24	1.56	1.35	<BG	1.71	2.88	2.07	<BG	0.78	<BG	0.71	1.10	<BG	3.56
C27	<BG	2.74	1.59	1.25	<BG	1.39	1.02	1.26	<BG	0.79	<BG	<BG	<BG	<BG	1.02
C28	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	0.71
C29	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	0.91	<BG	<BG	<BG	<BG	<BG
C30	ND	<BG	<BG	<BG	<BG	<BG	ND	ND	<BG	<BG	<BG	ND	<BG	ND	0.29
C31	ND	<BG	<BG	ND	0.41	<BG	ND	ND	<BG	0.51	<BG	ND	ND	ND	0.20
C32	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C33	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C34	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C35	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C36	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample ID	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
Start Date	012703	012803	012803	012803	012903	012903	012903	013003	013003	013003	020503	020503	020603	020603	020703
Start Time	1830	1230	820	1800	30	745	1837	30	810	1830	700	1825	735	1745	110
Stop Date	012803	012803	012803	012903	012903	012903	013003	013003	013003	013103	020503	020603	020603	020703	020703
Stop Time	802	800	1734	30	630	1831	30	630	1830	1830	1820	735	1740	110	710
Conc	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3	ng/m^3
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
C10	0.11	0.35	0.25	0.11	0.33	0.22	0.21	0.15	ND	0.13	0.06	0.08	0.09	0.12	0.05
C11	0.60	1.55	0.88	<BG	0.86	0.51	<BG	<BG	ND	0.45	<BG	0.38	<BG	<BG	<BG
C12	1.78	4.41	2.37	<BG	1.57	1.24	<BG	<BG	<BG	0.74	<BG	0.98	<BG	<BG	<BG
C13	5.29	12.47	6.14	<BG	4.18	2.80	<BG	3.41	<BG	1.73	<BG	2.67	<BG	<BG	<BG
C14	10.37	23.45	12.99	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C15	18.57	35.58	28.14	16.27	29.98	16.78	20.49	35.99	15.20	9.95	6.52	19.25	10.11	6.31	12.84
C16	32.20	39.76	52.41	25.44	56.09	36.79	60.34	63.02	36.62	20.21	13.73	41.89	26.78	13.02	26.78
C17	27.32	22.37	56.22	23.76	57.81	55.45	37.68	64.84	56.56	30.59	18.82	41.63	35.25	19.22	31.86
C18	8.52	4.87	32.34	10.94	33.24	50.76	48.08	40.32	36.67	18.70	9.51	36.46	20.01	15.05	20.80
C19	1.50	0.83	11.75	3.32	20.00	32.92	16.58	22.10	23.58	13.09	4.97	13.81	11.61	10.71	13.60
C20	<BG	<BG	2.13	<BG	8.87	17.59	22.39	10.22	12.71	6.76	1.67	6.60	4.15	7.64	7.63
C21	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C22	0.32	0.74	1.84	2.62	3.53	1.93	1.91	3.82	1.54	1.20	0.56	0.99	2.28	3.41	1.42
C23	<BG	<BG	0.97	1.49	1.90	<BG	<BG	1.87	<BG	<BG	<BG	<BG	1.29	1.71	<BG
C24	0.19	0.34	0.43	0.82	0.90	0.24	0.40	0.83	0.28	0.20	0.29	0.33	0.68	0.97	0.40
C25	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	0.51	<BG	<BG
C26	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C27	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C28	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C29	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C30	<BG	<BG	ND	<BG	ND	<BG	<BG	ND	<BG	<BG	<BG	<BG	<BG	<BG	<BG
C31	<BG	<BG	ND	<BG	<BG	<BG	ND	ND	<BG	ND	<BG	<BG	<BG	ND	<BG
C32	<BG	0.10	ND	ND	ND	ND	ND	ND	<BG	ND	<BG	ND	ND	ND	<BG
C33	ND	0.11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C34	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C35	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
C36	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample ID	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 8	MT 9	MT 10	MT 11	MT 12	MT 13	MT 16	MT 17
Start Date	032302	032402	032802	032902	033002	033102	040202	040302	040402	040802	040902	041002	041402	041502
Start Time	1906	1914	1920	2016	1809	1936	1927	1924	1930	1720	1835	1905	1555	1834
Stop Date	032402	032502	032902	033002	033102	040102	040302	040402	040502	040902	041002	041102	041502	041602
Stop Time	1800	1740	1901	1706	1802	1750	1758	1813	325	1808	1823	1826	1802	742
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Tm	763	559	642	552	276	389	433	373	511	703	522	574	242	824
a,b - norhopane	2576	2063	2404	1909	1116	1462	1955	1326	1745	2831	1865	2368	1599	3483
a,a + b, a-norhopane	445	409	370	421	220	256	420	261	309	523	404	369	236	690
a-hopane	2503	1913	2422	2083	1085	1479	1991	1271	1682	2670	2092	1996	1331	3386
moretane	267	173	242	254	131	166	196	121	152	324	212	218	126	380
a,b-S-Homohopane	1314	1041	1316	970	604	777	1161	717	916	1532	1004	1219	843	1982
a,b-R-Homohopane	1037	857	988	787	479	587	892	564	726	1194	782	962	663	1589

Sample ID	MT 18	MT 19	MT 20	MT 21	MT 22	MT 23	MT 25	MT 26	MT 27	MT 28	MT 29	MT 30	MT 32
Start Date	041602	041602	041702	041702	042202	042302	042402	042402	042502	042502	042602	042702	042902
Start Time	0846	1957	0855	1856	1833	0834	0913	1926	0855	1840	1905	1710	1734
Stop Date	041602	041702	041702	041802	042302	042302	042402	042502	042502	042602	042702	042802	043002
Stop Time	1854	735	1759	1745	808	1839	1933	800	1814	1843	1700	1645	1704
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Tm	620	968	919	843	338	462	501	191	763	443	366	506	293
a,b - norhopane	2281	3691	3661	2951	1234	1629	1549	813	2564	1881	1525	1909	1141
a,a + b, a-norhopane	420	708	766	672	222	273	222	141	646	234	254	390	232
a-hopane	2763	3921	4252	3445	1239	1701	1546	719	3291	1674	1448	2144	1122
moretane	396	470	515	450	145	196	164	99	459	196	164	265	120
a,b-S-Homohopane	1533	2095	2425	1660	633	871	866	429	1299	983	854	1017	600
a,b-R-Homohopane	1259	1737	1902	1261	537	727	571	328	1008	751	690	800	486

	MT 33	MT 34	MT 35	MT 36	MT 37	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43	MT 45	MT 46
Start Date	070902	071002	071102	071202	071302	071402	071502	071602	071702	071802	071902	072102	072202
Start Time	1705	1845	1915	1835	1923	1921	1903	1850	1905	1853	1935	1819	1832
Stop Date	071002	071102	071202	071302	071402	071502	071602	071702	071802	071902	072002	072202	072302
Stop Time	1745	1805	1720	1820	1811	1757	1754	1801	1804	1850	1828	1740	727
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Tm	585	221	279	189	333	368	441	252	263	333	97	163	746
a,b - norhopane	2096	909	1176	670	1007	1263	1418	1091	885	1125	383	707	2581
a,a + b, a-norhopane	474	194	234	168	283	298	337	278	252	251		171	638
a-hopane	2525	980	1350	942	1377	1570	1786	1232	1032	1350	413	892	3268
moretane	330	129	118	138	208	199	217	167	144	193		92	459
a,b-S-Homohopane	1191	549	789	471	572	758	785	815	519	612	258	605	1375
a,b-R-Homohopane	932	443	682	386	477	599	606	641	413	495	191	494	1081

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	MT 47	MT 49	MT 51	MT 52	MT 53	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63
Start Date	072302	072902	072902	073002	073002	073002	080102	080502	080602	080602	080602	080702	080702	080802	080802
Start Time	734	620	1854	650	1250	1824	1759	1900	100	700	1900	745	1900	800	1900
Stop Date	072402	072902	073002	073002	073002	073102	080202	080602	080602	080602	080702	080702	080802	080802	080902
Stop Time	800	1124	605	1245	1814	750	807	100	700	1900	746	1900	754	1900	803
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Tm	351	657	291	481	521	271	286	310	927	718	449	329	323	446	445
a,b - norhopane	1200	1935	994	1561	1739	954	1203	1161	2848	2365	1605	1136	1330	1370	1729
a,a + b, a-norhopane	274	572	320	564	486	255	273	360	694	449	391	203	340	349	311
a-hopane	1487	2469	1213	1857	2077	1103	1415	1355	3626	2694	1850	1219	1433	1639	1877
moretane	181	329	162	267	305	136	197	170	444	377	258	149	195	183	223
a,b-S-Homohopane	716	1134	545	980	966	517	806	643	1361	1443	868	747	812	824	1043
a,b-R-Homohopane	565	893	453	728	914	477	645	467	1202	1141	676	672	669	650	827

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	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
Start Date	012703	012803	012803	012803	012903	012903	012903	013003	013003	013003	020503	020503	020603	020603	020703
Start Time	1830	1230	820	1800	30	745	1837	30	810	1830	700	1825	735	1745	110
Stop Date	012803	012803	012803	012903	012903	012903	013003	013003	013003	013103	020503	020603	020603	020703	020703
Stop Time	802	800	1734	30	630	1831	30	630	1830	1830	1820	735	1740	110	710
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Tm	532	702	430	676	508	601	907	826	1207	355	623	791	406	928	976
a,b - norhopane	1913	2636	1749	2110	2006	2282	3299	2932	4153	1403	2147	3176	1697	3042	3229
a,a + b, a-norhopane	287	458	251	656	259	444	857	746	891	178	383	448	266	726	759
a-hopane	1611	2229	1419	2365	1770	2165	3635	2695	4676	1200	2011	2606	1408	3700	3500
moretane	118	177	126	303	200	264	429	344	600	122	235	244	154	531	492
a,b-S-Homohopane	1006	1355	922	1126	1171	1128	1526	1338	2043	791	1224	1612	932	1424	1557
a,b-R-Homohopane	808	1140	888	858	812	882	1379	1133	1637	611	998	1267	725	1122	1190

	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 8	MT 9	MT 10
Sample ID	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 8	MT 9	MT 10
Start Date	032302	032402	032802	032902	033002	033102	040202	040302	040402
Start Time	1906	1914	1920	2016	1809	1936	1927	1924	1930
Stop Date	032402	032502	032902	033002	033102	040102	040302	040402	040502
Stop Time	1800	1740	1901	1706	1802	1750	1758	1813	325
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter

Surrogate (% Recovery)

	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 8	MT 9	MT 10
d8-Naphthalene	40.5%	48.2%	44.1%	30.9%	39.1%	45.6%	35.1%	39.9%	40.8%
d10-Fluorene	127.9%	144.0%	147.3%	116.5%	133.4%	120.1%	138.0%	125.9%	126.8%
d10-Fluoranthene	71.9%	77.4%	86.6%	70.7%	82.9%	81.9%	90.2%	79.9%	83.1%
d12-Perylene	82.9%	88.5%	93.6%	81.5%	83.7%	94.4%	92.1%	93.7%	96.0%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	7.8E+01	3.7E+01	6.3E+01	2.1E+01	2.8E+01	2.7E+01	3.3E+01	1.7E+01	3.3E+01
2-Methylnaphthalene	1.1E+02	5.1E+01	8.9E+01	2.6E+01	3.4E+01	2.6E+01	4.3E+01	2.3E+01	3.8E+01
Azulene	3.8E+00	ND	ND	ND	1.4E+00	4.8E+00	3.2E+00	3.3E+00	5.0E+00
1-Methylnaphthalene	5.7E+01	2.2E+01	3.9E+01	1.0E+01	1.3E+01	1.1E+01	1.8E+01	1.1E+01	1.9E+01
Biphenyl	1.3E+01	1.3E+01	1.3E+01	7.2E+00	7.2E+00	7.6E+00	1.3E+01	6.3E+00	1.2E+01
2,7-Dimethylnaphthalene	1.2E+02	2.6E+01	4.3E+01	1.8E+01	1.5E+01	2.0E+01	2.8E+01	3.5E+01	6.9E+01
1,3-Dimethylnaphthalene	1.0E+02	4.6E+01	5.1E+01	2.2E+01	2.0E+01	2.1E+01	3.5E+01	4.3E+01	7.1E+01
1,6-Dimethylnaphthalene	5.7E+01	2.3E+01	4.6E+01	1.4E+01	1.6E+01	9.1E+00	2.7E+01	1.3E+01	2.0E+01
1,4-Dimethylnaphthalene	2.0E+01	8.0E+00	1.3E+01	4.3E+00	5.3E+00	4.2E+00	7.4E+00	3.5E+00	5.2E+00
1,5-Dimethylnaphthalene	5.5E+01	3.2E+01	4.7E+01	3.1E+01	2.6E+01	1.9E+01	7.7E+01	2.6E+01	4.2E+01
Acenapthylene	9.2E+00	2.1E+01	1.6E+01	9.3E+00	6.4E+00	7.7E+00	1.5E+01	8.5E+00	1.5E+01
1,2-Dimethylnapthalene	8.1E+01	3.1E+01	2.8E+01	1.9E+01	1.7E+01	1.4E+01	2.2E+01	2.1E+01	5.2E+01
1,8-Dimethylnapthalene	3.6E+01	2.7E+01	<BG	<BG	<BG	<BG	<BG	ND	ND
Acenapthene	5.4E+00	ND	1.2E+01	9.4E+00	7.2E+00	8.7E+00	6.7E+00	1.1E+01	1.2E+01
2,3,5-Trimethylnapthalene	3.1E+01	7.0E+01	2.2E+01	ND	1.8E+01	ND	ND	ND	4.3E+01
Fluorene	2.3E+01	2.8E+01	3.0E+01	1.3E+01	1.3E+01	1.4E+01	2.2E+01	1.4E+01	2.1E+01
1-Methylfuorene	5.0E+01	4.2E+01	2.3E+01	ND	ND	ND	ND	1.4E+01	2.0E+01
Dibenzothiophene	2.6E+01	3.0E+01	2.4E+01	1.4E+01	1.5E+01	2.5E+01	2.1E+01	3.4E+01	4.7E+01
Phenanthrene	2.2E+02	3.0E+02	2.5E+02	1.4E+02	1.1E+02	1.7E+02	2.4E+02	2.0E+02	2.9E+02
Anthracene	2.7E+01	4.7E+01	3.9E+01	1.8E+01	1.0E+01	2.2E+01	3.4E+01	2.8E+01	4.1E+01
2-Methyldibenzothiophene	5.5E+01	2.2E+01	1.4E+01	1.7E+01	1.1E+01	2.2E+01	1.8E+01	2.8E+01	3.7E+01
4-Methyldibenzothiophene	1.9E+01	2.4E+01	1.7E+01	1.2E+01	9.4E+00	1.8E+01	2.2E+01	2.9E+01	3.9E+01
2-Methylphenanthrene	9.0E+01	9.1E+01	8.3E+01	4.7E+01	4.1E+01	6.5E+01	9.5E+01	9.1E+01	1.2E+02
2-Methylanthracene	2.1E+01	2.5E+01	2.3E+01	1.3E+01	1.5E+01	8.5E+00	2.7E+01	1.0E+01	1.6E+01
4,5-Methylenephenanthrene	1.6E+01	3.0E+01	2.0E+01	9.5E+00	8.5E+00	1.4E+01	2.3E+01	2.3E+01	2.9E+01
1-Methylanthracene	3.0E+01	2.8E+01	2.7E+01	1.2E+01	9.7E+00	1.6E+01	3.1E+01	2.2E+01	3.3E+01
1-Methylphenanthrene	1.5E+01	2.2E+01	1.4E+01	9.7E+00	8.6E+00	1.3E+01	1.7E+01	1.5E+01	2.2E+01
9-Methylanthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
9,10-Dimethylanthracene	2.0E+01	2.2E+01	1.9E+01	9.7E+00	9.9E+00	1.7E+01	2.4E+01	2.6E+01	3.6E+01
Fluoranthene	2.5E+02	4.8E+02	3.2E+02	1.8E+02	1.9E+02	2.7E+02	4.6E+02	3.4E+02	5.5E+02
3,6-Dimethylphenanthrene	1.7E+02	1.6E+02	ND	4.4E+01	4.1E+01	8.3E+01	1.2E+02	1.4E+02	2.4E+02
Pyrene	2.6E+02	4.2E+02	3.0E+02	1.8E+02	1.5E+02	2.5E+02	4.3E+02	3.5E+02	5.4E+02
3,6-Dimethylphenanthrene	1.7E+02	1.6E+02	ND	4.4E+01	4.1E+01	8.3E+01	1.2E+02	1.4E+02	2.4E+02
Benzo[a]fluorene	4.7E+01	6.4E+01	4.5E+01	2.3E+01	2.6E+01	3.7E+01	7.6E+01	5.1E+01	8.6E+01
Retene	5.1E+01	5.1E+01	3.8E+01	1.9E+01	2.4E+01	2.2E+01	4.6E+01	3.5E+01	6.3E+01
Benzo[b]fluorene	3.4E+01	5.6E+01	3.5E+01	1.9E+01	2.4E+01	3.0E+01	7.6E+01	3.9E+01	6.8E+01
Cyclopenta[c,d]pyrene	1.8E+02	ND	1.1E+02	8.4E+01	6.3E+01	ND	ND	ND	ND
Benz[a]anthracene	1.4E+02	2.3E+02	1.3E+02	7.0E+01	6.0E+01	9.3E+01	3.2E+02	1.3E+02	2.3E+02
Chrysene+Triphenylene	2.6E+02	3.6E+02	2.6E+02	1.7E+02	1.4E+02	1.9E+02	4.3E+02	2.4E+02	3.6E+02
Napthacene	1.9E+01	4.0E+01	3.0E+01	1.6E+01	8.1E+00	1.5E+01	2.5E+01	2.0E+01	4.0E+01
4-Methylchrysene	3.1E+01	4.4E+01	3.7E+01	1.9E+01	1.1E+01	1.7E+01	5.0E+01	2.6E+01	3.5E+01
Benzo[b]fluoranthene	3.9E+02	5.8E+02	3.8E+02	2.5E+02	2.3E+02	2.5E+02	9.4E+02	3.2E+02	4.5E+02
Benzo[k]fluoranthene	2.0E+02	3.0E+02	2.0E+02	1.3E+02	1.2E+02	1.2E+02	5.6E+02	1.7E+02	2.5E+02
Dimethylbenz[a]anthracene	1.5E+01	2.6E+01	2.2E+01	1.3E+01	7.6E+00	9.5E+00	2.6E+01	1.4E+01	1.9E+01
Benzo[e]pyrene	2.0E+02	3.0E+02	2.0E+02	1.4E+02	1.1E+02	1.3E+02	4.4E+02	1.6E+02	2.4E+02
Benzo[a]pyrene	1.7E+02	2.8E+02	1.5E+02	1.0E+02	6.6E+01	1.1E+02	3.4E+02	1.6E+02	2.5E+02
Perylene	3.3E+01	4.4E+01	3.7E+01	2.1E+01	1.3E+01	2.4E+01	6.6E+01	2.7E+01	5.0E+01
3-Methylchloanthrene	4.4E+00	7.1E+00	6.9E+00	4.4E+00	<BG	4.8E+00	8.3E+00	6.4E+00	8.7E+00
Indeno[1,2,3-c,d]pyrene	2.3E+02	3.4E+02	2.1E+02	1.4E+02	1.3E+02	1.5E+02	5.8E+02	1.8E+02	2.8E+02
Dibenz[a,h+ac]anthracene	1.1E+01	2.1E+01	1.5E+01	9.8E+00	9.4E+00	9.4E+00	4.2E+01	1.3E+01	2.0E+01
Benzo[g,h,i]perylene	2.3E+02	2.7E+02	1.7E+02	1.3E+02	1.0E+02	1.2E+02	3.3E+02	1.4E+02	2.1E+02
Anthanthrene	1.4E+01	2.5E+01	8.4E+00	9.8E+00	5.0E+00	8.6E+00	1.8E+01	1.3E+01	1.5E+01
Coronene	1.3E+02	1.1E+02	6.9E+01	6.7E+01	4.8E+01	5.1E+01	1.1E+02	6.1E+01	9.5E+01

Sample ID	MT 11	MT 12	MT 13	MT 16	MT 17	MT 18	MT 19	MT 20	MT 20 Back
Start Date	040802	040902	041002	041402	041502	041602	041602	041702	041702
Start Time	1720	1835	1905	1555	1834	0846	1957	0855	0855
Stop Date	040902	041002	041102	041502	041602	041602	041702	041702	041702
Stop Time	1808	1823	1826	1802	742	1854	735	1759	1759
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter

Surrogate (% Recovery)

d8-Naphthalene	32.6%	37.0%	4.7%	44.2%	34.5%	37.3%	42.1%	40.7%	53.5%
d10-Fluorene	112.8%	129.1%	137.7%	129.9%	144.7%	201.9%	164.8%	187.8%	138.4%
d10-Fluoranthene	74.5%	88.7%	88.5%	84.4%	81.0%	96.1%	83.4%	87.7%	93.5%
d12-Perylene	80.9%	92.1%	90.7%	91.3%	83.6%	84.8%	87.4%	84.0%	92.0%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	5.0E+01	2.1E+01	<BG	2.5E+01	5.8E+01	1.0E+02	7.6E+01	2.3E+02	<BG
2-Methylnaphthalene	7.0E+01	2.5E+01	<BG	2.9E+01	8.8E+01	1.3E+02	1.0E+02	3.1E+02	<BG
Azulene	1.7E+00	4.1E+00	5.6E-01	1.9E+00	ND	ND	ND	8.6E+00	4.2E+00
1-Methylnaphthalene	3.0E+01	9.7E+00	3.2E+00	1.2E+01	3.0E+01	5.2E+01	3.3E+01	1.4E+02	5.1E+01
Biphenyl	1.4E+01	8.8E+00	2.7E+00	7.7E+00	2.6E+01	4.5E+01	2.7E+01	7.9E+01	1.7E+01
2,7-Dimethylnaphthalene	4.2E+01	1.7E+01	7.4E+00	1.7E+01	5.2E+01	1.1E+02	8.4E+01	2.0E+02	8.3E+01
1,3-Dimethylnaphthalene	3.4E+01	2.5E+01	4.8E+00	1.5E+01	4.7E+01	6.6E+01	4.9E+01	1.5E+02	3.5E+01
1,6-Dimethylnaphthalene	3.6E+01	1.2E+01	6.6E+00	2.3E+01	4.8E+01	5.0E+01	6.8E+01	1.3E+02	2.4E+01
1,4-Dimethylnaphthalene	1.2E+01	3.3E+00	7.2E+00	4.4E+00	1.3E+01	2.3E+01	1.4E+01	4.4E+01	3.5E+00
1,5-Dimethylnaphthalene	2.3E+01	2.9E+01	1.7E+01	4.4E+01	4.2E+01	1.0E+02	3.8E+01	3.8E+02	1.5E+02
Acenapthylene	2.4E+01	8.3E+00	4.3E+00	1.2E+01	2.8E+01	4.1E+01	4.9E+01	6.7E+01	3.4E+01
1,2-Dimethylnapthalene	1.2E+01	1.7E+01	4.0E+00	8.6E+00	2.4E+01	1.9E+01	2.4E+01	5.7E+01	3.4E+01
1,8-Dimethylnapthalene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	ND	<BG
Acenapthene	2.3E+01	3.9E+00	1.6E+00	8.3E+00	1.5E+01	1.8E+01	1.8E+01	6.0E+01	1.2E+01
2,3,5-Trimethylnapthalene	4.4E+01	ND	ND	ND	5.5E+01	ND	5.5E+01	1.2E+02	3.2E+01
Fluorene	4.5E+01	1.4E+01	2.5E+01	1.3E+01	5.5E+01	5.0E+01	6.1E+01	1.1E+02	3.9E+01
1-Methylfuorene	2.0E+01	2.6E+01	ND	9.8E+00	ND	3.4E+01	3.8E+01	5.8E+01	ND
Dibenzothiophene	3.6E+01	1.7E+01	2.5E+01	1.5E+01	4.3E+01	4.8E+01	4.5E+01	8.4E+01	1.5E+01
Phenanthrene	4.8E+02	1.4E+02	2.3E+02	1.4E+02	5.2E+02	4.9E+02	4.8E+02	9.5E+02	2.7E+01
Anthracene	7.0E+01	1.8E+01	3.4E+01	1.6E+01	4.5E+01	5.7E+01	5.5E+01	1.5E+02	3.1E+00
2-Methyldibenzothiophene	2.6E+01	1.3E+01	1.7E+01	1.2E+01	3.6E+01	3.3E+01	4.4E+01	6.2E+01	2.1E+01
4-Methyldibenzothiophene	2.4E+01	1.8E+01	3.8E+01	1.2E+01	5.1E+01	4.5E+01	3.9E+01	7.5E+01	3.7E+01
2-Methylphenanthrene	1.2E+02	6.2E+01	8.8E+01	4.9E+01	2.3E+02	1.5E+02	2.1E+02	2.8E+02	1.3E+01
2-Methylanthracene	2.9E+01	1.3E+01	2.9E+01	1.6E+01	6.8E+01	9.8E+01	7.3E+01	1.4E+02	2.6E+00
4,5-Methylenephenanthrene	4.2E+01	1.2E+01	1.3E+01	8.2E+00	3.7E+01	2.7E+01	3.2E+01	5.8E+01	9.8E-01
1-Methylanthracene	3.8E+01	1.8E+01	2.6E+01	1.3E+01	5.8E+01	3.6E+01	5.2E+01	6.7E+01	4.3E+00
1-Methylphenanthrene	2.2E+01	1.0E+01	1.5E+01	8.3E+00	3.7E+01	2.9E+01	3.9E+01	5.7E+01	2.2E+00
9-Methylanthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
9,10-Dimethylanthracene	2.7E+01	1.9E+01	1.8E+01	1.3E+01	8.2E+01	3.7E+01	6.9E+01	5.9E+01	5.8E+00
Fluoranthene	8.3E+02	2.3E+02	3.2E+02	1.8E+02	8.3E+02	8.7E+02	6.4E+02	1.4E+03	3.2E+01
3,6-Dimethylphenanthrene	5.8E+01	7.7E+00	1.1E+02	4.1E+01	2.4E+02	8.3E+01	2.0E+02	1.3E+02	5.2E+01
Pyrene	7.2E+02	2.5E+02	3.7E+02	1.6E+02	6.6E+02	5.8E+02	6.2E+02	1.1E+03	2.5E+01
3,6-Dimethylphenanthrene	5.8E+01	7.7E+00	1.1E+02	4.1E+01	2.4E+02	8.3E+01	2.0E+02	1.3E+02	5.2E+01
Benzo[a]fluorene	7.3E+01	3.3E+01	4.8E+01	2.1E+01	7.9E+01	6.4E+01	7.6E+01	1.2E+02	4.3E+00
Retene	4.2E+01	3.1E+01	2.4E+01	1.4E+01	ND	4.3E+01	7.4E+01	9.1E+01	3.1E+01
Benzo[b]fluorene	7.1E+01	2.5E+01	3.8E+01	1.7E+01	7.9E+01	4.8E+01	6.8E+01	8.9E+01	1.9E+00
Cyclopenta[c,d]pyrene	ND	ND	ND	ND	ND	ND	7.8E+02	3.0E+02	1.0E+01
Benz[a]anthracene	3.2E+02	9.3E+01	1.6E+02	7.0E+01	2.6E+02	1.9E+02	2.8E+02	3.8E+02	<BG
Chrysene+Triphenylene	4.2E+02	2.0E+02	2.7E+02	1.3E+02	3.8E+02	3.5E+02	4.0E+02	6.5E+02	1.3E+01
Napthacene	6.5E+01	2.1E+01	3.6E+01	1.5E+01	3.7E+01	4.2E+01	4.3E+01	8.1E+01	4.0E+00
4-Methylchrysene	5.2E+01	2.7E+01	3.2E+01	1.8E+01	5.0E+01	4.3E+01	4.6E+01	6.5E+01	<BG
Benzo[b]fluoranthene	6.5E+02	2.4E+02	4.8E+02	2.2E+02	5.2E+02	6.3E+02	5.3E+02	9.3E+02	2.5E+01
Benzo[k]fluoranthene	3.6E+02	1.1E+02	2.3E+02	1.1E+02	2.5E+02	3.2E+02	3.1E+02	4.3E+02	1.5E+01
Dimethylbenz[a]anthracene	2.9E+01	1.3E+01	1.9E+01	1.1E+01	2.2E+01	2.5E+01	4.5E+01	3.3E+01	<BG
Benzo[e]pyrene	3.2E+02	1.2E+02	2.7E+02	1.2E+02	2.9E+02	3.7E+02	3.0E+02	4.4E+02	1.8E+01
Benzo[a]pyrene	3.8E+02	1.2E+02	2.4E+02	1.1E+02	3.3E+02	3.0E+02	4.5E+02	4.2E+02	2.1E+01
Perylene	8.2E+01	2.7E+01	4.5E+01	2.3E+01	6.1E+01	5.2E+01	7.1E+01	8.8E+01	<BG
3-Methylchloanthrene	1.3E+01	7.2E+00	8.1E+00	3.4E+00	6.9E+00	9.9E+00	9.6E+00	1.5E+01	<BG
Indeno[1,2,3-c,d]pyrene	3.5E+02	1.4E+02	3.3E+02	1.2E+02	3.1E+02	3.8E+02	4.0E+02	4.3E+02	3.3E+01
Dibenz[a,h+ac]anthracene	3.3E+01	9.4E+00	1.6E+01	8.8E+00	2.2E+01	2.8E+01	1.9E+01	3.3E+01	<BG
Benzo[g,h,i]perylene	2.3E+02	1.2E+02	4.8E+02	1.1E+02	3.6E+02	4.5E+02	4.0E+02	3.8E+02	3.7E+01
Anthanthrene	2.2E+01	1.1E+01	2.2E+01	9.9E+00	2.8E+01	1.6E+01	6.4E+01	2.1E+01	<BG
Coronene	8.8E+01	5.9E+01	2.5E+02	5.6E+01	1.9E+02	2.6E+02	2.6E+02	2.1E+02	ND

	MT 21	MT 22	MT 23	MT 25	MT 26	MT 27	MT 29	MT 30	MT 32
Sample ID	MT 21	MT 22	MT 23	MT 25	MT 26	MT 27	MT 29	MT 30	MT 32
Start Date	041702	042202	042302	042402	042402	042502	042602	042702	042902
Start Time	1856	1833	0834	0913	1926	0855	1905	1710	1734
Stop Date	041802	042302	042302	042402	042502	042502	042702	042802	043002
Stop Time	1745	808	1839	1933	800	1814	1700	1645	1704
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Surrogate (% Recovery)									
d8-Naphthalene	44.8%	43.4%	48.2%	47.9%	33.0%	48.8%	25.0%	36.6%	35.9%
d10-Fluorene	158.9%	130.6%	108.0%	141.1%	111.1%	120.5%	120.6%	123.9%	121.5%
d10-Fluoranthene	98.8%	92.5%	79.7%	100.1%	92.1%	78.3%	88.9%	91.8%	93.2%
d12-Perylene	90.6%	92.6%	97.2%	103.0%	99.6%	86.1%	90.8%	87.6%	88.9%
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	6.6E+01	1.6E+01	6.1E+01	5.1E+01	2.0E+01	2.7E+01	3.0E+01	4.6E+01	<BG
2-Methylnaphthalene	8.5E+01	2.0E+01	5.1E+01	4.7E+01	1.8E+01	2.4E+01	3.2E+01	4.1E+01	1.5E+01
Azulene	3.0E+00	2.2E+00	ND	1.6E+01	ND	ND	3.2E+00	4.8E+00	8.9E-01
1-Methylnaphthalene	3.6E+01	8.9E+00	2.2E+01	2.2E+01	7.9E+00	7.5E+00	1.4E+01	1.6E+01	3.6E+00
Biphenyl	2.0E+01	6.4E+00	1.3E+01	2.3E+01	6.6E+00	7.5E+00	1.2E+01	1.2E+01	3.6E+00
2,7-Dimethylnaphthalene	4.6E+01	2.6E+01	3.4E+01	4.9E+01	1.6E+01	1.7E+01	6.0E+01	4.6E+01	7.7E+00
1,3-Dimethylnaphthalene	3.8E+01	3.4E+01	3.4E+01	5.3E+01	1.2E+01	1.2E+01	4.1E+01	3.2E+01	5.5E+00
1,6-Dimethylnaphthalene	5.3E+01	8.5E+00	1.9E+01	2.1E+01	9.6E+00	8.7E+00	1.5E+01	2.1E+01	1.1E+01
1,4-Dimethylnaphthalene	1.4E+01	3.5E+00	7.7E+00	1.2E+01	2.7E+00	2.8E+00	5.2E+00	5.0E+00	1.4E+01
1,5-Dimethylnaphthalene	5.9E+00	2.0E+01	1.7E+01	1.3E+02	1.6E+01	6.4E+00	4.7E+01	4.4E+01	1.1E+01
Acenapthylene	2.6E+01	7.0E+00	1.7E+01	1.4E+01	5.0E+00	7.3E+00	2.0E+01	2.2E+01	3.5E+00
1,2-Dimethylnapthalene	1.4E+01	2.8E+01	5.4E+00	3.2E+01	1.1E+01	4.6E+01	4.3E+01	3.9E+01	3.1E+00
1,8-Dimethylnapthalene	<BG	<BG	ND	ND	ND	ND	ND	ND	<BG
Acenapthene	2.9E+01	6.2E+00	2.6E+01	2.2E+01	5.2E+00	5.4E+00	8.5E+00	4.4E+00	4.9E+00
2,3,5-Trimethylnapthalene	3.3E+01	1.5E+01	2.5E+01	2.9E+01	1.3E+01	9.9E+00	5.0E+01	4.2E+01	7.9E+00
Fluorene	4.9E+01	1.4E+01	3.7E+01	2.8E+01	8.9E+00	1.2E+01	2.3E+01	1.7E+01	5.9E+00
1-Methylfuorene	2.4E+01	1.1E+01	1.4E+01	1.6E+01	8.1E+00	9.8E+00	1.7E+01	6.4E+01	7.7E+00
Dibenzothiophene	3.6E+01	3.2E+01	4.3E+01	4.6E+01	1.1E+01	1.3E+01	2.6E+01	2.0E+01	6.1E+00
Phenanthrene	3.9E+02	1.4E+02	3.1E+02	2.6E+02	9.6E+01	1.2E+02	2.8E+02	1.7E+02	5.5E+01
Anthracene	4.6E+01	1.6E+01	5.0E+01	4.7E+01	9.7E+00	1.4E+01	3.3E+01	2.3E+01	6.2E+00
2-Methyldibenzothiophene	2.9E+01	2.6E+01	4.2E+01	3.2E+01	1.1E+01	1.7E+01	1.9E+01	1.7E+01	7.4E+00
4-Methyldibenzothiophene	3.6E+01	2.1E+01	4.2E+01	5.1E+01	1.1E+01	1.5E+01	1.7E+01	1.6E+01	1.0E+01
2-Methylphenanthrene	1.1E+02	7.3E+01	1.2E+02	9.2E+01	3.3E+01	5.3E+01	1.0E+02	5.6E+01	2.5E+01
2-Methylanthracene	4.9E+01	6.9E+00	1.6E+01	1.4E+01	5.3E+00	6.5E+00	2.0E+01	2.0E+01	7.7E+00
4,5-Methylenephenanthrene	3.1E+01	1.6E+01	2.9E+01	2.1E+01	6.4E+00	1.1E+01	2.0E+01	1.1E+01	5.0E+00
1-Methylanthracene	2.9E+01	2.3E+01	3.8E+01	2.4E+01	1.1E+01	1.4E+01	2.7E+01	1.5E+01	6.6E+00
1-Methylphenanthrene	2.0E+01	1.4E+01	2.1E+01	1.6E+01	6.4E+00	9.3E+00	1.9E+01	9.6E+00	4.2E+00
9-Methylanthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
9,10-Dimethylanthracene	3.0E+01	2.8E+01	3.6E+01	2.1E+01	1.1E+01	1.6E+01	2.9E+01	1.6E+01	8.6E+00
Fluoranthene	6.7E+02	2.9E+02	5.1E+02	4.2E+02	1.4E+02	2.1E+02	4.5E+02	2.5E+02	8.9E+01
3,6-Dimethylphenanthrene	5.0E+01	9.2E+01	1.1E+02	6.2E+01	4.8E+01	4.4E+01	1.5E+02	8.6E+01	6.7E+00
Pyrene	5.7E+02	3.2E+02	5.1E+02	3.5E+02	1.2E+02	2.3E+02	4.1E+02	2.3E+02	8.3E+01
3,6-Dimethylphenanthrene	5.0E+01	9.2E+01	1.1E+02	6.2E+01	4.8E+01	4.4E+01	1.5E+02	8.6E+01	6.7E+00
Benzo[a]fluorene	6.0E+01	5.6E+01	7.6E+01	4.6E+01	2.0E+01	3.1E+01	5.0E+01	2.7E+01	8.7E+00
Retene	3.4E+01	3.1E+01	3.8E+01	6.8E+01	1.5E+01	3.9E+01	3.6E+01	2.2E+01	2.1E+01
Benzo[b]fluorene	5.1E+01	5.1E+01	6.1E+01	4.4E+01	1.4E+01	2.2E+01	4.4E+01	2.6E+01	8.0E+00
Cyclopenta[c,d]pyrene	1.3E+02	8.8E+01	1.5E+02	1.1E+02	3.3E+01	6.6E+01	1.5E+02	1.1E+02	3.3E+01
Benz[a]anthracene	1.8E+02	1.0E+02	2.0E+02	1.4E+02	4.6E+01	8.2E+01	1.8E+02	1.0E+02	2.8E+01
Chrysene+Triphenylene	3.1E+02	1.6E+02	3.2E+02	2.4E+02	1.0E+02	1.3E+02	3.1E+02	1.7E+02	5.9E+01
Napthacene	4.3E+01	1.9E+01	4.0E+01	2.3E+01	9.7E+00	1.3E+01	3.5E+01	1.8E+01	4.7E+00
4-Methylchrysene	3.4E+01	1.7E+01	4.0E+01	2.2E+01	1.0E+01	1.3E+01	3.3E+01	1.9E+01	6.5E+00
Benzo[b]fluoranthene	4.1E+02	2.2E+02	3.3E+02	3.4E+02	2.6E+02	1.6E+02	4.3E+02	3.0E+02	1.3E+02
Benzo[k]fluoranthene	2.4E+02	1.3E+02	1.8E+02	1.7E+02	1.0E+02	9.2E+01	2.4E+02	1.7E+02	5.6E+01
Dimethylbenz[a]anthracene	2.0E+01	1.4E+01	1.7E+01	1.4E+01	9.7E+00	6.0E+00	1.7E+01	1.7E+01	5.4E+00
Benzo[e]pyrene	2.3E+02	1.1E+02	1.8E+02	1.8E+02	1.3E+02	8.6E+01	2.3E+02	1.6E+02	6.3E+01
Benzo[a]pyrene	2.4E+02	1.4E+02	2.3E+02	1.8E+02	7.3E+01	9.5E+01	2.6E+02	1.5E+02	4.5E+01
Perylene	5.1E+01	1.8E+01	4.3E+01	3.0E+01	1.3E+01	2.2E+01	4.0E+01	2.4E+01	1.6E+01
3-Methylchloanthrene	1.0E+01	5.8E+00	1.0E+01	8.0E+00	<BG	<BG	8.7E+00	5.2E+00	<BG
Indeno[1,2,3-c,d]pyrene	2.3E+02	1.4E+02	2.0E+02	3.9E+02	2.9E+02	1.1E+02	2.6E+02	1.9E+02	9.1E+01
Dibenz[a,h+ac]anthracene	2.0E+01	1.3E+01	1.9E+01	4.5E+01	3.3E+01	8.5E+00	1.7E+01	1.2E+01	5.0E+00
Benzo[g,h,i]perylene	2.1E+02	1.2E+02	1.6E+02	2.9E+02	2.1E+02	1.1E+02	2.4E+02	1.8E+02	7.8E+01
Anthanthrene	2.2E+01	1.6E+01	2.5E+01	4.1E+01	1.5E+01	1.3E+01	1.6E+01	8.3E+00	3.7E+00
Coronene	1.1E+02	6.4E+01	7.1E+01	1.6E+02	1.0E+02	5.7E+01	1.3E+02	1.1E+02	4.9E+01

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	MT 33	MT 34	MT 35	MT 36	MT 37	MT 38	MT 39	MT 40	MT 41
Sample ID									
Start Date	070902	071002	071102	071202	071302	071402	071502	071602	071702
Start Time	1705	1845	1915	1835	1923	1921	1903	1850	1905
Stop Date	071002	071102	071202	071302	071402	071502	071602	071702	071802
Stop Time	1745	1805	1720	1820	1811	1757	1754	1801	1804
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter

Surrogate (% Recovery)

	MT 33	MT 34	MT 35	MT 36	MT 37	MT 38	MT 39	MT 40	MT 41
d8-Naphthalene	7.2%	22.0%	5.0%	44.2%	16.4%	13.7%	39.0%	22.0%	8.2%
d10-Fluorene	97.4%	113.5%	96.5%	137.2%	78.3%	85.6%	127.4%	107.1%	92.0%
d10-Fluoranthene	78.4%	73.0%	67.8%	75.5%	70.2%	73.6%	71.9%	67.3%	73.2%
d12-Perylene	94.5%	92.6%	84.6%	93.5%	90.5%	88.5%	94.2%	83.9%	91.7%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	1.0E+01	1.4E+01	<BG	1.6E+01	<BG	<BG	2.0E+01	4.1E+01	<BG
2-Methylnaphthalene	1.3E+01	1.2E+01	1.4E+01	1.7E+01	6.4E+00	1.1E+01	2.2E+01	4.9E+01	1.3E+01
Azulene	ND	ND	2.1E+00	ND	ND	1.2E+00	ND	ND	ND
1-Methylnaphthalene	3.6E+00	4.6E+00	4.5E+00	5.8E+00	<BG	3.4E+00	9.1E+00	1.7E+01	2.4E+00
Biphenyl	4.8E+00	4.4E+00	4.3E+00	4.5E+00	<BG	3.4E+00	6.6E+00	1.2E+01	4.1E+00
2,7-Dimethylnaphthalene	2.1E+01	1.1E+01	8.3E+00	1.9E+01	9.9E+00	1.3E+01	2.4E+01	3.3E+01	2.3E+01
1,3-Dimethylnaphthalene	ND	5.5E+00	8.2E+00	ND	2.4E+00	5.3E+00	8.5E+00	1.9E+01	ND
1,6-Dimethylnaphthalene	ND	7.2E+00	1.4E+01	ND	8.9E+00	1.4E+01	2.6E+01	1.6E+01	ND
1,4-Dimethylnaphthalene	2.5E+00	2.8E+00	5.4E+00	1.6E+00	<BG	1.6E+00	5.2E+00	9.9E+00	2.3E+00
1,5-Dimethylnaphthalene	9.9E+00	5.7E+00	2.1E+00	1.7E+00	4.3E+00	7.9E+00	8.8E+00	9.7E+00	1.7E+01
Acenapthylene	1.2E+01	6.7E+00	7.1E+00	5.1E+00	2.4E+00	5.3E+00	7.5E+00	2.0E+01	7.6E+00
1,2-Dimethylnapthalene	3.2E+00	ND	3.9E+00	ND	1.3E+00	ND	5.0E+00	6.7E+00	ND
1,8-Dimethylnapthalene	ND	<BG	<BG	ND	<BG	<BG	<BG	<BG	ND
Acenapthene	1.0E+01	7.3E+00	9.5E+00	1.1E+01	3.7E+00	6.7E+00	8.4E+00	1.8E+01	5.6E+00
2,3,5-Trimethylnapthalene	1.6E+01	5.6E+00	1.2E+01	4.2E+00	6.8E+00	6.8E+00	6.9E+00	1.1E+01	ND
Fluorene	2.1E+01	1.3E+01	1.6E+01	8.7E+00	4.4E+00	9.2E+00	1.3E+01	4.7E+01	1.2E+01
1-Methylfuorene	2.0E+01	6.9E+00	9.5E+00	6.2E+00	4.7E+00	8.2E+00	9.9E+00	2.3E+01	1.2E+01
Dibenzothiophene	2.0E+01	1.0E+01	1.9E+01	1.2E+01	2.9E+00	7.5E+00	1.3E+01	3.0E+01	1.1E+01
Phenanthrene	3.2E+02	1.2E+02	1.8E+02	7.1E+01	4.4E+01	1.1E+02	1.5E+02	4.7E+02	1.6E+02
Anthracene	4.2E+01	2.5E+01	7.9E+01	4.7E+01	4.1E+00	1.7E+01	6.6E+01	1.1E+02	6.0E+01
2-Methyldibenzothiophene	1.9E+01	1.0E+01	1.4E+01	5.6E+00	3.7E+00	8.3E+00	1.0E+01	2.7E+01	8.5E+00
4-Methyldibenzothiophene	1.3E+01	1.5E+01	1.0E+01	5.3E+00	1.8E+00	5.8E+00	8.2E+00	2.0E+01	5.6E+00
2-Methylphenanthrene	9.5E+01	4.2E+01	6.8E+01	2.5E+01	1.3E+01	3.7E+01	4.8E+01	1.3E+02	5.0E+01
2-Methylanthracene	1.8E+01	9.7E+00	2.4E+01	1.2E+01	4.2E+00	7.2E+00	1.2E+01	2.7E+01	1.6E+01
4,5-Methylenephenanthrene	2.8E+01	8.5E+00	1.2E+01	5.8E+00	2.5E+00	7.2E+00	1.1E+01	2.8E+01	1.1E+01
1-Methylanthracene	5.1E+01	2.1E+01	3.6E+01	1.2E+01	6.4E+00	1.6E+01	2.6E+01	6.5E+01	2.4E+01
1-Methylphenanthrene	3.7E+01	1.7E+01	2.2E+01	8.4E+00	4.8E+00	1.3E+01	1.9E+01	4.6E+01	1.9E+01
9-Methylanthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
9,10-Dimethylanthracene	1.8E+01	7.7E+00	1.1E+01	4.7E+00	2.3E+00	5.6E+00	9.0E+00	2.3E+01	7.2E+00
Fluoranthene	5.6E+02	1.8E+02	2.1E+02	8.2E+01	5.8E+01	1.4E+02	2.4E+02	4.3E+02	2.1E+02
3,6-Dimethylphenanthrene	1.0E+01	4.9E+00	6.7E+00	4.8E+00	4.2E+00	6.8E+00	8.4E+00	4.8E+00	5.9E+00
Pyrene	5.1E+02	1.8E+02	2.1E+02	7.4E+01	5.1E+01	1.3E+02	2.0E+02	3.5E+02	1.9E+02
3,6-Dimethylphenanthrene	1.0E+01	4.9E+00	6.7E+00	4.8E+00	4.2E+00	6.8E+00	8.4E+00	4.8E+00	5.9E+00
Benzo[a]fluorene	6.3E+01	2.1E+01	2.5E+01	9.0E+00	6.0E+00	1.2E+01	2.3E+01	3.7E+01	1.9E+01
Retene	2.1E+01	1.5E+01	1.2E+01	8.8E+00	6.4E+00	7.6E+00	1.1E+01	1.5E+01	7.5E+00
Benzo[b]fluorene	3.7E+01	1.6E+01	1.5E+01	7.3E+00	3.9E+00	9.8E+00	1.8E+01	2.7E+01	1.3E+01
Cyclopenta[c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benz[a]anthracene	2.8E+02	9.3E+01	1.0E+02	2.8E+01	2.4E+01	6.3E+01	8.6E+01	1.5E+02	7.9E+01
Chrysene+Triphenylene	3.9E+02	1.7E+02	1.7E+02	5.8E+01	4.7E+01	1.2E+02	1.8E+02	2.0E+02	1.4E+02
Napthacene	5.4E+01	1.7E+01	2.3E+01	6.5E+00	6.7E+00	1.5E+01	1.6E+01	2.5E+01	2.0E+01
4-Methylchrysene	3.7E+01	2.3E+01	2.3E+01	6.4E+00	4.6E+00	1.4E+01	1.7E+01	2.1E+01	1.3E+01
Benzo[b]fluoranthene	5.2E+02	1.7E+02	2.4E+02	8.6E+01	7.7E+01	1.6E+02	2.4E+02	3.7E+02	2.0E+02
Benzo[k]fluoranthene	3.1E+02	1.1E+02	1.4E+02	4.8E+01	3.9E+01	7.9E+01	1.1E+02	2.2E+02	1.2E+02
Dimethylbenz[a]anthracene	2.5E+01	1.1E+01	1.5E+01	6.8E+00	2.7E+00	8.5E+00	1.2E+01	1.5E+01	1.4E+01
Benzo[e]pyrene	2.9E+02	1.1E+02	1.5E+02	5.4E+01	4.5E+01	9.9E+01	1.3E+02	2.2E+02	1.2E+02
Benzo[a]pyrene	3.4E+02	1.0E+02	1.3E+02	3.9E+01	2.5E+01	8.6E+01	1.2E+02	2.0E+02	9.7E+01
Perylene	7.0E+01	1.9E+01	2.4E+01	8.7E+00	6.3E+00	1.8E+01	2.2E+01	4.3E+01	1.6E+01
3-Methylchloanthrene	ND	5.1E+00	ND	ND	ND	ND	7.3E+00	ND	ND
Indeno[1,2,3-c,d]pyrene	4.9E+02	1.6E+02	2.3E+02	9.5E+01	7.5E+01	1.6E+02	1.9E+02	3.7E+02	1.9E+02
Dibenz[a,h+ac]anthracene	5.0E+01	1.6E+01	2.1E+01	6.8E+00	6.3E+00	1.3E+01	1.9E+01	2.8E+01	1.4E+01
Benzo[g,h,i]perylene	4.2E+02	2.0E+02	2.8E+02	1.2E+02	8.3E+01	2.1E+02	2.1E+02	3.8E+02	2.1E+02
Anthanthrene	6.6E+01	2.4E+01	3.0E+01	1.1E+01	7.0E+00	1.9E+01	2.8E+01	4.0E+01	2.1E+01
Coronene	1.5E+02	1.1E+02	1.8E+02	8.7E+01	5.9E+01	1.4E+02	1.3E+02	1.9E+02	1.3E+02

Sample ID	MT 42	MT 43	MT 45	MT 46	MT 47	MT 49	MT 51	MT 52	MT 53
Start Date	071802	071902	072102	072202	072302	072902	072902	073002	073002
Start Time	1853	1935	1819	1832	734	620	1854	650	1250
Stop Date	071902	072002	072202	072302	072402	072902	073002	073002	073002
Stop Time	1850	1828	1740	727	800	1124	605	1245	1814
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter

Surrogate (% Recovery)									
d8-Naphthalene	37.0%	21.4%	25.8%	42.9%	28.6%	19.6%	63.9%	68.1%	34.8%
d10-Fluorene	108.4%	89.3%	95.3%	128.5%	82.8%	76.3%	144.0%	161.5%	119.0%
d10-Fluoranthene	75.1%	73.9%	71.6%	75.0%	73.6%	71.5%	73.9%	76.9%	76.1%
d12-Perylene	91.8%	86.0%	84.0%	90.4%	95.3%	94.9%	93.9%	96.0%	99.6%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	3.2E+01	1.3E+01	2.3E+01	3.1E+01	1.6E+01	<BG	5.3E+01	5.4E+01	<BG
2-Methylnaphthalene	2.5E+01	2.0E+01	2.5E+01	4.1E+01	2.2E+01	3.8E+01	4.9E+01	5.8E+01	3.6E+01
Azulene	ND	3.5E+00	ND	ND	ND	ND	ND	ND	ND
1-Methylnaphthalene	6.3E+00	6.5E+00	6.8E+00	1.3E+01	6.3E+00	1.6E+01	1.5E+01	1.9E+01	1.3E+01
Biphenyl	7.2E+00	5.4E+00	6.0E+00	8.5E+00	4.2E+00	1.3E+01	1.4E+01	1.6E+01	1.4E+01
2,7-Dimethylnaphthalene	2.0E+01	7.2E+00	3.0E+01	4.4E+01	1.9E+01	2.4E+01	3.2E+01	4.8E+01	3.9E+01
1,3-Dimethylnaphthalene	8.0E+00	8.1E+00	1.1E+01	ND	7.4E+00	1.7E+01	1.6E+01	2.5E+01	1.5E+01
1,6-Dimethylnaphthalene	3.1E+01	2.8E+01	2.2E+01	ND	2.0E+01	1.4E+01	1.2E+01	1.5E+01	1.4E+01
1,4-Dimethylnaphthalene	2.5E+00	3.2E+00	5.1E+00	6.5E+00	2.1E+00	8.7E+00	8.5E+00	8.1E+00	3.7E+00
1,5-Dimethylnaphthalene	3.7E+01	3.1E+01	2.1E+01	1.4E+01	2.8E+00	9.8E+00	1.0E+01	1.3E+01	1.3E+01
Acenapthylene	7.2E+00	4.9E+00	7.4E+00	1.4E+01	8.7E+00	1.2E+01	9.2E+00	1.5E+01	9.5E+00
1,2-Dimethylnapthalene	4.2E+00	5.4E+00	3.8E+00	8.5E+00	3.0E+00	ND	ND	ND	ND
1,8-Dimethylnapthalene	<BG	ND	ND	<BG	<BG	<BG	<BG	ND	<BG
Acenapthene	6.5E+00	5.5E+00	8.5E+00	1.5E+01	6.4E+00	1.8E+01	1.4E+01	1.5E+01	1.3E+01
2,3,5-Trimethylnapthalene	7.8E+00	8.0E+00	ND	1.0E+01	8.8E+00	8.8E+00	9.7E+00	ND	ND
Fluorene	1.3E+01	1.0E+01	1.3E+01	2.6E+01	1.2E+01	2.0E+01	2.3E+01	2.4E+01	2.3E+01
1-Methylfuorene	9.3E+00	9.7E+00	1.4E+01	1.8E+01	9.0E+00	2.7E+01	1.2E+01	1.3E+01	1.2E+01
Dibenzothiophene	9.9E+00	1.1E+01	1.5E+01	1.9E+01	1.2E+01	1.5E+01	1.2E+01	1.9E+01	1.5E+01
Phenanthrene	1.4E+02	9.1E+01	1.6E+02	2.0E+02	1.5E+02	2.3E+02	1.5E+02	2.2E+02	1.8E+02
Anthracene	2.8E+01	1.9E+01	1.9E+01	4.3E+01	2.4E+01	2.6E+01	1.3E+01	3.2E+01	7.8E+01
2-Methyldibenzothiophene	8.2E+00	6.6E+00	1.3E+01	1.3E+01	1.1E+01	1.7E+01	9.1E+00	1.5E+01	1.5E+01
4-Methyldibenzothiophene	6.3E+00	4.5E+00	7.2E+00	9.9E+00	8.7E+00	1.7E+01	9.4E+00	2.3E+01	1.5E+01
2-Methylphenanthrene	4.2E+01	3.0E+01	5.3E+01	6.0E+01	5.4E+01	7.0E+01	4.3E+01	7.0E+01	6.1E+01
2-Methylanthracene	2.1E+01	1.9E+01	1.8E+01	2.2E+01	1.3E+01	7.3E+00	1.6E+01	9.1E+00	1.2E+01
4,5-Methylenephenanthrene	1.2E+01	5.7E+00	1.1E+01	1.1E+01	1.3E+01	1.4E+01	6.6E+00	1.7E+01	1.2E+01
1-Methylanthracene	2.2E+01	1.3E+01	2.7E+01	2.9E+01	3.0E+01	3.0E+01	2.1E+01	3.4E+01	3.1E+01
1-Methylphenanthrene	1.5E+01	1.1E+01	1.9E+01	2.2E+01	1.9E+01	2.8E+01	1.6E+01	2.4E+01	2.5E+01
9-Methylanthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
9,10-Dimethylanthracene	6.2E+00	4.3E+00	7.9E+00	1.2E+01	1.1E+01	1.5E+01	1.2E+01	1.2E+01	1.0E+01
Fluoranthene	2.3E+02	1.1E+02	2.0E+02	2.5E+02	2.7E+02	3.0E+02	1.6E+02	3.6E+02	2.8E+02
3,6-Dimethylphenanthrene	1.0E+01	4.5E+00	ND	2.2E+01	3.6E+00	1.2E+01	3.5E+00	ND	ND
Pyrene	2.0E+02	8.9E+01	1.7E+02	2.1E+02	2.3E+02	2.7E+02	1.4E+02	3.1E+02	2.5E+02
3,6-Dimethylphenanthrene	1.0E+01	4.5E+00	ND	2.2E+01	3.6E+00	1.2E+01	3.5E+00	ND	ND
Benzo[a]fluorene	2.2E+01	1.1E+01	2.0E+01	2.5E+01	2.9E+01	2.5E+01	1.3E+01	3.2E+01	2.9E+01
Retene	9.0E+00	9.3E+00	1.5E+01	2.9E+01	1.2E+01	2.0E+01	1.2E+01	2.1E+01	1.9E+01
Benzo[b]fluorene	1.6E+01	9.2E+00	1.3E+01	1.6E+01	1.7E+01	1.9E+01	1.2E+01	2.1E+01	1.8E+01
Cyclopenta[c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benz[a]anthracene	9.6E+01	4.1E+01	7.7E+01	7.7E+01	1.1E+02	1.1E+02	3.8E+01	1.4E+02	1.2E+02
Chrysene+Triphenylene	1.5E+02	8.5E+01	1.2E+02	1.3E+02	1.9E+02	2.0E+02	9.1E+01	2.5E+02	2.2E+02
Napthacene	2.2E+01	6.9E+00	1.2E+01	1.4E+01	1.8E+01	1.7E+01	ND	3.1E+01	2.0E+01
4-Methylchrysene	1.3E+01	1.0E+01	1.4E+01	1.3E+01	2.0E+01	1.5E+01	8.2E+00	2.2E+01	2.2E+01
Benzo[b]fluoranthene	2.0E+02	1.2E+02	1.7E+02	1.7E+02	2.3E+02	2.0E+02	1.1E+02	2.6E+02	2.2E+02
Benzo[k]fluoranthene	1.1E+02	5.7E+01	9.6E+01	7.6E+01	1.1E+02	1.1E+02	5.4E+01	1.6E+02	1.1E+02
Dimethylbenz[a]anthracene	8.9E+00	6.3E+00	9.0E+00	1.2E+01	1.1E+01	1.2E+01	6.9E+00	1.3E+01	1.3E+01
Benzo[e]pyrene	1.1E+02	6.9E+01	1.0E+02	9.2E+01	1.3E+02	1.2E+02	6.0E+01	1.5E+02	1.2E+02
Benzo[a]pyrene	1.3E+02	5.0E+01	8.1E+01	7.7E+01	1.2E+02	1.2E+02	4.2E+01	1.7E+02	1.3E+02
Perylene	2.5E+01	8.3E+00	1.7E+01	1.7E+01	2.8E+01	2.0E+01	7.9E+00	3.0E+01	2.6E+01
3-Methylchloanthrene	5.8E+00	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	1.7E+02	1.1E+02	1.6E+02	1.6E+02	2.1E+02	1.9E+02	9.2E+01	2.5E+02	1.9E+02
Dibenz[a,h+ac]anthracene	1.8E+01	1.1E+01	1.6E+01	1.5E+01	2.1E+01	1.5E+01	7.2E+00	2.5E+01	2.2E+01
Benzo[g,h,i]perylene	1.7E+02	1.2E+02	1.8E+02	1.7E+02	2.1E+02	2.4E+02	1.1E+02	2.8E+02	2.1E+02
Anthanthrene	2.5E+01	1.4E+01	2.7E+01	2.8E+01	3.1E+01	3.2E+01	1.4E+01	4.5E+01	3.7E+01
Coronene	1.0E+02	7.5E+01	9.4E+01	1.0E+02	1.2E+02	1.4E+02	6.8E+01	1.3E+02	1.3E+02

	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63
Sample ID	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63
Start Date	073002	080102	080502	080602	080602	080602	080702	080702	080802	080802
Start Time	1824	1759	1900	100	700	1900	745	1900	800	1900
Stop Date	073102	080202	080602	080602	080602	080702	080702	080802	080802	080902
Stop Time	750	807	100	700	1900	746	1900	754	1900	803
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter

Surrogate (% Recovery)

	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63
d8-Naphthalene	43.2%	28.2%	43.7%	58.2%	45.0%	32.8%	43.7%	36.3%	40.0%	39.0%
d10-Fluorene	123.6%	117.0%	95.6%	123.2%	124.0%	96.1%	99.4%	75.0%	95.6%	106.5%
d10-Fluoranthene	74.2%	66.7%	75.6%	74.9%	75.2%	83.7%	77.4%	70.7%	79.3%	83.7%
d12-Perylene	94.2%	84.8%	96.1%	98.4%	100.9%	101.1%	99.7%	92.2%	99.7%	102.8%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	2.0E+01	2.4E+01	<BG	4.8E+01	4.6E+01	1.8E+01	3.7E+01	2.6E+01	3.7E+01	4.9E+01
2-Methylnaphthalene	1.8E+01	3.4E+01	<BG	4.5E+01	4.4E+01	1.7E+01	3.6E+01	2.8E+01	2.3E+01	4.1E+01
Azulene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1-Methylnaphthalene	6.9E+00	1.2E+01	<BG	1.4E+01	1.5E+01	8.9E+00	1.6E+01	8.8E+00	1.2E+01	1.6E+01
Biphenyl	7.5E+00	1.1E+01	<BG	1.2E+01	1.2E+01	5.9E+00	1.1E+01	7.4E+00	8.0E+00	1.1E+01
2,7-Dimethylnaphthalene	1.7E+01	1.9E+01	1.6E+01	3.1E+01	5.6E+01	1.1E+01	ND	1.6E+01	ND	3.4E+01
1,3-Dimethylnaphthalene	1.1E+01	1.9E+01	9.1E+00	1.8E+01	2.7E+01	1.8E+01	2.5E+01	1.9E+01	1.8E+01	3.9E+01
1,6-Dimethylnaphthalene	2.1E+01	4.4E+01	<BG	9.6E+00	1.8E+01	6.3E+00	1.0E+01	2.2E+01	8.5E+00	9.8E+00
1,4-Dimethylnaphthalene	3.0E+00	8.0E+00	2.2E+00	6.1E+00	1.1E+01	3.6E+00	2.8E+01	4.2E+00	3.8E+00	ND
1,5-Dimethylnaphthalene	1.4E+01	9.5E+00	ND	4.7E+00	2.0E+01	7.6E+00	4.8E+00	6.1E+00	9.3E+00	ND
Acenapthylene	9.9E+00	1.8E+01	7.2E+00	8.8E+00	1.8E+01	6.7E+00	1.1E+01	1.1E+01	3.8E+01	6.7E+01
1,2-Dimethylnapthalene	7.7E+00	1.4E+01	4.0E+00	7.2E+00	8.7E+00	7.7E+00	1.4E+01	1.3E+01	ND	1.9E+01
1,8-Dimethylnapthalene	<BG	<BG	<BG	<BG	<BG	ND	<BG	<BG	<BG	<BG
Acenapthene	9.3E+00	ND	1.2E+01	4.3E+01	5.0E+01	1.1E+01	3.2E+01	1.5E+01	1.9E+01	3.3E+01
2,3,5-Trimethylnapthalene	ND	ND	ND	1.0E+01	ND	4.3E+00	5.2E+00	3.4E+00	5.3E+00	8.0E+00
Fluorene	1.1E+01	2.3E+01	1.9E+01	3.8E+01	4.9E+01	1.4E+01	3.8E+01	1.6E+01	2.7E+01	4.6E+01
1-Methylfuorene	8.9E+00	1.4E+01	1.2E+01	1.2E+01	1.7E+01	1.1E+01	9.6E+00	1.1E+01	1.5E+01	1.7E+01
Dibenzothiophene	1.3E+01	2.7E+01	1.5E+01	1.7E+01	3.5E+01	1.4E+01	2.5E+01	1.7E+01	3.2E+01	4.1E+01
Phenanthrene	1.2E+02	2.3E+02	1.7E+02	2.0E+02	3.6E+02	1.3E+02	2.6E+02	1.5E+02	3.1E+02	4.3E+02
Anthracene	2.4E+01	8.6E+01	2.5E+01	2.8E+01	5.5E+01	2.1E+01	4.2E+01	3.6E+01	6.2E+01	1.4E+02
2-Methyldibenzothiophene	1.1E+01	1.5E+01	1.4E+01	1.3E+01	3.0E+01	1.5E+01	2.2E+01	1.1E+01	3.1E+01	3.6E+01
4-Methyldibenzothiophene	8.0E+00	9.9E+00	8.8E+00	1.2E+01	4.7E+01	1.8E+01	3.2E+01	1.5E+01	4.2E+01	4.5E+01
2-Methylphenanthrene	4.4E+01	7.8E+01	4.7E+01	5.4E+01	1.2E+02	5.0E+01	8.8E+01	6.3E+01	1.2E+02	1.2E+02
2-Methylanthracene	1.7E+01	3.3E+01	9.5E+00	5.8E+00	1.8E+01	5.8E+00	1.3E+01	1.2E+01	2.5E+01	3.7E+01
4,5-Methylenephenanthrene	8.0E+00	1.1E+01	1.4E+01	1.5E+01	3.4E+01	1.0E+01	2.3E+01	1.1E+01	4.9E+01	6.3E+01
1-Methylanthracene	2.4E+01	3.5E+01	2.5E+01	2.8E+01	6.5E+01	2.8E+01	4.6E+01	3.3E+01	7.1E+01	8.4E+01
1-Methylphenanthrene	1.5E+01	2.4E+01	1.7E+01	2.0E+01	4.6E+01	1.9E+01	3.1E+01	2.2E+01	4.8E+01	5.2E+01
9-Methylanthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9,10-Dimethylanthracene	9.6E+00	1.4E+01	1.1E+01	1.1E+01	2.5E+01	1.4E+01	2.0E+01	1.6E+01	2.7E+01	2.5E+01
Fluoranthene	1.6E+02	2.4E+02	2.7E+02	3.2E+02	5.8E+02	2.0E+02	4.0E+02	2.1E+02	5.8E+02	7.8E+02
3,6-Dimethylphenanthrene	ND	6.6E+00	ND	1.1E+01	5.9E+00	6.0E+00	ND	7.7E+00	ND
Pyrene	1.5E+02	2.0E+02	2.4E+02	3.1E+02	5.1E+02	2.1E+02	3.5E+02	2.1E+02	6.0E+02	8.4E+02
3,6-Dimethylphenanthrene	ND	6.6E+00	ND	1.1E+01	5.9E+00	6.0E+00	ND	ND	7.7E+00	ND
Benzo[a]fluorene	2.0E+01	2.4E+01	2.6E+01	3.8E+01	6.4E+01	2.5E+01	4.3E+01	3.0E+01	8.7E+01	1.3E+02
Retene	ND	1.4E+01	2.0E+01	2.1E+01	2.5E+01	ND	2.2E+01	1.7E+01	2.2E+01	ND
Benzo[b]fluorene	1.2E+01	1.6E+01	2.1E+01	2.8E+01	4.3E+01	1.7E+01	3.1E+01	2.1E+01	6.1E+01	9.7E+01
Cyclopenta[c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benz[a]anthracene	6.7E+01	8.9E+01	1.1E+02	2.1E+02	2.9E+02	9.1E+01	2.2E+02	1.1E+02	3.6E+02	5.0E+02
Chrysene+Triphenylene	1.2E+02	1.7E+02	1.8E+02	2.8E+02	5.6E+02	1.7E+02	3.8E+02	1.8E+02	4.3E+02	4.9E+02
Napthacene	9.5E+00	1.8E+01	2.6E+01	4.4E+01	5.7E+01	1.6E+01	4.0E+01	1.7E+01	5.8E+01	7.9E+01
4-Methylchrysene	1.4E+01	1.7E+01	1.9E+01	2.5E+01	6.8E+01	2.1E+01	4.4E+01	2.4E+01	4.4E+01	5.3E+01
Benzo[b]fluoranthene	1.3E+02	1.8E+02	1.8E+02	2.9E+02	5.5E+02	1.9E+02	3.8E+02	2.2E+02	4.4E+02	6.9E+02
Benzo[k]fluoranthene	8.1E+01	9.8E+01	1.3E+02	2.0E+02	3.0E+02	1.0E+02	2.1E+02	1.2E+02	2.8E+02	4.7E+02
Dimethylbenz[a]anthracene	8.3E+00	7.6E+00	1.2E+01	1.4E+01	3.2E+01	1.3E+01	2.6E+01	1.2E+01	2.1E+01	3.4E+01
Benzo[e]pyrene	8.3E+01	1.1E+02	1.1E+02	1.7E+02	3.3E+02	1.1E+02	2.1E+02	1.3E+02	2.6E+02	4.1E+02
Benzo[a]pyrene	7.0E+01	9.0E+01	1.3E+02	1.9E+02	3.3E+02	1.0E+02	2.7E+02	1.1E+02	4.1E+02	6.8E+02
Perylene	1.6E+01	2.2E+01	2.3E+01	5.0E+01	7.5E+01	2.4E+01	5.4E+01	2.5E+01	6.9E+01	1.1E+02
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	1.3E+02	1.6E+02	1.7E+02	2.6E+02	4.6E+02	1.8E+02	3.2E+02	2.1E+02	4.3E+02	7.3E+02
Dibenz[a,h+ac]anthracene	1.1E+01	1.5E+01	1.6E+01	3.0E+01	5.3E+01	1.7E+01	3.5E+01	1.8E+01	5.0E+01	8.4E+01
Benzo[g,h,i]perylene	1.5E+02	2.0E+02	1.9E+02	2.5E+02	4.5E+02	2.1E+02	3.1E+02	2.4E+02	3.7E+02	6.5E+02
Anthanthrene	2.1E+01	2.2E+01	4.0E+01	5.0E+01	6.3E+01	3.3E+01	4.5E+01	3.2E+01	7.3E+01	1.4E+02
Coronene	8.7E+01	1.3E+02	1.2E+02	1.3E+02	1.8E+02	1.0E+02	1.3E+02	1.5E+02	1.1E+02	1.9E+02

	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72
Sample ID	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72
Start Date	012703	012803	012803	012803	012903	012903	012903	013003	013003
Start Time	1830	1230	820	1800	30	745	1837	30	810
Stop Date	012803	012803	012803	012903	012903	012903	013003	013003	013003
Stop Time	802	800	1734	30	630	1831	30	630	1830
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Surrogate (% Recovery)									
d8-Naphthalene	41.8%	72.1%	21.8%	51.8%	51.9%	38.1%	72.6%	73.2%	49.7%
d10-Fluorene	120.4%	148.6%	61.6%	125.6%	116.5%	92.5%	128.8%	139.2%	102.4%
d10-Fluoranthene	76.9%	75.9%	49.0%	79.1%	79.1%	75.5%	73.9%	76.3%	73.0%
d12-Perylene	100.0%	94.7%	61.9%	100.6%	96.9%	97.7%	96.7%	96.6%	95.3%
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	5.8E+01	1.1E+02	5.6E+01	5.0E+01	5.3E+01	3.8E+01	9.4E+01	6.5E+01	5.1E+01
2-Methylnaphthalene	5.1E+01	1.2E+02	6.2E+01	3.6E+01	5.3E+01	3.7E+01	8.4E+01	5.5E+01	4.6E+01
Azulene	ND	ND	5.3E+00	1.3E+01	ND	8.6E+00	3.1E+01	1.7E+01	ND
1-Methylnaphthalene	2.4E+01	5.2E+01	2.7E+01	1.6E+01	2.3E+01	1.1E+01	3.4E+01	2.4E+01	1.5E+01
Biphenyl	2.6E+01	5.2E+01	1.9E+01	1.7E+01	1.8E+01	1.3E+01	5.3E+01	2.7E+01	2.2E+01
2,7-Dimethylnaphthalene	8.8E+01	1.3E+02	6.0E+01	1.1E+02	1.6E+02	5.4E+01	5.2E+01	3.4E+01	ND
1,3-Dimethylnaphthalene	1.6E+02	2.8E+02	1.0E+02	1.1E+02	2.0E+02	8.5E+01	2.0E+02	1.6E+02	6.3E+01
1,6-Dimethylnaphthalene	2.6E+01	7.0E+01	2.0E+01	1.1E+01	2.2E+01	8.6E+00	2.9E+01	2.2E+01	9.3E+00
1,4-Dimethylnaphthalene	2.4E+01	5.2E+01	4.4E+01	4.1E+01	6.7E+01	1.2E+01	2.9E+01	1.7E+01	3.2E+01
1,5-Dimethylnaphthalene	5.9E+01	6.8E+01	2.2E+01	2.1E+01	3.8E+01	3.0E+01	6.8E+01	4.2E+01	1.3E+01
Acenapthylene	8.3E+01	1.1E+02	3.2E+01	2.5E+01	4.4E+01	2.6E+01	7.6E+01	3.9E+01	2.7E+01
1,2-Dimethylnapthalene	1.6E+02	1.8E+02	5.1E+01	8.8E+01	1.1E+02	6.8E+01	1.0E+02	8.7E+01	5.0E+01
1,8-Dimethylnapthalene	8.3E+01	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Acenapthene	2.1E+01	4.5E+01	1.8E+01	1.5E+01	2.5E+01	ND	ND	3.4E+01	1.3E+01
2,3,5-Trimethylnapthalene	ND	2.2E+02	ND	3.4E+01	ND	ND	ND	ND	3.0E+01
Fluorene	1.3E+02	2.4E+02	6.8E+01	5.4E+01	7.2E+01	3.1E+01	9.4E+01	6.5E+01	1.7E+01
1-Methylfuorene	2.2E+02	4.0E+02	6.2E+01	8.2E+01	8.6E+01	4.8E+01	1.3E+02	9.8E+01	2.3E+01
Dibenzothiophene	3.2E+02	3.2E+02	2.2E+02	1.7E+02	2.3E+02	6.4E+01	1.6E+02	2.4E+02	6.6E+01
Phenanthrene	2.2E+03	2.9E+03	1.1E+03	9.2E+02	1.2E+03	6.5E+02	1.1E+03	9.4E+02	3.2E+02
Anthracene	1.6E+02	1.7E+02	8.4E+01	4.4E+01	9.9E+01	5.8E+01	9.3E+01	8.3E+01	3.7E+01
2-Methyldibenzothiophene	2.5E+02	4.4E+02	1.5E+02	1.8E+02	3.2E+02	1.6E+02	2.1E+02	3.1E+02	1.0E+02
4-Methyldibenzothiophene	3.2E+02	3.9E+02	2.3E+02	1.9E+02	3.4E+02	2.2E+02	2.5E+02	ND	1.2E+02
2-Methylphenanthrene	1.3E+03	1.9E+03	4.9E+02	5.5E+02	8.3E+02	4.6E+02	8.0E+02	9.4E+02	2.1E+02
2-Methylanthracene	7.3E+01	1.0E+02	3.9E+01	3.2E+01	7.0E+01	6.2E+01	7.0E+01	7.3E+01	2.2E+01
4,5-Methylenephenanthrene	2.7E+02	3.6E+02	1.1E+02	7.6E+01	1.4E+02	9.8E+01	1.3E+02	1.4E+02	4.1E+01
1-Methylanthracene	6.2E+02	8.8E+02	2.3E+02	2.4E+02	4.3E+02	2.5E+02	4.1E+02	4.8E+02	1.2E+02
1-Methylphenanthrene	4.9E+02	7.5E+02	2.3E+02	2.1E+02	3.4E+02	2.4E+02	3.2E+02	3.9E+02	1.0E+02
9-Methylanthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
9,10-Dimethylanthracene	4.3E+02	6.0E+02	2.2E+02	1.7E+02	2.9E+02	1.8E+02	2.8E+02	4.6E+02	1.0E+02
Fluoranthene	2.4E+03	3.2E+03	1.6E+03	1.1E+03	1.7E+03	1.7E+03	1.4E+03	1.5E+03	9.7E+02
3,6-Dimethylphenanthrene	4.7E+02	5.0E+02	2.9E+02	2.0E+02	5.7E+02	4.6E+02	ND	5.9E+02	ND
Pyrene	2.6E+03	3.4E+03	1.5E+03	9.0E+02	1.9E+03	1.8E+03	1.6E+03	2.0E+03	1.1E+03
3,6-Dimethylphenanthrene	4.7E+02	5.0E+02	2.9E+02	2.0E+02	5.7E+02	4.6E+02	ND	5.9E+02	ND
Benzo[a]fluorene	4.1E+02	5.0E+02	2.6E+02	1.7E+02	2.9E+02	3.5E+02	3.6E+02	3.7E+02	2.0E+02
Retene	2.3E+02	2.9E+02	3.7E+02	3.4E+02	2.7E+02	1.7E+02	6.6E+02	3.8E+02	2.7E+02
Benzo[b]fluorene	3.4E+02	4.4E+02	2.1E+02	1.3E+02	2.2E+02	2.7E+02	2.7E+02	2.8E+02	1.3E+02
Cyclopenta[c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benz[a]anthracene	7.5E+02	9.4E+02	5.4E+02	2.6E+02	6.3E+02	8.9E+02	1.0E+03	8.6E+02	4.2E+02
Chrysene+Triphenylene	8.6E+02	1.1E+03	7.1E+02	5.3E+02	8.4E+02	9.5E+02	1.2E+03	9.7E+02	8.5E+02
Napthacene	7.9E+01	1.0E+02	6.4E+01	2.7E+01	7.9E+01	9.1E+01	1.0E+02	8.3E+01	4.8E+01
4-Methylchrysene	5.4E+01	6.2E+01	4.5E+01	2.7E+01	5.2E+01	5.5E+01	7.4E+01	7.3E+01	3.5E+01
Benzo[b]fluoranthene	7.9E+02	1.0E+03	7.3E+02	6.1E+02	7.6E+02	9.9E+02	1.4E+03	1.0E+03	8.6E+02
Benzo[k]fluoranthene	5.5E+02	7.1E+02	5.0E+02	3.9E+02	6.1E+02	8.3E+02	1.0E+03	6.6E+02	6.2E+02
Dimethylbenz[a]anthracene	2.9E+01	2.4E+01	2.3E+01	2.3E+01	2.6E+01	6.7E+01	4.9E+01	3.7E+01	2.7E+01
Benzo[e]pyrene	4.2E+02	5.1E+02	3.9E+02	3.2E+02	4.1E+02	5.3E+02	7.2E+02	5.0E+02	4.7E+02
Benzo[a]pyrene	6.9E+02	8.1E+02	5.2E+02	3.4E+02	6.2E+02	7.7E+02	1.1E+03	7.8E+02	2.5E+02
Perylene	9.4E+01	1.2E+02	7.6E+01	4.6E+01	8.3E+01	1.0E+02	1.3E+02	1.1E+02	5.7E+01
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	8.9E+02	1.2E+03	8.0E+02	6.3E+02	8.0E+02	1.2E+03	1.6E+03	1.0E+03	9.9E+02
Dibenz[a,h+ac]anthracene	6.8E+01	8.1E+01	7.1E+01	4.9E+01	5.6E+01	8.2E+01	1.1E+02	7.1E+01	5.2E+01
Benzo[g,h,i]perylene	7.7E+02	1.0E+03	6.9E+02	5.3E+02	6.7E+02	1.0E+03	1.4E+03	8.8E+02	1.0E+03
Anthanthrene	1.9E+02	2.1E+02	1.1E+02	7.1E+01	1.3E+02	1.8E+02	2.6E+02	1.9E+02	6.0E+01
Coronene	4.6E+02	6.0E+02	3.0E+02	2.1E+02	2.8E+02	4.5E+02	8.1E+02	4.4E+02	3.9E+02

Sample ID	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
Start Date	013003	020503	020503	020603	020603	020703
Start Time	1830	700	1825	735	1745	110
Stop Date	013103	020503	020603	020603	020703	020703
Stop Time	1830	1820	735	1740	110	710
Media	Filter	Filter	Filter	Filter	Filter	Filter

Surrogate (% Recovery)

	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
d8-Naphthalene	44.6%	35.5%	40.8%	28.7%	65.6%	73.8%
d10-Fluorene	113.6%	108.6%	126.1%	97.0%	137.8%	149.4%
d10-Fluoranthene	73.1%	75.7%	82.5%	85.7%	76.0%	75.4%
d12-Perylene	92.5%	97.8%	96.3%	98.0%	99.5%	97.9%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	3.0E+01	3.2E+01	7.7E+01	3.0E+01	6.1E+01	5.1E+01
2-Methylnaphthalene	3.2E+01	3.3E+01	6.9E+01	3.0E+01	4.2E+01	3.7E+01
Azulene	ND	ND	7.7E+00	ND	ND	ND
1-Methylnaphthalene	1.0E+01	1.3E+01	2.9E+01	1.4E+01	1.7E+01	1.6E+01
Biphenyl	2.2E+01	1.5E+01	3.1E+01	1.2E+01	1.4E+01	1.6E+01
2,7-Dimethylnaphthalene	ND	2.5E+01	6.8E+01	ND	ND	2.6E+01
1,3-Dimethylnaphthalene	3.8E+01	8.3E+01	2.2E+02	4.9E+01	5.0E+01	4.2E+01
1,6-Dimethylnaphthalene	8.3E+00	1.8E+01	3.1E+01	1.2E+01	1.2E+01	1.3E+01
1,4-Dimethylnaphthalene	2.7E+01	1.2E+01	4.7E+01	1.1E+01	2.4E+01	4.7E+00
1,5-Dimethylnaphthalene	6.4E+00	3.4E+01	6.9E+01	2.8E+01	ND	1.5E+01
Acenapthylene	2.1E+01	2.1E+01	9.1E+01	2.2E+01	1.4E+01	2.7E+01
1,2-Dimethylnapthalene	3.1E+01	9.2E+01	1.7E+02	6.1E+01	2.9E+01	1.8E+01
1,8-Dimethylnapthalene	<BG	<BG	7.9E+01	<BG	<BG	<BG
Acenapthene	7.4E+00	1.6E+01	3.8E+01	1.0E+01	6.9E+00	8.1E+00
2,3,5-Trimethylnapthalene	ND	8.5E+01	ND	ND	ND	ND
Fluorene	1.5E+01	7.9E+01	1.6E+02	4.1E+01	1.7E+01	3.5E+01
1-Methylfuorene	2.1E+01	9.3E+01	2.0E+02	3.8E+01	1.9E+01	3.1E+01
Dibenzothiophene	3.5E+01	2.5E+02	6.5E+02	1.8E+02	3.1E+01	5.7E+01
Phenanthrene	2.6E+02	1.1E+03	2.3E+03	6.3E+02	2.8E+02	4.8E+02
Anthracene	2.5E+01	8.4E+01	2.1E+02	5.7E+01	2.0E+01	3.6E+01
2-Methyldibenzothiophene	4.5E+01	1.7E+02	5.2E+02	8.7E+01	3.6E+01	6.7E+01
4-Methyldibenzothiophene	5.8E+01	1.9E+02	5.2E+02	1.6E+02	6.4E+01	8.0E+01
2-Methylphenanthrene	1.6E+02	5.5E+02	1.5E+03	2.5E+02	1.6E+02	2.5E+02
2-Methylanthracene	1.5E+01	3.3E+01	1.4E+02	3.0E+01	1.2E+01	2.1E+01
4,5-Methylenephenanthrene	3.0E+01	1.1E+02	2.6E+02	5.6E+01	2.4E+01	6.1E+01
1-Methylanthracene	8.2E+01	2.6E+02	8.3E+02	1.4E+02	7.7E+01	1.2E+02
1-Methylphenanthrene	6.4E+01	2.3E+02	6.5E+02	1.1E+02	6.8E+01	1.1E+02
9-Methylanthracene	ND	ND	ND	ND	ND	ND
9,10-Dimethylanthracene	6.9E+01	1.9E+02	6.7E+02	1.2E+02	4.5E+01	1.1E+02
Fluoranthene	6.6E+02	1.5E+03	2.9E+03	1.2E+03	4.5E+02	1.1E+03
3,6-Dimethylphenanthrene	ND	ND	ND	3.2E+02	ND	ND
Pyrene	7.1E+02	1.4E+03	3.4E+03	1.2E+03	4.0E+02	1.2E+03
3,6-Dimethylphenanthrene	ND	ND	ND	3.2E+02	ND	ND
Benzo[a]fluorene	1.2E+02	1.9E+02	5.3E+02	1.9E+02	7.2E+01	2.2E+02
Retene	1.8E+02	9.6E+01	3.8E+02	1.3E+02	1.1E+02	7.3E+01
Benzo[b]fluorene	9.1E+01	1.6E+02	4.6E+02	1.5E+02	5.5E+01	1.8E+02
Cyclopenta[c,d]pyrene	ND	ND	ND	ND	ND	ND
Benz[a]anthracene	3.9E+02	4.6E+02	1.2E+03	4.7E+02	1.2E+02	4.0E+02
Chrysene+Triphenylene	6.4E+02	6.7E+02	1.3E+03	6.7E+02	3.8E+02	8.3E+02
Napthacene	4.8E+01	8.5E+01	1.6E+02	6.2E+01	2.1E+01	3.2E+01
4-Methylchrysene	3.5E+01	4.8E+01	1.1E+02	3.4E+01	2.4E+01	4.0E+01
Benzo[b]fluoranthene	7.1E+02	6.9E+02	1.3E+03	6.8E+02	4.3E+02	8.6E+02
Benzo[k]fluoranthene	4.3E+02	4.4E+02	9.1E+02	4.8E+02	2.8E+02	6.0E+02
Dimethylbenz[a]anthracene	2.0E+01	3.0E+01	6.1E+01	2.3E+01	1.7E+01	1.0E+01
Benzo[e]pyrene	3.5E+02	3.7E+02	6.9E+02	3.8E+02	2.2E+02	4.3E+02
Benzo[a]pyrene	2.5E+02	4.3E+02	1.1E+03	4.3E+02	1.2E+02	2.9E+02
Perylene	4.8E+01	7.1E+01	1.7E+02	6.5E+01	2.2E+01	5.7E+01
3-Methylchloanthrene	ND	1.6E+01	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	7.5E+02	6.6E+02	1.3E+03	7.8E+02	4.4E+02	9.6E+02
Dibenz[a,h+ac]anthracene	4.3E+01	6.0E+01	1.1E+02	6.4E+01	3.4E+01	6.7E+01
Benzo[g,h,i]perylene	7.7E+02	5.9E+02	1.2E+03	7.1E+02	3.8E+02	7.8E+02
Anthanthrene	5.4E+01	9.8E+01	3.0E+02	1.0E+02	3.1E+01	6.6E+01
Coronene	3.1E+02	2.0E+02	4.6E+02	2.4E+02	1.5E+02	3.0E+02

Sample ID	MT 2	MT 3	MT 4	MT 5	MT 6 Back	MT 6	MT 7	MT 8	MT 9
Start Date	032302	032402	032802	032902	033002	033002	033102	040202	040302
Start Time	1906	1914	1920	2016	1809	1809	1936	1927	1924
Stop Date	032402	032502	032902	033002	033102	033102	040102	040302	040402
Stop Time	1800	1740	1901	1706	1802	1802	1750	1758	1813
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Surrogate (% Recovery)									
d8-Naphthalene	65.3%	68.0%	61.4%	58.1%	34.9%	30.9%	51.1%	55.8%	74.6%
d10-Fluorene	100.9%	106.1%	105.9%	92.0%	69.8%	68.0%	74.4%	80.1%	132.3%
d10-Fluoranthene	170.0%	199.2%	208.6%	175.0%	65.7%	70.2%	164.3%	198.8%	108.7%
d12-Perylene	102.5%	97.4%	99.7%	103.3%	50.5%	59.8%	97.0%	113.0%	101.6%
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	6.2E+02	4.3E+02	4.5E+02	2.3E+02	5.3E+02	3.7E+02	6.5E+02	4.3E+02	1.1E+03
2-Methylnaphthalene	7.0E+02	6.5E+02	5.7E+02	3.2E+02	7.1E+02	5.2E+02	9.1E+02	5.5E+02	1.5E+03
Azulene	ND	1.2E+01	ND	4.0E+00	1.9E+00	2.8E+01	3.3E+00	1.5E+00	6.1E+00
1-Methylnaphthalene	2.8E+02	2.5E+02	2.4E+02	1.2E+02	2.8E+02	2.2E+02	3.6E+02	2.4E+02	5.8E+02
Biphenyl	1.5E+02	1.8E+02	1.6E+02	8.6E+01	1.6E+02	1.2E+02	1.6E+02	1.9E+02	3.0E+02
2,7-Dimethylnaphthalene	2.7E+02	2.8E+02	3.3E+02	1.6E+02	2.8E+02	2.6E+02	3.7E+02	3.3E+02	7.5E+02
1,3-Dimethylnaphthalene	2.9E+02	3.0E+02	4.3E+02	1.6E+02	2.8E+02	2.9E+02	4.0E+02	3.6E+02	7.2E+02
1,6-Dimethylnaphthalene	1.5E+02	1.6E+02	2.1E+02	9.5E+01	1.7E+02	1.5E+02	2.3E+02	2.1E+02	4.4E+02
1,4-Dimethylnaphthalene	8.6E+01	1.1E+02	1.3E+02	7.0E+01	9.0E+01	1.1E+02	1.3E+02	1.2E+02	2.1E+02
1,5-Dimethylnaphthalene	3.4E+01	3.5E+01	4.9E+01	2.0E+01	3.3E+01	2.8E+01	4.2E+01	4.8E+01	9.9E+01
Acenapthylene	1.1E+02	2.8E+02	1.3E+02	4.6E+01	8.5E+01	1.4E+02	1.3E+02	2.3E+02	3.8E+02
1,2-Dimethylnapthalene	6.8E+01	8.1E+01	1.1E+02	4.4E+01	6.1E+01	7.0E+01	8.7E+01	8.6E+01	1.5E+02
1,8-Dimethylnapthalene	ND	<BG	<BG	<BG	ND	<BG	ND	ND	ND
Acenapthene	2.2E+02	1.6E+02	1.7E+02	2.2E+02	2.2E+02	2.2E+02	3.4E+02	3.1E+02	3.8E+02
2,3,5-Trimethylnapthalene	4.1E+02	3.6E+02	5.5E+02	2.1E+02	3.8E+02	2.9E+02	6.1E+02	6.8E+02	8.1E+02
Fluorene	1.6E+03	1.3E+03	1.2E+03	9.4E+02	1.1E+03	9.2E+02	2.2E+03	2.1E+03	2.1E+03
1-Methylfuorene	2.2E+03	2.1E+03	1.7E+03	5.6E+02	4.0E+02	5.4E+02	1.2E+03	9.9E+02	1.1E+03
Dibenzothiophene	1.8E+03	2.6E+03	2.0E+03	1.1E+03	1.6E+02	7.1E+02	1.6E+03	2.0E+03	9.4E+02
Phenanthrene	1.7E+04	2.2E+04	1.5E+04	1.4E+04	1.4E+02	7.9E+03	1.8E+04	2.5E+04	9.7E+03
Anthracene	6.0E+02	1.2E+03	5.7E+02	4.3E+02	4.5E+01	2.9E+02	4.5E+02	1.5E+03	4.5E+02
2-Methyldibenzothiophene	1.5E+03	3.1E+03	1.8E+03	1.0E+03	3.7E+01	5.3E+02	9.6E+02	2.3E+03	7.6E+02
4-Methyldibenzothiophene	9.5E+02	2.1E+03	1.3E+03	6.7E+02	1.5E+01	3.8E+02	6.0E+02	1.7E+03	4.7E+02
2-Methylphenanthrene	4.0E+03	7.5E+03	3.7E+03	2.9E+03	2.2E+01	1.3E+03	2.6E+03	5.7E+03	2.0E+03
2-Methylanthracene	6.1E+01	3.5E+02	1.0E+02	1.1E+02	1.4E+01	2.8E+01	5.0E+01	2.6E+02	ND
4,5-Methylenephenanthrene	7.5E+02	1.1E+03	6.3E+02	5.9E+02	6.1E+00	3.4E+02	6.2E+02	1.5E+03	5.0E+02
1-Methylanthracene	2.0E+03	3.9E+03	2.0E+03	1.5E+03	1.0E+01	6.8E+02	1.2E+03	3.4E+03	9.5E+02
1-Methylphenanthrene	1.7E+03	3.1E+03	1.7E+03	1.3E+03	7.2E+00	5.8E+02	1.0E+03	2.6E+03	8.6E+02
9-Methylanthracene	ND	9.5E+01	4.3E+01	2.9E+01	<BG	1.4E+01	2.0E+01	6.1E+01	ND
9,10-Dimethylanthracene	1.2E+03	2.7E+03	1.6E+03	1.4E+03	<BG	3.2E+02	8.8E+02	1.5E+03	5.4E+02
Fluoranthene	4.0E+03	4.8E+03	4.4E+03	5.8E+03	<BG	1.9E+03	5.2E+03	1.1E+04	2.3E+03
3,6-Dimethylphenanthrene	1.2E+02	4.8E+02	3.9E+02	2.5E+02	ND	4.0E+01	2.7E+02	7.1E+02	ND
Pyrene	4.0E+03	5.1E+03	3.8E+03	4.0E+03	<BG	1.3E+03	3.4E+03	8.7E+03	1.8E+03
3,6-Dimethylphenanthrene	1.2E+02	4.8E+02	3.9E+02	2.5E+02	ND	4.0E+01	2.7E+02	7.1E+02	ND
Benzo[a]fluorene	1.2E+02	2.2E+02	1.9E+02	1.4E+02	ND	4.9E+01	1.1E+02	4.4E+02	6.5E+01
Retene	2.1E+02	3.3E+02	3.5E+02	2.6E+02	ND	7.4E+01	1.7E+02	3.8E+02	5.7E+01
Benzo[b]fluorene	1.3E+02	2.4E+02	1.7E+02	1.2E+02	ND	5.1E+01	1.4E+02	5.5E+02	6.4E+01
Cyclopenta[c,d]pyrene	3.0E+00	1.3E+01	4.0E+00	2.4E+00	ND	3.8E+00	1.7E+00	8.0E+01	7.9E-01
Benz[a]anthracene	ND	3.4E+01	9.3E+01	2.4E+01	<BG	7.4E+01	1.8E+01	2.2E+02	3.2E+00
Chrysene+Triphenylene	8.2E+01	2.3E+02	2.1E+02	2.0E+02	1.4E+00	6.5E+01	1.4E+02	9.7E+02	4.5E+01
Napthacene	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Methylchrysene	ND	5.7E+00	2.8E+00	4.9E+00	<BG	1.1E+00	7.6E+00	1.8E+01	2.0E+00
Benzo[b]fluoranthene	3.1E+00	1.5E+01	7.9E+00	2.6E+01	3.1E+00	7.4E+00	3.4E+01	7.4E+01	2.8E+00
Benzo[k]fluoranthene	ND	4.1E+00	ND	6.2E+00	<BG	<BG	5.9E+00	1.8E+01	<BG
Dimethylbenz[a]anthracene	ND	ND	ND	ND	<BG	ND	ND	ND	ND
Benzo[e]pyrene	<BG	5.0E+00	2.1E+00	9.7E+00	2.0E+00	3.0E+00	1.4E+01	2.0E+01	1.3E+00
Benzo[a]pyrene	ND	ND	ND	ND	<BG	<BG	ND	1.0E+01	ND
Perylene	ND	ND	ND	ND	<BG	ND	ND	ND	ND
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	ND	<BG	ND	7.6E+00	ND
Dibenz[a,h+ac]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	6.7E-01	1.8E+00	ND	6.9E+00	ND
Anthanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Coronene	ND	ND	ND	ND	ND	ND	ND	ND	ND

	MT 11	MT 12	MT 13	MT 16	MT 17	MT 18	MT 19	MT 20
Sample ID	MT 11	MT 12	MT 13	MT 16	MT 17	MT 18	MT 19	MT 20
Start Date	040802	040902	041002	041402	041502	041602	041602	041702
Start Time	1720	1835	1905	1555	1834	0846	1957	0855
Stop Date	040902	041002	041102	041502	041602	041602	041702	041702
Stop Time	1808	1823	1826	1802	742	1854	735	1759
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Surrogate (% Recovery)								
d8-Naphthalene	48.4%	50.9%	39.0%	56.5%	46.6%	59.6%	38.9%	39.9%
d10-Fluorene	1117.4%	82.1%	70.7%	78.0%	76.5%	105.9%	68.2%	48.8%
d10-Fluoranthene	188.7%	111.0%	103.9%	189.3%	121.4%	176.7%	161.6%	55.6%
d12-Perylene	105.8%	101.1%	62.2%	90.1%	87.7%	98.5%	94.8%	41.8%
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	3.1E+02	3.1E+02	1.7E+02	2.6E+02	2.3E+03	5.0E+02	3.6E+03	2.4E+02
2-Methylnaphthalene	5.4E+02	3.6E+02	2.5E+02	2.9E+02	3.3E+03	6.8E+02	4.5E+03	3.2E+02
Azulene	1.1E+00	8.2E-01	ND	6.0E-01	1.6E+01	1.7E+01	ND	8.2E+00
1-Methylnaphthalene	2.4E+02	1.3E+02	8.7E+01	1.2E+02	1.4E+03	2.7E+02	1.9E+03	1.2E+02
Biphenyl	1.9E+02	8.8E+01	6.7E+01	6.1E+01	8.6E+02	2.1E+02	1.0E+03	1.1E+02
2,7-Dimethylnaphthalene	4.2E+02	1.6E+02	1.4E+02	1.6E+02	1.8E+03	3.4E+02	2.1E+03	1.7E+02
1,3-Dimethylnaphthalene	4.6E+02	1.6E+02	1.4E+02	1.4E+02	1.9E+03	3.3E+02	2.5E+03	1.9E+02
1,6-Dimethylnaphthalene	2.8E+02	8.6E+01	7.4E+01	8.9E+01	1.1E+03	2.1E+02	1.4E+03	1.0E+02
1,4-Dimethylnaphthalene	2.1E+02	8.4E+01	5.5E+01	5.5E+01	7.1E+02	4.1E+02	9.3E+02	1.1E+02
1,5-Dimethylnaphthalene	2.4E+02	2.1E+01	1.3E+01	1.4E+01	1.8E+02	4.4E+01	2.6E+02	2.1E+01
Acenapthylene	1.0E+02	1.3E+02	1.2E+02	4.6E+01	7.8E+02	9.3E+01	1.4E+03	4.8E+01
1,2-Dimethylnapthalene	9.8E+01	3.3E+01	4.1E+01	3.3E+01	4.0E+02	7.7E+01	5.7E+02	4.8E+01
1,8-Dimethylnapthalene	<BG	ND	<BG	ND	<BG	ND	ND	<BG
Acenapthene	6.5E+02	1.4E+02	6.5E+01	2.6E+02	3.2E+03	5.7E+02	5.0E+03	2.0E+02
2,3,5-Trimethylnapthalene	9.4E+02	2.1E+02	1.4E+02	2.2E+02	3.4E+03	4.2E+02	4.8E+03	1.5E+02
Fluorene	2.5E+03	9.4E+02	3.5E+02	9.1E+02	1.2E+04	2.0E+03	2.0E+04	7.3E+02
1-Methylfuorene	1.4E+03	6.3E+02	4.5E+02	4.5E+02	3.5E+03	6.7E+02	4.9E+03	2.9E+02
Dibenzothiophene	2.4E+03	1.2E+03	9.4E+02	1.6E+03	5.0E+03	1.7E+03	6.2E+03	9.4E+02
Phenanthrene	2.4E+04	1.5E+04	1.1E+04	2.4E+04	7.1E+04	2.3E+04	7.9E+04	1.4E+04
Anthracene	7.7E+02	7.1E+02	7.1E+02	9.4E+02	2.9E+03	7.7E+02	2.9E+03	5.1E+02
2-Methyldibenzothiophene	2.9E+03	1.1E+03	1.4E+03	2.1E+03	3.1E+03	2.0E+03	3.5E+03	8.1E+02
4-Methyldibenzothiophene	2.1E+03	7.7E+02	1.0E+03	1.5E+03	1.3E+03	2.0E+03	1.7E+03	7.2E+02
2-Methylphenanthrene	6.1E+03	3.6E+03	3.9E+03	6.0E+03	8.8E+03	7.0E+03	9.4E+03	3.2E+03
2-Methylanthracene	3.5E+03	1.5E+02	2.3E+02	6.1E+01	4.3E+02	1.3E+02	4.1E+02	5.7E+01
4,5-Methylenephenanthrene	1.0E+03	8.5E+02	7.0E+02	1.2E+03	2.4E+03	1.7E+03	2.3E+03	1.0E+03
1-Methylanthracene	3.2E+03	1.9E+03	2.1E+03	2.9E+03	4.3E+03	4.1E+03	4.9E+03	1.7E+03
1-Methylphenanthrene	2.8E+03	1.5E+03	1.7E+03	2.5E+03	3.6E+03	3.2E+03	3.8E+03	1.5E+03
9-Methylanthracene	6.2E+01	3.8E+01	4.7E+01	6.5E+01	8.1E+01	1.1E+02	8.0E+01	3.2E+01
9,10-Dimethylanthracene	2.6E+03	9.5E+02	1.1E+03	1.8E+03	2.3E+03	2.6E+03	3.0E+03	8.2E+02
Fluoranthene	7.8E+03	5.3E+03	3.1E+03	9.0E+03	1.7E+04	2.4E+04	1.7E+04	1.1E+04
3,6-Dimethylphenanthrene	6.7E+02	ND	1.9E+02	4.2E+02	ND	ND	5.1E+02	1.1E+02
Pyrene	5.9E+03	3.3E+03	3.8E+03	6.0E+03	9.9E+03	1.7E+04	1.1E+04	5.7E+03
3,6-Dimethylphenanthrene	6.7E+02	ND	1.9E+02	4.2E+02	ND	ND	5.1E+02	1.1E+02
Benzo[a]fluorene	6.0E+02	1.0E+02	1.2E+02	1.9E+02	2.7E+02	4.6E+02	2.8E+02	1.1E+02
Retene	5.3E+02	1.6E+02	1.7E+02	3.7E+02	3.6E+02	8.7E+02	4.7E+02	2.4E+02
Benzo[b]fluorene	2.8E+02	1.1E+02	1.3E+02	1.6E+02	2.4E+02	2.9E+02	2.8E+02	1.0E+02
Cyclopenta[c,d]pyrene	2.3E+02	1.3E+01	9.6E+00	3.7E+00	6.3E+01	1.6E+01	3.8E+01	9.1E+00
Benz[a]anthracene	4.2E+01	1.8E+01	2.1E+01	3.7E+01	1.0E+02	1.1E+02	5.9E+01	2.3E+01
Chrysene+Triphenylene	4.9E+02	1.1E+02	1.1E+02	2.9E+02	3.3E+02	8.6E+02	2.7E+02	2.1E+02
Napthacene	8.2E+02	ND	1.7E+00	ND	8.3E+00	1.3E+01	1.3E+01	ND
4-Methylchrysene	3.8E+01	1.8E+00	1.9E+00	6.4E+00	9.7E+00	2.2E+01	1.1E+01	4.9E+00
Benzo[b]fluoranthene	4.5E+01	1.4E+01	6.1E+00	4.6E+01	2.1E+01	1.2E+02	1.5E+01	2.2E+01
Benzo[k]fluoranthene	4.2E+01	ND	<BG	8.1E+00	6.7E+00	3.4E+01	5.1E+00	4.8E+00
Dimethylbenz[a]anthracene	3.5E+00	ND	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	1.3E+01	4.9E+00	3.4E+00	1.9E+01	9.0E+00	5.1E+01	4.6E+00	8.5E+00
Benzo[a]pyrene	<BG	ND	4.2E+00	ND	5.2E+00	ND	ND	6.8E+00
Perylene	<BG	ND	ND	ND	ND	ND	ND	ND
3-Methylchloanthrene	<BG	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	<BG	ND	1.6E+00	ND	ND	ND	ND	ND
Dibenz[a,h+ac]anthracene	4.8E-01	ND	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	7.8E-01	ND	3.3E+00	ND	ND	ND	ND	ND
Anthanthrene	<BG	ND	ND	ND	ND	ND	ND	ND
Coronene	<BG	ND	ND	ND	ND	ND	ND	ND

	MT 21	MT 22	MT 23	MT 24	MT 25	MT 26	MT 27	MT 28
Sample ID	MT 21	MT 22	MT 23	MT 24	MT 25	MT 26	MT 27	MT 28
Start Date	041702	042202	042302	042302	042402	042402	042502	042502
Start Time	1856	1833	0834	1942	0913	1926	0855	1840
Stop Date	041802	042302	042302	042402	042402	042502	042502	042602
Stop Time	1745	808	1839	807	1933	800	1814	1843
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF

Surrogate (% Recovery)

	MT 21	MT 22	MT 23	MT 24	MT 25	MT 26	MT 27	MT 28
d8-Naphthalene	42.5%	54.7%	57.8%	77.2%	64.8%	58.5%	56.9%	56.0%
d10-Fluorene	73.5%	370.0%	146.0%	152.4%	119.8%	121.1%	124.8%	107.0%
d10-Fluoranthene	175.6%	105.8%	130.6%	143.7%	140.2%	177.1%	182.8%	197.4%
d12-Perylene	105.0%	103.2%	104.4%	93.4%	90.2%	96.5%	101.8%	96.2%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	3.4E+02	1.9E+03	8.1E+02	6.2E+03	8.2E+02	1.3E+03	8.1E+02	2.8E+02
2-Methylnaphthalene	7.0E+02	2.7E+03	1.3E+03	1.1E+04	1.2E+03	1.9E+03	1.2E+03	4.2E+02
Azulene	1.4E+01	1.2E+01	3.2E+00	3.5E+01	4.7E+00	4.5E+00	2.7E+00	1.7E+00
1-Methylnaphthalene	2.9E+02	1.2E+03	4.8E+02	4.8E+03	5.2E+02	8.2E+02	5.3E+02	1.8E+02
Biphenyl	2.0E+02	6.9E+02	3.4E+02	2.6E+03	3.7E+02	4.5E+02	2.8E+02	1.3E+02
2,7-Dimethylnaphthalene	4.8E+02	1.8E+03	8.1E+02	6.0E+03	7.1E+02	1.1E+03	6.7E+02	3.5E+02
1,3-Dimethylnaphthalene	5.1E+02	2.0E+03	7.5E+02	7.1E+03	8.1E+02	1.2E+03	7.5E+02	3.6E+02
1,6-Dimethylnaphthalene	3.0E+02	1.1E+03	4.9E+02	4.0E+03	4.9E+02	6.9E+02	4.2E+02	2.3E+02
1,4-Dimethylnaphthalene	2.4E+02	8.2E+02	2.4E+02	2.1E+03	2.7E+02	3.8E+02	2.6E+02	1.1E+02
1,5-Dimethylnaphthalene	5.1E+01	9.2E+02	7.8E+01	8.2E+02	1.1E+02	1.4E+02	8.8E+01	4.9E+01
Acenapthylene	1.3E+02	9.2E+02	2.3E+02	2.5E+02	2.0E+02	1.9E+02	2.2E+02	4.8E+01
1,2-Dimethylnapthalene	1.1E+02	4.0E+02	1.8E+02	1.4E+03	1.7E+02	2.3E+02	1.8E+02	8.0E+01
1,8-Dimethylnapthalene	2.1E+01	3.6E+01	<BG	<BG	<BG	<BG	<BG	<BG
Acenapthene	7.1E+02	7.6E+02	5.9E+02	4.8E+03	7.3E+02	5.4E+02	6.6E+02	2.3E+02
2,3,5-Trimethylnapthalene	6.7E+02	2.1E+03	1.2E+03	6.0E+03	1.5E+03	1.4E+03	1.7E+03	5.1E+02
Fluorene	2.9E+03	3.4E+03	3.4E+03	7.5E+03	4.7E+03	2.8E+03	4.1E+03	1.4E+03
1-Methylfuorene	7.3E+02	1.1E+03	1.4E+03	2.1E+03	1.6E+03	9.0E+02	1.8E+03	1.4E+03
Dibenzothiophene	1.3E+03	8.1E+02	1.3E+03	1.2E+03	1.4E+03	8.4E+02	1.4E+03	1.5E+03
Phenanthrene	1.6E+04	7.5E+03	1.4E+04	1.2E+04	1.3E+04	6.9E+03	1.4E+04	1.8E+04
Anthracene	5.4E+02	3.9E+02	6.5E+02	5.3E+02	4.5E+02	7.2E+03	5.2E+02	7.5E+02
2-Methyldibenzothiophene	1.1E+03	5.9E+02	8.3E+02	1.1E+03	9.6E+02	4.6E+02	9.3E+02	1.1E+03
4-Methyldibenzothiophene	9.7E+02	3.7E+02	5.0E+02	6.7E+02	6.2E+02	3.0E+02	5.7E+02	6.6E+02
2-Methylphenanthrene	4.6E+03	1.4E+03	2.6E+03	2.6E+03	2.3E+03	1.2E+03	2.7E+03	3.6E+03
2-Methylanthracene	1.5E+02	5.5E+01	4.5E+01	3.9E+01	ND	1.0E+01	9.4E+01	5.4E+01
4,5-Methylenephenanthrene	1.3E+03	3.7E+02	5.9E+02	5.3E+02	4.5E+02	2.5E+02	5.2E+02	7.1E+02
1-Methylanthracene	2.5E+03	6.8E+02	1.3E+03	1.3E+03	1.2E+03	6.1E+02	1.3E+03	1.8E+03
1-Methylphenanthrene	2.1E+03	5.9E+02	1.1E+03	1.1E+03	9.7E+02	5.2E+02	1.2E+03	1.5E+03
9-Methylanthracene	6.0E+01	ND	ND	ND	ND	ND	ND	3.6E+01
9,10-Dimethylanthracene	1.7E+03	3.5E+02	8.6E+02	9.3E+02	6.8E+02	5.4E+02	1.4E+03	1.8E+03
Fluoranthene	1.5E+04	1.6E+03	4.2E+03	2.7E+03	3.3E+03	2.8E+03	4.8E+03	5.9E+03
3,6-Dimethylphenanthrene	3.4E+02	3.7E+01	7.9E+01	ND	4.9E+01	1.1E+02	3.0E+02	2.4E+02
Pyrene	9.4E+03	1.3E+03	2.9E+03	2.4E+03	2.1E+03	2.0E+03	3.9E+03	5.2E+03
3,6-Dimethylphenanthrene	3.4E+02	3.7E+01	7.9E+01	ND	4.9E+01	1.1E+02	3.0E+02	2.4E+02
Benzo[a]fluorene	2.9E+02	3.6E+01	7.4E+01	5.0E+01	1.3E+02	1.2E+02	1.1E+02	1.7E+02
Retene	3.7E+02	3.7E+01	9.3E+01	6.8E+01	9.4E+01	1.1E+02	2.4E+02	1.8E+02
Benzo[b]fluorene	2.5E+02	4.8E+01	4.8E+01	8.0E+01	6.1E+01	1.3E+02	1.2E+02	1.8E+02
Cyclopenta[c,d]pyrene	7.9E+00	<BG	ND	ND	ND	ND	ND	9.8E+00
Benz[a]anthracene	5.8E+01	4.7E+00	4.4E+00	ND	3.0E+00	6.4E+00	2.4E+01	ND
Chrysene+Triphenylene	3.2E+02	4.1E+00	2.6E+01	2.9E+01	3.5E+01	1.5E+02	1.2E+01	1.3E+02
Napthacene	ND	5.1E+01	ND	ND	ND	ND	6.0E+00	ND
4-Methylchrysene	5.4E+00	<BG	ND	ND	5.4E+00	1.2E+01	5.6E+00	3.5E+00
Benzo[b]fluoranthene	1.3E+01	<BG	ND	ND	1.2E+01	5.4E+01	2.5E+01	6.2E+00
Benzo[k]fluoranthene	ND	<BG	ND	ND	<BG	1.3E+01	ND	ND
Dimethylbenz[a]anthracene	ND	<BG	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	2.8E+00	<BG	ND	ND	ND	2.5E+01	1.6E+01	ND
Benzo[a]pyrene	ND	<BG	ND	ND	ND	ND	ND	ND
Perylene	ND	<BG	ND	ND	ND	ND	ND	ND
3-Methylchloanthrene	ND	<BG	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	ND	<BG	ND	ND	ND	ND	ND	ND
Dibenz[a,h+ac]anthracene	ND	<BG	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	<BG	ND	ND	ND	ND	ND	ND
Anthanthrene	ND	<BG	ND	ND	ND	ND	ND	ND
Coronene	ND	<BG	ND	ND	ND	ND	ND	ND

Sample ID	MT 29	MT 30	MT 31	MT 32	MT 33	MT 34
Start Date	042602	042702	042802	042902	070902	071002
Start Time	1905	1710	1655	1734	1705	1845
Stop Date	042702	042802	042902	043002	071002	071102
Stop Time	1700	1645	1720	1704	1745	1805
Media	PUF	PUF	PUF	PUF	PUF	PUF

Surrogate (% Recovery)						
d8-Naphthalene	63.3%	69.1%	56.4%	60.2%	66.1%	77.3%
d10-Fluorene	101.1%	102.1%	126.3%	124.8%	141.0%	130.5%
d10-Fluoranthene	198.5%	113.3%	124.5%	252.0%	170.2%	142.4%
d12-Perylene	92.7%	99.1%	107.5%	90.3%	110.3%	117.5%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	2.0E+02	4.1E+02	4.9E+02	3.1E+02	9.6E+01	1.2E+02
2-Methylnaphthalene	2.8E+02	9.0E+02	5.8E+02	4.8E+02	1.5E+02	1.6E+02
Azulene	1.1E+01	2.8E+00	1.6E+00	2.2E+00	2.1E+00	2.2E+00
1-Methylnaphthalene	1.0E+02	4.1E+02	2.3E+02	1.9E+02	7.0E+01	7.2E+01
Biphenyl	8.5E+01	2.7E+02	1.4E+02	1.6E+02	4.6E+01	5.0E+01
2,7-Dimethylnaphthalene	1.4E+02	6.7E+02	3.0E+02	3.7E+02	1.1E+02	1.1E+02
1,3-Dimethylnaphthalene	1.7E+02	7.3E+02	3.0E+02	3.5E+02	1.0E+02	1.5E+02
1,6-Dimethylnaphthalene	7.8E+01	4.5E+02	1.8E+02	2.4E+02	5.5E+01	7.5E+01
1,4-Dimethylnaphthalene	5.2E+01	2.6E+02	1.1E+02	1.2E+02	5.4E+01	6.2E+01
1,5-Dimethylnaphthalene	1.9E+01	8.5E+01	2.8E+01	4.8E+01	1.1E+01	1.6E+01
Acenapthylene	4.3E+01	1.4E+02	1.9E+02	4.2E+01	5.8E+01	4.6E+01
1,2-Dimethylnapthalene	5.1E+01	1.3E+02	7.0E+01	7.6E+01	2.5E+01	2.9E+01
1,8-Dimethylnapthalene	<BG	ND	<BG	<BG	ND	<BG
Acenapthene	1.1E+02	3.1E+02	2.2E+02	3.4E+02	1.4E+02	2.3E+02
2,3,5-Trimethylnapthalene	1.5E+02	8.0E+02	4.5E+02	7.6E+02	1.6E+02	1.8E+02
Fluorene	6.1E+02	1.8E+03	1.3E+03	1.8E+03	6.3E+02	7.9E+02
1-Methylfuorene	8.2E+02	1.4E+03	6.8E+02	1.2E+03	3.7E+02	3.6E+02
Dibenzothiophene	1.5E+03	1.9E+03	8.9E+02	1.0E+03	7.1E+02	7.1E+02
Phenanthrene	1.6E+04	2.3E+04	1.1E+04	1.4E+04	1.2E+04	9.8E+03
Anthracene	6.1E+02	8.7E+02	4.5E+02	4.7E+02	5.7E+02	5.4E+02
2-Methyldibenzothiophene	1.6E+03	1.3E+03	7.4E+02	8.2E+02	9.9E+02	6.8E+02
4-Methyldibenzothiophene	1.0E+03	8.1E+02	4.6E+02	5.0E+02	8.3E+02	5.1E+02
2-Methylphenanthrene	4.2E+03	3.2E+03	2.5E+03	2.8E+03	4.3E+03	2.1E+03
2-Methylanthracene	1.4E+02	1.3E+02	9.4E+01	1.9E+01	1.4E+02	8.8E+01
4,5-Methylenephenanthrene	7.3E+02	8.5E+02	5.5E+02	4.8E+02	1.2E+03	5.9E+02
1-Methylanthracene	2.1E+03	1.7E+03	1.2E+03	1.3E+03	2.2E+03	1.1E+03
1-Methylphenanthrene	1.8E+03	1.4E+03	1.1E+03	1.1E+03	1.9E+03	9.6E+02
9-Methylanthracene	4.9E+01	3.2E+01	2.6E+01	ND	4.8E+01	2.3E+01
9,10-Dimethylanthracene	2.1E+03	8.1E+02	7.5E+02	1.8E+03	1.4E+03	6.2E+02
Fluoranthene	5.5E+03	5.1E+03	3.4E+03	6.3E+03	1.2E+04	3.9E+03
3,6-Dimethylphenanthrene	3.4E+02	1.7E+02	1.5E+02	2.0E+02	1.3E+02	4.4E+01
Pyrene	5.0E+03	3.1E+03	2.3E+03	4.3E+03	6.3E+03	2.6E+03
3,6-Dimethylphenanthrene	3.4E+02	1.7E+02	1.5E+02	2.0E+02	1.3E+02	4.4E+01
Benzo[a]fluorene	1.4E+02	1.1E+02	8.7E+01	1.2E+02	1.6E+02	7.1E+01
Retene	2.4E+02	2.0E+02	1.1E+02	1.9E+02	2.4E+02	1.2E+02
Benzo[b]fluorene	1.5E+02	1.3E+02	8.7E+01	8.7E+01	1.6E+02	8.0E+01
Cyclopenta[c,d]pyrene	8.0E+00	1.4E+01	1.1E+01	ND	1.3E+01	6.5E+00
Benz[a]anthracene	1.1E+01	3.4E+01	2.2E+01	ND	2.5E+01	1.3E+01
Chrysene+Triphenylene	1.9E+02	1.6E+02	8.8E+01	1.5E+02	1.9E+02	8.0E+01
Napthacene	3.1E+02	3.7E+02	ND	ND	ND	ND
4-Methylchrysene	7.7E+00	7.5E+00	5.5E+00	4.3E+00	2.8E+00	1.6E+00
Benzo[b]fluoranthene	2.3E+01	1.2E+01	1.3E+01	6.0E+00	9.8E+00	6.5E+00
Benzo[k]fluoranthene	ND	2.5E+00	4.0E+00	3.3E+00	1.8E+00	<BG
Dimethylbenz[a]anthracene	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	9.4E+00	4.0E+00	5.6E+00	ND	3.7E+00	3.3E+00
Benzo[a]pyrene	4.2E+00	ND	ND	ND	<BG	ND
Perylene	ND	ND	ND	ND	ND	ND
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	ND	ND
Dibenz[a,h+ac]anthracene	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	ND	ND
Anthanthrene	ND	ND	ND	ND	ND	ND
Coronene	ND	ND	ND	ND	ND	ND

	MT 35	MT 37	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43
Sample ID	MT 35	MT 37	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43
Start Date	071102	071302	071402	071502	071602	071702	071802	071902
Start Time	1915	1923	1921	1903	1850	1905	1853	1935
Stop Date	071202	071402	071502	071602	071702	071802	071902	072002
Stop Time	1720	1811	1757	1754	1801	1804	1850	1828
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF

Surrogate (% Recovery)

	MT 35	MT 37	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43
d8-Naphthalene	77.4%	68.3%	83.3%	77.6%	63.1%	60.2%	67.8%	84.3%
d10-Fluorene	112.3%	6541.3%	131.8%	132.4%	138.2%	130.6%	124.7%	165.1%
d10-Fluoranthene	203.0%	143.7%	177.9%	137.3%	206.7%	151.8%	188.5%	192.9%
d12-Perylene	114.4%	118.0%	121.6%	111.4%	122.8%	112.2%	125.0%	133.4%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	1.9E+02	1.4E+02	1.3E+02	1.1E+02	1.4E+02	1.2E+02	3.1E+02	2.8E+02
2-Methylnaphthalene	2.4E+02	1.4E+02	1.6E+02	1.6E+02	1.6E+02	1.6E+02	4.4E+02	3.5E+02
Azulene	2.1E+00	1.1E+00	2.2E+00	3.7E+00	ND	ND	3.7E+01	3.9E+00
1-Methylnaphthalene	8.6E+01	5.8E+01	6.0E+01	6.5E+01	6.8E+01	6.9E+01	2.0E+02	1.5E+02
Biphenyl	8.8E+01	4.6E+01	5.5E+01	5.1E+01	6.0E+01	4.0E+01	1.1E+02	8.8E+01
2,7-Dimethylnaphthalene	1.5E+02	7.5E+01	1.1E+02	1.1E+02	1.3E+02	8.2E+01	1.5E+02	2.5E+02
1,3-Dimethylnaphthalene	1.2E+02	5.9E+01	9.4E+01	9.9E+01	1.1E+02	8.3E+01	2.8E+02	1.9E+02
1,6-Dimethylnaphthalene	6.7E+01	3.5E+01	5.4E+01	5.0E+01	5.7E+01	4.4E+01	1.6E+02	1.1E+02
1,4-Dimethylnaphthalene	7.1E+01	4.5E+01	6.6E+01	5.6E+01	4.8E+01	4.2E+01	9.3E+01	7.2E+01
1,5-Dimethylnaphthalene	1.5E+01	7.6E+00	1.1E+01	1.2E+01	9.4E+00	9.1E+00	6.3E+01	2.3E+01
Acenapthylene	4.3E+01	3.4E+01	3.0E+01	2.7E+01	4.2E+01	2.8E+01	1.3E+02	7.9E+01
1,2-Dimethylnapthalene	4.8E+01	1.6E+01	2.2E+01	3.3E+01	2.5E+01	2.0E+01	8.2E+01	4.6E+01
1,8-Dimethylnapthalene	2.2E+01	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Acenapthene	1.4E+02	8.4E+01	1.6E+02	2.4E+02	2.7E+02	2.1E+02	5.4E+02	3.6E+02
2,3,5-Trimethylnapthalene	1.1E+02	6.6E+01	1.1E+02	1.0E+02	1.6E+02	9.8E+01	2.4E+02	1.9E+02
Fluorene	6.9E+02	3.9E+02	5.3E+02	8.0E+02	1.0E+03	5.8E+02	1.3E+03	1.0E+03
1-Methylfuorene	3.4E+02	2.3E+02	2.2E+02	1.8E+02	3.3E+02	1.7E+02	2.9E+02	2.2E+02
Dibenzothiophene	1.2E+03	9.2E+02	6.0E+02	7.5E+02	1.1E+03	4.2E+02	6.9E+02	4.9E+02
Phenanthrene	1.6E+04	1.6E+04	8.7E+03	1.2E+04	1.7E+04	5.8E+03	9.9E+03	6.5E+03
Anthracene	7.3E+02	4.8E+02	4.9E+02	6.9E+02	8.3E+02	2.3E+02	3.1E+02	2.1E+02
2-Methyldibenzothiophene	1.4E+03	7.2E+02	6.2E+02	5.2E+02	1.3E+03	3.9E+02	6.9E+02	4.4E+02
4-Methyldibenzothiophene	1.2E+03	5.2E+02	5.5E+02	4.8E+02	1.3E+03	3.5E+02	6.0E+02	4.0E+02
2-Methylphenanthrene	5.2E+03	2.0E+03	2.7E+03	2.3E+03	7.0E+03	1.8E+03	2.9E+03	1.9E+03
2-Methylanthracene	2.1E+02	3.8E+01	1.1E+02	7.7E+01	3.1E+02	4.6E+01	5.2E+01	4.3E+01
4,5-Methylenephenanthrene	1.2E+03	7.0E+02	7.7E+02	8.7E+02	2.3E+03	5.6E+02	8.1E+02	5.2E+02
1-Methylanthracene	2.7E+03	1.0E+03	1.4E+03	1.1E+03	3.7E+03	9.3E+02	1.4E+03	1.0E+03
1-Methylphenanthrene	2.4E+03	8.7E+02	1.2E+03	1.1E+03	3.2E+03	8.8E+02	1.3E+03	9.2E+02
9-Methylanthracene	6.1E+01	2.3E+01	2.7E+01	1.8E+01	7.1E+01	2.0E+01	3.5E+01	6.7E+00
9,10-Dimethylanthracene	1.8E+03	5.4E+02	1.1E+03	8.5E+02	2.0E+03	8.4E+02	1.2E+03	7.8E+02
Fluoranthene	1.0E+04	6.2E+03	8.5E+03	1.2E+04	1.9E+04	9.6E+03	1.0E+04	9.3E+03
3,6-Dimethylphenanthrene	3.0E+02	4.2E+01	1.3E+02	8.3E+01	2.0E+02	8.6E+01	2.1E+01	9.7E+01
Pyrene	7.4E+03	2.8E+03	4.9E+03	5.8E+03	1.2E+04	5.1E+03	5.4E+03	5.1E+03
3,6-Dimethylphenanthrene	3.0E+02	4.2E+01	1.3E+02	8.3E+01	2.0E+02	8.6E+01	2.1E+01	9.7E+01
Benzo[a]fluorene	2.2E+02	6.7E+01	1.2E+02	1.1E+02	3.5E+02	1.3E+02	1.3E+02	1.3E+02
Retene	3.6E+02	1.4E+02	2.4E+02	1.8E+02	4.3E+02	2.2E+02	2.4E+02	2.6E+02
Benzo[b]fluorene	2.0E+02	8.5E+01	1.2E+02	1.1E+02	3.7E+02	1.2E+02	1.9E+02	1.3E+02
Cyclopenta[c,d]pyrene	1.9E+01	8.6E+00	1.5E+01	9.5E+00	5.8E+01	1.7E+01	1.5E+01	1.4E+01
Benz[a]anthracene	4.2E+01	1.5E+01	3.0E+01	1.4E+01	1.5E+02	2.7E+01	2.1E+01	2.1E+01
Chrysene+Triphenylene	2.3E+02	1.0E+02	1.5E+02	1.6E+02	4.4E+02	1.9E+02	1.7E+02	1.8E+02
Napthacene	3.5E+00	ND	ND	ND	ND	ND	ND	ND
4-Methylchrysene	6.0E+00	2.1E+00	3.6E+00	2.4E+00	1.4E+01	4.3E+00	9.5E+00	5.0E+00
Benzo[b]fluoranthene	1.0E+01	8.4E+00	2.1E+01	4.2E+00	5.4E+01	5.9E+00	6.2E+00	2.1E+01
Benzo[k]fluoranthene	1.9E+00	<BG	3.8E+00	ND	8.7E+00	<BG	<BG	5.1E+00
Dimethylbenz[a]anthracene	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	4.3E+00	2.7E+00	8.4E+00	1.6E+00	1.5E+01	2.8E+00	ND	8.0E+00
Benzo[a]pyrene	ND	ND	ND	ND	ND	ND	ND	ND
Perylene	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND	1.7E+00	ND
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND
Dibenz[a,h+ac]anthracene	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	ND	ND	ND	ND
Anthanthrene	ND	ND	ND	ND	ND	ND	1.1E+00	ND
Coronene	ND	ND	ND	ND	ND	ND	ND	ND

Sample ID	MT 44	MT 45	MT 46	MT 47	MT 49 Back	MT 49	MT 50	MT 50 Back	MT 51
Start Date	072002	072102	072202	072302	072902	072902	072902	072902	072902
Start Time	1849	1819	1832	734	620	620	1206	1206	1854
Stop Date	072102	072202	072302	072402	072902	072902	072902	072902	073002
Stop Time	1800	1740	727	800	1124	1124	1758	1758	605
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Surrogate (% Recovery)									
d8-Naphthalene	78.4%	27.8%	85.2%	67.9%	76.9%	79.4%	81.1%	49.8%	77.5%
d10-Fluorene	155.1%	427.2%	70.2%	11951.4%	137.6%	80.2%	130.5%	61.1%	111.1%
d10-Fluoranthene	153.8%	87.6%	137.3%	145.5%	110.5%	130.4%	136.9%	86.3%	146.4%
d12-Perylene	130.1%	39.2%	86.9%	113.5%	116.9%	89.0%	121.4%	82.0%	114.2%
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	1.5E+02	1.2E+02	7.2E+02	2.6E+02	3.0E+02	4.0E+02	5.9E+02	2.5E+02	9.9E+02
2-Methylnaphthalene	2.1E+02	1.6E+02	1.1E+03	3.4E+02	3.7E+02	4.9E+02	7.6E+02	4.2E+02	1.5E+03
Azulene	5.0E+00	5.8E+00	8.4E+00	2.8E+00	3.3E+00	8.1E+00	ND	ND	1.2E+01
1-Methylnaphthalene	9.4E+01	6.5E+01	5.6E+02	1.6E+02	1.6E+02	2.2E+02	3.1E+02	1.3E+02	7.1E+02
Biphenyl	7.5E+01	4.9E+01	4.9E+02	1.0E+02	1.5E+02	2.1E+02	2.2E+02	8.6E+01	4.8E+02
2,7-Dimethylnaphthalene	1.5E+02	1.1E+02	1.1E+03	2.2E+02	2.5E+02	3.2E+02	3.9E+02	1.5E+02	1.0E+03
1,3-Dimethylnaphthalene	1.5E+02	1.1E+02	1.1E+03	2.3E+02	2.6E+02	3.1E+02	3.3E+02	1.7E+02	1.2E+03
1,6-Dimethylnaphthalene	8.2E+01	5.8E+01	6.3E+02	1.3E+02	1.4E+02	1.8E+02	2.1E+02	9.6E+01	6.7E+02
1,4-Dimethylnaphthalene	8.7E+01	6.7E+01	4.0E+02	1.1E+02	1.0E+02	1.9E+02	1.2E+02	1.5E+02	4.0E+02
1,5-Dimethylnaphthalene	1.3E+01	9.1E+00	1.3E+02	2.2E+01	2.1E+01	3.9E+01	4.1E+01	2.3E+01	1.3E+02
Acenapthylene	6.1E+01	3.3E+01	3.2E+02	1.2E+02	8.5E+01	1.2E+02	9.6E+01	4.8E+01	2.7E+02
1,2-Dimethylnapthalene	3.9E+01	2.4E+01	2.4E+02	5.3E+01	5.6E+01	7.7E+01	6.9E+01	2.8E+02	2.2E+02
1,8-Dimethylnapthalene	<BG	<BG	<BG	<BG	<BG	ND	<BG	<BG	<BG
Acenapthene	2.1E+02	1.3E+02	1.8E+03	2.3E+02	6.7E+02	8.7E+02	8.7E+02	4.4E+02	1.6E+03
2,3,5-Trimethylnapthalene	1.7E+02	1.2E+02	1.1E+03	2.5E+02	3.3E+02	3.8E+02	3.5E+02	2.0E+02	1.0E+03
Fluorene	9.9E+02	5.1E+02	6.3E+03	9.8E+02	1.9E+03	2.6E+03	2.7E+03	1.3E+03	4.1E+03
1-Methylfuorene	3.9E+02	2.1E+02	1.7E+03	4.4E+02	9.8E+02	1.0E+03	6.8E+02	3.9E+02	1.2E+03
Dibenzothiophene	9.8E+02	5.1E+02	3.1E+03	1.1E+03	9.9E+02	2.2E+03	2.0E+03	9.2E+02	2.5E+03
Phenanthrene	1.4E+04	6.5E+03	4.9E+04	1.5E+04	1.0E+04	3.0E+04	2.8E+04	1.1E+04	4.0E+04
Anthracene	3.9E+02	2.7E+02	1.1E+03	5.7E+02	5.3E+02	1.7E+03	1.7E+03	5.6E+02	8.6E+02
2-Methyldibenzothiophene	6.3E+02	5.9E+02	1.8E+03	8.5E+02	2.6E+02	1.5E+03	1.2E+03	3.3E+02	1.4E+03
4-Methyldibenzothiophene	4.9E+02	5.7E+02	1.3E+03	7.6E+02	9.7E+01	1.0E+03	9.2E+02	1.3E+02	9.8E+02
2-Methylphenanthrene	1.8E+03	2.8E+03	6.0E+03	3.4E+03	2.5E+02	4.6E+03	3.8E+03	3.7E+02	4.4E+03
2-Methylanthracene	5.9E+01	7.2E+01	6.8E+01	1.2E+02	1.3E+01	2.1E+02	1.7E+02	1.3E+01	9.4E+01
4,5-Methylenephenanthrene	6.3E+02	7.0E+02	1.9E+03	9.6E+02	8.3E+01	1.3E+03	1.6E+03	1.8E+02	1.8E+03
1-Methylanthracene	8.4E+02	1.5E+03	2.8E+03	1.7E+03	1.2E+02	2.3E+03	1.8E+03	1.8E+02	2.1E+03
1-Methylphenanthrene	7.8E+02	1.4E+03	2.4E+03	1.5E+03	9.0E+01	2.0E+03	1.7E+03	1.3E+02	1.9E+03
9-Methylanthracene	ND	3.4E+01	ND	ND	ND	ND	ND	ND	6.6E+00
9,10-Dimethylanthracene	4.6E+02	1.4E+03	1.5E+03	1.1E+03	1.5E+01	1.2E+03	1.0E+03	1.7E+01	1.1E+03
Fluoranthene	5.5E+03	1.1E+04	1.3E+04	1.2E+04	4.0E+01	1.2E+04	1.6E+04	9.4E+01	1.3E+04
3,6-Dimethylphenanthrene	8.8E+01	3.2E+02	1.3E+02	ND	ND	ND	ND	ND	ND
Pyrene	2.6E+03	6.2E+03	6.6E+03	6.2E+03	<BG	6.8E+03	8.3E+03	4.2E+01	6.6E+03
3,6-Dimethylphenanthrene	8.8E+01	3.2E+02	1.3E+02	ND	ND	ND	ND	ND	ND
Benzo[a]fluorene	6.7E+01	2.3E+02	1.5E+02	1.5E+02	ND	1.6E+02	1.6E+02	ND	1.5E+02
Retene	9.1E+01	3.6E+02	3.7E+02	2.6E+02	ND	3.4E+02	3.0E+02	ND	2.3E+02
Benzo[b]fluorene	6.7E+01	1.8E+02	1.7E+02	1.4E+02	ND	2.4E+02	1.6E+02	ND	1.7E+02
Cyclopenta[c,d]pyrene	3.2E+00	1.1E+01	1.3E+01	1.7E+01	ND	3.1E+01	1.4E+01	ND	1.3E+01
Benz[a]anthracene	1.1E+01	5.5E+01	1.8E+01	2.7E+01	ND	3.9E+01	4.8E+01	ND	2.1E+01
Chrysene+Triphenylene	6.3E+01	3.5E+02	2.0E+02	1.8E+02	ND	1.3E+02	2.6E+02	ND	1.4E+02
Napthacene	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Methylchrysene	ND	1.8E+01	7.4E+00	2.8E+00	ND	<BG	7.7E+00	ND	2.8E+00
Benzo[b]fluoranthene	2.7E+00	5.3E+01	2.3E+01	8.4E+00	ND	1.3E+01	2.8E+01	ND	8.5E+00
Benzo[k]fluoranthene	<BG	2.5E+00	3.8E+00	2.3E+00	ND	<BG	7.6E+00	ND	<BG
Dimethylbenz[a]anthracene	ND	2.0E+00	ND	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	ND	2.2E+01	9.5E+00	3.6E+00	ND	ND	1.2E+01	ND	4.6E+00
Benzo[a]pyrene	ND	ND	ND	4.2E+00	ND	ND	ND	ND	<BG
Perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenz[a,h+ac]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Anthanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Coronene	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample ID	MT 52	MT 53	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60
Start Date	073002	073002	073002	080102	080502	080602	080602	080602	080702
Start Time	650	1250	1824	1759	1900	100	700	1900	745
Stop Date	073002	073002	073102	080202	080602	080602	080602	080702	080702
Stop Time	1245	1814	750	807	100	700	1900	746	1900
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF

Surrogate (% Recovery)

d8-Naphthalene	85.6%	72.8%	71.9%	75.6%	67.4%	70.5%	59.4%	54.8%	61.1%
d10-Fluorene	139.4%	90.9%	126.5%	2315.2%	4680.6%	127.7%	119.7%	67.7%	74.0%
d10-Fluoranthene	135.8%	115.5%	163.6%	147.3%	131.7%	129.3%	150.1%	103.1%	119.0%
d12-Perylene	124.4%	84.3%	123.0%	96.9%	120.5%	132.0%	126.9%	79.0%	90.3%

Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	2.7E+02	5.0E+02	8.8E+02	8.3E+02	7.9E+02	9.2E+02	4.2E+02	6.0E+02	5.1E+02
2-Methylnaphthalene	4.0E+02	8.3E+02	1.3E+03	1.0E+03	8.7E+02	1.5E+03	5.8E+02	8.9E+02	7.0E+02
Azulene	4.0E+00	ND	6.1E+00	1.7E+01	ND	ND	ND	ND	ND
1-Methylnaphthalene	2.0E+02	4.1E+02	6.2E+02	4.4E+02	3.8E+02	7.2E+02	2.9E+02	4.0E+02	3.0E+02
Biphenyl	1.5E+02	2.9E+02	3.5E+02	3.2E+02	2.8E+02	4.5E+02	1.8E+02	2.8E+02	1.8E+02
2,7-Dimethylnaphthalene	2.7E+02	5.9E+02	8.4E+02	5.9E+02	2.9E+02	1.4E+03	4.5E+02	7.3E+02	3.9E+02
1,3-Dimethylnaphthalene	2.9E+02	6.7E+02	1.0E+03	5.4E+02	4.6E+02	1.5E+03	5.1E+02	7.2E+02	3.6E+02
1,6-Dimethylnaphthalene	1.6E+02	3.7E+02	5.6E+02	3.2E+02	2.8E+02	8.8E+02	2.8E+02	4.2E+02	2.1E+02
1,4-Dimethylnaphthalene	1.4E+02	3.1E+02	3.3E+02	1.9E+02	1.7E+02	5.0E+02	1.7E+02	2.4E+02	1.2E+02
1,5-Dimethylnaphthalene	3.5E+01	6.3E+01	1.2E+02	7.2E+01	5.7E+01	1.6E+02	5.6E+01	8.6E+01	3.9E+01
Acenapthylene	7.8E+01	1.6E+02	3.9E+02	2.7E+02	9.0E+01	3.5E+02	1.8E+02	2.6E+02	1.1E+02
1,2-Dimethylnapthalene	6.1E+01	1.5E+02	2.1E+02	1.1E+02	1.3E+02	3.5E+02	1.5E+02	1.7E+02	8.5E+01
1,8-Dimethylnapthalene	<BG	<BG	<BG	<BG	<BG	ND	<BG	ND	<BG
Acenapthene	7.2E+02	1.8E+03	1.3E+03	6.9E+02	1.1E+03	1.4E+03	9.9E+02	9.0E+02	6.8E+02
2,3,5-Trimethylnapthalene	3.3E+02	9.5E+02	1.2E+03	6.7E+02	5.3E+02	1.8E+03	6.6E+02	9.5E+02	3.9E+02
Fluorene	2.2E+03	4.7E+03	5.2E+03	4.0E+03	3.6E+03	4.3E+03	3.1E+03	3.4E+03	1.9E+03
1-Methylfuorene	7.3E+02	1.2E+03	1.6E+03	1.5E+03	1.1E+03	1.2E+03	1.2E+03	1.2E+03	5.6E+02
Dibenzothiophene	1.8E+03	2.5E+03	2.6E+03	3.2E+03	2.3E+03	1.7E+03	2.4E+03	1.4E+03	1.3E+03
Phenanthrene	2.3E+04	3.2E+04	3.1E+04	4.3E+04	3.3E+04	2.1E+04	2.9E+04	1.6E+04	1.7E+04
Anthracene	1.5E+03	1.9E+03	1.0E+03	1.3E+03	6.1E+02	6.9E+02	1.8E+03	9.5E+02	1.1E+03
2-Methyldibenzothiophene	1.2E+02	1.4E+03	1.8E+03	1.9E+03	1.5E+03	1.1E+03	1.7E+03	1.1E+03	1.1E+03
4-Methyldibenzothiophene	8.8E+02	9.4E+02	1.2E+03	1.4E+03	1.0E+03	7.6E+02	1.3E+03	7.7E+02	8.4E+02
2-Methylphenanthrene	3.7E+03	3.7E+03	4.6E+03	6.1E+03	4.1E+03	2.7E+03	4.3E+03	2.7E+03	3.1E+03
2-Methylanthracene	1.9E+02	2.0E+02	1.9E+02	2.3E+02	5.2E+01	1.2E+02	1.6E+02	1.8E+02	1.3E+02
4,5-Methylenephenanthrene	1.2E+03	1.4E+03	1.2E+03	1.9E+03	1.3E+03	8.2E+02	1.4E+03	7.0E+02	9.2E+02
1-Methylanthracene	1.8E+03	1.7E+03	2.2E+03	2.8E+03	1.9E+03	1.3E+03	2.2E+03	1.3E+03	1.5E+03
1-Methylphenanthrene	1.7E+03	1.6E+03	1.9E+03	2.5E+03	1.7E+03	1.1E+03	1.9E+03	1.2E+03	1.3E+03
9-Methylanthracene	9.4E+00	4.7E+01	ND	ND	ND	<BG	ND	ND	ND
9,10-Dimethylanthracene	9.3E+02	9.2E+02	1.2E+03	1.8E+03	1.1E+03	6.1E+02	1.3E+03	6.9E+02	8.0E+02
Fluoranthene	9.7E+03	1.3E+04	8.7E+03	1.5E+04	9.6E+03	6.3E+03	1.1E+04	3.5E+03	7.5E+03
3,6-Dimethylphenanthrene	ND	ND	ND	ND	1.6E+02	ND	ND	ND	ND
Pyrene	5.6E+03	7.0E+03	5.1E+03	7.7E+03	4.9E+03	3.3E+03	6.2E+03	2.5E+03	4.5E+03
3,6-Dimethylphenanthrene	ND	ND	ND	ND	1.6E+02	ND	ND	ND	ND
Benzo[a]fluorene	1.2E+02	1.2E+02	1.3E+02	2.0E+02	1.3E+02	9.7E+01	1.4E+02	7.9E+01	1.1E+02
Retene	2.2E+02	1.9E+02	2.1E+02	2.7E+02	2.3E+02	1.5E+02	2.5E+02	1.1E+02	1.9E+02
Benzo[b]fluorene	2.0E+02	2.6E+02	1.6E+02	2.0E+02	1.4E+02	8.9E+01	1.3E+02	8.3E+01	1.0E+02
Cyclopenta[c,d]pyrene	1.9E+01	7.9E+00	1.4E+01	1.6E+01	1.1E+01	ND	4.1E+00	7.2E+00	3.3E+00
Benz[a]anthracene	2.9E+01	2.3E+01	2.4E+01	2.0E+01	1.9E+01	1.6E+01	9.1E+00	1.2E+01	1.1E+01
Chrysene+Triphenylene	1.3E+02	1.4E+02	1.3E+02	1.7E+02	1.3E+02	8.5E+01	1.3E+02	6.1E+01	1.0E+02
Napthacene	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-Methylchrysene	7.3E+00	ND	5.0E+00	1.0E+01	ND	ND	ND	2.1E+00	ND
Benzo[b]fluoranthene	1.8E+01	ND	1.1E+01	1.2E+01	2.2E+01	1.8E+01	1.3E+01	ND	7.2E+00
Benzo[k]fluoranthene	<BG	ND	<BG	1.3E+01	ND	9.8E+00	6.0E+00	ND	ND
Dimethylbenz[a]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	9.3E+00	ND	3.8E+00	6.0E+00	4.4E+00	ND	8.8E+00	ND	<BG
Benzo[a]pyrene	<BG	ND	ND	ND	<BG	ND	1.2E+01	ND	ND
Perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenz[a,h+ac]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Anthanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Coronene	ND	ND	ND	ND	ND	ND	ND	ND	ND

	MT 61	MT 62	MT 63	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69
Sample ID	MT 61	MT 62	MT 63	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69
Start Date	080702	080802	080802	012703	012803	012803	012803	012903	012903
Start Time	1900	800	1900	1830	1230	820	1800	30	745
Stop Date	080802	080802	080902	012803	012803	012803	012903	012903	012903
Stop Time	754	1900	803	802	800	1734	30	630	1831
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Surrogate (% Recovery)									
d8-Naphthalene	57.3%	68.5%	37.3%	38.6%	48.1%	57.2%	47.8%	68.6%	80.9%
d10-Fluorene	54.8%	119.6%	45.1%	101.7%	97.7%	96.2%	62.8%	108.6%	88.1%
d10-Fluoranthene	110.3%	137.3%	117.0%	84.0%	88.0%	87.5%	81.8%	90.3%	104.1%
d12-Perylene	92.1%	123.3%	87.5%	87.0%	89.9%	91.2%	82.1%	88.2%	90.4%
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	8.2E+02	3.5E+02	5.9E+02	1.2E+04	2.7E+04	1.4E+04	1.0E+04	2.9E+04	2.8E+04
2-Methylnaphthalene	1.3E+03	4.1E+02	6.8E+02	1.6E+04	3.4E+04	1.9E+04	1.5E+04	4.3E+04	3.7E+04
Azulene	ND	ND	ND	8.9E+01	2.0E+02	5.3E+01	6.7E+01	1.7E+02	1.5E+02
1-Methylnaphthalene	6.2E+02	1.8E+02	2.8E+02	7.0E+03	1.5E+04	6.2E+03	6.6E+03	1.8E+04	1.6E+04
Biphenyl	3.5E+02	1.1E+02	2.1E+02	4.5E+03	6.7E+03	6.9E+03	4.7E+03	1.0E+04	8.5E+03
2,7-Dimethylnaphthalene	1.0E+03	2.3E+02	3.9E+02	1.0E+04	1.6E+04	1.0E+04	8.7E+03	2.7E+04	1.8E+04
1,3-Dimethylnaphthalene	1.1E+03	2.2E+02	3.9E+02	1.2E+04	1.7E+04	9.0E+03	9.4E+03	3.0E+04	2.1E+04
1,6-Dimethylnaphthalene	6.6E+02	1.3E+02	2.3E+02	6.4E+03	9.4E+03	5.6E+03	5.3E+03	1.7E+04	1.1E+04
1,4-Dimethylnaphthalene	3.6E+02	8.5E+01	1.5E+02	3.5E+03	4.3E+03	3.0E+03	2.8E+03	8.9E+03	6.7E+03
1,5-Dimethylnaphthalene	1.2E+02	2.2E+01	4.4E+01	1.2E+03	1.8E+03	9.8E+02	9.2E+02	2.4E+03	2.3E+03
Acenapthylene	3.5E+02	7.9E+01	3.4E+02	4.6E+03	6.9E+03	5.0E+03	4.1E+03	7.6E+03	1.8E+04
1,2-Dimethylnapthalene	2.4E+02	7.7E+01	1.1E+02	2.3E+03	3.0E+03	2.1E+03	1.8E+03	5.7E+03	4.3E+03
1,8-Dimethylnapthalene	ND	<BG	<BG	ND	<BG	<BG	<BG	<BG	8.6E+01
Acenapthene	9.8E+02	4.3E+02	4.6E+02	2.2E+03	2.4E+03	2.5E+03	2.4E+03	5.1E+03	4.7E+03
2,3,5-Trimethylnapthalene	1.4E+03	2.2E+02	5.7E+02	6.7E+03	6.9E+03	8.3E+03	4.4E+03	1.7E+04	1.6E+04
Fluorene	4.1E+03	1.3E+03	2.6E+03	5.9E+03	6.3E+03	8.7E+03	5.0E+03	1.2E+04	1.5E+04
1-Methylfuorene	1.6E+03	3.8E+02	1.2E+03	2.4E+03	2.3E+03	4.0E+03	1.7E+03	5.1E+03	5.6E+03
Dibenzothiophene	2.3E+03	1.0E+03	1.9E+03	1.2E+03	1.1E+03	1.2E+03	6.3E+02	2.4E+03	2.6E+03
Phenanthrene	2.8E+04	1.3E+04	2.4E+04	1.3E+04	1.4E+04	1.7E+04	9.6E+03	2.2E+04	2.8E+04
Anthracene	1.3E+03	8.6E+02	1.0E+03	2.8E+02	4.1E+02	5.7E+02	3.4E+02	1.1E+03	2.5E+03
2-Methyldibenzothiophene	1.6E+03	7.5E+02	1.3E+03	1.1E+03	1.0E+03	1.3E+03	5.9E+02	2.7E+03	2.3E+03
4-Methyldibenzothiophene	1.1E+03	5.8E+02	9.6E+02	6.1E+02	5.7E+02	6.4E+02	3.3E+02	1.9E+03	1.5E+03
2-Methylphenanthrene	4.4E+03	2.3E+03	3.6E+03	3.0E+03	2.4E+03	4.8E+03	1.9E+03	7.1E+03	6.4E+03
2-Methylanthracene	2.9E+02	1.2E+02	1.9E+02	ND	9.8E+00	ND	ND	2.5E+02	4.0E+02
4,5-Methylenephenanthrene	1.2E+03	6.9E+02	1.1E+03	6.2E+02	6.6E+02	8.6E+02	4.8E+02	9.9E+02	1.4E+03
1-Methylanthracene	2.2E+03	1.2E+03	1.8E+03	1.3E+03	1.1E+03	2.2E+03	8.2E+02	3.2E+03	3.2E+03
1-Methylphenanthrene	1.9E+03	1.0E+03	1.6E+03	1.2E+03	1.0E+03	2.0E+03	8.2E+02	2.9E+03	2.8E+03
9-Methylanthracene	2.4E+01	ND	ND	9.8E+00	ND	3.0E+01	ND	6.5E+01	6.0E+01
9,10-Dimethylanthracene	1.2E+03	6.0E+02	9.6E+02	2.1E+02	1.2E+02	7.4E+02	2.8E+02	1.2E+03	1.3E+03
Fluoranthene	6.3E+03	5.8E+03	6.4E+03	1.0E+03	7.5E+02	1.9E+03	1.5E+03	2.2E+03	3.6E+03
3,6-Dimethylphenanthrene	ND	ND	ND	ND	1.0E+01	1.2E+01	ND	6.7E+01	9.3E+01
Pyrene	4.2E+03	3.5E+03	4.3E+03	4.8E+02	4.3E+02	1.5E+03	1.1E+03	2.2E+03	3.7E+03
3,6-Dimethylphenanthrene	ND	ND	ND	ND	1.0E+01	1.2E+01	ND	6.7E+01	9.3E+01
Benzo[a]fluorene	1.4E+02	8.6E+01	1.5E+02	5.4E+00	7.2E+00	1.0E+01	1.7E+01	6.2E+01	1.4E+02
Retene	1.7E+02	1.4E+02	1.5E+02	9.1E+00	1.2E+01	1.3E+01	1.9E+01	6.7E+01	1.5E+02
Benzo[b]fluorene	1.4E+02	8.3E+01	1.5E+02	1.3E+01	1.4E+01	9.1E+00	6.7E+01	6.7E+01	1.3E+02
Cyclopenta[c,d]pyrene	6.4E+00	2.6E+00	1.2E+01	3.6E+00	1.8E+01	ND	6.2E+00	1.3E+01	2.7E+01
Benz[a]anthracene	1.9E+01	9.9E+00	1.6E+01	3.2E+00	1.3E+01	<BG	5.0E+00	4.9E+00	1.5E+01
Chrysene+Triphenylene	9.8E+01	5.6E+01	1.3E+02	4.2E+00	1.7E+01	4.4E+00	1.4E+01	2.1E+01	3.7E+01
Napthacene	ND	ND	ND	ND	ND	ND	ND	ND	2.3E+00
4-Methylchrysene	ND	ND	1.7E+00	ND	<BG	ND	ND	ND	ND
Benzo[b]fluoranthene	7.9E+00	ND	3.3E+00	4.6E+00	1.9E+01	<BG	1.2E+01	6.7E+00	4.7E+00
Benzo[k]fluoranthene	3.8E+00	ND	6.0E+00	3.6E+00	6.5E+00	<BG	<BG	<BG	6.4E+00
Dimethylbenz[a]anthracene	ND	ND	ND	ND	ND	<BG	ND	ND	ND
Benzo[e]pyrene	<BG	ND	ND	<BG	1.1E+01	<BG	5.2E+00	<BG	ND
Benzo[a]pyrene	ND	ND	ND	<BG	1.2E+01	<BG	1.0E+01	ND	ND
Perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenz[a,h+ac]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	1.4E+01	ND	ND	ND	ND
Anthanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Coronene	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample ID	MT 70	MT 71	MT 72	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
Start Date	012903	013003	013003	013003	020503	020503	020603	020603	020703
Start Time	1837	30	810	1830	700	1825	735	1745	110
Stop Date	013003	013003	013003	013103	020503	020603	020603	020703	020703
Stop Time	30	630	1830	1830	1820	735	1740	110	710
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Surrogate (% Recovery)									
d8-Naphthalene	38.3%	35.4%	48.3%	60.2%	40.7%	89.3%	51.5%	36.9%	36.5%
d10-Fluorene	82.1%	98.4%	149.0%	79.0%	69.4%	149.1%	80.9%	62.9%	59.5%
d10-Fluoranthene	83.1%	92.7%	99.5%	98.2%	91.6%	107.6%	85.8%	96.0%	57.4%
d12-Perylene	77.3%	83.7%	84.1%	86.2%	82.4%	88.1%	78.9%	91.8%	55.6%
Conc	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Naphthalene	1.6E+04	1.7E+04	1.1E+04	8.0E+03	5.3E+03	1.8E+04	9.4E+03	3.6E+03	1.1E+04
2-Methylnaphthalene	2.2E+04	2.6E+04	1.9E+04	1.1E+04	8.2E+03	3.1E+04	1.2E+04	4.7E+03	1.4E+04
Azulene	8.4E+01	9.4E+01	5.9E+01	3.3E+01	3.0E+01	1.4E+01	3.5E+01	1.3E+01	4.2E+01
1-Methylnaphthalene	1.1E+04	1.0E+04	7.9E+03	4.0E+03	3.4E+03	1.4E+04	4.9E+03	1.8E+03	5.8E+03
Biphenyl	7.8E+03	6.5E+03	5.6E+03	3.4E+03	1.5E+03	7.8E+03	3.0E+03	2.0E+03	3.6E+03
2,7-Dimethylnaphthalene	1.6E+04	1.6E+04	1.0E+04	5.4E+03	4.0E+03	2.2E+04	5.4E+03	3.0E+03	9.1E+03
1,3-Dimethylnaphthalene	1.9E+04	1.7E+04	1.1E+04	5.4E+03	4.3E+03	2.6E+04	6.1E+03	2.9E+03	9.6E+03
1,6-Dimethylnaphthalene	1.0E+04	9.6E+03	6.3E+03	3.1E+03	2.4E+03	1.4E+04	3.4E+03	1.8E+03	5.4E+03
1,4-Dimethylnaphthalene	6.0E+03	5.1E+03	3.6E+03	1.7E+03	1.4E+03	7.9E+03	1.9E+03	9.8E+02	2.9E+03
1,5-Dimethylnaphthalene	1.9E+03	1.7E+03	1.4E+03	5.1E+02	5.1E+02	3.3E+03	7.6E+02	3.6E+02	9.7E+02
Acenapthylene	1.5E+04	9.0E+03	1.0E+04	4.8E+03	1.8E+03	1.1E+04	4.5E+03	2.4E+03	6.4E+03
1,2-Dimethylnapthalene	4.2E+03	3.5E+03	2.7E+03	1.2E+03	9.0E+02	5.3E+03	1.4E+03	6.8E+02	1.9E+03
1,8-Dimethylnapthalene	<BG	<BG	<BG	<BG	<BG	7.3E+01	<BG	<BG	<BG
Acenapthene	4.7E+03	3.1E+03	3.0E+03	1.6E+03	1.2E+03	4.5E+03	1.7E+03	1.0E+03	1.6E+03
2,3,5-Trimethylnapthalene	1.6E+04	1.3E+04	1.1E+04	5.4E+03	4.1E+03	1.7E+04	5.3E+03	3.7E+03	7.6E+03
Fluorene	1.8E+04	9.9E+03	1.3E+04	8.3E+03	4.1E+03	1.2E+04	5.3E+03	4.6E+03	6.3E+03
1-Methylfuorene	5.5E+03	4.5E+03	4.8E+03	2.7E+03	1.5E+03	5.3E+03	2.1E+03	1.8E+03	2.5E+03
Dibenzothiophene	2.7E+03	2.2E+03	2.0E+03	1.3E+03	7.4E+02	2.3E+03	7.9E+02	9.2E+02	1.5E+03
Phenanthrene	3.2E+04	2.2E+04	2.5E+04	1.8E+04	9.5E+03	2.3E+04	1.0E+04	1.0E+04	1.3E+04
Anthracene	2.8E+03	1.5E+03	1.9E+03	1.5E+03	2.8E+02	1.5E+03	6.2E+02	5.6E+02	1.3E+03
2-Methyldibenzothiophene	2.3E+03	2.5E+03	2.0E+03	1.3E+03	7.1E+02	2.6E+03	8.9E+02	7.2E+02	1.3E+03
4-Methyldibenzothiophene	1.6E+03	1.6E+03	1.3E+03	8.1E+02	4.2E+02	1.8E+03	5.3E+02	4.6E+02	9.7E+02
2-Methylphenanthrene	6.4E+03	6.0E+03	6.0E+03	3.5E+03	2.3E+03	6.3E+03	2.9E+03	2.5E+03	3.4E+03
2-Methylanthracene	4.9E+02	3.5E+02	3.7E+02	2.4E+02	ND	2.2E+02	ND	5.5E+01	2.2E+02
4,5-Methylenephenanthrene	1.7E+03	1.1E+03	1.3E+03	9.0E+02	4.8E+02	1.0E+03	5.7E+02	5.5E+02	7.5E+02
1-Methylanthracene	3.1E+03	2.9E+03	3.0E+03	1.8E+03	1.0E+03	3.1E+03	1.4E+03	1.2E+03	1.7E+03
1-Methylphenanthrene	2.9E+03	2.5E+03	2.7E+03	1.5E+03	9.3E+02	2.6E+03	1.3E+03	1.1E+03	1.5E+03
9-Methylanthracene	2.4E+01	5.1E+01	6.4E+01	ND	ND	5.4E+01	2.5E+01	2.6E+01	3.4E+01
9,10-Dimethylanthracene	1.0E+03	1.2E+03	1.3E+03	6.2E+02	3.3E+02	1.2E+03	5.2E+02	5.6E+02	7.2E+02
Fluoranthene	4.3E+03	2.4E+03	3.7E+03	3.0E+03	1.4E+03	2.5E+03	1.5E+03	2.1E+03	2.2E+03
3,6-Dimethylphenanthrene	6.2E+01	5.9E+01	7.3E+01	ND	1.1E+01	3.3E+01	2.1E+01	4.9E+01	6.7E+01
Pyrene	4.1E+03	2.6E+03	3.9E+03	2.9E+03	8.8E+02	2.4E+03	1.5E+03	2.0E+03	2.2E+03
3,6-Dimethylphenanthrene	6.2E+01	5.9E+01	7.3E+01	ND	1.1E+01	3.3E+01	2.1E+01	4.9E+01	6.7E+01
Benzo[a]fluorene	1.4E+02	8.8E+01	1.1E+02	9.6E+01	1.9E+01	4.4E+01	2.5E+01	7.2E+01	8.8E+01
Retene	5.2E+02	1.4E+02	1.1E+02	1.3E+02	1.2E+01	2.7E+01	1.1E+01	1.5E+02	1.1E+02
Benzo[b]fluorene	1.8E+02	9.9E+01	1.3E+02	1.1E+02	1.9E+01	4.3E+01	3.6E+01	8.0E+01	1.1E+02
Cyclopenta[c,d]pyrene	7.6E+01	2.7E+01	1.6E+01	4.2E+01	2.8E+00	6.2E+00	1.7E+01	7.3E+01	3.4E+01
Benz[a]anthracene	2.5E+01	1.4E+01	8.1E+00	1.1E+01	3.4E+00	6.0E+00	<BG	6.5E+00	1.5E+01
Chrysene+Triphenylene	5.8E+01	3.0E+01	2.9E+01	3.7E+01	7.9E+00	1.1E+01	7.1E+00	3.1E+01	3.6E+01
Napthacene	7.1E+00	2.6E+00	ND	ND	ND	ND	ND	ND	<BG
4-Methylchrysene	ND	ND	ND	ND	ND	ND	ND	<BG	ND
Benzo[b]fluoranthene	1.2E+01	ND	4.6E+00	3.1E+00	7.3E+00	7.9E+00	ND	ND	5.4E+00
Benzo[k]fluoranthene	ND	ND	ND	<BG	<BG	3.6E+00	ND	ND	ND
Dimethylbenz[a]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[e]pyrene	ND	ND	ND	ND	3.5E+00	3.6E+00	ND	<BG	ND
Benzo[a]pyrene	ND	ND	ND	ND	<BG	7.1E+00	ND	ND	ND
Perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Methylchloanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Indeno[1,2,3-c,d]pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dibenz[a,h+ac]anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Anthanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
Coronene	ND	ND	ND	ND	ND	ND	ND	ND	ND

Sample ID	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 8	MT 9	MT 10	MT 11	MT 12	MT 13	MT 16	MT 17
Start Date	032302	032402	032802	032902	033002	033102	040202	040302	040402	040802	040902	041002	041402	041502
Start Time	1906	1914	1920	2016	1809	1936	1927	1924	1930	1720	1835	1905	1555	1834
Stop Date	032402	032502	032902	033002	033102	040102	040302	040402	040502	040902	041002	041102	041502	041602
Stop Time	1800	1740	1901	1706	1802	1750	1758	1813	325	1808	1823	1826	1802	742
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Surrogate (% Recovery)														
1N-Napthalene-d7	12.4%	25.4%	15.2%	16.3%	21.3%	19.5%	32.3%	23.5%	23.0%	19.5%	26.8%	22.7%	30.1%	19.8%
1N-anthracene d9	33.8%	44.9%	29.9%	23.5%	40.7%	47.8%	61.5%	55.2%	41.2%	47.4%	48.3%	46.0%	60.3%	43.7%
1N-pyrene d9	30.6%	27.0%	25.8%	26.2%	35.2%	45.5%	29.5%	48.1%	34.3%	33.9%	46.8%	29.0%	42.9%	38.6%
Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	6.7E+00	2.2E+00	6.3E+00	2.8E+00	3.5E+00	5.2E+00	3.9E+00	3.2E+00	5.1E+00	5.4E+00	3.2E+00	2.4E+00	3.5E+00	1.1E+01
2N-napthalene	8.2E+00	5.5E+00	5.1E+00	6.4E+00	4.3E+00	6.1E+00	4.1E+00	7.0E+00	1.3E+01	5.5E+00	3.5E+00	4.0E+00	3.6E+00	1.3E+01
2N-biphenyl	1.6E+00	1.5E+00	1.6E+00	1.7E+00	8.4E-01	4.2E-01	6.7E-01	1.6E+00	1.3E+00	4.5E-01	1.1E+00	1.2E+00	1.1E+00	1.3E+00
3N-biphenyl	5.3E-01	5.7E-01	4.6E-01	8.7E-01	5.4E-01	4.4E-01	3.3E-01	4.6E-01	6.0E-01	3.0E-01	5.6E-01	2.6E-01	4.6E-01	1.6E+00
4-Nitrobiphenyl	8.7E-01	3.6E-01	ND	5.1E-01	3.2E-01	1.4E+00	7.8E-01	8.5E-01	2.8E+00	5.3E-01	3.9E-01	ND	1.2E+00	3.6E+00
3N-dibenzofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-dinitronaphthalene	ND	ND	8.2E-01	ND	4.0E-01	ND	ND	4.2E-01	ND	ND	ND	ND	2.6E-01	7.6E-01
1,5-dinitronaphthalene	ND	ND	ND	ND	1.0E-01	ND	ND	1.2E-01	ND	ND	ND	ND	1.1E-01	1.4E-01
5N-acenapthene	1.3E+00	2.4E-01	4.8E-01	8.3E-01	4.4E-01	6.3E-01	2.4E-01	6.5E-01	6.0E-01	1.3E+00	5.5E-01	2.8E-01	5.1E-01	3.9E+00
2N-fluorene	2.3E+00	2.3E-01	5.3E-01	2.3E-01	1.7E-01	4.9E+00	3.2E-01	9.8E-01	3.3E+00	4.1E-01	2.0E-01	2.3E-01	3.9E-01	2.2E+00
2,2'-dinitrobiphenyl	2.1E+00	2.8E+00	2.6E+00	3.0E+01	1.8E+00	<BG	1.2E+00	1.2E+00	1.4E+00	2.0E+00	1.4E+00	1.3E+00	1.3E+00	3.2E+00
9N-anthracene	1.4E+02	2.4E+02	1.2E+02	3.9E+01	8.9E+01	2.3E+01	6.7E+01	5.1E+01	1.1E+02	5.1E+01	2.7E+01	9.5E+01	3.1E+01	3.0E+02
2N-anthracene	ND	<BG	ND	ND	8.5E-01	1.6E+00	ND	<BG	ND	ND	<BG	ND	ND	<BG
9N-phenanthrene	1.5E+01	2.5E+00	3.2E+00	1.5E+00	1.5E+00	2.0E+01	1.8E+00	4.1E+00	9.7E+00	2.8E+00	1.2E+00	2.0E+00	3.6E+00	1.7E+01
3N-phenanthrene	5.5E+00	2.1E+00	2.1E+00	2.4E+00	1.9E+00	9.7E+00	1.7E+00	2.3E+00	3.5E+00	3.3E+00	1.8E+00	1.6E+00	2.8E+00	1.7E+01
4N-phenanthrene	5.4E-01	6.4E-01	2.8E-01	3.3E-01	7.4E-01	3.8E-01	4.9E-01	2.2E-01	3.8E-01	7.9E-01	2.8E-01	3.2E-01	3.4E-01	2.8E+00
2N-fluoranthene	3.7E+01	1.2E+02	4.1E+01	4.4E+01	4.0E+01	1.4E+01	1.7E+01	8.2E+00	3.6E+01	2.0E+01	2.5E+01	7.8E+01	2.9E+01	3.7E+02
3N-fluoranthene	1.1E+00	5.4E-01	1.7E+00	2.1E-01	2.1E-01	3.4E+00	4.1E-01	8.3E-01	6.1E-01	2.3E+00	3.2E-01	3.6E-01	2.8E+00	1.8E+00
1N-pyrene	6.5E+01	9.1E+01	4.8E+01	2.4E+01	1.5E+01	8.4E+01	2.4E+01	2.2E+01	4.1E+01	9.6E+01	2.8E+01	8.2E+01	8.5E+01	1.2E+02
2N-pyrene	2.8E+00	7.2E+00	2.3E+00	4.5E+00	2.1E+00	1.3E+00	1.4E+00	4.9E-01	1.1E+00	2.8E+00	1.8E+00	6.9E+00	2.3E+00	2.3E+01
7-nitrobenz[a]anthracene	1.9E+01	1.6E+02	1.4E+01	5.0E+00	1.2E+01	9.2E+00	2.6E+01	3.7E+00	1.0E+01	3.0E+01	3.9E+00	5.1E+01	1.9E+01	4.6E+01
6N-chrysene	1.5E+00	6.4E+00	1.3E+00	3.5E-01	2.0E-01	3.8E+00	ND	8.2E-01	1.1E+00	7.7E+00	2.6E-01	2.0E+00	3.6E+00	1.8E+00

	MT 18	MT 19	MT 20	MT 20 Back	MT 21	MT 22	MT 23	MT 25	MT 26	MT 27	MT 28	MT 29	MT 30	MT 32
Sample ID	MT 18	MT 19	MT 20	MT 20 Back	MT 21	MT 22	MT 23	MT 25	MT 26	MT 27	MT 28	MT 29	MT 30	MT 32
Start Date	041602	041602	041702	041702	041702	042202	042302	042402	042402	042502	042502	042602	042702	042902
Start Time	0846	1957	0855	0855	1856	1833	0834	0913	1926	0855	1840	1905	1710	1734
Stop Date	041602	041702	041702	041702	041802	042302	042302	042402	042502	042502	042602	042702	042802	043002
Stop Time	1854	735	1759	1759	1745	808	1839	1933	800	1814	1843	1700	1645	1704
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Surrogate (% Recovery)														
1N-Napthalene-d7	36.9%	28.7%	6.7%	0.0%	25.2%	19.3%	0.0%	72.8%	44.0%	21.7%	19.9%	17.6%	17.6%	12.6%
1N-anthracene d9	59.7%	42.7%	14.0%	0.0%	47.7%	44.2%	0.0%	56.7%	46.0%	51.0%	41.0%	37.3%	49.4%	26.6%
1N-pyrene d9	41.0%	38.0%	13.6%	0.0%	37.8%	49.1%	0.0%	57.2%	54.4%	52.2%	33.0%	31.3%	51.1%	26.5%
Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	5.5E+00	8.7E+00	1.4E+01	ND	6.0E+00	4.7E+00	1.5E+00	4.3E+00	8.9E-01	2.0E+00	7.3E+00	4.7E+00	2.7E+00	6.0E+00
2N-napthalene	9.0E+00	1.3E+01	1.9E+01	5.1E-01	5.1E+00	5.5E+00	3.4E+00	4.6E+00	1.3E+00	1.9E+00	9.0E+00	7.5E+00	1.9E+00	5.0E+00
2N-biphenyl	1.9E+00	1.4E+00	5.1E+00	4.0E-01	5.6E-01	ND	4.8E+00	2.0E+00	ND	2.6E-01	1.9E+00	2.4E+00	ND	2.6E+01
3N-biphenyl	1.2E+00	1.1E+00	4.8E+00	1.1E-01	6.6E-01	3.2E-01	2.6E-01	1.9E+00	2.0E-01	3.4E-01	3.8E-01	5.2E-01	1.6E-01	3.6E-01
4-Nitrobiphenyl	ND	9.7E-01	ND	ND	ND	1.6E+00	1.1E+00	2.2E+00	6.7E-01	<BG	1.1E+00	ND	6.6E-01	4.4E-01
3N-dibenzofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-dinitronaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,5-dinitronaphthalene	ND	ND	ND	2.2E-01	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5N-acenapthene	2.2E+00	3.3E+00	6.0E+00	1.3E+00	2.3E+00	7.9E-01	6.2E-01	1.9E+00	3.2E-01	2.9E-01	6.9E-01	9.8E-01	5.5E-01	1.6E+00
2N-fluorene	2.1E-01	1.2E+00	8.1E-01	ND	5.2E-01	2.2E+00	9.2E-01	1.6E+00	4.1E+00	3.9E-01	1.7E+00	1.8E-01	5.0E-01	8.6E-01
2,2'-dinitrobiphenyl	3.2E+00	5.7E+00	<BG	3.1E+00	4.0E+00	<BG	<BG	<BG	<BG	<BG	1.5E+00	2.6E+00	1.2E+00	<BG
9N-anthracene	1.5E+02	2.6E+02	6.5E+02	<BG	6.0E+01	6.0E+01	2.0E+01	2.0E+01	2.3E+01	9.3E+00	9.2E+01	1.5E+02	1.1E+01	6.0E+01
2N-anthracene	ND	<BG	ND	ND	ND	1.4E+00	<BG	ND	2.5E+00	<BG	ND	ND	<BG	2.1E+00
9N-phenanthrene	1.5E+00	8.8E+00	4.2E+00	ND	3.9E+00	4.9E+00	4.8E+00	3.8E+00	3.3E+01	3.7E+00	1.6E+01	2.1E+00	2.9E+00	4.3E+00
3N-phenanthrene	6.8E+00	1.1E+01	2.7E+01	ND	8.9E+00	2.6E+00	2.5E+00	3.8E+00	1.1E+01	2.4E+00	8.0E+00	1.5E+00	1.8E+00	3.9E+00
4N-phenanthrene	2.1E+00	2.2E+00	8.2E+00	ND	1.5E+00	2.7E-01	2.9E-01	4.7E-01	3.7E-01	1.9E-01	3.4E-01	4.5E-01	3.0E-01	4.0E-01
2N-fluoranthene	2.7E+02	3.7E+02	1.2E+03	ND	1.5E+02	1.1E+01	5.6E+00	1.6E+01	7.1E+00	8.1E+00	3.6E+01	7.5E+01	1.2E+01	2.2E+01
3N-fluoranthene	6.8E-01	1.0E+00	2.0E+00	ND	2.2E+00	3.9E-01	2.6E-01	5.3E-01	4.0E+00	2.1E-01	3.8E+00	3.5E-01	7.4E-01	3.9E+00
1N-pyrene	3.8E+01	7.6E+01	1.2E+02	ND	5.4E+01	2.3E+01	2.3E+01	2.0E+01	9.1E+01	2.3E+01	1.5E+02	3.9E+01	2.1E+01	7.4E+01
2N-pyrene	1.4E+01	1.1E+01	7.1E+01	ND	6.9E+00	6.0E-01	ND	4.6E-01	1.1E+00	1.1E+00	3.9E+00	4.2E+00	9.5E-01	6.9E-01
7-nitrobenz[a]anthracene	6.4E+00	2.3E+01	1.7E+01	ND	1.9E+01	3.1E+00	2.0E+00	1.9E+00	1.4E+01	1.4E+00	3.3E+01	3.2E+01	2.2E+00	6.5E+00
6N-chrysene	1.3E+00	1.1E+00	5.5E+00	ND	3.6E+00	3.5E-01	ND	ND	2.5E+00	2.3E-01	6.2E+00	1.2E+00	5.3E-01	2.7E+00

	MT 33	MT 34	MT 35	MT 36	MT 37	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43	MT 45	MT 46	MT 47
Sample ID														
Start Date	070902	071002	071102	071202	071302	071402	071502	071602	071702	071802	071902	072102	072202	072302
Start Time	1705	1845	1915	1835	1923	1921	1903	1850	1905	1853	1935	1819	1832	734
Stop Date	071002	071102	071202	071302	071402	071502	071602	071702	071802	071902	072002	072202	072302	072402
Stop Time	1745	1805	1720	1820	1811	1757	1754	1801	1804	1850	1828	1740	727	800
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Surrogate (% Recovery)														
1N-Napthalene-d7	44.9%	53.3%	32.8%	72.3%	28.5%	54.5%	53.8%	39.7%	22.0%	50.1%	55.1%	34.5%	49.1%	32.0%
1N-anthracene d9	57.9%	48.4%	46.2%	63.0%	51.1%	49.8%	53.5%	48.9%	28.8%	54.8%	54.0%	48.2%	40.8%	37.4%
1N-pyrene d9	45.1%	49.3%	41.4%	59.2%	55.1%	53.4%	49.7%	41.7%	28.2%	56.2%	57.2%	59.3%	42.6%	45.9%
Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	1.2E+00	2.9E-01	8.9E-01	4.7E-01	2.5E-01	6.3E-01	9.1E-01	1.7E+00	1.2E+00	1.1E+00	7.6E-01	6.5E-01	2.8E+00	1.1E+00
2N-napthalene	1.1E+00	8.3E-01	ND	6.1E-01	5.9E-01	1.5E+00	1.0E+00	2.3E+00	1.9E+00	7.8E-01	7.8E-01	7.0E-01	1.6E+00	9.7E-01
2N-biphenyl	ND	2.4E-01	3.2E-01	3.2E-02	8.7E-02	ND	5.2E-02	ND	ND	ND	1.7E-01	ND	<BG	7.5E-02
3N-biphenyl	1.4E-01	8.6E-02	2.8E-01	6.9E-02	ND	1.2E-01	2.1E-01	3.5E-01	3.8E-01	6.6E-02	1.6E-01	1.6E-01	1.8E-01	8.0E-02
4-Nitrobiphenyl	4.1E-01	2.0E-01	4.8E-01	2.4E-01	ND	3.7E-01	ND	4.8E-01	ND	ND	5.5E-01	3.6E-01	4.4E-01	3.9E-01
3N-dibenzofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-dinitronaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.6E-01	ND	ND	ND
1,5-dinitronaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.7E-02	ND	ND	ND
5N-acenapthene	7.4E-01	3.4E-01	5.6E-01	4.6E-01	3.3E-01	3.9E-01	8.1E-01	1.9E+00	ND	8.1E-01	8.8E-01	5.1E-01	1.3E+00	4.1E-01
2N-fluorene	2.5E-01	1.3E-01	2.1E-01	1.2E-01	4.6E-02	3.0E-01	ND	1.7E-01	2.1E-01	ND	ND	2.8E-01	4.5E-01	4.4E-01
2,2'-dinitrobiphenyl	1.5E+00	<BG	1.2E+00	<BG	<BG	9.1E-01	<BG	1.2E+00	<BG	<BG	1.1E+00	<BG	ND	<BG
9N-anthracene	3.3E+01	2.9E+01	1.4E+02	3.2E+01	6.9E+00	1.4E+01	7.7E+01	1.5E+02	7.4E+01	8.5E+01	6.3E+01	4.3E+01	3.4E+02	4.2E+01
2N-anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9N-phenanthrene	1.6E+00	9.5E-01	2.3E+00	1.2E+00	3.6E-01	1.2E+00	8.0E-01	1.3E+00	1.1E+00	4.8E-01	6.6E-01	2.0E+00	3.4E+00	2.3E+00
3N-phenanthrene	2.9E+00	1.4E+00	3.2E+00	1.2E+00	1.0E+00	2.8E+00	1.9E+00	4.6E+00	2.7E+00	1.7E+00	1.7E+00	3.1E+00	6.0E+00	3.0E+00
4N-phenanthrene	3.3E-01	3.1E-01	1.1E+00	2.2E-01	1.2E-01	2.5E-01	5.5E-01	1.1E+00	2.8E-01	2.6E-01	4.0E-01	2.9E-01	1.3E+00	3.2E-01
2N-fluoranthene	5.2E+01	1.4E+01	7.1E+01	2.0E+01	3.1E+01	6.2E+01	4.5E+01	8.1E+01	5.5E+01	2.8E+01	4.2E+01	8.1E+01	1.1E+02	2.9E+01
3N-fluoranthene	4.6E-01	1.6E-01	5.7E-01	3.8E-01	1.9E-01	7.1E-01	3.7E-01	3.3E-01	9.8E-01	2.1E-01	1.7E-01	4.9E-01	1.2E+00	1.8E+00
1N-pyrene	2.8E+01	1.4E+01	3.5E+01	1.1E+01	6.7E+00	2.1E+01	1.1E+01	2.6E+01	2.3E+01	9.9E+00	7.0E+00	2.1E+01	4.5E+01	6.3E+01
2N-pyrene	1.5E+00	6.5E-01	4.8E+00	7.6E-01	8.5E-01	2.4E+00	9.3E-01	9.1E+00	1.6E+00	5.4E-01	7.2E-01	2.0E+00	2.0E+00	1.1E+00
7-nitrobenz[a]anthracene	7.4E+00	3.3E+00	1.3E+01	2.1E+00	1.2E+00	2.1E+00	3.3E+00	1.2E+01	5.8E+00	1.6E+00	2.2E+00	2.9E+00	6.4E+00	3.2E+00
6N-chrysene	3.9E-01	1.1E-01	7.1E-01	2.1E-01	1.3E-01	2.8E-01	1.9E-01	3.4E-01	6.8E-01	1.9E-01	1.1E-01	2.2E-01	5.5E-01	1.0E+00

Sample ID	MT 49	MT 51	MT 53	MT 53 Back	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63
Start Date	072902	072902	073002	073002	073002	080102	080502	080602	080602	080602	080702	080702	080802	080802
Start Time	620	1854	1250	1250	1824	1759	1900	100	700	1900	745	1900	800	1900
Stop Date	072902	073002	073002	073002	073102	080202	080602	080602	080602	080702	080702	080802	080802	080902
Stop Time	1124	605	1814	1814	750	807	100	700	1900	746	1900	754	1900	803
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter
Surrogate (% Recovery)														
1N-Napthalene-d7	23.2%	57.3%	55.4%	46.6%	48.1%	33.6%	42.1%	57.1%	68.4%	55.5%	57.6%	38.4%	36.3%	69.7%
1N-anthracene d9	30.3%	53.0%	49.1%	37.1%	40.2%	37.9%	54.5%	57.6%	57.3%	56.2%	60.9%	47.7%	47.9%	53.2%
1N-pyrene d9	35.6%	61.1%	55.7%	36.3%	47.7%	41.3%	58.0%	59.7%	47.6%	60.2%	56.7%	51.9%	51.2%	54.8%
Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	1.7E+00	1.3E+00	4.1E-01	5.0E-01	2.3E+00	3.0E+00	6.6E-01	4.4E-01	5.3E-01	4.5E-01	3.9E-01	7.5E-01	6.4E-01	8.8E-01
2N-napthalene	3.1E+00	9.3E-01	9.9E-01	1.3E+00	1.7E+00	4.1E+00	1.1E+00	1.4E+00	1.7E+00	9.3E-01	1.2E+00	1.3E+00	1.5E+00	1.6E+00
2N-biphenyl	2.3E+00	1.2E-01	ND	ND	ND	ND	ND	ND	ND	5.5E-01	2.7E-01	3.3E-01	4.0E-01	9.0E-02
3N-biphenyl	8.1E-01	8.7E-02	2.1E-01	2.0E-01	1.0E-01	3.3E-01	2.1E-01	<BG	1.4E-01	1.3E-01	1.0E-01	2.0E-01	1.9E-01	1.7E-01
4-Nitrobiphenyl	ND	ND	ND	ND	ND	1.0E+00	ND	<BG	3.6E-01	<BG	<BG	ND	ND	4.5E-01
3N-dibenzofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-dinitronaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,5-dinitronaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5N-acenapthene	3.4E+00	7.2E-01	1.4E+00	ND	1.0E+00	1.7E+00	ND	ND	1.4E+00	6.0E-01	1.6E+00	7.2E-01	2.1E+00	8.8E-01
2N-fluorene	6.2E-01	2.9E-01	<BG	ND	1.7E-01	3.4E-01	<BG	4.4E-01	7.2E-01	6.1E-01	2.3E-01	4.4E-01	2.1E-01	3.9E-01
2,2'-dinitrobiphenyl	<BG	<BG	<BG	<BG	<BG	2.2E+00	<BG	3.1E+00	3.1E+00	<BG	<BG	2.2E+00	<BG	3.7E+00
9N-anthracene	2.9E+01	2.1E+02	5.4E+01	1.2E+01	1.3E+02	4.3E+02	1.5E+01	1.1E+01	2.1E+01	1.1E+01	1.5E+01	3.2E+01	1.7E+01	6.0E+01
2N-anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9N-phenanthrene	2.5E+00	1.9E+00	6.4E-01	5.6E-01	1.4E+00	3.7E+00	9.3E-01	1.4E+00	8.4E+00	4.5E+00	1.7E+00	4.3E+00	2.6E+00	4.4E+00
3N-phenanthrene	4.9E+00	3.2E+00	3.2E+00	2.7E+00	3.8E+00	1.2E+01	1.6E+00	2.6E+00	6.2E+00	2.2E+00	3.0E+00	4.0E+00	3.0E+00	4.2E+00
4N-phenanthrene	3.2E-01	5.2E-01	6.7E-01	2.2E-01	1.2E+00	2.9E+00	1.2E-01	2.6E-01	4.5E-01	2.0E-01	3.4E-01	1.0E+00	3.0E-01	1.0E+00
2N-fluoranthene	5.8E+01	4.6E+01	2.8E+01	3.7E+01	5.7E+01	8.5E+02	4.6E+01	2.7E+01	2.7E+01	1.4E+01	1.7E+01	6.3E+01	1.6E+01	6.1E+01
3N-fluoranthene	8.3E-01	4.7E-01	3.3E-01	2.0E-01	2.7E-01	1.7E+00	1.5E-01	4.3E-01	6.7E-01	4.6E-01	3.5E-01	2.4E-01	5.8E-01	5.2E-01
1N-pyrene	3.2E+01	2.4E+01	1.4E+01	1.8E+01	1.9E+01	5.2E+01	8.3E+00	1.4E+01	2.5E+01	2.8E+01	1.5E+01	3.6E+01	1.2E+01	4.2E+01
2N-pyrene	2.6E+00	1.9E+00	1.0E+00	2.3E+00	1.3E+00	6.4E+00	9.2E-01	1.6E+00	1.4E+00	1.1E+00	7.6E-01	4.6E+00	7.7E-01	5.7E+00
7-nitrobenz[a]anthracene	1.7E+00	5.2E+00	1.2E+00	1.7E+00	3.7E+00	1.1E+01	2.4E+00	1.8E+00	7.0E+00	2.8E+00	2.9E+00	6.8E+00	2.2E+00	8.5E+00
6N-chrysene	<BG	2.2E-01	ND	4.0E-01	1.7E-01	5.5E-01	<BG	ND	ND	1.2E-01	ND	2.0E-01	1.5E-01	2.0E-01

Sample ID	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
Start Date	012703	012803	012803	012803	012903	012903	012903	013003	013003	013003	020503	020503	020603	020603	020703
Start Time	1830	1230	820	1800	30	745	1837	30	810	1830	700	1825	735	1745	110
Stop Date	012803	012803	012803	012903	012903	012903	013003	013003	013003	013103	020503	020603	020603	020703	020703
Stop Time	802	800	1734	30	630	1831	30	630	1830	1830	1820	735	1740	110	710
Media	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter	Filter

Surrogate (% Recovery)

	MT 64	MT 65	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
1N-Napthalene-d7	43.3%	45.4%	35.8%	96.5%	69.0%	56.4%	69.1%	48.5%	84.3%	60.7%	60.2%	44.1%	57.2%	67.5%	61.3%
1N-anthracene d9	35.9%	34.9%	32.1%	50.2%	46.2%	36.8%	38.7%	40.8%	39.2%	40.8%	49.7%	27.1%	47.1%	51.7%	52.3%
1N-pyrene d9	62.7%	50.2%	37.8%	50.8%	52.6%	33.4%	35.5%	51.5%	44.8%	45.0%	56.8%	39.7%	54.2%	63.7%	55.8%

Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	1.7E+02	5.6E+02	1.8E+01	1.8E+01	9.4E+00	6.4E+00	3.3E+01	1.3E+01	1.3E+00	5.3E-01	1.2E+01	2.9E+01	7.3E+00	1.8E+00	2.8E+00
2N-napthalene	1.1E+02	2.6E+02	2.3E+01	2.6E+01	1.2E+01	8.7E+00	1.9E+01	1.2E+01	7.7E+00	2.7E+00	1.7E+01	4.2E+01	1.3E+01	3.0E+00	5.1E+00
2N-biphenyl	1.9E+01	3.3E+01	6.9E+00	8.7E+00	1.9E+00	1.4E+00	5.0E+00	4.3E+00	1.3E+00	1.2E+00	7.4E+00	1.9E+01	2.9E+00	2.7E-01	8.1E-01
3N-biphenyl	1.1E+02	1.4E+02	2.4E+01	1.9E+01	3.0E+00	4.8E+00	9.1E+00	6.7E+00	3.7E+00	1.4E+00	6.0E+00	1.0E+01	1.1E+01	8.6E+00	1.1E+00
4-Nitrobiphenyl	6.4E+01	1.4E+02	2.9E+01	4.6E+01	1.5E+01	3.2E+00	9.3E+00	1.8E+02	2.1E+00	1.1E+00	3.9E+01	1.6E+02	1.4E+01	1.0E+00	7.9E+00
3N-dibenzofuran	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,3-dinitronaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,5-dinitronaphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
5N-acenapthene	1.1E+01	1.8E+01	1.1E+01	3.1E+00	4.9E+00	2.4E+00	3.8E+00	1.3E+01	1.5E+00	1.1E+00	4.4E+00	2.0E+01	4.3E+00	4.3E-01	4.0E+00
2N-fluorene	1.2E+01	2.1E+01	3.7E+00	3.2E+00	7.2E+00	2.8E+00	1.9E+00	5.7E+01	3.5E+00	3.5E+00	6.8E+00	3.9E+01	2.4E+00	5.9E-01	1.0E+01
2,2'-dinitrobiphenyl	2.4E+00	8.0E+00	<BG	<BG	4.6E+00	<BG	6.9E+00	<BG	4.2E+00	2.5E+00	<BG	5.8E+00	2.0E+00	<BG	<BG
9N-anthracene	9.0E+01	6.9E+01	3.6E+01	8.9E+01	9.8E+01	9.3E+01	6.3E+01	5.9E+01	4.7E+01	4.0E+01	1.9E+01	2.1E+02	2.6E+01	1.7E+01	2.7E+01
2N-anthracene	3.6E+00	5.7E+00	ND	ND	ND	ND	<BG	5.2E+00	ND	ND	ND	7.2E+00	ND	ND	ND
9N-phenanthrene	3.3E+01	5.7E+01	1.6E+01	4.7E+00	1.5E+01	1.5E+01	9.2E+00	6.9E+01	1.0E+01	2.3E+01	2.4E+01	6.2E+01	1.1E+01	5.8E+00	2.2E+01
3N-phenanthrene	1.8E+01	3.4E+01	8.1E+00	3.7E+00	1.1E+01	9.0E+00	6.3E+00	6.1E+01	8.1E+00	7.1E+00	9.2E+00	4.6E+01	4.8E+00	2.4E+00	2.1E+01
4N-phenanthrene	5.4E+00	8.4E+00	2.0E+00	1.1E+00	2.6E+00	1.4E+00	1.9E+00	4.4E+00	6.8E-01	7.5E-01	1.0E+00	5.8E+00	6.6E-01	1.2E-01	6.2E-01
2N-fluoranthene	7.4E+01	8.8E+01	4.3E+01	8.7E+01	2.5E+02	1.6E+02	1.1E+02	5.3E+01	6.1E+01	2.8E+01	1.2E+01	3.0E+02	7.8E+01	3.0E+01	3.4E+01
3N-fluoranthene	1.3E+01	1.4E+01	2.4E+00	1.3E+00	1.6E+00	1.0E+00	6.8E-01	2.7E+00	9.4E-01	1.0E+00	1.5E+00	5.9E+00	6.5E-01	1.1E+00	2.2E+00
1N-pyrene	5.9E+02	8.0E+02	1.2E+02	6.4E+01	1.6E+02	1.3E+02	1.5E+02	2.4E+02	1.3E+02	9.4E+01	9.4E+01	3.6E+02	4.6E+01	3.9E+01	3.4E+02
2N-pyrene	1.0E+01	1.1E+01	4.8E+00	6.2E+00	1.5E+01	9.7E+00	1.2E+01	8.7E+00	7.4E+00	3.6E+00	1.3E+00	1.2E+01	3.3E+00	2.1E+00	5.0E+00
7-nitrobenz[a]anthracene	3.6E+01	4.0E+01	4.8E+00	7.0E+01	1.3E+02	2.8E+01	2.9E+01	3.9E+01	8.1E+00	6.4E+00	3.5E+00	6.5E+01	2.7E+00	3.7E+00	1.3E+01
6N-chrysene	4.5E+00	6.2E+00	1.1E+00	1.4E+00	1.5E+00	1.6E+00	2.0E+00	2.2E+00	1.6E+00	1.2E+00	8.4E-01	2.8E+00	3.9E-01	5.1E-01	1.8E+00

	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 9	MT 10	MT 11	MT 12	MT 13	MT 16	MT 17	MT 18
Sample ID	MT 2	MT 3	MT 4	MT 5	MT 6	MT 7	MT 9	MT 10	MT 11	MT 12	MT 13	MT 16	MT 17	MT 18
Start Date	032302	032402	032802	032902	033002	033102	040302	040402	040802	040902	041002	041402	041502	041602
Start Time	1906	1914	1920	2016	1809	1936	1924	1930	1720	1835	1905	1555	1834	0846
Stop Date	032402	032502	032902	033002	033102	040102	040402	040502	040902	041002	041102	041502	041602	041602
Stop Time	1800	1740	1901	1706	1802	1750	1813	325	1808	1823	1826	1802	742	1854
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Surrogate (% Recovery)														
1N-Napthalene-d7	37.4%	42.1%	26.0%	21.8%	11.7%	16.7%	16.9%	11.8%	18.5%	13.8%	12.5%	21.1%	16.8%	16.1%
1N-anthracene-d9	66.0%	84.1%	52.0%	61.8%	40.8%	46.5%	72.3%	23.6%	53.7%	44.1%	15.6%	49.7%	18.0%	54.7%
1N-pyrene-d9	77.5%	76.9%	64.3%	57.0%	51.1%	59.4%	58.8%	32.6%	65.6%	70.9%	24.4%	57.6%	25.7%	64.4%
Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	2.7E+03	3.9E+02	3.1E+03	1.5E+02	3.4E+02	2.7E+03	6.5E+02	1.2E+03	1.3E+03	5.7E+02	2.5E+02	5.6E+02	6.5E+03	8.9E+02
2N-napthalene	9.8E+02	3.5E+02	1.1E+03	1.7E+02	2.8E+02	1.5E+03	1.9E+02	4.3E+02	7.3E+02	3.1E+02	4.0E+02	5.5E+02	2.5E+03	1.2E+03
2N-biphenyl	2.1E+02	2.1E+01	5.5E+01	1.3E+01	6.5E+01	7.0E+01	8.7E+00	2.4E+01	1.3E+02	3.4E+01	5.0E+01	2.1E+02	1.9E+02	2.9E+02
3N-biphenyl	1.4E+02	4.1E+01	3.5E+01	2.3E+01	8.4E+01	3.0E+01	5.0E+00	2.1E+01	1.0E+02	2.4E+01	7.9E+01	1.2E+02	1.2E+02	7.9E+02
4-Nitrobiphenyl	9.1E+01	1.3E+01	1.0E+02	6.9E+00	<BG	3.2E+02	2.1E+01	4.9E+01	9.4E+01	5.4E+01	2.9E+01	2.0E+02	1.3E+02	6.2E+01
3N-dibenzofuran	2.8E+01	6.1E+00	2.9E+01	4.4E+00	<BG	6.8E+01	4.5E+00	8.4E+00	4.0E+01	1.7E+01	2.2E+01	7.0E+01	8.3E+01	3.6E+01
1,3-dinitronaphthalene	1.5E+00	4.9E-01	1.8E+00	3.5E-01	5.4E-01	3.6E+00	2.7E-01	<BG	5.3E+00	1.7E+00	2.1E+00	9.8E+00	4.9E+00	7.8E+00
1,5-dinitronaphthalene	3.2E-01	1.3E-01	8.2E-01	2.2E-01	<BG	1.4E+00	1.8E-01	<BG	2.3E+00	7.1E-01	8.0E-01	2.2E+00	5.2E+00	1.4E+00
5N-acenapthene	8.3E+01	5.8E+00	1.3E+01	7.6E+00	6.7E+01	1.3E+01	1.6E+00	6.0E+00	1.1E+02	2.1E+01	2.3E+01	1.6E+02	4.5E+02	4.1E+02
2N-fluorene	6.7E+01	2.1E+00	1.1E+01	1.2E+00	5.4E+01	2.8E+01	2.7E+00	3.5E+00	8.1E+01	4.5E+00	6.0E+00	1.0E+02	1.8E+01	1.3E+02
2,2'-dinitrobiphenyl	2.8E+00	9.7E+00	1.0E+01	4.8E+00	4.9E+00	3.3E+01	1.1E+00	1.1E+01	2.9E+00	1.8E+01	8.3E+01	3.6E+00	8.8E+01	7.7E+00
9N-anthracene	2.1E+02	2.0E+02	1.4E+02	4.1E+01	9.5E+01	7.3E+01	1.2E+01	4.7E+01	3.0E+02	7.3E+01	2.5E+02	4.5E+02	8.3E+02	6.2E+02
2N-anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	2.9E-01	<BG	<BG	<BG	<BG
9N-phenanthrene	8.0E+01	6.0E+00	3.1E+01	4.3E+00	4.7E+01	8.7E+01	1.1E+01	1.0E+01	1.3E+02	1.4E+01	2.6E+01	2.6E+02	6.7E+01	1.4E+02
3N-phenanthrene	3.2E+01	3.5E+00	6.8E+00	2.4E+00	3.1E+01	1.2E+01	8.9E-01	1.4E+00	4.4E+01	5.8E+00	1.3E+01	5.8E+01	5.6E+01	1.1E+02
4N-phenanthrene	2.4E+00	1.6E+00	2.0E+00	7.6E-01	<BG	4.1E+00	5.9E-01	1.6E+00	3.8E+00	1.8E+00	6.1E+00	9.3E+00	2.7E+01	1.3E+01
2N-fluoranthene	5.3E+01	3.0E+00	2.4E+00	2.8E+00	4.4E+01	3.0E+00	3.3E-01	6.4E-01	5.7E+01	3.9E+00	9.1E+00	6.6E+01	5.2E+01	2.7E+02
3N-fluoranthene	3.6E+01	<BG	1.4E-01	<BG	3.0E+01	3.0E-01	<BG	<BG	3.2E+01	7.6E-02	<BG	3.6E+01	<BG	9.0E+01
1N-pyrene	5.4E+01	1.2E+00	2.0E+00	9.6E-01	4.8E+01	4.8E+00	2.4E-01	4.2E-01	7.9E+01	2.4E+00	7.0E+00	7.2E+01	1.2E+01	1.6E+02
2N-pyrene	3.1E+01	<BG	<BG	<BG	2.1E+01	<BG	<BG	<BG	2.2E+01	<BG	<BG	2.7E+01	<BG	7.0E+01
7-nitrobenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	2.4E-01	7.5E-02	<BG	4.4E-01	8.1E-01	<BG
6N-chrysene	4.2E+01	<BG	<BG	<BG	3.6E+01	<BG	<BG	<BG	4.2E+01	<BG	<BG	4.8E+01	<BG	1.2E+02

Sample ID	MT 20	MT 23	MT 24	MT 25	MT 26	MT 27	MT 28	MT 29	MT 30	MT 31	MT 32	MT 33	MT 34	MT 37
Start Date	041702	042302	042302	042402	042402	042502	042502	042602	042702	042802	042902	070902	071002	071302
Start Time	0855	0834	1942	0913	1926	0855	1840	1905	1710	1655	1734	1705	1845	1923
Stop Date	041702	042302	042402	042402	042502	042502	042602	042702	042802	042902	043002	071002	071102	071402
Stop Time	1759	1839	807	1933	800	1814	1843	1700	1645	1720	1704	1745	1805	1811
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF

Surrogate (% Recovery)														
1N-Napthalene-d7	27.7%	21.0%	32.1%	21.9%	0.0%	0.0%	1.0%	2.1%	18.3%	23.4%	8.8%	46.7%	78.6%	78.0%
1N-anthracene-d9	56.8%	67.5%	59.1%	64.4%	0.0%	0.0%	0.0%	0.0%	58.0%	65.7%	0.0%	37.7%	53.2%	34.0%
1N-pyrene-d9	52.9%	52.2%	52.8%	61.8%	0.0%	0.0%	0.0%	0.0%	72.0%	69.4%	0.0%	53.1%	55.5%	45.9%

Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	1.4E+03	1.0E+03	8.9E+02	1.0E+03	1.8E+03	5.4E+02	3.0E+03	7.0E+02	6.2E+02	1.1E+03	4.3E+02	3.2E+01	4.3E+01	6.9E+01
2N-napthalene	7.4E+02	6.8E+02	5.9E+02	7.5E+02	1.0E+03	4.0E+02	1.2E+03	5.8E+02	2.8E+02	4.7E+02	2.5E+02	4.1E+01	3.7E+01	1.0E+02
2N-biphenyl	4.6E+01	1.7E+02	1.6E+02	1.9E+02	1.8E+02	9.8E+01	1.3E+02	1.2E+02	3.0E+01	3.5E+01	3.4E+01	1.5E+01	5.4E+00	1.5E+01
3N-biphenyl	1.0E+02	2.6E+02	1.9E+02	2.7E+02	2.0E+02	1.4E+02	7.2E+01	9.3E+01	2.2E+01	1.3E+01	3.4E+01	2.1E+01	6.3E+00	1.2E+01
4-Nitrobiphenyl	1.9E+02	1.1E+01	1.7E+01	1.3E+01	6.7E+01	1.5E+01	1.1E+02	1.6E+01	4.0E+01	6.7E+01	5.1E+01	2.8E+01	9.1E+00	1.4E+01
3N-dibenzofuran	7.3E+01	2.9E+00	4.0E+00	2.2E+00	1.3E+01	5.5E+00	3.3E+01	7.2E+00	2.5E+01	4.3E+01	1.2E+01	2.1E+01	3.4E+00	8.7E+00
1,3-dinitronaphthalene	<BG	1.4E+00	8.9E-01	1.4E+00	1.8E+00	1.2E+00	2.5E+00	8.4E-01	1.2E+00	1.9E+00	9.8E-01	1.0E+00	3.5E-01	5.7E-01
1,5-dinitronaphthalene	<BG	<BG	<BG	<BG	4.7E-01	1.7E-01	8.9E-01	1.3E-01	5.5E-01	7.7E-01	3.3E-01	2.9E+00	1.5E-01	1.3E+00
5N-acenapthene	7.3E+02	1.9E+02	1.3E+02	1.8E+02	1.4E+02	9.9E+01	4.1E+01	5.1E+01	1.9E+01	2.3E+01	3.8E+01	1.1E+02	1.9E+01	6.7E+01
2N-fluorene	2.5E+01	1.4E+02	9.4E+01	1.4E+02	1.1E+02	6.7E+01	4.7E+01	3.0E+01	1.2E+01	1.6E+01	3.4E+01	6.8E+00	1.4E+00	2.4E+00
2,2'-dinitrobiphenyl	2.1E+01	1.2E+01	7.4E+01	5.9E+00	9.8E+00	5.4E+01	1.6E+00	4.3E+00	2.3E+00	5.0E+00	1.1E+01	4.5E+00	3.5E+00	7.9E+00
9N-anthracene	2.6E+03	2.7E+02	2.5E+02	2.6E+02	2.2E+02	1.5E+02	1.3E+02	1.7E+02	5.5E+01	1.3E+02	9.1E+01	3.1E+02	9.4E+01	1.3E+02
2N-anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	4.0E-01	<BG	<BG	<BG	<BG	<BG
9N-phenanthrene	1.2E+02	1.4E+02	9.1E+01	1.2E+02	1.1E+02	6.9E+01	1.2E+02	3.3E+01	6.1E+01	7.0E+01	6.7E+01	4.4E+01	7.4E+00	1.8E+01
3N-phenanthrene	8.6E+01	8.3E+01	5.6E+01	7.6E+01	6.4E+01	4.4E+01	2.4E+01	1.8E+01	9.2E+00	9.5E+00	2.6E+01	2.2E+01	4.5E+00	1.3E+01
4N-phenanthrene	2.4E+01	7.3E-01	7.7E-01	4.8E-01	1.5E+00	1.0E+00	3.8E+00	1.4E+00	3.3E+00	3.9E+00	1.4E+00	7.4E+00	1.8E+00	4.0E+00
2N-fluoranthene	1.6E+02	1.8E+02	1.0E+02	1.5E+02	1.2E+02	8.2E+01	3.2E+01	3.8E+01	4.7E+00	3.3E+00	3.0E+01	3.2E+01	3.4E+00	3.4E+01
3N-fluoranthene	2.0E+00	1.2E+02	7.1E+01	1.0E+02	8.4E+01	5.5E+01	2.1E+01	2.4E+01	2.8E-01	4.6E-01	2.0E+01	3.7E-01	<BG	2.6E-01
1N-pyrene	2.5E+00	2.2E+02	9.9E+01	1.4E+02	1.3E+02	7.9E+01	3.0E+01	4.3E+01	4.9E+00	8.7E+00	2.7E+01	7.6E+00	1.6E+00	6.3E+00
2N-pyrene	<BG	1.1E+02	6.3E+01	8.5E+01	6.5E+01	4.7E+01	2.0E+01	2.0E+01	<BG	<BG	1.6E+01	<BG	<BG	<BG
7-nitrobenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	1.4E-01	1.8E-01	<BG	2.7E-01	<BG	2.8E-01
6N-chrysene	<BG	3.8E+02	1.0E+02	1.7E+02	1.4E+02	9.5E+01	3.6E+01	4.1E+01	<BG	9.9E-02	2.3E+01	<BG	<BG	<BG

Sample ID	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43	MT 45	MT 46	MT 47	MT 49	MT 49 Back	MT 50	MT 50 Back	MT 51
Start Date	071402	071502	071602	071702	071802	071902	072102	072202	072302	072902	072902	072902	072902	072902
Start Time	1921	1903	1850	1905	1853	1935	1819	1832	734	620	620	1206	1206	1854
Stop Date	071502	071602	071702	071802	071902	072002	072202	072302	072402	072902	072902	072902	072902	073002
Stop Time	1757	1754	1801	1804	1850	1828	1740	727	800	1124	1124	1758	1758	605
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF

Surrogate (% Recovery)

	MT 38	MT 39	MT 40	MT 41	MT 42	MT 43	MT 45	MT 46	MT 47	MT 49	MT 49 Back	MT 50	MT 50 Back	MT 51
1N-Napthalene-d7	46.8%	59.6%	97.0%	45.1%	46.4%	87.9%	39.0%	37.2%	159.0%	52.7%	62.2%	13.3%	39.1%	109.3%
1N-anthracene-d9	34.0%	41.5%	41.1%	39.6%	45.3%	47.2%	44.6%	34.1%	45.8%	54.7%	51.9%	13.6%	68.2%	68.6%
1N-pyrene-d9	50.8%	44.7%	52.2%	43.1%	41.8%	54.3%	65.1%	40.8%	52.1%	46.4%	57.4%	8.7%	60.1%	61.7%

Conc (Surrogate corrected)

	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	1.5E+02	1.8E+01	9.8E+01	8.2E+01	5.3E+01	5.1E+01	8.3E+01	7.1E+02	1.1E+02	2.8E+02	3.3E+02	6.9E+01	2.6E+02	6.0E+02
2N-napthalene	1.0E+02	2.7E+01	8.0E+01	7.3E+01	6.5E+01	7.3E+01	5.8E+01	2.3E+02	1.0E+02	2.9E+02	1.5E+02	2.4E+01	1.7E+02	2.7E+02
2N-biphenyl	1.8E+01	3.6E+00	1.5E+01	7.1E+00	8.7E+00	1.0E+01	7.0E+00	3.1E+01	1.5E+01	2.3E+01	7.5E+00	4.5E+00	1.2E+01	4.3E+01
3N-biphenyl	2.7E+01	1.1E+01	6.2E+01	1.5E+01	1.7E+01	6.6E+00	2.5E+01	1.7E+01	1.8E+01	2.5E+01	<BG	<BG	1.0E+01	1.0E+01
4-Nitrobiphenyl	5.5E+01	9.9E+00	3.5E+01	3.8E+01	2.2E+01	2.4E+00	1.4E+02	4.8E+01	2.5E+01	8.9E+01	2.4E+00	<BG	3.0E+01	2.7E+01
3N-dibenzofuran	1.8E+01	1.2E+01	2.9E+01	1.8E+01	1.4E+01	3.6E+00	6.2E+01	1.9E+01	1.5E+01	2.0E+01	<BG	<BG	9.4E+00	1.1E+01
1,3-dinitronaphthalene	2.9E+00	1.9E+00	2.3E+00	3.7E+00	4.0E+00	3.5E-01	4.5E+00	1.9E+00	1.5E+00	3.4E+00	<BG	<BG	2.9E+00	<BG
1,5-dinitronaphthalene	1.7E+00	8.6E-01	2.1E+00	3.3E+00	2.4E+00	6.7E-01	4.3E+00	2.7E+00	2.4E+00	2.3E+00	<BG	5.0E-01	1.7E+00	1.8E+00
5N-acenapthene	7.6E+01	1.1E+02	3.2E+02	1.6E+02	7.6E+01	4.2E+01	1.6E+02	1.8E+02	1.5E+02	7.9E+01	<BG	<BG	1.2E+02	1.5E+02
2N-fluorene	8.9E+00	2.6E+00	5.1E+00	7.7E+00	4.0E+00	6.8E-01	3.9E+01	7.4E+00	4.8E+00	1.6E+01	<BG	<BG	5.8E+00	4.4E+00
2,2'-dinitrobiphenyl	4.2E+01	5.3E+00	2.5E+00	1.9E+00	7.7E+00	1.2E+01	2.0E+00	3.2E+01	8.3E+01	4.2E+00	3.3E+00	<BG	1.3E+01	6.9E+00
9N-anthracene	1.4E+02	2.9E+02	1.9E+03	6.9E+02	3.6E+02	1.2E+02	5.6E+02	6.0E+02	2.6E+02	1.0E+02	<BG	<BG	9.0E+01	7.4E+02
2N-anthracene	<BG	<BG	<BG	<BG	7.2E-01	<BG	<BG	<BG	<BG	2.7E+00	<BG	<BG	<BG	<BG
9N-phenanthrene	3.9E+01	2.7E+01	1.8E+01	4.4E+01	1.8E+01	7.8E+00	1.4E+02	4.6E+01	2.5E+01	4.7E+01	1.1E+00	<BG	1.5E+01	2.5E+01
3N-phenanthrene	2.2E+01	2.1E+01	4.8E+01	2.9E+01	1.8E+01	6.7E+00	3.9E+01	2.6E+01	2.1E+01	3.7E+01	<BG	<BG	2.0E+01	2.4E+01
4N-phenanthrene	7.0E+00	4.4E+00	2.9E+01	9.3E+00	2.5E+00	1.7E+00	1.0E+01	4.7E+00	8.6E+00	1.4E+01	<BG	<BG	7.5E+00	7.6E+00
2N-fluoranthene	2.6E+01	4.5E+01	1.0E+02	6.5E+01	5.5E+01	1.3E+01	2.6E+01	2.3E+01	2.6E+01	1.6E+01	<BG	<BG	1.8E+01	2.9E+01
3N-fluoranthene	2.6E-01	2.7E-01	3.5E-01	4.1E-01	4.7E-01	<BG	2.1E+00	3.6E-01	3.6E-01	6.2E-01	<BG	<BG	<BG	<BG
1N-pyrene	5.0E+00	4.9E+00	2.1E+01	8.2E+00	7.5E+00	1.7E+00	6.5E+01	6.4E+00	5.7E+00	1.3E+01	<BG	<BG	5.5E+00	5.7E+00
2N-pyrene	<BG	<BG	4.4E+00	5.0E-01	<BG	<BG	5.7E-01	<BG	<BG	<BG	<BG	<BG	<BG	<BG
7-nitrobenz[a]anthracene	2.1E-01	9.9E-02	1.1E+00	3.8E-01	2.7E-01	1.6E-01	7.2E-01	3.1E-01	<BG	<BG	<BG	<BG	<BG	6.0E-01
6N-chrysene	<BG	<BG	<BG	<BG	<BG	<BG	1.4E-01	<BG	<BG	<BG	<BG	<BG	<BG	<BG

	MT 52	MT 53	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63	MT 64	MT 65
Sample ID	MT 52	MT 53	MT 54	MT 55	MT 56	MT 57	MT 58	MT 59	MT 60	MT 61	MT 62	MT 63	MT 64	MT 65
Start Date	073002	073002	073002	080102	080502	080602	080602	080602	080702	080702	080802	080802	012703	012803
Start Time	650	1250	1824	1759	1900	100	700	1900	745	1900	800	1900	1830	1230
Stop Date	073002	073002	073102	080202	080602	080602	080602	080702	080702	080802	080802	080902	012803	012803
Stop Time	1245	1814	750	807	100	700	1900	746	1900	754	1900	803	802	800
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Surrogate (% Recovery)														
1N-Napthalene-d7	43.9%	46.7%	74.7%	31.4%	31.9%	73.7%	47.0%	54.5%	41.4%	57.2%	43.6%	65.9%	53.5%	38.2%
1N-anthracene-d9	57.9%	46.3%	48.6%	23.7%	41.2%	90.9%	59.9%	66.6%	58.9%	62.5%	74.0%	80.5%	60.8%	47.2%
1N-pyrene-d9	59.4%	53.5%	41.8%	19.1%	40.0%	68.2%	35.8%	44.1%	41.4%	46.8%	44.1%	63.1%	41.2%	28.7%
Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	7.3E+01	7.7E+01	3.0E+02	6.8E+02	2.9E+02	2.5E+02	8.9E+01	2.9E+02	7.6E+01	2.4E+02	5.8E+01	1.4E+02	1.6E+02	3.5E+02
2N-napthalene	1.2E+02	9.2E+01	2.4E+02	5.7E+02	2.7E+02	1.3E+02	6.0E+01	1.0E+02	8.0E+01	2.2E+02	4.8E+01	1.7E+01	4.5E+01	3.6E+02
2N-biphenyl	1.6E+01	6.2E+00	3.2E+01	3.1E+01	2.9E+01	2.0E+01	4.8E+00	9.1E+00	3.3E+00	1.4E+01	2.5E+00	5.0E-01	8.2E-01	1.8E+01
3N-biphenyl	1.5E+01	9.1E+00	1.2E+01	4.3E+01	1.2E+01	6.0E+00	4.7E+00	2.9E+00	5.4E+00	9.9E+00	5.2E+00	3.1E-01	<BG	2.0E+01
4-Nitrobiphenyl	1.2E+01	1.7E+01	1.5E+01	7.6E+01	1.2E+01	2.3E+01	2.2E+01	1.2E+01	8.3E+00	9.0E+00	5.0E+00	1.8E+00	<BG	1.2E+01
3N-dibenzofuran	6.1E+00	7.6E+00	1.1E+01	3.0E+01	1.8E+01	5.1E+00	4.5E+00	5.1E+00	3.1E+00	5.8E+00	2.4E+00	<BG	<BG	1.1E+01
1,3-dinitronaphthalene	1.1E+00	2.4E+00	8.6E-01	5.1E+00	<BG	<BG	3.4E-01	<BG	<BG	4.7E-01	<BG	<BG	<BG	8.0E-01
1,5-dinitronaphthalene	4.7E-01	<BG	1.5E+00	3.6E+00	2.2E+00	8.0E-01	1.9E-01	2.0E-01	9.4E-02	1.3E-01	9.0E-02	<BG	<BG	2.6E-01
5N-acenapthene	5.7E+01	9.1E+01	9.5E+01	4.1E+02	9.7E+01	2.5E+01	2.0E+01	1.5E+01	2.0E+01	7.6E+01	2.0E+01	<BG	<BG	1.5E+02
2N-fluorene	2.4E+00	4.0E+00	2.3E+00	7.6E+00	2.2E+00	2.9E+00	2.6E+00	2.5E+00	1.8E+00	1.7E+00	1.8E+00	<BG	<BG	3.4E+00
2,2'-dinitrobiphenyl	4.7E+00	<BG	3.4E+01	1.1E+01	<BG	1.2E+01	2.6E+00	6.0E+00	1.6E+00	2.4E+00	1.3E+00	<BG	2.4E+01	<BG
9N-anthracene	9.1E+01	8.3E+01	3.6E+02	1.5E+03	2.8E+02	1.1E+02	2.9E+01	1.1E+02	3.1E+01	3.6E+02	2.7E+01	2.6E+00	1.0E+00	7.9E+02
2N-anthracene	<BG	<BG	<BG	<BG	<BG	<BG	8.3E-01	<BG	<BG	<BG	1.1E+00	<BG	<BG	<BG
9N-phenanthrene	1.0E+01	1.4E+01	1.8E+01	8.0E+01	1.6E+01	1.0E+01	1.4E+01	1.5E+01	1.5E+01	1.1E+01	2.1E+01	1.8E-01	<BG	3.6E+01
3N-phenanthrene	1.7E+01	2.1E+01	1.7E+01	8.4E+01	1.7E+01	6.2E+00	5.3E+00	4.4E+00	5.2E+00	1.4E+01	5.0E+00	<BG	<BG	2.5E+01
4N-phenanthrene	8.1E+00	6.3E+00	3.8E+00	1.8E+01	7.4E+00	1.8E+00	2.2E+00	1.5E+00	1.8E+00	4.5E+00	2.4E+00	<BG	<BG	7.2E+00
2N-fluoranthene	1.3E+01	7.9E+00	2.2E+01	2.1E+02	2.6E+01	1.3E+01	2.7E+00	3.2E+00	3.9E+00	8.9E+00	1.8E+00	4.0E-01	<BG	1.5E+01
3N-fluoranthene	4.7E-01	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
1N-pyrene	5.4E+00	2.2E+00	3.6E+00	1.1E+01	5.7E+00	1.9E+00	7.8E-01	2.8E+00	1.1E+00	3.1E+00	8.2E-01	1.5E+00	<BG	3.0E+00
2N-pyrene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
7-nitrobenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
6N-chrysene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG

	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
Sample ID	MT 66	MT 67	MT 68	MT 69	MT 70	MT 71	MT 72	MT 73	MT 74	MT 75	MT 76	MT 77	MT 78
Start Date	012803	012803	012903	012903	012903	013003	013003	013003	020503	020503	020603	020603	020703
Start Time	820	1800	30	745	1837	30	810	1830	700	1825	735	1745	110
Stop Date	012803	012903	012903	012903	013003	013003	013003	013103	020503	020603	020603	020703	020703
Stop Time	1734	30	630	1831	30	630	1830	1830	1820	735	1740	110	710
Media	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF	PUF
Surrogate (% Recovery)													
1N-Napthalene-d7	48.5%	56.6%	62.6%	79.4%	77.8%	59.5%	110.9%	235.5%	69.5%	71.2%	68.1%	56.7%	38.4%
1N-anthracene-d9	70.1%	64.1%	50.6%	52.0%	54.1%	62.9%	61.5%	63.4%	52.8%	70.4%	66.4%	59.1%	35.9%
1N-pyrene-d9	46.1%	37.0%	38.8%	56.5%	43.3%	45.0%	54.5%	59.7%	50.3%	60.9%	67.9%	57.9%	27.1%
Conc (Surrogate corrected)	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
1N-napthalene	4.2E+02	2.2E+02	5.7E+02	4.5E+02	1.0E+02	1.0E+03	5.7E+02	2.2E+02	3.5E+02	1.2E+03	2.6E+02	2.0E+02	1.3E+03
2N-napthalene	1.7E+02	1.1E+02	4.0E+02	3.1E+02	1.3E+02	3.5E+02	4.2E+02	1.9E+02	1.5E+02	4.7E+02	1.5E+02	9.6E+01	5.2E+02
2N-biphenyl	3.1E+00	2.1E+00	8.6E+00	1.7E+01	8.5E+00	4.5E+01	1.5E+01	1.0E+01	1.5E+00	1.8E+01	3.2E+00	7.1E+00	2.3E+01
3N-biphenyl	2.3E+00	1.4E+00	1.8E+01	4.0E+01	4.0E+01	2.1E+01	6.9E+01	6.1E+01	7.3E-01	8.5E+00	6.3E+00	1.5E+01	1.7E+01
4-Nitrobiphenyl	3.0E+00	2.4E+00	3.2E+01	3.2E+01	1.2E+01	1.1E+02	4.0E+01	2.2E+01	2.5E+00	7.1E+00	3.9E+00	1.9E+01	1.5E+02
3N-dibenzofuran	<BG	<BG	3.5E+00	7.6E+00	4.2E+00	5.1E+00	3.2E+00	5.7E+00	<BG	8.2E-01	<BG	4.3E+00	1.3E+01
1,3-dinitronaphthalene	<BG	<BG	<BG	3.3E-01	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
1,5-dinitronaphthalene	<BG	<BG	<BG	1.4E-01	<BG	<BG	<BG	1.5E-01	8.4E-02	<BG	<BG	<BG	3.6E-01
5N-acenapthene	<BG	<BG	1.3E+00	3.8E+00	<BG	1.6E+00	1.9E+00	2.2E+00	3.6E-01	7.9E-01	<BG	3.2E+00	7.1E+00
2N-fluorene	<BG	<BG	<BG	1.1E+00	<BG	7.3E-01	<BG	<BG	<BG	1.6E-01	<BG	1.2E+00	5.6E+00
2,2'-dinitrobiphenyl	<BG	<BG	<BG	3.9E+01	5.9E+01	1.3E+02	1.5E+02	2.7E+01	6.7E+01	1.8E+01	2.1E+01	1.9E+01	4.2E+02
9N-anthracene	<BG	6.1E+00	2.0E+01	3.2E+01	2.9E+01	2.6E+01	1.7E+01	2.1E+01	3.1E+00	9.1E+00	2.3E+00	2.6E+01	4.9E+01
2N-anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
9N-phenanthrene	<BG	<BG	<BG	3.7E+00	1.0E+00	1.6E+00	1.0E+00	1.3E+00	5.1E-01	2.2E-01	1.6E-01	3.7E+00	5.2E+00
3N-phenanthrene	<BG	<BG	<BG	9.8E-01	<BG	4.3E-01	<BG	3.0E-01	2.3E-01	2.2E-01	<BG	6.3E-01	1.8E+00
4N-phenanthrene	<BG	<BG	<BG	7.1E-01	4.2E-01	3.5E-01	4.4E-01	2.5E-01	1.8E-01	1.1E-01	<BG	4.3E-01	8.4E-01
2N-fluoranthene	<BG	9.2E-01	<BG	1.1E+00	1.4E+00	6.3E-01	4.7E-01	8.0E-01	5.0E-01	6.6E-01	3.1E-01	1.0E+00	2.1E+00
3N-fluoranthene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
1N-pyrene	<BG	<BG	<BG	5.6E-01	<BG	<BG	<BG	<BG	3.6E-01	5.0E-01	2.5E-01	1.1E+00	1.6E+00
2N-pyrene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
7-nitrobenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
6N-chrysene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG

Appendix B

Berner Low Pressure Impactor PAH and NPAH Size Distributions

April 15, 2002
Night Sample

222

April 16, 2002
Day Sample

April 16, 2002
Night Sample

224

April 17-18, 2002
24 hr Sample

225

April 22, 2002
Night Sample

226

April 23, 2002
Day Sample

April 23, 2002
Night Sample

228

Fluoranthene | Pyrene | 3,6-Dimethylphenanthrene | 9,10-Dimethylanthracene

MDL

Benzo[a]fluorene | Benzo[b]fluorene | Benz[a]anthracene | Cyclopenta[c,d]pyrene

Chrysene + Triphenylene | Napthacene | Retene | Benzo[b]fluoranthene

Benzo[k]fluoranthene | Benzo[e]pyrene | Benzo[a]pyrene | Perylene

Indeno[c,d]pyrene | Benzo[g,h,i]perylene | Anthanthrene | Dibenz[ah,ac]anthracene

Coronene | Mass

Concentration, pg m^{-3}

D_p (μm)

μg m^{-3}

April 24, 2002
Day Sample

April 24, 2002
Night Sample

April 25, 2002
Day Sample

April 17, 2002
Day Sample

232

April 15, 2002
Night Sample

233

April 16, 2002
Day Sample

April 16, 2002
Night Sample

235

April 17, 2002
Day Sample

236

2N-Fluorene · 9N-Anthracene · 2N-Anthracene · 9N-Phenanthrene · MDL · 3N-Phenanthrene · 4N-Phenanthrene · 2N-Fluoranthene · 3N-Fluoranthene · 1N-Pyrene · 2N-Pyrene · 7N-Benz[a]anthracene · 6N-Chrysene · Mass

Concentration, pg m^{-3}

D_p (μm)

μg m^{-3}

April 17 - 18, 2002
Night and Day Sample

April 22, 2002
Night Sample

238

April 23, 2002
Day Sample

April 23, 2002
Night Sample

April 24, 2002
Day Sample
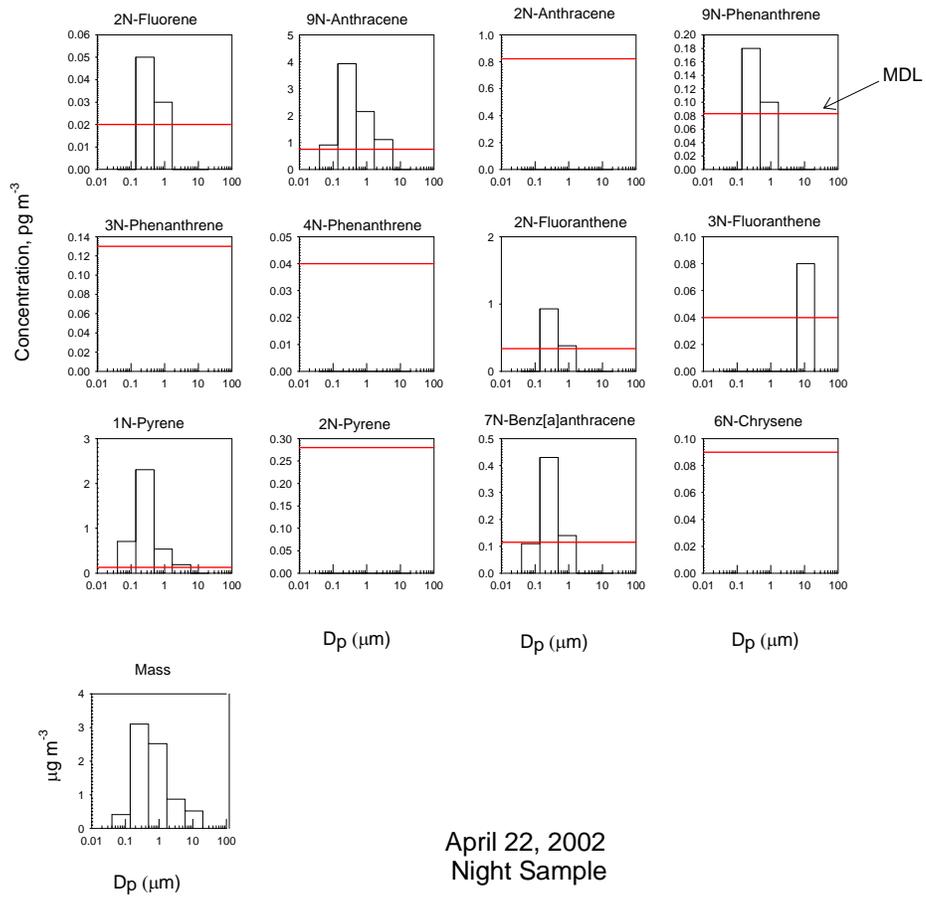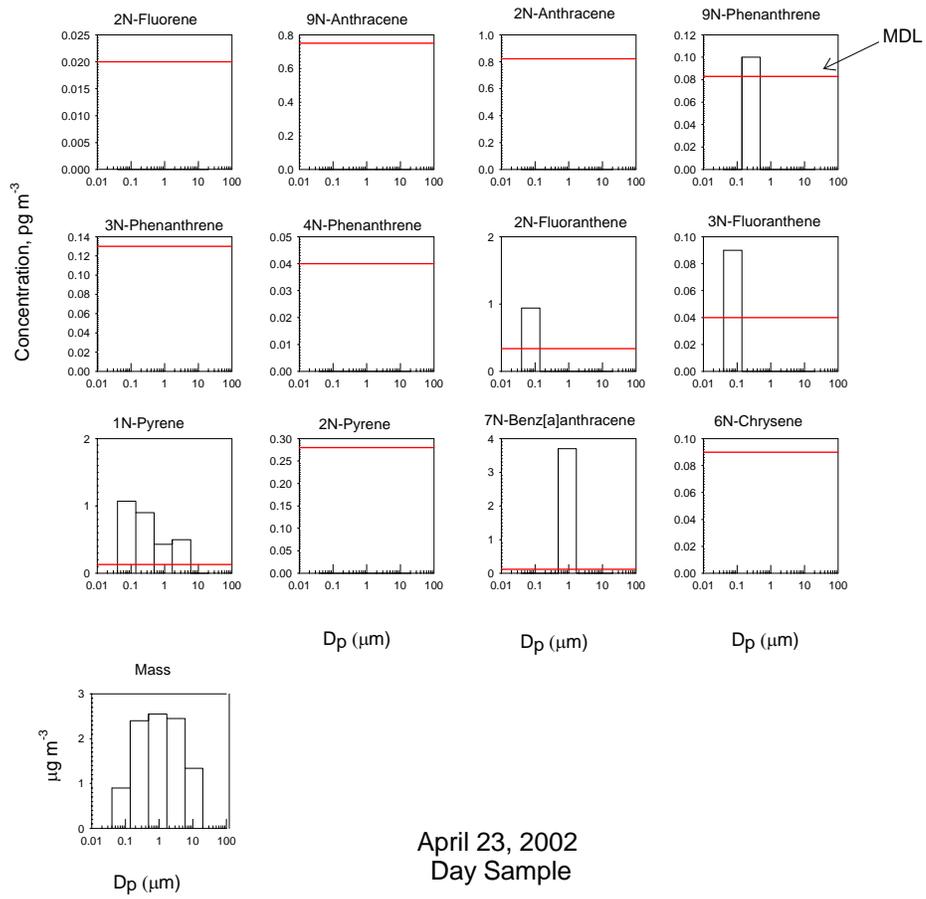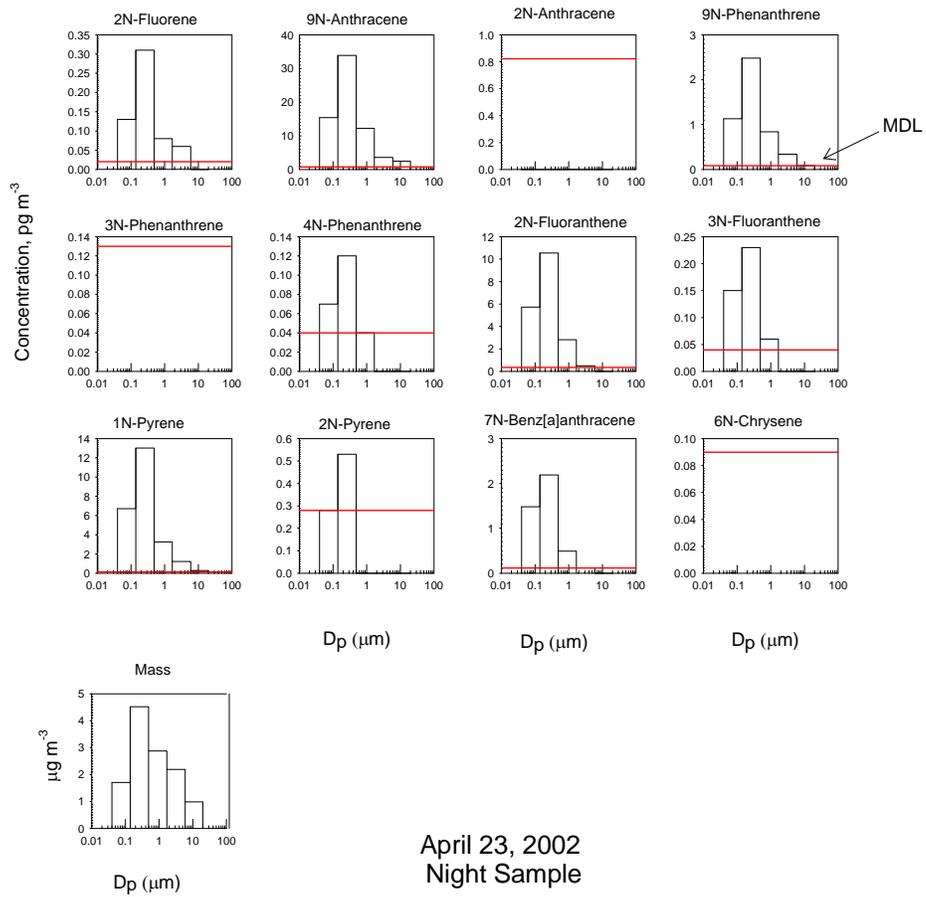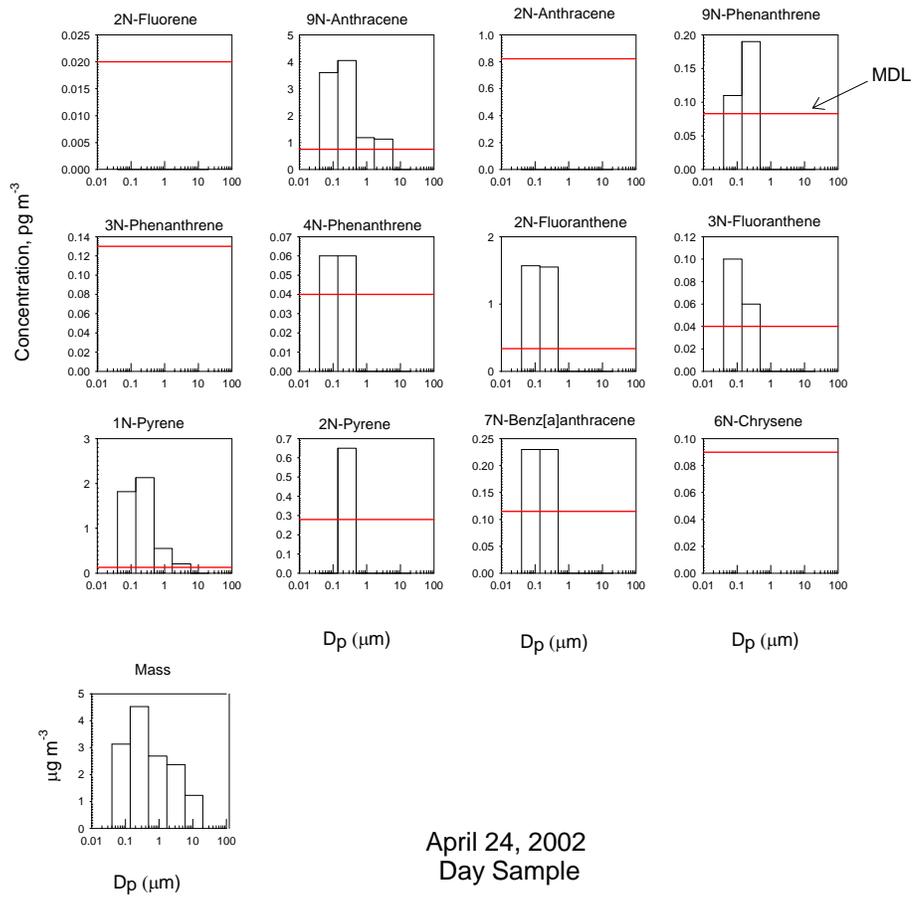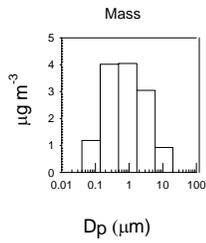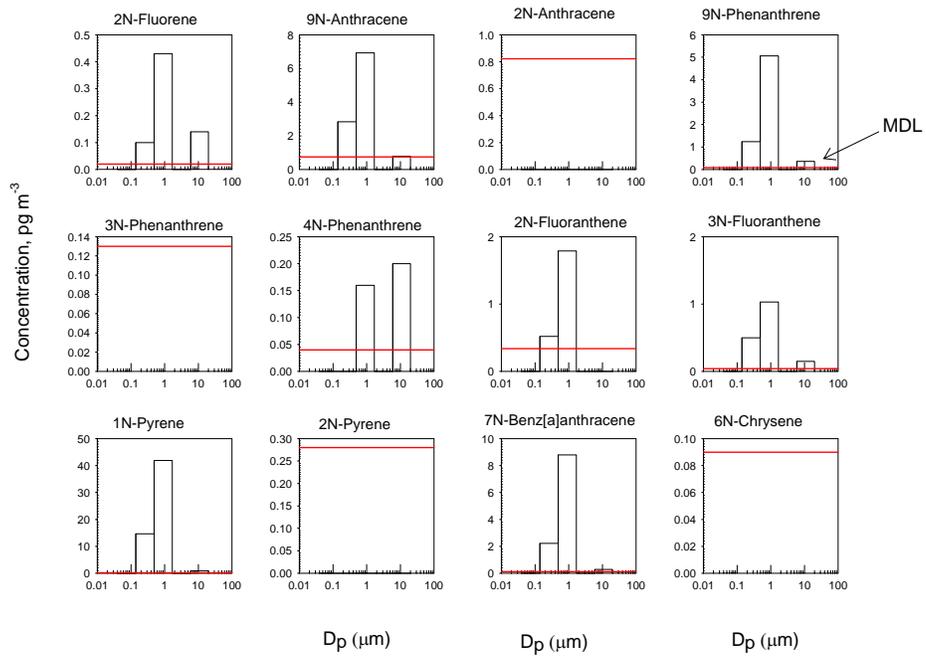
April 24, 2002
Night Sample
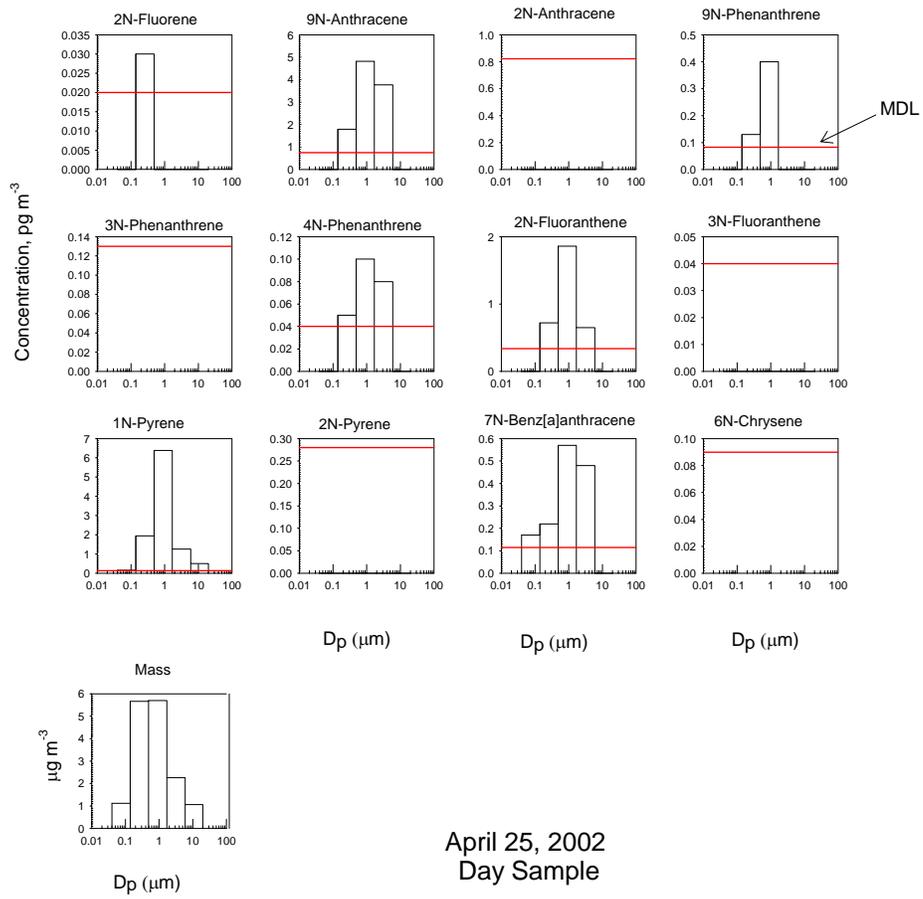
April 25, 2002
Day Sample

Appendix C

PAH and NPAH Berner Impactor Concentration Summary

Sample ID	MT 17	MT 17	MT 17	MT 17	MT 17	MT 18	MT 18	MT 18	MT 18	MT 18
Start Date	041502	041502	041502	041502	041502	041602	041602	041602	041602	041602
Start Time	1834	1834	1834	1834	1834	0846	0846	0846	0846	0846
Stop Date	041602	041602	041602	041602	041602	041602	041602	041602	041602	041602
Stop Time	742	742	742	742	742	1854	1854	1854	1854	1854
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um

Surrogates (% Recovery)

	MT 17	MT 17	MT 17	MT 17	MT 17	MT 18	MT 18	MT 18	MT 18	MT 18
d8 Napthalene	9%	10%	11%	9%	8%	11%	10%	12%	9%	7%
d10 Fluorene	75%	78%	79%	77%	76%	77%	85%	68%	82%	74%
d10 Fluoranthene	93%	87%	84%	87%	93%	95%	96%	83%	106%	100%
d12 Perylene	91%	93%	92%	92%	92%	96%	93%	86%	107%	97%

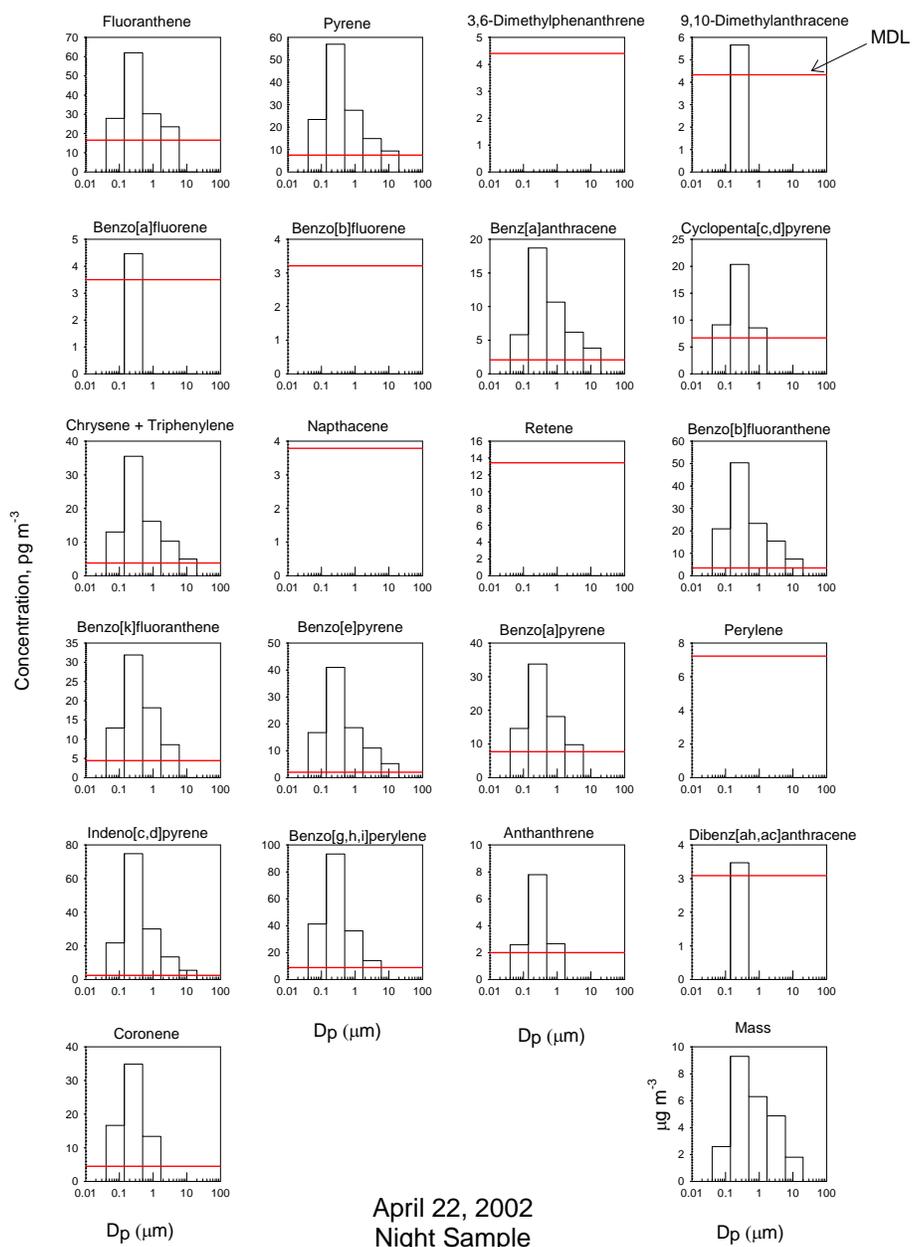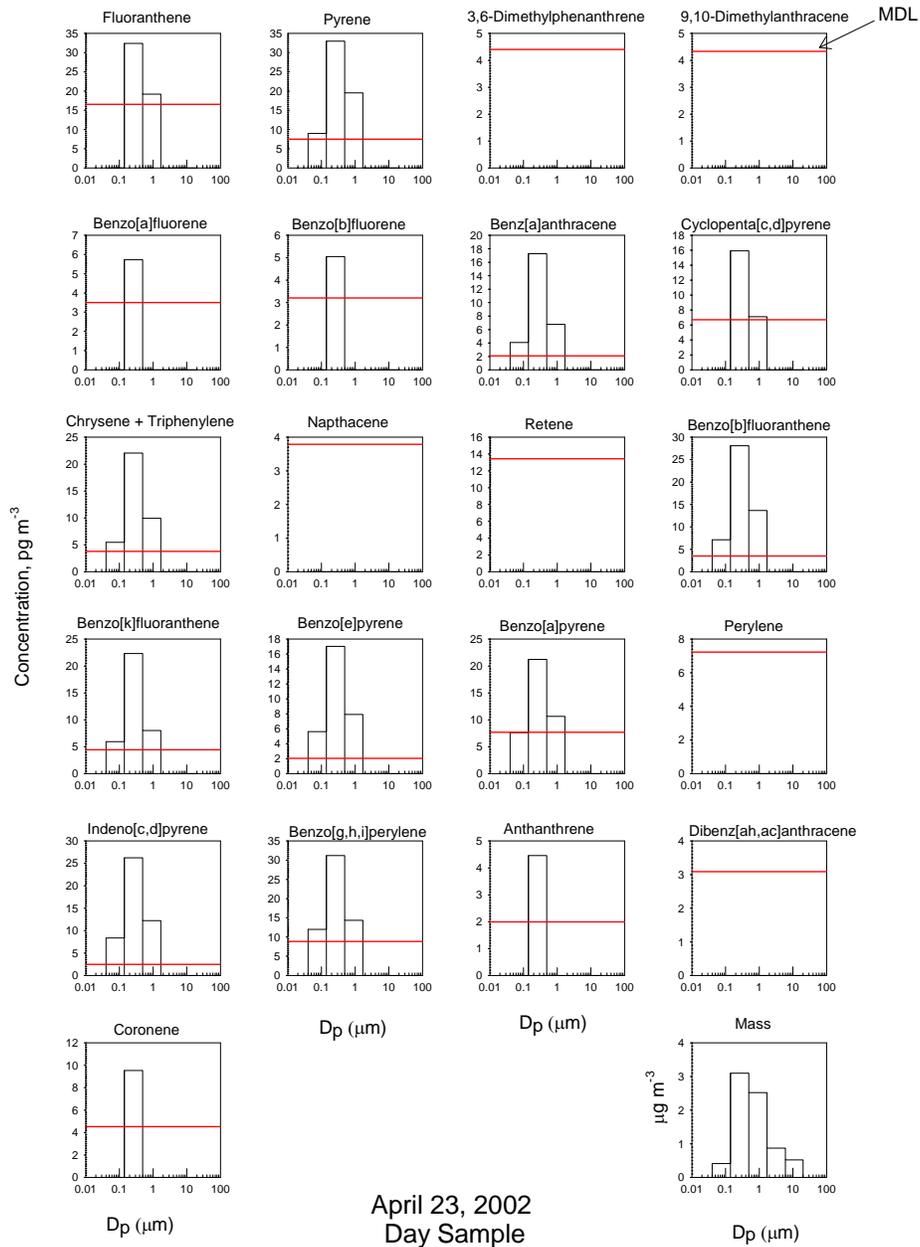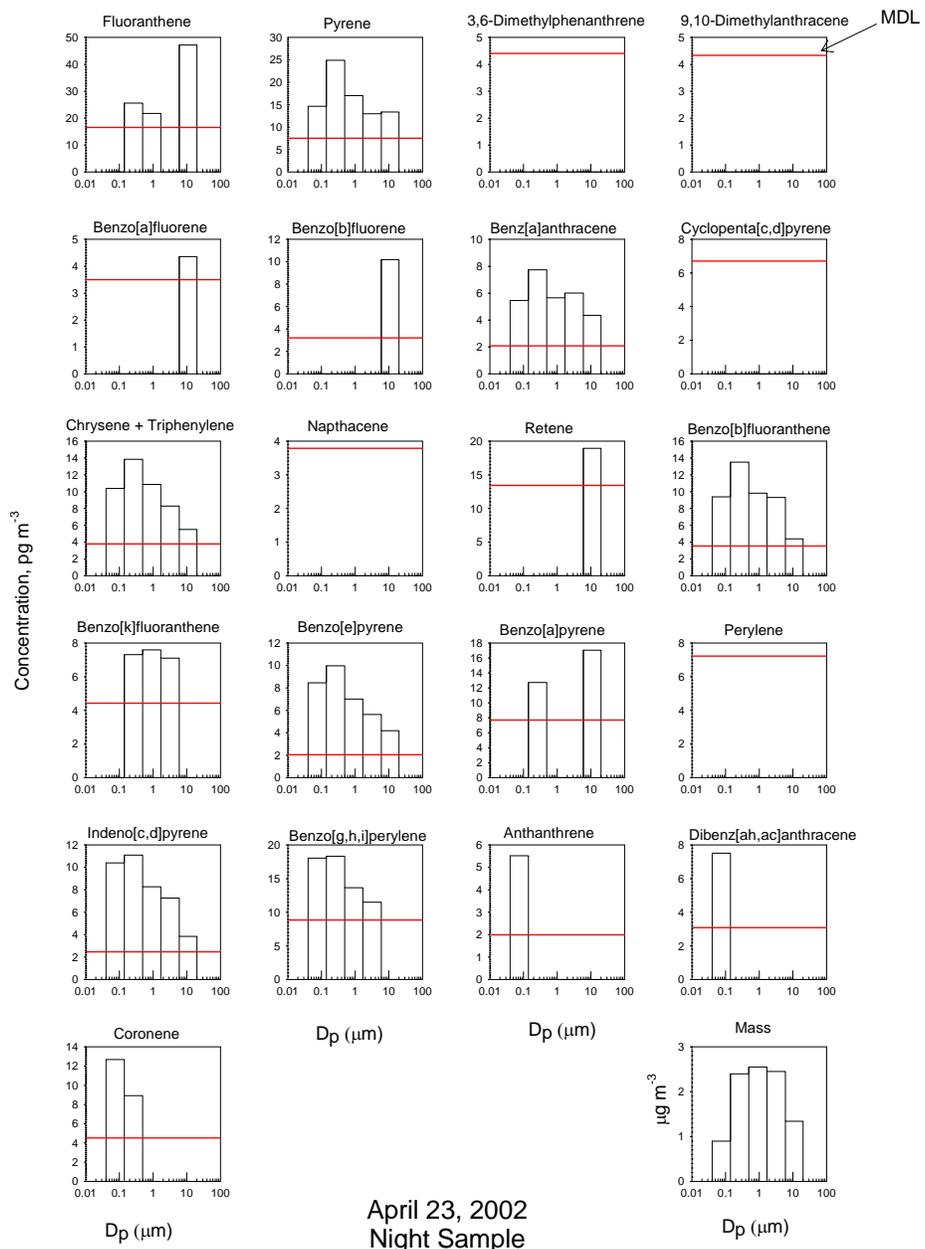| Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Fluoranthene	6.2E+01	1.4E+02	7.4E+01	3.7E+01	<BG	3.5E+01	8.2E+01	3.8E+01	<BG	<BG
Pyrene	4.4E+01	1.2E+02	5.8E+01	2.9E+01	7.2E+00	3.2E+01	8.1E+01	3.5E+01	1.4E+01	<BG
3,6Dimethylphenanthrene	4.8E+00	1.0E+01	5.8E+00	<BG	<BG	<BG	7.4E+00	<BG	<BG	<BG
9,10,dimethylanthracene	6.8E+00	1.7E+01	6.2E+00	<BG	<BG	<BG	9.5E+00	<BG	<BG	<BG
Benzo[a]fluorene	5.0E+00	1.5E+01	6.9E+00	3.7E+00	<BG	<BG	7.5E+00	4.7E+00	<BG	<BG
Benzo[b]fluorene	4.2E+00	1.2E+01	4.9E+00	<BG	<BG	<BG	5.4E+00	3.8E+00	<BG	<BG
Benz[a]anthracene	2.4E+01	6.4E+01	2.4E+01	8.6E+00	2.6E+00	9.9E+00	3.6E+01	1.4E+01	5.0E+00	<BG
Cyclopenta(c,d)pyrene	3.6E+01	9.6E+01	3.1E+01	1.0E+01	<BG	1.8E+01	4.6E+01	1.3E+01	<BG	<BG
Chrysene + Triphenylene	3.9E+01	1.0E+02	3.4E+01	1.5E+01	<BG	2.2E+01	6.6E+01	2.4E+01	9.2E+00	<BG
Napthacene	5.5E+00	1.0E+01	5.9E+00	<BG	<BG	7.0E+00	6.8E+00	<BG	<BG	<BG
Retene	<BG	1.9E+01	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Benzo[b]fluoranthene	4.6E+01	1.2E+02	3.9E+01	1.2E+01	3.5E+00	4.8E+01	1.4E+02	3.8E+01	1.4E+01	4.9E+00
Benzo[k]fluoranthene	3.6E+01	8.8E+01	2.7E+01	8.2E+00	<BG	2.4E+01	7.2E+01	2.1E+01	7.8E+00	<BG
Benzo[e]pyrene	3.5E+01	8.0E+01	2.4E+01	8.5E+00	2.0E+00	3.4E+01	9.3E+01	2.6E+01	8.8E+00	2.6E+00
Benzo[a]pyrene	3.8E+01	9.1E+01	3.4E+01	1.1E+01	<BG	2.6E+01	6.7E+01	2.4E+01	<BG	<BG
Perylene	8.3E+00	1.6E+01	<BG	1.2E+01	1.2E+01	<BG	1.1E+01	<BG	<BG	<BG
Dimethylbenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
3Methylcholanthrene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Indeno[1,2,3-c,d]pyrene	5.1E+01	1.5E+02	5.4E+01	1.2E+01	2.7E+00	5.3E+01	2.0E+02	4.3E+01	8.5E+00	<BG
Benzo[g,h,i]perylene	7.0E+01	1.6E+02	5.1E+01	1.7E+01	<BG	8.9E+01	2.2E+02	5.1E+01	1.3E+01	<BG
Anthanthrene	1.1E+01	2.0E+01	6.5E+00	2.1E+00	<BG	4.8E+00	1.4E+01	4.7E+00	<BG	<BG
Dibenz[a,h+ac]anthracene	6.8E+00	1.4E+01	4.1E+00	<BG	<BG	3.5E+00	2.1E+01	3.7E+00	<BG	<BG
Coronene	2.6E+01	4.3E+01	1.7E+01	5.0E+00	<BG	3.4E+01	8.8E+01	1.6E+01	<BG	<BG
Mass Conc (ug/m^3)	1.9E+00	8.0E+00	8.1E+00	6.5E+00	1.0E+00	3.1E+00	1.2E+01	9.3E+00	6.7E+00	1.4E+00

	MT 19	MT 19	MT 19	MT 19	MT 19	MT 20	MT 20	MT 20	MT 20	MT 20
Sample ID	MT 19	MT 19	MT 19	MT 19	MT 19	MT 20	MT 20	MT 20	MT 20	MT 20
Start Date	041602	041602	041602	041602	041602	041702	041702	041702	041702	041702
Start Time	1957	1957	1957	1957	1957	0855	0855	0855	0855	0855
Stop Date	041702	041702	041702	041702	041702	041702	041702	041702	041702	041702
Stop Time	735	735	735	735	735	1759	1759	1759	1759	1759
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um
Surrogates (% Recovery)										
d8 Napthalene	9%	11%	10%	9%	8%	9%	10%	8%	9%	8%
d10 Fluorene	85%	75%	77%	86%	90%	84%	82%	89%	84%	96%
d10 Fluoranthene	114%	94%	86%	109%	117%	109%	101%	107%	110%	111%
d12 Perylene	98%	95%	93%	99%	105%	104%	93%	97%	101%	104%
Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Fluoranthene	5.5E+01	1.3E+02	6.2E+01	3.2E+01	<BG	6.1E+01	1.4E+02	9.2E+01	5.2E+01	<BG
Pyrene	4.8E+01	1.4E+02	5.3E+01	3.0E+01	<BG	4.3E+01	1.3E+02	7.3E+01	3.8E+01	1.3E+01
3,6Dimethylphenanthrene	<BG	7.4E+00	<BG	<BG	<BG	<BG	1.1E+01	<BG	<BG	<BG
9,10,dimethylanthracene	7.9E+00	1.5E+01	5.0E+00	<BG	<BG	<BG	1.7E+01	7.4E+00	<BG	4.8E+01
Benzo[a]fluorene	5.9E+00	1.4E+01	5.6E+00	4.3E+00	<BG	4.8E+00	1.2E+01	6.9E+00	5.0E+00	<BG
Benzo[b]fluorene	3.8E+00	1.3E+01	5.3E+00	3.9E+00	<BG	<BG	8.9E+00	4.8E+00	<BG	<BG
Benz[a]anthracene	2.6E+01	7.4E+01	2.1E+01	8.5E+00	<BG	1.3E+01	4.6E+01	2.5E+01	1.3E+01	4.7E+00
Cyclopenta(c,d)pyrene	6.7E+01	2.0E+02	4.3E+01	1.1E+01	<BG	1.8E+01	5.0E+01	2.0E+01	<BG	<BG
Chrysene + Triphenylene	3.4E+01	9.9E+01	2.9E+01	1.5E+01	3.5E+00	2.9E+01	9.4E+01	4.6E+01	2.1E+01	6.8E+00
Napthacene	4.4E+00	1.1E+01	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Retene	<BG	1.2E+01	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Benzo[b]fluoranthene	5.5E+01	1.4E+02	3.6E+01	1.6E+01	3.4E+00	4.2E+01	1.1E+02	4.7E+01	2.7E+01	9.7E+00
Benzo[k]fluoranthene	3.1E+01	1.1E+02	1.9E+01	9.4E+00	<BG	2.2E+01	8.1E+01	3.6E+01	2.0E+01	8.8E+00
Benzo[e]pyrene	3.9E+01	9.5E+01	2.5E+01	1.3E+01	5.0E+00	3.0E+01	8.4E+01	3.3E+01	2.0E+01	6.7E+00
Benzo[a]pyrene	4.7E+01	1.4E+02	3.6E+01	1.3E+01	<BG	2.1E+01	5.5E+01	3.1E+01	2.4E+01	<BG
Perylene	9.2E+00	2.5E+01	<BG	<BG	<BG	<BG	9.9E+00	<BG	<BG	<BG
Dimethylbenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
3Methylcholanthrene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Indeno[1,2,3-c,d]pyrene	5.8E+01	2.0E+02	5.6E+01	8.9E+00	3.6E+00	3.3E+01	1.1E+02	5.8E+01	2.7E+01	7.4E+00
Benzo[g,h,i]perylene	9.1E+01	2.4E+02	6.5E+01	1.5E+01	<BG	5.6E+01	1.5E+02	5.4E+01	2.6E+01	1.1E+01
Anthanthrene	1.2E+01	5.0E+01	1.5E+01	<BG	<BG	6.4E+00	1.2E+01	3.9E+00	<BG	<BG
Dibenz[a,h+ac]anthracene	<BG	7.3E+00	<BG	<BG	<BG	<BG	5.8E+00	<BG	<BG	<BG
Coronene	3.1E+01	9.0E+01	2.7E+01	5.0E+00	<BG	2.3E+01	5.4E+01	2.1E+01	7.7E+00	<BG
Mass Conc (ug/m^3)	2.2E+00	8.6E+00	1.2E+01	8.1E+00	1.7E+00	4.1E+00	1.4E+01	1.1E+01	1.0E+01	2.8E+00

Sample ID	MT 21	MT 21	MT 21	MT 21	MT 21	MT 22	MT 22	MT 22	MT 22	MT 22
Start Date	041702	041702	041702	041702	041702	042202	042202	042202	042202	042202
Start Time	1856	1856	1856	1856	1856	1833	1833	1833	1833	1833
Stop Date	041802	041802	041802	041802	041802	042302	042302	042302	042302	042302
Stop Time	1745	1745	1745	1745	1745	808	808	808	808	808
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um
Surrogates (% Recovery)										
d8 Napthalene	8%	11%	11%	9%	8%	8%	7%	8%	8%	7%
d10 Fluorene	89%	87%	82%	83%	88%	81%	85%	76%	88%	91%
d10 Fluoranthene	117%	96%	86%	94%	109%	99%	112%	95%	114%	115%
d12 Perylene	101%	91%	96%	97%	104%	97%	104%	98%	83%	113%
Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Fluoranthene	2.8E+01	6.2E+01	3.0E+01	2.3E+01	1.3E+01	<BG	3.2E+01	1.9E+01	<BG	<BG
Pyrene	2.3E+01	5.7E+01	2.8E+01	1.5E+01	9.4E+00	9.0E+00	3.3E+01	2.0E+01	<BG	<BG
3,6Dimethylphenanthrene	<BG	4.2E+00	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
9,10,dimethylanthracene	2.6E+00	5.7E+00	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Benzo[a]fluorene	<BG	4.5E+00	2.7E+00	2.0E+00	<BG	<BG	5.7E+00	3.4E+00	<BG	<BG
Benzo[b]fluorene	<BG	3.2E+00	2.0E+00	<BG	<BG	<BG	5.0E+00	2.9E+00	<BG	<BG
Benz[a]anthracene	5.8E+00	1.9E+01	1.1E+01	6.2E+00	3.8E+00	4.1E+00	1.7E+01	6.8E+00	2.0E+00	<BG
Cyclopenta(c,d)pyrene	9.1E+00	2.0E+01	8.5E+00	3.8E+00	<BG	<BG	1.6E+01	7.1E+00	<BG	<BG
Chrysene + Triphenylene	1.3E+01	3.6E+01	1.6E+01	1.0E+01	5.0E+00	5.5E+00	2.2E+01	9.9E+00	<BG	<BG
Napthacene	<BG	<BG	<BG	2.6E+00	<BG	<BG	<BG	<BG	<BG	<BG
Retene	<BG	<BG	<BG	1.0E+01	<BG	<BG	<BG	<BG	<BG	<BG
Benzo[b]fluoranthene	2.1E+01	5.0E+01	2.3E+01	1.5E+01	7.5E+00	7.1E+00	2.8E+01	1.4E+01	3.5E+00	<BG
Benzo[k]fluoranthene	1.3E+01	3.2E+01	1.8E+01	8.6E+00	3.9E+00	5.9E+00	2.2E+01	8.0E+00	<BG	<BG
Benzo[e]pyrene	1.7E+01	4.1E+01	1.9E+01	1.1E+01	5.2E+00	5.6E+00	1.7E+01	7.9E+00	<BG	1.8E+00
Benzo[a]pyrene	1.5E+01	3.4E+01	1.8E+01	9.8E+00	6.5E+00	7.6E+00	2.1E+01	1.1E+01	<BG	<BG
Perylene	<BG	5.7E+00	<BG	<BG	<BG	<BG	7.0E+00	<BG	<BG	<BG
Dimethylbenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
3Methylcholanthrene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Indeno[1,2,3-c,d]pyrene	2.2E+01	7.5E+01	3.0E+01	1.3E+01	5.5E+00	8.4E+00	2.6E+01	1.2E+01	<BG	<BG
Benzo[g,h,i]perylene	4.1E+01	9.3E+01	3.6E+01	1.4E+01	7.6E+00	1.2E+01	3.1E+01	1.4E+01	<BG	<BG
Anthanthrene	2.6E+00	7.8E+00	2.7E+00	<BG	<BG	<BG	4.5E+00	<BG	<BG	<BG
Dibenz[a,h+ac]anthracene	<BG	3.5E+00	2.4E+00	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Coronene	1.7E+01	3.5E+01	1.3E+01	4.4E+00	<BG	4.3E+00	9.5E+00	4.4E+00	<BG	<BG
Mass Conc (ug/m^3)	2.6E+00	9.3E+00	6.3E+00	4.9E+00	1.8E+00	4.1E-01	3.1E+00	2.5E+00	8.7E-01	5.2E-01

	MT 23	MT 23	MT 23	MT 23	MT 23	MT 24	MT 24	MT 24	MT 24	MT 24
Sample ID	MT 23	MT 23	MT 23	MT 23	MT 23	MT 24	MT 24	MT 24	MT 24	MT 24
Start Date	042302	042302	042302	042302	042302	042302	042302	042302	042302	042302
Start Time	0834	0834	0834	0834	0834	1942	1942	1942	1942	1942
Stop Date	042302	042302	042302	042302	042302	042402	042402	042402	042402	042402
Stop Time	1839	1839	1839	1839	1839	807	807	807	807	807
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um
Surrogates (% Recovery)										
d8 Napthalene	8%	7%	8%	8%	12%	9%	12%	8%	8%	8%
d10 Fluorene	80%	76%	95%	90%	82%	73%	77%	74%	86%	94%
d10 Fluoranthene	103%	104%	117%	109%	103%	90%	90%	92%	108%	107%
d12 Perylene	107%	89%	106%	108%	100%	93%	95%	96%	109%	108%
Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Fluoranthene	<BG	2.6E+01	2.2E+01	<BG	4.7E+01	3.1E+01	8.7E+01	5.2E+01	2.0E+01	<BG
Pyrene	1.5E+01	2.5E+01	1.7E+01	1.3E+01	1.3E+01	3.8E+01	1.0E+02	4.8E+01	1.7E+01	9.9E+00
3,6Dimethylphenanthrene	<BG	<BG	<BG	<BG	<BG	<BG	6.1E+00	<BG	<BG	<BG
9,10,dimethylanthracene	<BG	<BG	<BG	<BG	<BG	4.3E+00	1.1E+01	<BG	<BG	<BG
Benzo[a]fluorene	<BG	<BG	<BG	<BG	4.4E+00	5.5E+00	1.5E+01	7.6E+00	<BG	<BG
Benzo[b]fluorene	<BG	<BG	<BG	<BG	1.0E+01	4.5E+00	1.5E+01	6.7E+00	<BG	<BG
Benz[a]anthracene	5.5E+00	7.7E+00	5.6E+00	6.0E+00	4.4E+00	2.6E+01	6.2E+01	2.7E+01	5.8E+00	3.4E+00
Cyclopenta(c,d)pyrene	<BG	<BG	<BG	<BG	<BG	2.7E+01	6.7E+01	2.7E+01	<BG	<BG
Chrysene + Triphenylene	1.0E+01	1.4E+01	1.1E+01	8.3E+00	5.5E+00	3.0E+01	7.6E+01	3.4E+01	8.8E+00	5.0E+00
Napthacene	<BG	<BG	<BG	<BG	<BG	<BG	1.3E+01	5.0E+00	<BG	<BG
Retene	<BG	<BG	<BG	<BG	1.9E+01	<BG	1.8E+01	<BG	<BG	<BG
Benzo[b]fluoranthene	9.4E+00	1.3E+01	9.8E+00	9.3E+00	4.4E+00	3.7E+01	9.7E+01	3.7E+01	8.3E+00	4.1E+00
Benzo[k]fluoranthene	<BG	7.3E+00	7.6E+00	7.1E+00	<BG	2.7E+01	7.3E+01	2.9E+01	5.6E+00	<BG
Benzo[e]pyrene	8.5E+00	1.0E+01	7.0E+00	5.6E+00	4.2E+00	2.3E+01	5.5E+01	1.9E+01	4.8E+00	2.9E+00
Benzo[a]pyrene	<BG	1.3E+01	<BG	<BG	1.7E+01	3.1E+01	7.6E+01	3.0E+01	8.1E+00	<BG
Perylene	<BG	<BG	<BG	<BG	<BG	<BG	1.4E+01	<BG	<BG	<BG
Dimethylbenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
3Methylcholanthrene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Indeno[1,2,3-c,d]pyrene	1.0E+01	1.1E+01	8.3E+00	7.3E+00	3.8E+00	3.8E+01	9.5E+01	4.2E+01	3.4E+00	2.9E+00
Benzo[g,h,i]perylene	1.8E+01	1.8E+01	1.4E+01	1.1E+01	<BG	4.8E+01	8.9E+01	3.4E+01	8.6E+00	<BG
Anthanthrene	5.5E+00	<BG	<BG	<BG	<BG	4.1E+00	1.1E+01	5.4E+00	<BG	<BG
Dibenz[a,h+ac]anthracene	7.5E+00	<BG	<BG	<BG	<BG	<BG	6.3E+00	<BG	<BG	<BG
Coronene	1.3E+01	8.9E+00	<BG	<BG	<BG	1.7E+01	3.5E+01	1.3E+01	<BG	<BG
Mass Conc (ug/m^3)	9.0E-01	2.4E+00	2.5E+00	2.5E+00	1.3E+00	1.7E+00	4.5E+00	2.9E+00	2.2E+00	9.9E-01

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	MT 25	MT 25	MT 25	MT 25	MT 25	MT 26	MT 26	MT 26	MT 26	MT 26
Sample ID	MT 25	MT 25	MT 25	MT 25	MT 25	MT 26	MT 26	MT 26	MT 26	MT 26
Start Date	042402	042402	042402	042402	042402	042402	042402	042402	042402	042402
Start Time	0913	0913	0913	0913	0913	1926	1926	1926	1926	1926
Stop Date	042402	042402	042402	042402	042402	042502	042502	042502	042502	042502
Stop Time	1933	1933	1933	1933	1933	800	800	800	800	800
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um
Surrogates (% Recovery)										
d8 Napthalene	8%	10%	8%	7%	10%	8%	9%	7%	7%	9%
d10 Fluorene	90%	82%	89%	80%	75%	81%	80%	89%	82%	81%
d10 Fluoranthene	111%	101%	102%	89%	100%	92%	86%	104%	106%	104%
d12 Perylene	106%	103%	84%	98%	101%	100%	94%	106%	102%	102%
Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Fluoranthene	2.8E+01	4.1E+01	2.3E+01	<BG	<BG	<BG	2.1E+01	1.8E+01	<BG	1.6E+01
Pyrene	2.1E+01	3.2E+01	1.5E+01	<BG	<BG	7.2E+00	1.9E+01	1.2E+01	<BG	<BG
3,6Dimethylphenanthrene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
9,10,dimethylanthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Benzo[a]fluorene	<BG	4.5E+00	<BG	<BG	<BG	<BG	3.9E+00	<BG	<BG	<BG
Benzo[b]fluorene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Benz[a]anthracene	1.1E+01	1.9E+01	6.2E+00	3.2E+00	<BG	3.9E+00	1.6E+01	4.7E+00	2.1E+00	2.1E+00
Cyclopenta(c,d)pyrene	1.1E+01	1.2E+01	<BG	<BG	<BG	<BG	1.2E+01	<BG	<BG	<BG
Chrysene + Triphenylene	2.3E+01	3.0E+01	1.2E+01	4.8E+00	<BG	8.7E+00	3.1E+01	1.4E+01	4.1E+00	<BG
Napthacene	<BG	<BG	<BG	<BG	<BG	<BG	4.8E+00	<BG	<BG	<BG
Retene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Benzo[b]fluoranthene	4.4E+01	7.3E+01	1.3E+01	6.1E+00	<BG	2.0E+01	1.1E+02	2.4E+01	4.6E+00	<BG
Benzo[k]fluoranthene	2.7E+01	4.3E+01	7.7E+00	<BG	<BG	1.6E+01	8.1E+01	1.4E+01	<BG	<BG
Benzo[e]pyrene	3.0E+01	5.2E+01	8.1E+00	3.1E+00	<BG	1.7E+01	8.7E+01	1.5E+01	2.2E+00	<BG
Benzo[a]pyrene	2.7E+01	4.2E+01	<BG	<BG	<BG	1.2E+01	6.1E+01	1.3E+01	<BG	<BG
Perylene	<BG	1.1E+01	<BG	<BG	<BG	<BG	1.3E+01	<BG	<BG	<BG
Dimethylbenz[a]anthracene	<BG	<BG	<BG	<BG	<BG	<BG	5.4E+00	<BG	<BG	<BG
3Methylcholanthrene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
Indeno[1,2,3-c,d]pyrene	5.3E+01	8.5E+01	1.1E+01	3.4E+00	<BG	3.3E+01	1.7E+02	2.4E+01	2.5E+00	<BG
Benzo[g,h,i]perylene	5.3E+01	8.4E+01	1.8E+01	<BG	<BG	3.5E+01	1.4E+02	2.5E+01	<BG	<BG
Anthanthrene	3.0E+00	4.8E+00	<BG	<BG	<BG	<BG	6.2E+00	<BG	<BG	<BG
Dibenz[a,h+ac]anthracene	7.6E+00	1.2E+01	<BG	<BG	<BG	3.5E+00	3.9E+01	3.7E+00	<BG	<BG
Coronene	1.4E+01	2.1E+01	<BG	<BG	<BG	8.4E+00	3.1E+01	6.2E+00	<BG	<BG
Mass Conc (ug/m^3)	3.1E+00	4.5E+00	2.7E+00	2.4E+00	1.2E+00	1.2E+00	4.0E+00	4.0E+00	3.0E+00	9.3E-01

Sample ID	MT 27	MT 27	MT 27	MT 27	MT 27
Start Date	042502	042502	042502	042502	042502
Start Time	0855	0855	0855	0855	0855
Stop Date	042502	042502	042502	042502	042502
Stop Time	1814	1814	1814	1814	1814
Media	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um
Surrogates (% Recovery)					
d8 Napthalene	8%	8%	8%	9%	8%
d10 Fluorene	76%	87%	78%	81%	83%
d10 Fluoranthene	93%	101%	85%	91%	96%
d12 Perylene	95%	100%	95%	99%	102%
Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
Fluoranthene	<BG	4.7E+01	2.4E+01	<BG	<BG
Pyrene	1.3E+01	4.3E+01	2.1E+01	1.0E+01	<BG
3,6Dimethylphenanthrene	<BG	<BG	<BG	<BG	<BG
9,10,dimethylanthracene	<BG	6.4E+00	<BG	<BG	<BG
Benzo[a]fluorene	<BG	8.4E+00	<BG	<BG	<BG
Benzo[b]fluorene	<BG	4.6E+00	<BG	<BG	<BG
Benz[a]anthracene	6.1E+00	2.7E+01	8.1E+00	4.0E+00	<BG
Cyclopenta(c,d)pyrene	<BG	2.9E+01	<BG	<BG	<BG
Chrysene + Triphenylene	1.1E+01	3.9E+01	1.4E+01	5.7E+00	<BG
Napthacene	<BG	<BG	<BG	<BG	<BG
Retene	<BG	2.8E+01	<BG	<BG	<BG
Benzo[b]fluoranthene	1.5E+01	6.7E+01	2.5E+01	6.7E+00	<BG
Benzo[k]fluoranthene	8.8E+00	4.4E+01	2.1E+01	<BG	<BG
Benzo[e]pyrene	9.9E+00	4.1E+01	1.8E+01	4.0E+00	<BG
Benzo[a]pyrene	1.2E+01	5.5E+01	1.8E+01	<BG	<BG
Perylene	<BG	1.2E+01	<BG	<BG	<BG
Dimethylbenz[a]anthracene	<BG	<BG	<BG	<BG	<BG
3Methylcholanthrene	<BG	<BG	<BG	<BG	<BG
Indeno[1,2,3-c,d]pyrene	1.3E+01	5.9E+01	3.4E+01	5.1E+00	<BG
Benzo[g,h,i]perylene	2.7E+01	8.1E+01	3.6E+01	<BG	<BG
Anthanthrene	<BG	7.8E+00	3.1E+00	<BG	<BG
Dibenz[a,h+ac]anthracene	<BG	4.5E+00	<BG	<BG	<BG
Coronene	6.6E+00	2.1E+01	8.8E+00	<BG	<BG
Mass Conc (ug/m^3)	1.1E+00	5.7E+00	5.7E+00	2.3E+00	1.1E+00

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Sample ID	MT 17	MT 17	MT 17	MT 17	MT 17	MT 18	MT 18	MT 18	MT 18	MT 18
Start Date	041502	041502	041502	041502	041502	041602	041602	041602	041602	041602
Start Time	1834	1834	1834	1834	1834	0846	0846	0846	0846	0846
Stop Date	041602	041602	041602	041602	041602	041602	041602	041602	041602	041602
Stop Time	742	742	742	742	742	1854	1854	1854	1854	1854
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um
Surrogate (% Recovery)										
1N-Napthalene-d7	78%	74%	37%	49%	64%	46%	53%	62%	48%	24%
1N-Anthracene-d9	83%	90%	69%	80%	89%	91%	93%	85%	79%	75%
1N-Pyrene-d9	66%	74%	56%	57%	68%	77%	80%	65%	82%	62%
Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
2N-fluorene	6.9E-02	2.4E-01	7.3E-02	ND	ND	ND	ND	8.4E-02	ND	5.3E-02
9N-anthracene	2.1E+01	1.0E+02	2.2E+01	3.3E+00	1.0E+00	5.7E+00	2.5E+01	1.2E+01	1.6E+00	<BG
2N-anthracene	ND	<BG	<BG	<BG	<BG	1.2E+00	1.1E+00	<BG	<BG	<BG
9N-phenanthrene	5.2E-01	1.9E+00	4.4E-01	2.7E-01	ND	1.2E-01	4.2E-01	2.0E-01	ND	<BG
3N-phenanthrene	5.8E-01	2.6E+00	6.5E-01	2.3E-01	ND	4.1E-01	2.0E+00	6.0E-01	2.2E-01	ND
4N-phenanthrene	1.9E-01	6.3E-01	1.4E-01	4.6E-02	4.2E-02	7.6E-02	2.1E-01	2.0E-01	<BG	ND
2N-fluoranthene	1.9E+01	7.0E+01	7.3E+00	1.9E+00	3.0E-01	1.5E+01	7.2E+01	1.3E+01	1.9E+00	<BG
3N-fluoranthene	1.4E-01	3.5E-01	7.6E-02	ND	ND	ND	1.4E-01	1.3E-01	ND	ND
1N-pyrene	8.0E+00	2.4E+01	2.2E+00	8.0E-01	<BG	2.5E+00	1.1E+01	2.0E+00	4.0E-01	1.7E-01
2N-pyrene	1.2E+00	3.9E+00	8.2E-01	1.4E+00	ND	1.3E+00	6.1E+00	7.0E-01	ND	<BG
7-nitrobenz[a]anthracen	1.6E+00	4.9E+00	5.5E-01	1.8E-01	<BG	1.4E-01	6.1E-01	1.9E-01	ND	ND
6N-chrysene	8.8E-02	1.1E-01	<BG	ND	<BG	<BG	4.3E-01	1.1E-01	ND	<BG

Sample ID	MT 19	MT 19	MT 19	MT 19	MT 19	MT 20	MT 20	MT 20	MT 20	MT 20
Start Date	041602	041602	041602	041602	041602	041702	041702	041702	041702	041702
Start Time	1957	1957	1957	1957	1957	0855	0855	0855	0855	0855
Stop Date	041702	041702	041702	041702	041702	041702	041702	041702	041702	041702
Stop Time	735	735	735	735	735	1759	1759	1759	1759	1759
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um

Surrogate (% Recovery)

	MT 19	MT 19	MT 19	MT 19	MT 19	MT 20	MT 20	MT 20	MT 20	MT 20
1N-Napthalene-d7	64%	40%	55%	64%	44%	61%	50%	55%	53%	44%
1N-Anthracene-d9	74%	66%	73%	72%	64%	75%	72%	72%	73%	62%
1N-Pyrene-d9	79%	81%	84%	69%	44%	70%	73%	69%	67%	50%

Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
2N-fluorene	ND	9.4E-02	4.0E-02	3.6E-02	<BG	ND	ND	ND	ND	ND
9N-anthracene	1.1E+01	6.1E+01	3.5E+01	1.5E+00	<BG	1.3E+01	3.8E+01	1.7E+01	3.7E+00	2.1E+00
2N-anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
9N-phenanthrene	2.4E-01	6.9E-01	4.2E-01	1.3E-01	ND	1.1E-01	3.5E-01	1.2E-01	ND	ND
3N-phenanthrene	3.2E-01	1.2E+00	5.3E-01	<BG	ND	5.6E-01	1.9E+00	6.8E-01	1.7E-01	ND
4N-phenanthrene	1.1E-01	2.7E-01	1.6E-01	<BG	ND	1.3E-01	2.5E-01	2.0E-01	5.4E-02	<BG
2N-fluoranthene	1.5E+01	4.8E+01	1.3E+01	1.4E+00	<BG	2.3E+01	7.8E+01	1.5E+01	2.8E+00	<BG
3N-fluoranthene	8.7E-02	1.4E-01	6.9E-02	ND	ND	5.1E-02	1.0E-01	<BG	<BG	<BG
1N-pyrene	3.3E+00	1.1E+01	1.4E+01	4.7E-01	8.6E-02	2.5E+00	7.3E+00	1.7E+00	4.4E-01	1.4E-01
2N-pyrene	5.8E-01	1.2E+00	5.1E-01	ND	ND	1.4E+00	5.0E+00	9.1E-01	<BG	ND
7-nitrobenz[a]anthracen	5.2E-01	1.9E+00	7.9E-01	1.2E-01	<BG	<BG	3.8E-01	<BG	<BG	ND
6N-chrysene	ND	<BG	<BG	ND	ND	<BG	<BG	<BG	ND	<BG

Sample ID	MT 21	MT 21	MT 21	MT 21	MT 21	MT 22	MT 22	MT 22	MT 22	MT 22
Start Date	041702	041702	041702	041702	041702	042202	042202	042202	042202	042202
Start Time	1856	1856	1856	1856	1856	1833	1833	1833	1833	1833
Stop Date	041802	041802	041802	041802	041802	042302	042302	042302	042302	042302
Stop Time	1745	1745	1745	1745	1745	808	808	808	808	808
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um
Surrogate (% Recovery)										
1N-Napthalene-d7	57%	47%	70%	48%	56%	60%	64%	59%	33%	42%
1N-Anthracene-d9	73%	68%	88%	73%	74%	75%	76%	70%	66%	66%
1N-Pyrene-d9	69%	68%	69%	71%	64%	74%	80%	76%	74%	50%
Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
2N-fluorene	2.6E-02	4.9E-02	5.1E-02	ND	<BG	<BG	5.0E-02	3.3E-02	ND	ND
9N-anthracene	3.6E+01	8.5E+01	3.0E+01	3.7E+00	1.2E+00	9.1E-01	3.9E+00	2.2E+00	1.1E+00	<BG
2N-anthracene	ND	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	ND
9N-phenanthrene	2.0E-01	4.4E-01	2.9E-01	5.4E-02	<BG	<BG	1.8E-01	1.0E-01	<BG	ND
3N-phenanthrene	4.2E-01	1.2E+00	5.9E-01	1.2E-01	<BG	<BG	1.4E-01	ND	<BG	ND
4N-phenanthrene	1.0E-01	2.6E-01	1.7E-01	3.7E-02	<BG	ND	ND	ND	<BG	ND
2N-fluoranthene	9.1E+00	2.2E+01	6.1E+00	9.3E-01	2.9E-01	<BG	9.3E-01	3.8E-01	<BG	<BG
3N-fluoranthene	1.1E-01	2.9E-01	1.0E-01	<BG	ND	ND	ND	ND	<BG	8.2E-02
1N-pyrene	3.6E+00	8.4E+00	2.2E+00	4.1E-01	1.1E-01	7.1E-01	2.3E+00	5.4E-01	1.9E-01	<BG
2N-pyrene	2.9E-01	7.5E-01	2.2E-01	ND	ND	ND	ND	ND	ND	ND
7-nitrobenz[a]anthracen	7.5E-01	1.8E+00	4.9E-01	<BG	<BG	1.1E-01	4.3E-01	1.4E-01	<BG	<BG
6N-chrysene	1.3E-01	2.0E-01	6.3E-02	<BG	<BG	ND	ND	ND	<BG	<BG

	MT 23	MT 23	MT 23	MT 23	MT 23	MT 24	MT 24	MT 24	MT 24	MT 24
Sample ID	MT 23	MT 23	MT 23	MT 23	MT 23	MT 24	MT 24	MT 24	MT 24	MT 24
Start Date	042302	042302	042302	042302	042302	042302	042302	042302	042302	042302
Start Time	0834	0834	0834	0834	0834	1942	1942	1942	1942	1942
Stop Date	042302	042302	042302	042302	042302	042402	042402	042402	042402	042402
Stop Time	1839	1839	1839	1839	1839	807	807	807	807	807
Media	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil	Foil
Stage	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um	0.04 - 0.14 um	0.14 - 0.49 um	0.49 - 1.7 um	1.7 - 6 um	6 - 20 um
Surrogate (% Recovery)										
1N-Napthalene-d7	59%	46%	61%	74%	74%	66%	58%	54%	63%	60%
1N-Anthracene-d9	74%	60%	71%	85%	84%	82%	72%	80%	84%	84%
1N-Pyrene-d9	74%	62%	66%	65%	69%	80%	66%	66%	69%	65%
Concentration	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3	pg/m^3
2N-fluorene	ND	ND	ND	ND	ND	1.3E-01	3.1E-01	7.6E-02	6.4E-02	ND
9N-anthracene	<BG	<BG	<BG	<BG	<BG	1.5E+01	3.4E+01	1.2E+01	3.6E+00	2.5E+00
2N-anthracene	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG	<BG
9N-phenanthrene	<BG	9.6E-02	<BG	ND	ND	1.1E+00	2.5E+00	8.4E-01	3.4E-01	9.2E-02
3N-phenanthrene	<BG	<BG	<BG	ND	ND	4.1E-01	8.3E-01	2.8E-01	<BG	<BG
4N-phenanthrene	<BG	<BG	<BG	ND	<BG	6.7E-02	1.2E-01	4.4E-02	<BG	ND
2N-fluoranthene	9.4E-01	<BG	<BG	<BG	<BG	5.7E+00	1.1E+01	2.8E+00	4.9E-01	<BG
3N-fluoranthene	9.4E-02	<BG	<BG	<BG	ND	1.5E-01	2.3E-01	5.7E-02	ND	ND
1N-pyrene	1.1E+00	9.0E-01	4.3E-01	5.0E-01	<BG	6.7E+00	1.3E+01	3.2E+00	1.2E+00	2.8E-01
2N-pyrene	ND	ND	ND	ND	ND	2.8E-01	5.3E-01	ND	ND	ND
7-nitrobenz[a]anthracene	ND	<BG	3.7E+00	<BG	<BG	1.5E+00	2.2E+00	4.9E-01	1.2E-01	ND
6N-chrysene	<BG	<BG	<BG	<BG	ND	9.4E-02	1.4E-01	ND	<BG	<BG

REFERENCES

Aceves, M. and Grimalt, J. O., 1993. Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. *Environmental Science and Technology* 27, 2896-2908.

Allen, J.O., Dookeran, N.M., Smith, K.A., Sarofim, A.F., Taghizadeh, K., and Lafleur, A.L., 1996. Measurement of polycyclic aromatic hydrocarbons associated with size segregated atmospheric aerosols in Massachusetts. *Environmental Science and Technology* 30, 1023-1031.

Alves, C.A., Pio, C.A., and Duarte, A. C., 2000. Particulate size distributed organic compounds in a forested atmosphere. *Environmental Science and Technology* 34, 4287-4293.

Arditsoglou, A., Petaloti,Ch, Terzi, E., Sofoniou, M., and Samara, C., 2004. Size distribution of trace elements and ploycyclic aromatic hydrocarbons in fly ashes generated in Greek lignite-fired power plants. *Science of the Total Environment* 323, 153-167.

Arey, J., 1998. Atmospheric reactions of PAHs including formation of nitroarenes. In: A.H. Neilson (Editor), The Handbook of Environmental Chemistry. Springer-Verlag, Berlin, pp. 347-385.

Arey, J., Zielinska, B., Harger, W. P., Atkinson, R., and Winer, A.M., 1988. The contribution of nitrofluoranthenes and nitropyrenes to the mutagenic activity of ambient particulate matter collected in southern California. *Mutation Research* 207, 45-71

Arey, J., Zielinska,B., Atkinson, R., Winer, A.M., Ramdahl,T., Pitts Jr., J.N., 1986. The formation of nitro-PAH from the gas phase reactions of fluorathene and pyrene with the OH radical in the presence of NOx. *Atmospheric Environment,* 20, 2339-2345

Atkinson, R., Arey, J., Zielinska, B., Ashmann, S.M., 1990. Kinetics and nitro-products of the gas-phase OH and NO_3 radical initiated reactions of naphthalene-d8, fluoranthene-d10, and pyrene. *International Journal of Chemical Kinetics*, 22, 999-1014.

Atkinson, R. and Arey, J., 1994. Atmospheric Chemistry of gas phase polycyclic aromatic hydrocarbons. *Environmental Health Perspectives* 102, 117-126.

Bamford, H. A.; Offenberg, J. H.; Larsen, R. K.; Ko, F.-C.; Baker, J. E., 1999. Diffusive Exchange of Polycyclic Aromatic Hydrocarbons across the Air-Water

Interface of the Patapsco River, an Urbanized Subestuary of the Chesapeake Bay. *Environmental Science and Technology* 33**,** 2138-2144

Bamford, H.A., Sources and Transport of Trace Organic Contaminants in a Mid-Atlantic Urban Atmosphere**,** Ph.D. Dissertation, University of Maryland, College Park, MD, 2002.

Bamford, H.A. and Baker, J.E., 2003. Sources and concentrations of nitro-PAHs in urban and sub-urban atmospheres of Maryland. *Atmospheric Environment* 37, 2077-2091.

Bamford, H.A., D.Z. Bezabeh, M.M. Schantz, S.A. Wise, and Baker, J.E., 2003. Determination and comparison of nitrated polycyclic aromatic hydrocarbons measured in air and diesel particulate reference materials. *Chemosphere* 50, 575-587.

Bonfanti, L., Careri, M., Mangia, A., Manini, P., and Maspero, M., 1996. Simultaneous identification of different classes of hydrocarbons and determination of nitro-polycyclic aromatic hydrocarbons by means of particle beam liquid chromatography-mass spectrometry. *Journal of Chromatography A* 728, 359-369.

Bosboom, J.C., Jannssen, H-G., Mol, H. G.J., Cramers, C.A., 1996. Large-volume injection in capillary gas chromatography using a programmed-temperature vaporizing injector in the on-column or solvent-vent injection mode, *Journal of Chromatography* 724, 384-391.

Brinkman, G., Vance, G., Hannigan, M.P., Milford, J.B., 2006. Use of synthetic data to evaluate Positive Matrix Factorization as source apportionment tool for PM2.5 Exposure data. *Environmental Science and Technology*, 40, 1892-1901.

Broman, D., Naf, C. and Zebuhr, Y., 1991. Long-term High- and Low-volume air sampling of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons along a transect from urban to remote areas on the Swedish Baltic Coast. *Environmental Science and Technology* 25, 1841-1849.

Brown, S.G., Herckes, P., ashbaugh, L., Hannigan, M.P., Kreidenweis, S. M., Collett Jr., J.L., 2002. Characterization of organic aerosol in Big Bend National Park, Texas. *Atmospheric Environment* 36, 5807-5818.

Cecinato, A., Marino, F., Filippo, P., D., Lepore, L., and Possanzini, M., 1996. Distribution of *n*-alkanes, polynuclear aromatic hydrocarbons and nitrated polynuclear aromatic hydrocarbons between the fine and coarse fractions of inhalable atmospheric particulates. *Journal of Chromatography A* 846, 255-264.

Cecinato, A., Marino, F., Filippo, P.D., Lepore, L., Possanzini, M., 1999. Distribution of n-alkanes, polynuclear aromatic hydrocarbons and nitrated polynuclear

hydrocarbons between fine and coarse fractions of inhalable atmospheric particulates. *Journal of Chromatography* 846, 255-264.

Cecinato, A., Mabilia, R., Marino, F., 2000. Relavent compounds in ambient particulate matter collected at Svalbad Islands (Norway). *Atmospheric Environment* 34, 5061-5066.

Certificate of Analysis, 2001. Standard Reference Material (SRM) 1649a, Urban Dust, National Institutes of Standards and Technology (NIST) Gaithersburg, MD.

Certificate of Analysis, 2000. Standard Reference Material (SRM) 1650a. Diesel Particulate Matter, National Institutes of Standards and Technology (NIST) Gaithersburg, MD.

Chen, Y., Bi, X, Mai, B., Sheng G., and Fu, J., 2004. Emission characterization of particulate and gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. *Fuel* 83, 781-790.

Ciccioli, P., Cecinato, A., Brancaleoni, E., Fattoni, M., Zacchei, P., 1996. Formation and transport of 2-nitrofluoranthene and 2-nitropyrene of photochemical origin in the troposphere. *Journal of Geophysical Research* 101, 19567-19581.

Crimmins, B.S, Dickerson, R.R., Doddridge, B.G., and Baker, J.E., 2004. Particulate polycyclic aromatic hydrocarbons in the Atlantic and Indian Ocean atmospheres during the Indian Ocean Experiment and Aerosols99: Continental sources to the marine atmosphere. *Journal of Geophysical Research*, 109, doi:10.1029/2003JD004192

Crimmins, B.S. and Baker J.E., 2006a. Improved GC/MS methods for measuring hourly PAH and Nitro-PAH concentrations in urban particulate matter. *Atmospheric Environment*, 40, 6764-6779.

Dachs, J. and Eisenreich, S.J., 2000. Adsorption onto soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons. *Environmental Science and Technology* 34, 3690-3697.

Daisey, J., Cheney, J., Lioy, P., J., 1986. Profiles of organic particulate emissions from air pollution sources; Status and needs for receptor source apportionment modeling. *Journal of the Air Pollution and Control Association* 36, 17-33.

Dimashki, M., Harrad, S., Harrison, R.M., 2000. Measurements of nitro-PAH in the atmospheres of two cities. *Atmospheric Environment* 34, 2459-2469.

Dockery, D.W., Pope, A.C., Xu, X., Spengler, J.D., Ware,J.H., Fay,M.E., Ferris Jr., B.G., and Speizer, F.E., 1993. An association between ait pollution and mortality in six U.S. cities. *The New England Journal of Medicine* 393, 1753-1759.

Doskey, P.V. and Andren, A.W., 1986. Particulate and vapor-phase *n*-alkanes in the northern Wisconsin atmosphere. *Atmospheric Environment* 20, 1735-1744.

Engewald, W., Teske, J., Efer, J., 1999. Programmed temperature vaporizors-based large volume injection in capillary gas chromatography, *Journal of Chromatography A* 842, 143-161.

EPA. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd ed.; EPA/625/R-96/010b; United States Environmental Protection Agency: Cincinati, OH, 1999.

Fan, Z., Chen, D., Birla, P. and Kamens, R.M., 1995. Modeling of nitro-polycylic aromatic hydrocarbon formation and decay in the atmosphere. *Atmospheric Environment* 29, 1171-1181.

Fan, Z., Kamens, R.M., Zhang, J., Hu,, J., 1996. Ozone-nitrogen dioxide-NPAH heterogeneous soot particle reactions and modeling NPAH in the atmosphere. *Environmental Science and Technology* 30, 2821-2827.

Feildberg, A., Poulsen, M.W.B., Nielsen, T., and Skov, H., 2001. Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. *Atmospheric Environment* 35, 353-366.

Fine, P.M., Chakrabarti, B., Krudysz, M., Schauer, J.J, and Sioutas, C., 2004. Diurnal variations of individual organic compound constituents of ultrafine and accumulation mode particulate matter in the Los Angeles basin. *Environmental Science and Technology* 38, 1296-1304.

Foreman, W.T. and Bidleman, T.F., 1990. Semivolatile organic compounds in the ambient air of Denver, CO. *Atmospheric Environment* 24A, 2405-2416.

Fraser, M.P., Cass, G.R., Simoneit, B.R.T. and Rasmussen, R.A., 1998. Air quality model evaluation data for organics. 5. C6 – C22 Nonpolar and semipolar aromatic compounds. *Environmental Science and Technology* 32, 1760-1770.

Fraser, M.P., Yue, Z.W., Tropp, R.J., Kohl, S.D. and Chow, J.C., 2002. Molecular composition of organic fine particulate matter in Houston, TX. *Atmospheric Environment* 36, 5751-5758.

Gatz, D. F.; Sweet, C. W.; Basu, I.; Vermette, S.; Harlin, K.; Bauer, S. *Great Lakes Integrated Atmospheric Deposition Network (IADN) Data Report 1990-1992*; Illinois State Water Survey: Champaign, IL, 1994.

Gigliotti, C.L., Dachs, J., Nelson, E.D., Brunciak, P.A. and Eisenreich, S.J., 2000. Polycyclic aromatic hydrocarbons in the New Jersey Coastal Atmosphere. *Environmental Science and Technology* 34, 3547-3554.

Gogou, A., Stratigakis,N., Kanakidou, M., Stephanou, E.G., 1996. Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. *Organic Geochemistry* 25, 79-96.

Gordon, G. E., 1988. Receptor models, Critical Review, *Environmental Science and Technology* 22, 1988.

Greenberg, J. W., Bozzelli, Cannova, F., Forstner, E., Giorgio, P., Stout, D., and Yokoyama, R., 1981. Correlations between lead and coronene concentrations at urban, suburban, and industrial sites in New Jersey *Environmental Science and Technology* 15, 566-570.

Grob, K and Biedermann, M., 1996. Vaporizing systems for large volume injection or on-line transfer into gas chromatography: classification, critical remarks and suggestions. *Journal of Chromatography A* 750, 11-23.

Gundel, L.A., Lee, V.C., Mahanama, K.R.R., Stevens, R.K., and Daisey, J.M., 1995. Direct determination of the phase distributions of semi-volatile polycyclic aromatic hydrocarbons using annular denuders. *Atmospheric Environment* 29, 1719-1733.

Gupta, P., Harger, W. P. and Arey, J., 1996. The contribution of nitro- and methylnitro- naphthalenes to the vapor-phase mutagenicity of ambient air samples. *Atmospheric Environment* 30, 3157-3166.

Halsall, C. J., Barrie, L. A., Fellin, P., Muir, D. C. G., Billeck, B. N., Lockhart, L., Rovinsky, F. Ya., Kononov, E. Ya., and Pastukhov, B., 1997. Spatial and Temporal Variation of Polycyclic Aromatic Hydrocarbons in the Arctic Atmosphere. *Environmental Science and Technology* 31, 3593-3599.

Harrison, J.M., Smith, D.J.T. and Luhhana, L., 1996. Source apportionment of polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. *Environmental Science and Technology* 30, 825-832.

Harrison, D., Park, S.S., Ondov, J.M., Buckley, T., Kim, S.R., and Jayanty, R.K.M., 2004. Highly time resolved fine particle nitrate measurements at the Baltimore Supersite. *Atmospheric Environment* 38, 5321-5332

Hays, M.D., Geron, C.D., Linna, K.J., Smith, N.D., and Schauer, J.J., 2002. Speciation of gas phase and fine particle emissions from burning of foliar fuels. *Environmental Science and Technology* 36, 2281-2297.

Hildemann, L.M., Rogge, W.F., Cass, G.R., Mazurek, M.A., Simoneit, B.R.T., 1996. Contribution of primary aerosol emissions from vegetative-derived sources to the fine particulate concentrations in Los Angelos. *Joural of Geophysical Research* 101, 19,541-19,549.

Hinds, W.C., Aerosol Technology Properties, Behavior, and Measurement, John Wiley and Sons, New York, 1982.

Hoff, R.M. and Chan, K., 1987. Measurement of polycyclic aromatic hydrocarbons in the air along the Niagara River. *Environmental Science and Technology* 21, 556-561.

Huang, S., Arimoto, R., Rahn, K.A., 2001. Sources and source variations for aerosol at Mace Head, Ireland. *Atmospheric Environment* 35, 1421-1437.

IARC Monograph 1989. Evaluation of carcinogenic risk to humans, diesel and gasoline engine exhausts and some nitroarenes Vol 46, pp. 458 International Agency for research on cancer, Lyon, France

Kamens, R.M., Fan, Z., Yao, Y., Chen, D., Chen, S., Vartiainen, M., 1994. A methodology for modeling the formation and decay of nitro-PAH in the atmosphere. Chemosphere 28, 1623-1632.

Kavouras, I.G., Lawrence, J., Koutrakis, P., Stephanou, E.G., and Oyola, P., 1999. Measurement of particulate aliphatic and ploynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts. *Atmospheric Environment* 33, 4977-4986.

Keller, C.D. and Bidleman T.F., 1984. Collection of airborne polycyclic aromatic hydrocarbons and other organics with a glass fiber filter-polyurethane foam system. *Atmospheric Environment* 18, 837-845.

Kim, E., Hopke, P. K., Pinto, J. P., Wilson, W. E., 2005. Spatial Variability of Fine Particle Mass, Components, and Source Contributions during the Regional Air Pollution Study in St. Louis. *Environmental Science and Technology* 39, 4172-4179.

Larsen, R.K. and Baker J.E., 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: A comparison of methods. *Environmental Science and Technology* 37, 1873-1881.

Lee, H.K., 1995. Recent applications of gas and high-performance liquid chromatographic techniques to the analysis of polycyclic aromatic hydrocarbons in airborne particulates. *Journal of Chromatography* 710, 79-92.

Li, H, and Westerholm, R., 1994. Determination of mono-nitro and di-nitro polycylic aromatic-hydrocarbons by online reduction and high-performance liquid chromatography with chemilluminescence detection. *Journal of Chromatography A*

664, 177-182.

Lim, L.H., Harrison, R.M., Harrard, S., 1999. The contribution of traffic to atmospheric concentrations of polycyclic aromatic hydrocarbons. *Environmental Science and Technology* 33, 3538-3542.

Mac Crehan, W.A., May, W., Yang, S.D., and Benner, B.A., 1988. Determination of nitro polynuclear aromatic-hydrocarbons in air and diesel particulate matter using liquid-chromatography with electrochemical and fluorescence detection. *Analytical Chemistry* 60, 194-199.

Mader, B.T. and Pankow, J. F., 2000. Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters. 1. Partitioning of polychlorinated dibenzodioxins, polychlorinated dibenzofurans and polycyclic aromatinc hydrocarbons to Teflon membrane filters. *Atmospheric Environment* 34, 4879-4887.

Malm, W.C., Schichtel, B.A., Pitchford, M.L., Ashbaugh, L.L. and Elred, R.A., 2004. Spatial and monthly trends in speciated fine particle concentrations in the United States. *Journal of Geophysical Research*, 109, doi:10.1029/2003JD/003739.

Marino, F., Cecinato, A., and Siskos, P.A., 2000. Nitro-PAH in ambient particulate matter in the atmosphere of Athens. *Chemosphere* 40, 533-537.

Miguel, A.H., Kirchstetter,T.W., Harley, R.A. and Hering, S.V., 1998. On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. *Environmental Science and Technology* 32, 450-455.

Miguel, A.H., Fernandez, A.E-., Jaques, P.A., Froines, J.R., Grant, B.L., Mayo, P.R., Sioutas, C., 2004. Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California. *Atmospheric Environment* 38, 3241-3251.

Mol, Hans G.J., Janssen, Hans-Gerd, Cramers, Carel A., and Brinkman, Udo A.Th., 1996. Large volume injection in gas chromatographic trace analysis using temperature-programmed (PTV) injectors. *Trends in Analytical Chemistry* 15, 206-214.

Mukerjee, S., Ellenson, W.D., Lewis, R.G., Stevens, R.K., Somerville, M.C., and Shadwick, D.S., 1997. An environmental scoping sstudy in the lower Rio Grande valley of Texas – I. Comparative assessment of air sampling methods. *Environment International* 22, 611-628.

Nielson, T., 1996. Traffic contributions of polycyclic aromatic hydrocarbons in the center of a large city. *Atmospheric Environment* 30, 3481-3490

Nytoft, H.P., Bojesen-Koefoed, J.A., and Christiansen, F.G., 2000. C26 and C28-C34 28-norhopanes in sediments and petroleum. *Organic Geochemistry* 31, 25-39.

Offenberg, J.H., Semi-volatile Organic Compounds in Urban and Over-water Atmospheres. Ph.D. Dissertation, University of Maryland, College Park, MD, 1998.

Offenberg, J.H. and Baker, J.E., 1999. Influence of Baltimore's urban atmosphere on organic contaminants over the northern Chesapeake Bay. *Journal of the Air and Waste Management Association* 49, 959-965.

Ogulei, D., Hopke, P. K., Zhou, L., Paatero, P. Park, S. S., Ondov, J. M., 2005. Receptor Modeling for Highly-time (hourly and 24-hourly) Resolved Species: The Baltimore Supersite. *Atmospheric Environment* 39, 3751-3762.

Oros, D.R. and Simoneit, B.R.T., 1999. Identification of molecular tracers in organic aerosols from temperate climate vegetation subjected to biomass burning, *Aerosol Science and Technology* 31, 433-445.

Oros, D.R., and Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel* 79, 515-536.

Paatero, P., and Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values**.** *Envirometrics* 5, 111-126.

Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. *Chemometrics and Intelligent Laboratory Systems* 37, 23-25.

Paatero, P., 1999. The multilinear Engine- A table driven least squares program for solving multilinear problems, including the n-way parallel factor analysis model. *Journal of Compuational and Graphical Statistics* 1, 845-888.

Pankow, J.F., 1987. Review and comparative analysis of the theories on partitioning between gas and aerosol particulate phases in the atmosphere. *Atmospheric Environment*, 21, 2275-2283.

Pankow, J.F., and Bidleman, T.F., 1992. Interdependence of slopes and intercepts from log-log correlations of measured gas-particle partitioning and vapor pressure-I. Theory and analysis of available data. *Atmospheric Environment* 26A, 1071-1080.

Pankow, J.F., 1994. An absorption model of gas/particle partitioning in the atmosphere. *Atmospheric Environment*, 28, 185-188.

Paputa-Peck, M. C., Marano, R. S., Schuetzle, D., Riley, T. L., Hampton, C. V., Prater, T. J., Skewes, L. M., Jensen, T. E., Ruehle, P. H., 1983. Determination of nitrated polynuclear aromatic hydrocarbons in particulate extracts by using capillary

column gas chromatography with nitrogen selective detection. *Analytical Chemistry* 55**,** 1946-1954.

Park, S.S, Ondov, J.M., Harrison, D., Nair, N.P., 2005a. Seasonal and shorter variations in particulate atmospheric nitrate in Baltimore. *Atmospheric Environment* 39, 2011-2020.

Park, S.S., Harrison, D., Pancras, J.P., Ondov, J.M., 2005b. Highly time-resolved organic and elemental carbon measurements at the Baltimore Supersite in 2002. *Journal of Geophysical Research-Atmospheres* 110, Art. No. D07S06

Peters, A. J., Lane, D. A., Gundel, L. A., Northcott, G. L., Jones, K. C., 2000. A Comparison of High Volume and Diffusion Denuder Samplers for Measuring Semivolatile Organic Compounds in the Atmosphere. *Environmental Science and Technology* 34, 5001-5006.

Pierce, R.C. and Katz, M., 1975. Dependency of polynuclear aromatic hydrocarbon content on size distribution of atmospheric aerosols. *Environmental Science and Technology* 9, 347-353.

Pitts Jr., 1987. Nitration of gaseous polycyclic aromatic hydrocarbons in simulated and ambient urban atmospheres: a source of mutagenic nitroarenes. *Atmospheric Environment* 21, 2531-2547.

Polissar, A.V., Hopke, P.K., Paatero, P, Kaufmann, Y.J., Hall, D.K., Bodhaine, B.A., Dutton, E.G., Harris, J.M., 1999. The aerosol at Barrow, Alaska: long-term trends and source locations. *Environmental Science and Technology* 33, 2441-2458.

Polissar, A.V., Hopke, P.K., Poirot, R.L., 2001. Atmospheric aerosol over Vermont: Chemical composition and sources. *Environmental Science and Technology* 35, 4604-4621.

Pope III, C.A., 1996. Adverse health effects of particulate matter in a nonsmoking population. *Toxicology* 111, 149-155.

Pope, C.A., 2000. Epidemiology of fine particulate air pollution and human health: Biologic mechanisms and who's at risk? *Environmental Health Perspectives* 108, 713-723.

Possanzini, M., Di Palo, V., Gigliucci, P, Concetta, M.T.S., Cicinato, A., 2004. Determination of phase distributed PAH in Rome ambient air by denuder/GCMS method. *Atmospheric Environment* 38, 1727-1734.

Poster, D. L., Baker, J. E., 1996a. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 1. Concentrations and distributions of

polycyclic aromatic hydrocarbons and polychlorinated biphenyls in rainwater. *Environmental Science and Technology* 30, 341-348.

Poster, D. L., Baker, J. E., 1996b. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 2. Scavenging of polycyclic aromatic hydrocarbons by rain, *Environmental Science and Technology* 30, 349-354.

Prince, R.C., Elmendorf, D.L., Lute, J.R., Hsu, C.S., Halth, C.E., Senius, J.D., Dechert, G.J., Douglas, G.S., Butler, E.L., 1994. 17α(H), 21β(H)-Hopane as a conserved internal marker for estimating the biodegradation of crude oil. *Environmental Science and Technology* 28, 142-145.

Reisen, F, Wheeler, S. and Arey, J., 2003. Methyl and diethyl-nitronaphthalenes measured in ambient air in Southern California. *Atmospheric Environment* 37, 3653-3657.

Reisen, F. and Arey, J., 2005. Secondary PAH and nitro-PAH concentrations in the Los Angeles Basin. *Environmental Science and Technology* 39, 64-73.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T., 1993b. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. Environmental Science and Technology 27, 2700-2711.

Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simineit, B.R.T., 1993a. Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. *Atmospheric Environment* 27A, 1309-1330.

Rogge, W.F., Hildeman, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993c. Sources of fine organic aerosol. 5. Natural gas home appliances. *Environmental Science and Technology* 27, 2736-2744.

Rogge, W.F., Hildeman, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1997a. Sources of fine organic aerosol. 7. Hot asphalt roofing tar pot fumes. *Environmental Science and Technology* 31, 2726-2730.

Rogge, W.F., Hildeman, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993d. Sources of fine organic aerosol. 3. Road dust, tire debris, and organometalic brake lining dust. *Environmental Science and Technology* 27, 1892-1904.

Rogge, W.F., Hildeman, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993e. Sources of fine organic aerosol: 2. Noncatalyst and catalyst equipped automobiles and heavy duty diesel trucks. *Environmental Science and Technology* 27, 636-651.

Rogge, W.F., Hildeman, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1997b. Sources of fine organic aerosol. 8. Boilers burning No.2 Distillate fuel oil. *Environmental Science and Technology* 31, 2731-2737.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1997. Sources of fine organic aerosol. 8. Boilers burning No. 2 distillate fuel oil. *Environmental Science and Technology* 31, 2731-2737.

Rogge, W.F., Hildemann, M.A., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T., 1998. Sources of fine organic aerosl. 9. Pine, Oak, and Synthetic log combustion in residential fireplaces. *Environmental Science and Technology* 32, 13-22.

Sanderson, E. G., Farant, J.-P., 2005. Atmospheric size distribution of PAHs: evidence of a high-volume sampling artifact. *Environmental Science and Technology* 39, 7631-7637.

Schauer, J. J., Rogge, W. F., Hildemann, L.M.., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T., 1996. Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers. *Atmospheric Environ*ment 30, 3837-3855.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999b. Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks. *Environmental Science and Technology* 33, 1578-1587.

Schauer, J. J., M. J. Kleeman, G. R . Cass, and B. R. T. Simoneit 1999a. Measurement of Emissions from Air Pollution Sources. 1. C1 through C29 Organic Compounds from Meat Carbroiling. *Environmental Science and Technology* 33, 1566-1577.

Schauer, J.J. and Cass, G.R., 2000. Source apportionment of winter time gas-phase and particle phase air pollutants using organic compounds as tracers. *Environmental Science and Technology* 34, 1821-1832.

Schauer, J.J., Kleeman, M.J., Cass, G.R., and Simoneit, B.R.T., 2001. Measurement of emissions from air pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood. *Enviromental Science and Technology* 35, 1716-1728.

Schauer, J. J., M. J . Kleeman, G. R . Cass, and B. R . T. Simoneit, 2002a. Measurement of Emissions from Air Pollution Sources. 4. C1-C27 Organic Compounds from Cooking with Seed Oils, *Environmental Science and Technology* 36, 567-575.

Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit., 2002b. Measurement of Emissions from Air Pollution Sources. 5. C1-C32 Organic Compounds from Gasoline-Powered Motor Vehicles. *Environmental Science and Technology* 36, 1169-1180.

Schauer, C., Niessner, R. and Poschl, 2003. Polycyclic aromatic hydrocarbons in urban

air particulate matter: Decadal and seasonal trends, chemical degradation and sampling artifacts. *Environmental Science and Technology* 37, 2861-2868.

Schnelle-Kreis, J., Gebafugi, I., Welzl, G., Jaensch, T. and Kettrup, A., 2001. Occurrence of particle associated polycyclic aromatic compounds in ambient air of the city of Munich. *Atmospheric Environment* 35, S71-S81.

Sehmel, G.A., 1980. Particle and gas deposition, a review. *Atmospheric Environment* 14, 983-1011.

Seinfeld, J.H. and Pandis, S.N., Atmospheric Chemistry and Physics, From Air Pollution to Climate Change. John Wiley and Sons, New York, 1998.

Shah, S.D., Ogunyoku, T.A., Miller, J.W., and Cocker, D.R., 2005. On-road emission rates of PAH and *n*-alkane compounds from heavy duty diesel vehicles. Environmental Science and Technology 39, 5276-5284.

Sheesley, R.J., Schauer, J.J., Bean, E., Kenski, D., 2004. Trends in Secondary organic aerosol at a remote site in Michigan's upper peninsula. *Environmental Science and Technology* 38, 6491-6500.

Simicik, M.F., Zhang, H., Eisenreich, S.J., Franz, T.P., 1997. Urban contamination of the Chicago/Coastal Lake Michigan Atmosphere by PCBs and PAHs during AEOLOS, *Environmental Science and Technology* 31, 2141-2147.

Simcik, M.F., Eisenreich, S.J. and Lioy, P.J., 1999. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmospheric Environment* 33, 5071-5079.

Simo, R., Colom-Altes, M., Grimalt, J.O., and Albaiges, J., 1991. Background levels of atmospheric hydrocarbons, sulphate and nitrate over the western Mediterranean. *Atmospheric Environment* 25a, 1463-1471.

Simoneit, B.R.T., 1984. Organic matter of the troposphere-III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. *Atmospheric Environment* 18, 51-67.

Simoneit, B.R.T. and Mazurek M.A., 1982. Organic matter of the troposphere-II. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmospheric Environment* 16, 2139-2159.

Simoneit, B.R.T., Cox, R.E., Standley, L.J., 1988. Organic matter of the troposphere-IV. Lipids in Harmattan aerosols of Nigeria. *Atmospheric Environment* 22,983-1004.

Simoneit, B.R.T., 1989. Organic matter of the troposphere-V: Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *Journal of Atmospheric Chemistry* 8, 251-275.

Simoneit, B.R.T., 1984. Organic matter of the troposphere-III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. *Atmospheric Environment* 18, 51-67.

Simoneit, B.R.T., Rogge, W.F., Lang, Q., and Jaffe, R., 2000. Molecular characterization of smoke from campfire burning of pine wood (*Pinus elliottii*). *Chemosphere-Global Change Science* 2, 107-122.

Simoneit, B.R.T., Medeiros, P.M. and Didyk, B.M., 2005. Combustion products of plastics as indicators for refuse burning in the atmosphere. *Environmental Science and Technology* 39, 6961-6970.

Slinn, S.A. and Slinn W.G.N., 1980. Predictions for particle deposition on natural waters. *Atmospheric Environment* 14, 1013-1016.

Standley, L.J., Simoneit, B.R.T., 1987. Characterization of extractable plant wax, resin, and thermally matured components in smoke particles from prescribed burns. *Environmental Science and Technology* 21, 163-169.

Sweet, C. W.; Harlin, K.; Gatz, D. F.; Bauer, S. *Great Lakes Integrated Atmospheric Deposition Network (IADN) Data Report 1993-1994*; Illinois State Water Survey: Champaign, IL, 1996.

Teske, J. and Engewald, W., 2002. Methods for, and applications of, large-volume injection in capillary gas chromatography, *Trends in Analytical Chemistry* 21, 584-593.

Tobias, H. J., Beving, D.E., Ziemann, P.J., Sakurai, H., Zuk, M., McMurry, P. H., Zarling, D., Waytulonis, R., Kittelson, D. B., 2001. Chemical analysis of diesel engine nanoparticles using a nano-DMA/thermal desorption particle beam mass spectrometer. *Environmental Science and Technology* 35, 2233-2243.

Tsuda, A., Rogers, R.A., Hydon, P.E., and Butler, J.P., 2002. Chaotic mixing deep in the lung. *Proceedings of the National Academy of Sciences 99*, 10173-10178.

Turpin, B.J., Saxena, P., and Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmospheric Environment* 34, 2983-3013.

Van Vaeck, L. and Van Cauwenberghe, K.A., 1985. Characteristic parameters of particle size distributions of primary organic constituents of ambient aerosols. *Environmental Science and Technology* 19, 707-716.

Venkataraman, C., Lyons, J.M. and Friedlander, S.K., 1994. Size distributions of ploycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization. *Environmental Science and Technology* 28, 555-562.

Venkataraman, C. and Friedlander, S.K., 1994. Source resolution of fine particulate polycyclic aromatic hydrocarbons using a receptor model modified for reactivity. *Journal of the Air Waste Management Association* 44, 1103-1108.

Venkataraman, C., Negi, G., Brata, S.B., Rastogi, R., 2002. Size distributions of polycyclic aromatic hydrocarbons in aerosol emissions from biofuel combustion. *Aerosol Science*, 33, 503-518.

Vogt, W., Jacob, K., Obwexer, H.W., 1979. Sampling method in capillary column gas-liquid chromatography allowing injections of up to 250μL. *Journal of Chromatography A* 174, 437-439.

Volckens, J. and Leith, D., 2003. Comparison of methods for measuring gas-particle partitioning of semivolatile compounds. *Atmospheric Environment* 37, 3177-3188.

Watson, J.G. and Chow, J.C., 1992. Ambient air sampling. in aerosol measurement: Priciples, Techniques and Applications. K. Willeke and P.A. Baron eds. pp. 622. John Wiley and Sons.

Watson, J.G., Chow, J.C., and Fujita, E.M., 2001. Review of volatile organic compound source apportionment by chemical mass balance. *Atmospheric Environment* 35, 1567-1584.

Yamasaki, H., Kuwata, K., and Miyamoto, K., 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. *Environmental Science and Technology* 16, 189-194.

Yang, H., Chiang, C., Lee, W., Hwang, K., and Wu, E.M., 1999. Size distribution and dry deposition of road dust PAHs. *Environment International* 25, 585-597.

Yang, H., Chien,S., Chao, M., Lin, C., 2005. Particle size distribution of polycyclic aromatic hydrocarbons in motorcycle exhaust emissions. *Journal of Hazardous Materials* B125, 154-159.

Zheng, M., Cass, G.R., Schauer, J.J. and Edgerton, E.S., 2002. Source apportionment of PM2.5 in the southeastern United States using solvent-extractable organic compounds as tracers. *Environmental Science and Technology* 36, 2361-2371.

Zielinska, B., Arey, J., Atkinson, J., Winer, A.M., 1989a. The nitroarenes of molecular weight -247 in ambient particulate matter samples collected in Southern California, *Atmospheric Environment* 23, 223-229.

Zielinska, B., Arey, J., Atkinson, R., McElroy, P.A., 1989b. Formation of methylnitronaphthalenes from the gas-phase reactions of 1- and 2-methylnaphthalene with OH radicals and N_2O_5 and their occurrence in ambient air. *Environmental Science and Technology* 23, 723-729.

Zielinska, B., Sagebiel, J., McDonald, J.D., Whitney, K., Lawson, D. R., 2004. Emission rates and comparative chemical composition from selected in-use diesel and gasoline fueled vehicles. *Journal of the Air and Waste Management Association* 54, 1138-1150.

Zrostlikova, J., Hajslova, J., Godula, M., Mastovska, K., 2001. Performance of programmed temperature vaporizer, pulsed splitless and on-column injection techniques in analysis of pesticide residues in plant matrices. *Journal of Chromatography A* 937, 73-86.