FORENSIC PAH ASSESSMENT OF THE SYDNEY TAR PONDS AND THE SURROUNDING ENVIRONMENT USING PAH FINGERPRINT ANALYSIS

by

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I would like to dedicate this thesis to my wife, Natalie MacAskill, whose support and patience gave me the opportunity to pursue and complete this research project.

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are the primary contaminant of concern at the remediated Sydney Tar Ponds, located in Sydney, Nova Scotia, Canada. PAHs have been identified in shallow marine sediments in Sydney Harbour and have historically been considered to be a result of effluents from the Tar Ponds. The purpose of this research was to develop PAH Fingerprints for soil and sediment samples from the Tar Ponds and the surrounding areas. The PAH Fingerprints were analyzed using six techniques to identify common sources of PAHS. Results indicate a common source of PAHs for Upstream Sediments, Urban Background Soils, Harbour Sediments and Coal Sediments. Based on activity at these sites, coal handling is likely the source of PAHs in these samples. Fingerprints in the Tar Ponds Sediments did not correlate with other samples, indicating a different source of PAHs, unrelated to the PAHs found in Sydney Harbour Sediments.

List of Abbreviations Used

Ant	Anthracene
B(a)A	Benzo(a)anthracene
B(a)P	Benzo(a)pyrene
B(g,h,i)Pl	Benzo(g,h,i)perylene
Fluor	Fluoranthene
HPAH	High Molecular Weight PAHs
Ideno(1,2,3)	Ideno(1,2,3)pyrene
LPAH	Low Molecular Weight PAHs
MPAH	Moderate Molecular Weight PAHs
PAHs	Polycyclic Aromatic Hydrocarbons
Phen	Phenanthrene
STPA	Sydney Tar Ponds Agency

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Chapter 1 - Introduction

In cooperation with previous employer Dillon Consulting Limited (Dillon) and the Sydney Tar Ponds Agency (STPA), this research is based in part, on a large environmental monitoring project that has multiple sub-studies within it. While the author conducted, supervised or participated in many aspects of this project, this thesis focuses on PAH impacts in Sydney Harbour marine sediments and PAH impacts at other locations within the Sydney Tar Ponds study area. The research goal is to confirm correlation between the PAH impacts in the Sydney Tar Ponds and the PAH impacts observed in Sydney Harbour, which have long been considered a result of effluents from the Sydney Tar Ponds.

This is believed to be the first research project conducting spatial and temporal PAH fingerprint analysis at the Sydney Tar Ponds site and the surrounding area. This research project should improve the understanding of PAH distribution in the vicinity of the Sydney Tar Ponds site. This information may provide some direction on other potential sources of PAHs within the study area and identify potential relationships between PAH compounds identified in soils and sediments at various locations across the study area.

The literature review conducted for this research project did not identify studies that combined more than two PAH Fingerprint techniques for the assessment of PAH contamination in soils and sediments. This research uses multiple techniques to present the same results, supporting the validity of the various techniques as well as providing a framework for using multiple techniques in a given study.

It is important to note that data used in this research project varies both spatially across the project site, including the marine environment, as well as temporally from the late 1980s to 2012. This includes a period of dredging harbour sediments in 2011/2012. While this coverage can be considered a benefit to the research project overall, there are a number of potential variables that have not been accounted for (e.g. sewer outfalls). The data set is not meant to be all-inclusive of the surrounding environment, and other potential sources of PAHs within the study area may not yet be identified. The Muggah Creek watershed and the Sydney Harbour have a complex human, industrial and geochemical history of which the Sydney Tar Ponds are but one component. A

holistic approach to PAH fingerprinting at the study area allows for the assessment of multiple potential sources of PAH impacts in environmental samples.

A large number of studies were reviewed in preparation for this research to develop a better understanding of PAHs and the various methods of source identification, also known as source apportionment. The literature review in Section 2.0 describes much of the background reviewed for this research project, as well as the documents that were used to support the approach of this research project.

1.1. Hypothesis

The purpose of this research project was to confirm correlations between identified PAHs in various media (e.g., Sydney Harbour Sediments) and potential sources related to the Sydney Tar Ponds remediation project. Given the environmental importance of PAHs, source identification and confirmation is a relevant part of the monitoring conducted during the remediation project. The research will confirm that PAHs identified in the study area are pyrogenic in nature (i.e., derived from combustion processes) and will present similar PAH fingerprints, both to each other and to source fingerprints (e.g. impacted Tar Ponds sediments).

The hypothesis of the research was PAH Fingerprinting techniques will confirm similarities between PAH profiles in Sydney Harbour and the PAH profiles identified at the Sydney Tar Ponds, suggesting these two areas of PAH impacts share the same contamination source. If true, the PAH profiles of the ASTM Coal Tar Reference Material and the Sydney Tar Ponds Sediments can be considered as reference profiles for the potential distribution of PAHs in Sydney Harbour.

1.2. Multiple Techniques Approach

This PAH Fingerprint Assessment will employ several different PAH fingerprint techniques, the benefits and constraints of which will be discussed in the evaluation of the results. Multiple lines of evidence will help support the findings while also indirectly evaluating the correlation of the techniques employed.

1.3. Project Background

The data presented herein has been collected from soil and sediment samples at the Sydney Tar Ponds site and the surrounding area since 1988. PAH contamination of the sediments in the Muggah Creek estuary was a major cause in the recent Solidification/Stabilization (S/S) project at the site to reduce potential exposure of contaminants to the environment. Environmental Monitoring Programs were established prior to, and during the S/S program to monitor changes in the surrounding environment during remediation. Based on historical, pre-construction and construction phase information, this research project aims to correlate PAH impacts in the surrounding environment with one of the potential source materials: contaminated sediments in the Sydney Tar Ponds and other Coke Ovens related sources.

I was the Project Coordinator for the Environmental Effects Monitoring and Surface Water Compliance Monitoring (EEM) contract between Dillon Consulting Limited and the Sydney Tar Ponds Agency (STPA) from 2009-2013. The project included a variety of monitoring components including surface water, groundwater and marine monitoring. This research project is, in a large part, an extension of the monitoring programs that the author participated in during the EEM program at the Sydney Tar Ponds.

Chapter 2 - Literature Review

2.1. Coke Production

Coking is the process of heating coal in coke ovens to drive volatile matter from it. Coke was used as a fuel and reducing agent in the production of iron during the operation of the Sydney Steel Plant. The coke making process involves carbonization of coal at high temperatures (1100°C) in an oxygen deficient atmosphere in order to concentrate the carbon (Joint Review Panel, 2006).

The coke making process can be summarized in the following steps: Before carbonization, the selected coals from specific mines were blended, pulverized, and oiled for proper bulk density control. The blended coal was charged into a number of slot type ovens wherein each oven shared a common heating flue with the adjacent oven. Coal was carbonized in a reducing atmosphere and the off-gas was collected and sent to a by-product plant where various by-products were recovered. Some of the by-products generated were considered waste and in the case of this study site, waste by-product was discharged into Coke Ovens Brook with subsequent deposition downstream at the Muggah Creek estuary. Over a period of almost 100 years, the Muggah Creek estuary was transformed into the Sydney Tar Ponds.

Coal Tar is a black, highly viscous by-product of the coking process. It is a complex and variable mixture of dangerous chemical compounds that will have varying amounts of Polycyclic Aromatic Hydrocarbons (PAHs) depending upon the source. Research suggests 8-12 gallons of coal tar can be produced for each ton of coal converted to coke. Research did not identify an estimated volume of by-products released into the Sydney Tar Ponds from the Coke Ovens.

Gu et al. (2003) conducted a source apportionment study in a similar setting as the Sydney Tar Ponds. Coke ovens at a US Steel Corp. facility in Ohio contaminated the Black River with PAHs. Impacted sediments were dredged 7 years following the closure of the coke ovens, significantly reducing the overall PAH impact in the river. The Gu et al. (2003) study indicated that PAH impacts peaked around 1954 and again following the completion of the dredging project. The latter spike in PAHs was considered to be due to a redistribution of PAH impacts

during the dredging project. It is important to recognize the similarities between this project in the Black River in Ohio and the Sydney Harbour in that both sites were exposed to dredging activities following an extended period of exposure to potential PAH contamination.

2.2. Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are found in aquatic sediments worldwide and can pose a variety of environmental implications. PAHs are generally considered a contaminant of concern (COC) due to the carcinogenicity of these compounds (Joint Review Panel, 2006). They are most commonly produced by combustion of a fuel in oxygen deficient, or low temperature conditions. Coke production is considered one of the main anthropogenic causes of PAHs in the environment, in addition to production of charcoal, power generation using fossil fuels, waste incineration and oil refining. By-products of these processes can be high in PAHs and a discharge of these by-products will result in a release of PAHs into the environment.

The unique PAH profile or "Fingerprint" for a particular source is dependent on the process that produced the PAHs. During oxygen-deficient, high temperature processes such as coke production, low molecular weight PAHs are usually formed, whereas sources of heavy hydrocarbons, such as coal, contain higher molecular weight PAHs (Mostert et al, 2010). PAHs can be transported from their original source (e.g. fossil fuel pyrolysis/combustion) via direct discharge, atmospheric deposition or urban runoff, which could contain a variety of potential PAH sources.

In 1985 and 1987, PAH data was collected from borehole cores throughout the Sydney Tar Ponds at depths between 0 and 0.6 m. The general order of PAHs in terms of their relative abundance was as follows: Naphthalene, Phenanthrene, Benzo(a)anthracene, Pyrene, Fluoranthene and Anthracene. Napthalene and Phenanthrene account for about 60% to 80% of the total PAH content but were also the two most variable as indicated by standard deviation data (Acres, 1988). This suggests that PAHs in the Sydney Tar Ponds are predominantly low molecular weight PAHs, formed in the oxygen-deficient conditions of the Coke Ovens.

Atmospheric PAHs are bound either to the gas phase or to particulate matter. Generally, PAHs lighter than Pyrene and Fluoranthene tend to be present in the gaseous phase, whereas PAHs heavier than Benzo(a)anthracene and Chrysene are mainly bound on particles (Tobiszewski and

Namiesnik, 2012). At category I steel plants, the lower molecular weight PAHs are predominant in the emissions, contributing 97% of the total PAH mass. These PAHs easily vaporize and exist in the gas phase, while PAHs of higher molecular weights are less likely to volatilize and are instead, adsorbed by particulate (Lee and Chen, 1995). This particulate can contribute to PAH impacts in shallow soil in the area surrounding the facility.

PAH analysis at certified commercial laboratories in Canada normally include 19 PAH parameters. These parameters include the 16 PAHs listed as priority pollutants by the US EPA (US EPA, 1982). Studies in the US tend to focus on these 16 priority parameters, such as Ranjan et al. (2012), which is referenced herein. The list of 16 Priority Pollutant PAH compounds, as classified by the US EPA, are shown below in Table 1.

Table 2-1 presents a classification of PAH compounds developed for the JDAC Environmental (2002) Contaminant Flux from Muggah Creek to Sydney Harbour. PAH compounds were classified into three groups according to molecular weight (MWT), solubility in water, environmental behaviour as indicated by the octonal-water partition coefficient (K_{OW}), and carcinogenicity (JDAC, 2002). Low molecular weight compounds (LPAH) are characterized by relatively high solubility in water. The medium molecular weight compounds (MPAH) have lower solubility than the LPAH compounds, but higher solubility than the high molecular weight PAH compounds (HPAH) (JDAC, 2002).

Table 2-1 - PAH Compounds Included in the Study

	Number of Rings	Molecular Weight (g/mole)	Solubility in Water (mg/L)	Log Kow	Cancer causing?
Low Molecular Weight PAH Compounds (LPAH)					
Naphthalene[1]	2	128	30	3.37	no
2-Methylnapthalene	2	142	25	5.08	no
1-Methylnapthalene	2	142	28	5.08	no
Acenapthylene[1]	3	152	16.3	4.08	no
Acenapthene[1]	3	154	4.13	3.96	no
Fluorene[1]	2+	166	1.86	4.17	no
Phenanthrene[1]	3	178	1.28	4.55	no
Medium Molecular Weight PAH Compounds (MPAH)					
Anthracene[1]	3	178	0.07	4.47	no
Fluoranthene[1]	3+	202	0.232	5.08	no
Pyrene[1]	4	202	0.137	5	no
High Molecular Weight PAH Compounds (HPAH)					
Benzo(a)anthracene[1]	4	228	0.014	5.61	yes
Chrysene[1]	4	228	0.00194	5.74	yes
Benzoflouranthene[1]	4+	252	0.004	6.19	yes
Perylene	5	252	0.0004	6.25	no
Benzo(a)pyrene[1]	5	252	0.0038	6.13	yes
Ideno(1,2,3-c-d)pyrene[1]	5+	276	0.0107	6.91	yes
Dibenzo(a,h)anthrecene[1]	5	278	0.00067	6.55	yes
Benzo(g,h,i)perylene[1]	6	276	0.00026	7.23	no

Note: The PLA 1991 report identified three groups of PAHs:

- The Chrysene group, including benzo(a)antracene, chrysene, benzofluoranthene, benzo(e)pyrene, indenopyrene and benzo(g,h,i)perylene: of low aqueous solubility and mainly associated with particulates when transported from Coke Ovens Brook.

- The Fluorene group including acenapthene, fluorene, acenapylene, and phenanthrene; mainly dissolved and associated with base flow in Coke Ovens Brook.

- The Fluoranthene group - remaining compounds which were either intermediate, or not otherwise correlated with the other groups. Some of these compounds were hypothesized to originate mainly from sediments within Muggah Creek. 1 – PAH parameter is included in the US EPA original list of 16 priority pollutants.
Source: Contaminant Flux from Muggah Creek to Sydney Harbour (2002). JDAC Environmental.

The US EPA (2009) defines the Octanol-Water Partition Coefficient (K_{OW}) as "A coefficient representing the ratio of the solubility of a compound in octanol (a non-polar solvent) to its solubility in water (a polar solvent). The higher K_{OW}, the more non-polar the compound. Log K_{OW} is generally used as a relative indicator of the tendency of an organic compound to adsorb to soil. Log K_{OW} values are generally inversely related to aqueous solubility and directly proportional to molecular weight." As presented in Table 1, naphthalene exhibits the highest solubility, the lowest K_{OW} and the lowest molecular weight of the PAHs summarized. Conversely, benzo(g,h,i)perylene exhibits the highest molecular weight and K_{OW}, with the lowest solubility in water.

2.3. PAH Risk and Toxicity

The toxicity of PAH parameters depends primarily on structure. PAH isomers may have the same number of rings and same chemical formula, however the structure of the isomers may make the PAH non-toxic or very toxic. Benzo(a)pyrene is considered to be the first discovery of a chemical carcinogen. Since then, the US EPA has identified seven PAH compounds as probable human carcinogens (US EPA, 1982):

- Benzo(a)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Chrysene
- Dibenzo(a,h)anthracene
- Ideno(1,2,3-cd)pyrene

2.4. PAH Partitioning and Environmental Fate Modelling

The solubility of PAHs in water was identified early as a potential complication in the source apportionment goals. The interaction between contaminated soils and sediments with surface water and groundwater is complicated and an evaluation of each PAH parameter based on solubility would provide little value in testing the hypothesis of this study. As such, an evaluation of the distribution of each PAH parameter was undertaken using an environmental fate model developed by Karl C. Nieman (2003).

The model evaluates equilibrium chemical distribution between environmental phases (air, water, soil and free-phase product). The use of this model does not assume that the PAH distributions in the samples used in the study have reached equilibrium, but it does provide an indication of the distribution of PAHs between the water and soil/sediment phases that the data set consists of.

Fugacity is a measure of the tendency for a chemical such as PAHs, to escape from one phase (soil/sediment) to another (water). This tendency to escape is called the fugacity of the PAH, and it will exist until the PAH distribution reaches equilibrium. In addition to Henry's Law constant H, the Koc, known as the soil organic carbon-water partitioning coefficient, of the PAH is also important. Koc values are useful in predicting mobility of organic soil contaminants; higher Koc values correlate to less mobile organic chemicals while lower Koc values correlate to more mobile organic chemicals. Using Henry's Law Constant H, the log Kow and log Koc values of a particular PAH parameter, the fugacity of that parameter can be determined.

PAH parameters that are included in the analytical suite of the samples in the data set were used in the Fugacity model developed by Nieman (2003). Results suggest that for most PAH parameters, over 95% of the PAH distribution will be found in the soil/sediment phase. Results of the model are presented in Appendix 1. With this in mind, the statistical interpretations of the data focus on the soil/sediment phase only. This focus will provide source apportionment information for PAH impacts found in Urban Background Soils, Upstream Sediments, Tar Ponds Sediments, Harbour Sediments and Coal Sediments.

2.5. Sydney Harbour Sediment Deposition Rates

Sediment Traps that were used during the EEM to capture sediments during deposition in Sydney Harbour, were constructed of 15 cm PVC pipes, 1.2 m long, secured to concrete blocks. The traps were deployed at the Sydney Harbour marine monitoring stations from April 21 to July 21, 2009. The 5:1 dimensions ratio suggested by Bloesch (1994) were used to avoid losses due to sediment re-suspension (Walker, 2005; Walker et al., 2009)

The sediment collection period was only three months long and was in the Spring and Summer. Results were extrapolated to determine an annual sediment deposition rate for Sydney Harbour. Rates were determined to be between 0.4 and 0.8 cm/year (Walker et. al., 2013). These results

were found to be comparable to previous estimates (Stewart et al., (2001) and Lee et al., (2002) and more recently by Smith et al. (2009) who estimated between 0.2 and 2.0 cm/year. Similar to the results of this study, Lee et al. noted that stations closest to Muggah Creek tended to have the highest sedimentation rates of stations within the harbour. This suggests that outflow from the subject site, or another nearby source of sediment in the harbour, is a major source of sediments in the harbour.

2.6. PAHs in Coal

According to Stout et al. (2003), the occurrence of coal particles in a soil or sediment could confound the interpretations surrounding TPH, PAH and biomarkers in the samples. PAH distributions can vary widely between coals with lower rank coals dominated by 3 and 4-ring PAHs and volatile bitumous A coal and anthracite are both dominated by 2-ring PAHs. If the coal handling facilities in Sydney Harbour are a potential source of PAHs in Harbour Sediments, then changes in the PAH Fingerprints should be evident between historic periods of exporting Cape Breton coal, to the current activity of importing international coals.

Stout et al. (2001) stated that PAHs are well known components of urban runoff and that PAHs associated with urban runoff are complex mixtures that tend to be dominated by higher molecular weight 4 to 6-ring PAHs. It is thought that urban storm water runoff may be the largest chronic contributor of anthropogenic background PAH to urban sediments. The setting for this study (Sydney Harbour, Sydney Tar Ponds and surrounding environment) are subject to urban runoff and any potential PAH impacts associated with it.

2.7. Degradation of PAHs

PAH compositional changes due to weathering can include a pronounced decrease in the Naphthalene's relative to other alkylated PAHs, development of a profile in each alkylated PAH family showing the distribution of $C_0<C_1<C_2<C_3$, and a significant decrease in the relative ratios of the sum of Naphthalene's, Phenanthrenes, Dibenzo-thiophenes, and Fluorenes to Chrysenes (Wang et al., 2003).

Short (2002) employed a first-order loss-rate (FOLR) kinetic model of PAH weathering developed by Short and Heintz (1997) on four independent case studies. The model evaluates a

goodness-of-fit metric between measured PAH compositions in environmental samples and suspected sources after correcting for PAH weathering loss based on FOLR kinetics (Wang et al., 2003).

Gu et al. (2003) found that their results of source apportionment that included a degradation factor did not differ greatly from the one without this factor. Therefore, in that study, the effect of degradation on PAH concentrations was determined to be negligible. Phenanthrene appeared to be the only PAH compound out of six PAHs that undergoes significant aerobic decay due to biodegradation, photolysis or desorption. The loss is found at concentrations >500 ppb. This is concluded based on a chemical mass balance model that includes a degradation factor for individual PAHs (Gu et al., 2003).

Degradation and weathering of PAHs in the environment are expected to affect the behaviour of PAH impacts in some matrices, however, based on the results of similar studies, the scope of this research project does not consider the effects of PAH degradation due to weathering when developing and analyzing PAH Fingerprints.

2.8. PAH Analytical Procedures

The Canadian Council of Ministers of the Environment's (CCME) remediation criteria for PAHs in soil range from 0.1 mg/kg (agricultural) to 10-100 mg/kg (commercial/industrial) (Maxxam Analytics Inc., 2012). The regular PAH analysis package, as provided by Maxxam Analytics Inc. includes the following parameters:

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo[a]anthracene
- Benzo[a]pyrene
- Benzo[b]fluoranthene
- Benzo[k]fluoranthene
- Benzo[ghi]perylene
- Chrysene
- Dibenzo[a,h]anthracene

- Fluoranthene
- Fluorene
- Indeno[1,2,3-cd]pyrene
- 1-Methylnaphthalene
- 2-Methylnaphthalene
- Naphthalene
- Perylene
- Phenanthrene
- Pyrene

2.8.1. Analysis

The PAH method involves solvent extraction of the components and chromatographic column clean up to remove interferences. The extract is then analyzed by capillary column gas chromatography mass spectrometry (GC/MS). Prior to extraction, three deuterated surrogate PAH compounds are added to the samples. These compounds represent a range of volatilities and are used to monitor the efficiency of the sample preparation steps (Maxxam Analytics Inc., 2012).

2.8.2. Quality Assurance

A method blank, spiked blanks, matrix spike and a duplicate sample are analyzed with each batch of twenty samples. The spiked blank QC results are control charted and must meet specific acceptance criteria before sample results are released (Maxxam Analytics Inc., 2012).

2.8.3. Detection Limits

Detection limits for PAH analysis at Maxxam are evaluated using U.S. EPA protocols. The reporting limit for individual PAH compounds in soil is 0.01 mg/kg, 0.005 mg/kg for low level (Maxxam Analytics Inc., 2012).

2.8.4. Determination of PAHs in Soil by GC-MS

This method was provided by Maxxam (Maxxam Analytics Inc., 2012) and is applicable to the determination of polycyclic aromatic hydrocarbons (PAHs) in soil and sediment samples.

A 10 g soil sample is extracted by vigorous shaking with 50:50 acetone/hexane. The hexane is separated from the acetone by the addition of reverse osmosis (R.O.) water. An aliquot of hexane is added to an aliquot of isooctane and this extract is analyzed by gas chromatography with mass selective detection. The compounds are introduced into the GC/MS by injecting the sample onto a fused silica 5% Methyl Siloxane capillary column. The sample is separated in the GC into its components based on the boiling point of the compounds using the fused silica column. Specific temperature program, injection, and column features are used to optimize the separation of the compounds.

2.9. Use of Non-Detect Data

Many of the parameters measured as part of the EEM program exhibit concentrations less than the laboratory reportable detection limits (RDL). RDLs are designed to meet specific method requirements, such as being less than applicable guidelines.

Frequent parameters concentrations less than RDLs make the determination of positive or negative changes over time difficult to assess. Analytical methods with high detection limits are insufficient to make claims about the presence or absence of target parameters (de Solla et al., 2011). There is inherent value in knowing that concentrations are less than a given value such as the RDL, however, there is no way to identify increasing or decreasing trends using this data.

Data that is less than the RDL is often referred to as censored data. There is normally a result for each analysis, however the analysis method determines the level of analytical precision and low concentrations within this level of analytical precision, must be censored to reflect the level of precision the laboratory analysis is able to accurately provide. This censored data presents a serious interpretation problem for data analysis (Helsel, 1990).

Censored data are unavoidable as there are lower limits of residues that analytical techniques, however sophisticated, can detect. Despite the importance of using optimal statistical models for compensating for values below RDLs, data suggests that choosing optimal RDLs is more important that the statistical methods used in response to RDLs (de Solla et al., 2011).

Following the Pre-Construction/Baseline phase of the project, the laboratory implemented a routine sample dilution that resulted in an increase in some RDLs. The RDLs of some parameters were increased by 10x due to parameter interference during analysis, likely due to the presence

of seawater in the samples. Basic observations such as means, medians, and frequency of detections and correlation of parameters can all be affected by such changes in the RDLs (de Solla et al., 2011).

There are several routine practices for making use of censored data in statistical analysis, the most popular of which is the use of substitution data. The first option in using replacement data is the replacement of the < RDL value with a value of zero. This implies that the parameter being analyzed is not present in the sample. This cannot be verified and potentially results in a statistical analysis that is biased low. A second approach is the replacement of the less than RDL value with a value equal to the RDL. This approach results in an analysis that will likely be biased higher than the actual. Helsel (1990), found that substitution of zero produced estimates of mean and median which were biased low, while substituting the reporting limit resulted in estimates above the true value. Depending on the method used for the replacement of observations below RDLs, means or medians will either be underestimated or overestimated (de Solla et al., 2011).

The third and most common approach is to use ½ of the RDL value as a substitution value. Similar to the first two options, this approach is also an assumption. Helsel, 1990, also found that substituting ½ of the RDL was less desirable than alternative methods.

An alternative to substitution methods is robust methods. These combine observed data above the detection limit with below limit values extrapolated assuming a distributional shape, in order to compute estimates of summary statistics (Helsel, 1990). A distribution is fit to the data above the reporting limit, but the fitted distribution is only used to extrapolate a collection of values below the reporting limit. These extrapolated values are not considered as estimates for specific samples, but only used collectively to estimate summary statistics (Helsel, 1990).

2.10. PAH Fingerprint Analysis

Environmental forensic investigations can utilize fingerprinting techniques to compare analytical parameters or sets of parameters to determine associations between data sets. Data sets used in fingerprint analysis most often include a potential source and environmental samples from another location in an attempt to confirm association between the analytical parameters.

The fingerprint can be a reliable indicator of a particular mix of contaminants. With the exception of potential weathering, the fingerprint does not change as the contaminant migrates and it can be selected based on constituents that migrate faster than other constituents. Multiple sources can be distinguished this way because the fingerprints can have the same contaminants, but different contaminant distributions.

The fingerprinting approach involves either qualitative visual comparisons (e.g., histogram plots) or a statistical comparison (e.g., correlation coefficients) of the distributions of analytical parameters in known source samples to the distributions in potential source samples, potential impacted areas and background areas (Stout and Uhler, 2003).

The Fingerprint Analysis of Leachate Contaminants (FALCON) described in Section 3.5, developed by the United States Environmental Protection Agency (EPA) is an empirical data assessment and visualization tool that produces contaminant fingerprint patterns by combining data from two or more parameters to produce visually distinctive and reproducible fingerprints (Plumb, 2005). The most common goal of contaminant fingerprint assessment is to correlate contamination in some environmental media with a potential source or sources.

Chemical fingerprinting of petroleum hydrocarbons has evolved into a science where the original sources of compounds such as PAHs can be identified by the abundance of target compounds forming a pattern or fingerprint, ratios of specific compounds or groups of compounds or by identifying source-specific compounds or markers in environmental samples (Boehm et al., 1997). Fabbri et al. (2003) studied PAH impacts in marine sediments at a lagoon in Italy and concluded that a relatively small data dispersion (relative standard deviations less than 20%) represents quite uniform PAH distribution, suggesting that PAHs derived from a predominant source.

Chapter 3 - Proposed Methodologies

3.1. Tiered Approach

PAH forensic analysis requires flexibility to gather information from a variety of environmental impacts as well as potential impact sources. A tiered approach aids in the focus of determining the nature, source and extent of PAH impacts in a given setting. Boehm et al. (1997), Page et al. (1995), Daling et al. (2002), Wang et al. (1997b, 1998b, 1999c, 2002, 2003) and Stout (2002) employed tiered approaches in their studies. Application of a tiered approach for this study can be summarized as follows:

- Tier 1 – analysis of PAH concentrations in soil and sediment samples;
- Tier 2 – product screening and determination of 19 PAH compound concentrations;
- Tier 3 – summarizing of PAH-containing samples from multiple soil and sediment locations across the project site including historical samples and reference materials;
- Tier 4 – statistical analysis of the data set using various methods to evaluate correlation between PAH contamination in various soils and sediments and at different locations across the site; and
- Tier 5 – determination of weathered percentages of residual PAHs (not included in this study).

This study made use of PAH sample data collected during several environmental assessment and environmental effects monitoring programs at the project site. The data set of 52 samples, each comprised of 19 PAH parameters, was reduced down from hundreds of samples that could have been used for this study. In order to make use of non-detect results, several substitution techniques were evaluated, which are described herein. The data set was also normalized in order to remove any bias due to heavily contaminated samples being compared to only slightly contaminated samples. Following the development of the data set, the steps taken in conducting the forensic assessment using PAH Fingerprint Techniques is outlined in the following flow chart.

Figure 3-1 – Forensic Analysis Flow Diagram

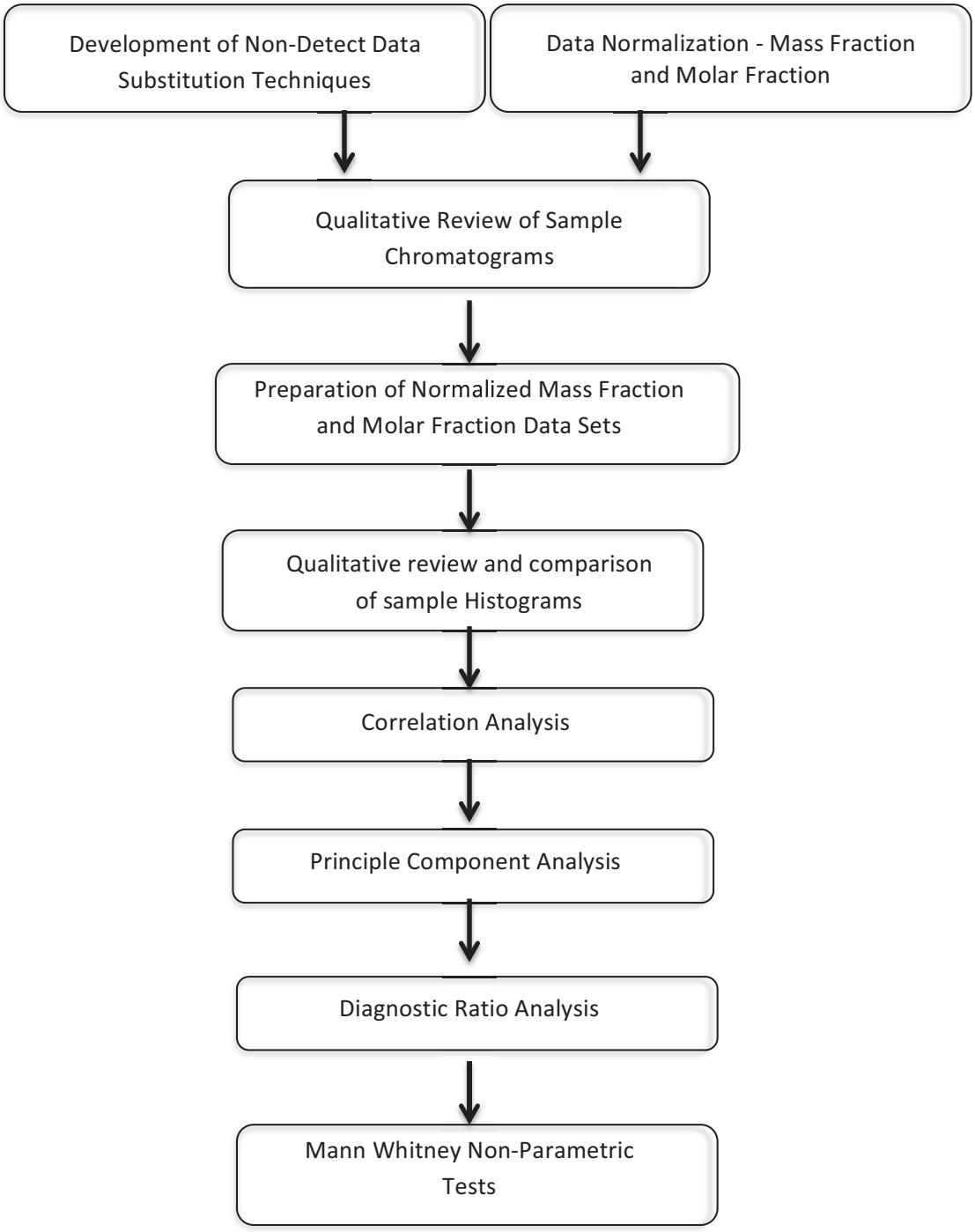


Figure 3-1 presents the steps taken in this study to develop the data set and conduct the forensic assessment using Fingerprint techniques. Following the completion of the data set as described

above, the available chromatograms were examined for similarities between samples. Then the normalized data set was used to generate histograms for a qualitative review of PAH compound distribution. This was followed by the Correlation Analysis of the data set, a Principle Component Analysis, generation of Diagnostic Ratio Plots and the conducting of Mann Whitney Non-Parametric Tests followed by the interpretation of the results and summary of the findings.

3.2. Use of Non-Detect Data

For the robust method, a regression of the log of concentrations versus normal score is used to extrapolate "fill-in" values below the detection limit. These "fill-ins" are retransformed back to original units and combined with data above the reporting limit to compute estimates of summary statistics. Helsel describes the process in four steps:

Step 1: Normal scores are computed with all non-detects set to slightly different values, all below the reporting limit.

Step 2: A linear regression equation is developed using only the above limit observations, where log of concentration is the y variable and normal scores the x variable.

Step 3: Estimates for the below-limit data are then extrapolated using this regression equation from normal scores for the below-limit data.

Step 4: Extrapolated estimates are retransformed into units of concentration, combined with the above-limit concentration data, and the summary statistics are computed.

A detailed description of the use of the Robust Method to assess the project-censored data is presented in APPENDIX 3.

Following the completion of the Robust Method analysis, mean concentrations were calculated for the COPCs using:

- The Robust Method;
- Exclusion of non-detects;
- Non-detects substituted with 0;
- Non-detects substituted with ½ RDL; and
- Non-detects substituted with RDL.

Means are summarized in the following Table 3-1.

Table 3-1 - Mean Concentrations Using Five Substitution Methods

Mean Concentrations	Cadmium	Chromium	Copper	Lead	Zinc	Acenaphthene	Acenaphthylene	Anthracene
Robust Method	0.57	39.14	367.30	34.02	444.50	0.049	0.031	0.037
ND=1/2 RDL	0.56	39.14	365.67	33.96	441.25	0.049	0.031	0.037
Exclude NDs	0.83	52.87	428.09	58.28	500.37	0.052	0.038	0.044
ND=Zero	0.53	38.01	364.41	31.79	438.34	0.048	0.030	0.036
ND=RDL	0.59	40.26	366.49	36.14	444.16	0.049	0.032	0.038

The means calculated using ND values based on the Robust Method are greater than means calculated with zero substituted for ND values. Using ½ of the RDL as a substitution resulted in means values not significantly different from the Robust Method. Even using the RDL in place of ND values did not always result in higher calculated means, as can be seen with copper, zinc and Acenapthene, which were lower or equal when the RDL was substituted. Exclusion of ND values results in much higher mean calculations for all parameters.

The Robust Method is only recommended for the assessment of summary statistics and the "fill-in" values should not be used other statistical analysis. However, as shown in the table, the substitution method that provided mean calculations most similar to the Robust Method is the substitution of the non-detects with ½ of the RDL.

Therefore, for consistency in the correlation analysis, all values in the PAH data set, concentrations below the RDL will be replaced with ½ of the RDL.

3.3. Data Normalization

Tabulated PAH parameter concentrations are normalized to facilitate statistical analysis. By converting PAH parameter concentrations to a % of the total PAH concentration, all sample

results become relative numbers from 0.0 to 1.0, with 0.0 being a non-detect parameter and 1.0 being 100% of the total PAH concentration. Data was normalized using both mass fractions and molar fractions as described in the next section. It is important to note the use of non-detect results in this research project; as described in detail in Section 3.2.

It was interesting to note during the normalization of the data set, that when ½ RDL is substituted for non-detect results, there is a direct effect on the total PAH concentration being used for the calculations. The reported Total PAH is less than the Total PAH that includes ½ RDL value substitutions for non-detects. This results in a larger % difference between the reported Total PAH and the value used for calculations.

3.4. Mass Fractions versus Molar Fractions

The mass fraction is the percentage of a particular PAH compound mass that contributes to the Total PAH mass of a sample. If analytical results are normalized so each PAH parameter becomes a percentage of the total PAH mass, mass fractions will be between 0 and 1.0. For example, if Naphthalene makes up 60% of the total mass of PAHs in a sample, the mass fraction for Naphthalene is 60% or 0.60. However, considering that Naphthalene is the lightest of the PAHs analyzed in these samples, a mass fraction of 0.3 Naphthalene may have the same mass as a mass fraction of 0.3 of Benzo(g,h,i)perylene, however because Benzo(g,h,i)perylene is heavier (i.e., a higher molecular weight) then there are effectively, fewer moles of Benzo(g,h,i)perylene in the sample. By conducting this study using mass fractions, the distribution of the masses are being compared and not the relative abundance of PAH parameters.

To account for this, the normalized mass fraction data set was converted into molar fractions. To do this, the values described above were used and assumed a base Total PAH mass of 100 g. This way, each mass fraction represents a mass of PAH, which cumulatively total 100. To convert this into the molar fraction, the mass fraction for Naphthalene, say 60% is used and divided by the molar mass:

60 g Naphthalene / 128 g/mol = 0.47 moles Naphthalene in the sample.

This was done for each PAH compound in the sample to determine how many moles of each compound are in each sample. Then the moles of each PAH compound were summed for a total

number of moles in each sample. The number of moles for each PAH compound was then divided by the total moles in each sample in order to obtain a molar fraction for each PAH compound in each sample.

0.47 moles Napthalene / 0.68 total moles = 0.69% Napthalene molar fraction in sample.

This way the distribution of PAHs can be evaluated by their relative abundance, and not by the relative mass. This was done for each of the 52 samples, generating a second, molar fraction, data set to compare with the mass fraction data set.

A set of histograms (Figures 3-2 and 3-3) was created to compare the mass fraction distribution of several samples with the molar fraction distributions, just to understand how they differ. One histograms was created using the PAH Fingerprint of an ASTM Reference Material for PAHs in Coal Tar, and a second histogram was created using the PAH Fingerprint of Coal Sediment, collected from beneath a coal handling facility on Sydney Harbour. As you can see in the two examples provided below, the PAH distribution fingerprint for each sample using molar fractions is relatively similar to the mass fraction distributions. In both histograms, it appears that lighter molecular weight PAHs are slightly more predominant when considering molar fractions, whereas heavier molecular weight PAHs are slightly more predominant when considering mass fraction. In either case, the mass fractions are not significantly different from the molar fraction distribution of PAHs.

Figure 3-2 - ASTM Reference Mass and Molar Fraction Histograms

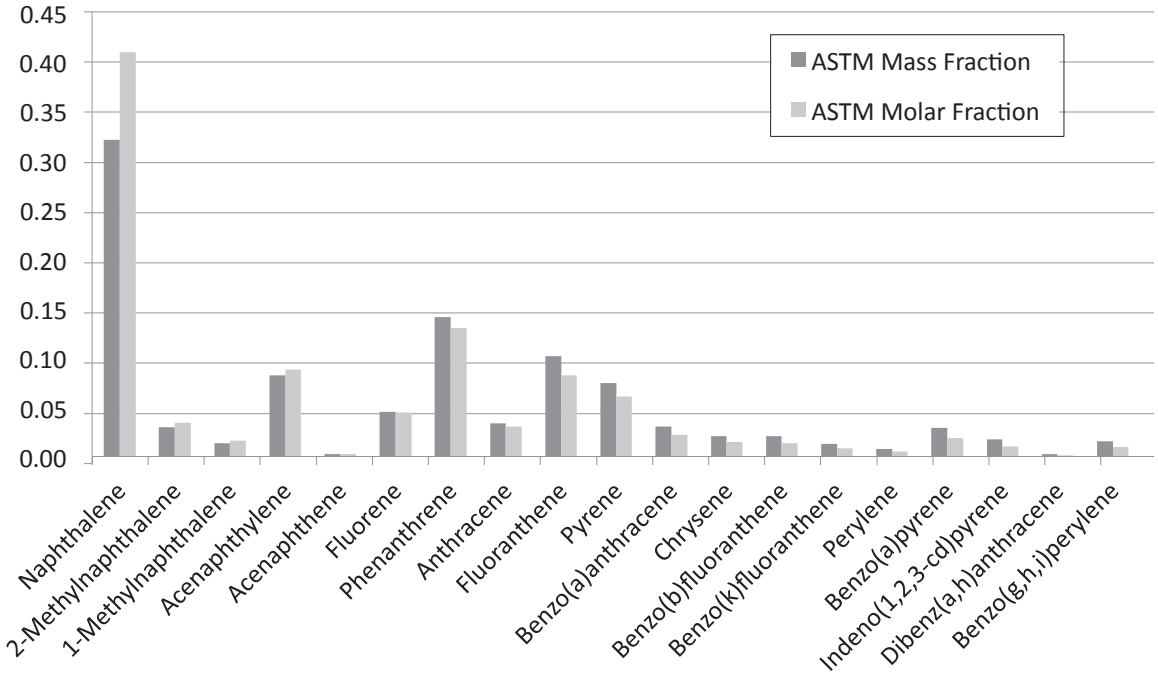
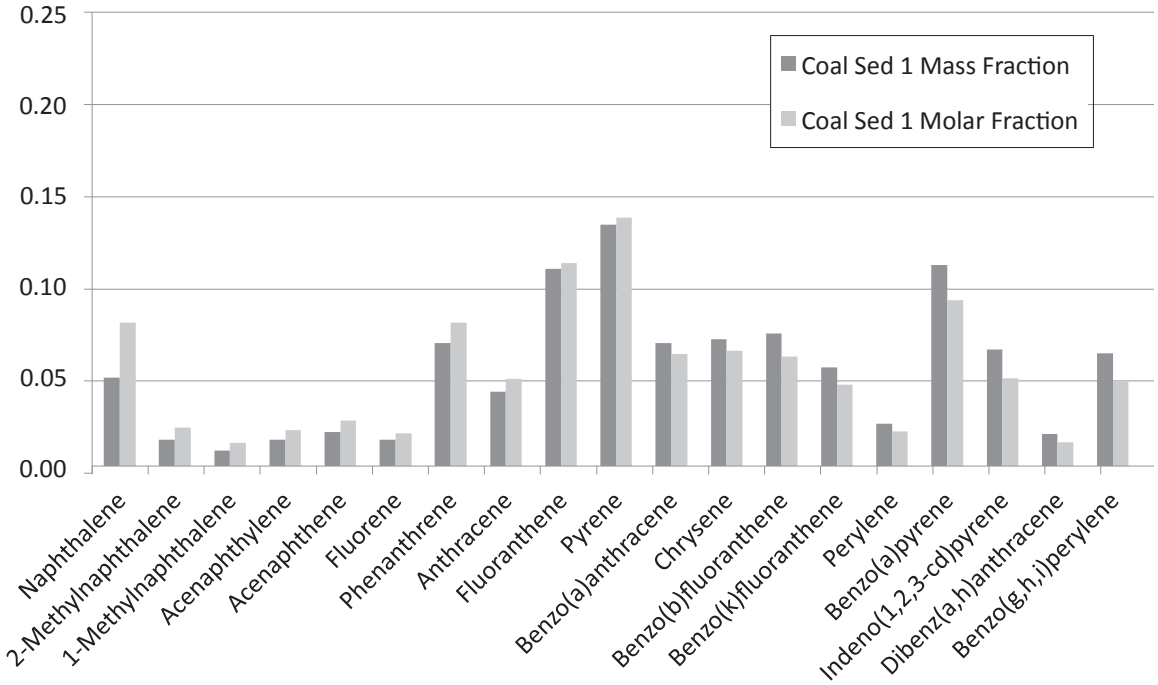


Figure 3-3 - Coal Sediment Mass and Molar Fraction Histograms



In an effort to emphasize the similarities between the results of Mass Fraction analysis and Molar Fraction analysis, several diagnostic ratio plots have been prepared, which use the Mass Fraction

data and Molar Fraction data, respectively. In the following Figures 3-4 and 3-5, the first was generated using Mass Fraction data and the second was generated using Molar Fraction data. It is obvious that the PAH distributions are the same using both of these data sets.

Figure 3-4 – Mass Fraction Diagnostic Ratio Example

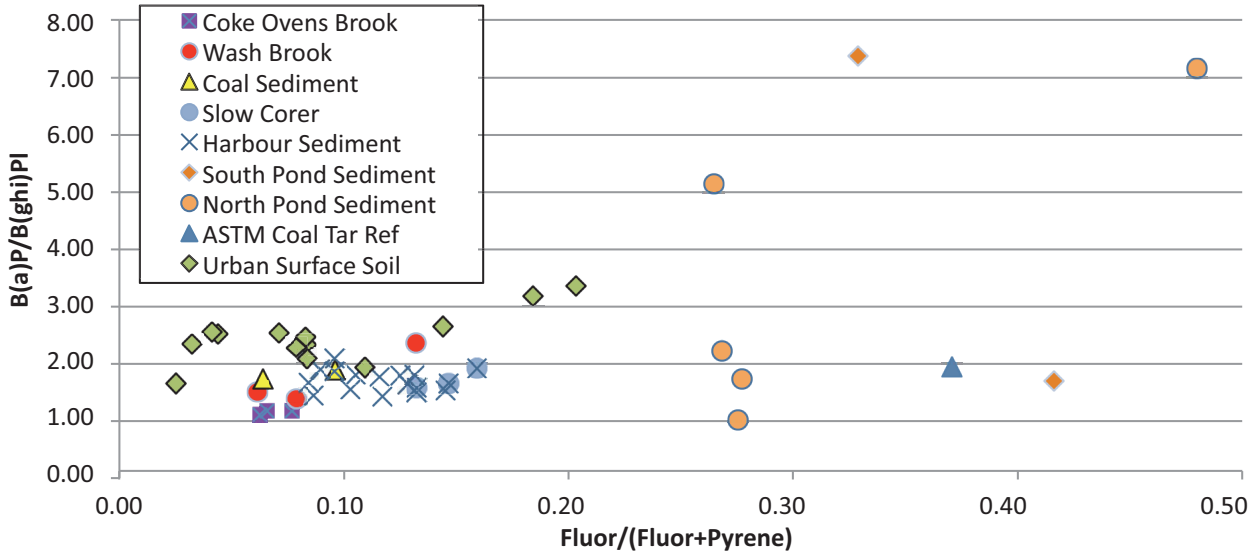
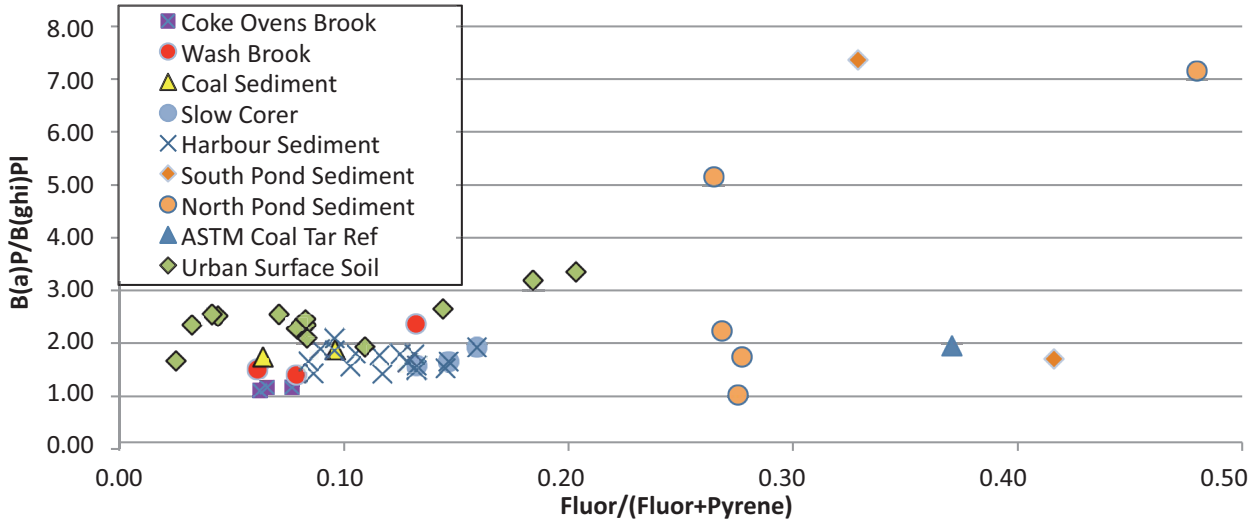


Figure 3-5 - Molar Fraction Diagnostic Ratio Example



As shown above, the distribution of PAHs in the samples included in the study does not differ between the Mass Fraction and Molar Fraction calculations. Considering the amount of amount of work that was initially conducted using the Mass Fractions of the PAH compounds, there is not sufficient evidence to require repeating of the various fingerprint techniques using the Molar Fractions of each PAH parameter in each sample. The remainder of this thesis will focus on Mass Fraction data only.

3.5. FALCON

This study consists of data collected during several different projects across locations throughout the study area. Available data was reviewed for applicability to this study and to confirm compatibility between projects (e.g., same number of PAH compounds in each sample). Analytical techniques were also confirmed to be similar. Due to complications of inter-matrix analysis due to solubility factors, only soil and sediment data (in addition to reference data) was used for this study. The locations of available data sets were also considered in order to include data from known sources, potential sources and background areas. Despite the similarities and commonalities between the data sets used for this process, the FALCON approach (Fingerprint Analysis of Leachate Contaminants) can be used with existing monitoring data because special analytical techniques are not required (Hazardous Waste Consultants, 2004).

The set of 19 PAH parameters was common throughout the analytical programs conducted during the previous reports referenced herein.

The FALCON Technical Resource document issued by the US EPA (Hazardous Waste Consultants, 2004) focused on a coking operation that generated coal tar impacts from 1920 to 1979. A second potential source was identified as an operation processing crude tar wastes to recover creosote, phenol and other chemicals. Using the FALCON process, the assessors were able to identify two distinct PAH fingerprints from each waste discharge source. These fingerprints were used to attribute PAH impacts within a contaminated water body to the primary source accordingly. In particular, PAH impacts identified in near shore sediments were attributed to one source, whereas mid-channel and deeper sediments were attributed to the other source.

3.6. Fingerprint Methods

A number of statistical and numerical analysis techniques have been developed and used in forensic environmental contaminant fingerprint assessments. Methods researched and employed in this study include:

- Qualitative assessment of sample PAH Chromatograms;
- Qualitative assessment of PAH Histograms;
- Correlation Analysis of the PAH sample set;
- Principal Components Analysis (PCA);
- Diagnostic Ratios; and,
- Mann-Whitney Non-Parametric Test.

3.6.1. Chromatograms

In some instances, qualitative chemical analysis and visual comparison of chromatograms of environmental samples, potential sources and background samples may sufficiently meet the needs of a forensic investigation (Wang et al., 2003). Prominent features such as peaks and unresolved complex mixtures (UCM) can provide important clues surrounding the potential source of PAH (Stout et al., 2003). However, if there are multiple potential sources or the correlation between environmental samples and the suspected sources are not visually obvious, the PAH concentrations and distributions are the most relevant information and a quantitative

PAH fingerprinting analysis of should be performed. Stout et al. (2003) found that sediments exhibiting a tar-like chromatogram had higher concentrations of total petroleum hydrocarbons and higher percentages of total PAH than other hydrocarbon resemblances (e.g., gasoline, diesel or crude oil). This led them to conclude that tar or tar distillates (in this case, manufactured gas plant) are a concentrated form of PAH which could have a significant effect on sediments even when present in low concentrations.

Many PAH compounds are more resistant to weathering than their saturated hydrocarbon counterparts and volatile alkyl benzene compounds, thus making PAHs one of the most valuable fingerprinting classes of hydrocarbons (Wange, 2003).

Chromatograms were not available for historical data from the Sydney Tar Ponds Sediments or the Urban Background Surface Soils. A chromatogram was also not available for the ASTM Coal Tar PAH Reference Material. Therefore, PAH chromatogram results were reviewed for Upstream Sediments, Harbour Sediments (both grab samples and sediment trap samples), as well as the Coal-1 and Coal-2 samples. Chromatograms were requested from Maxxam Analytics Inc. who provided analytical services during the Environmental Effects Monitoring program. Please note that PAH chromatograms were supplied by Maxxam Analytics Inc. for two samples that are not otherwise included in the forensic assessment study. Coke Ovens Brook and the Domtar facility sediments were collected prior to construction that removed the impacted sediments in these areas and replaced them with clean soil and stone.

Upstream surface water tributary sediment samples were collected at representative locations to assess sediment quality upstream of the Tar Ponds. One location, on Coke Ovens Brook (COB-SED), exhibited a variety of impacts that may originate from both on-site operations (e.g., coal and fill) or an off-site source (e.g., CBRM Municipal Solid Waste Management Facility). A second upstream sediment sample was collected from Cagney Brook (CB-SED), which could potentially be affected by upstream commercial or residential impacts. The third upstream sediment sample (DOMTAR-SED) was collected in a small ditch of running water near the former DOMTAR facility. This facility used Coke Ovens bi-products to generate a variety of commercial products. This area was previously identified as highly impacted by coal tar and other related by-products.

3.6.2. Histograms

Histograms were prepared using the normalized data for the PAH parameters. PAH parameters are listed along the x-axis and the relative abundance of each parameter is indicated on the y-axis. By presenting normalized data, sample results with wide ranges of concentrations can be presented on the same relative scale.

Qualitative visual comparison of normalized sample PAH histograms, including contaminated soil and sediments and suspected source materials may satisfy the requirements of a forensic environmental investigation. However, where multiple potential sources are involved, or when the visual similarity of sample histograms is not obvious, a qualitative approach may not be sufficient and a quantitative approach, as described in the following sections, may be warranted.

3.6.3. Correlation Analysis

Correlation analysis is a measure of linear association between two variables. Correlation is quantified with a single number, the Pearson Correlation Coefficient, which describes both the strength and direction of the relationship (Minitab, 2012). The correlation coefficient ranges from -1 to 1 where:

- -1 describes a relationship where an increase in one variable is accompanied by a predictable and consistent decrease in the other.
- 0 describes a random or non-existent relationship.
- 1 describes a relationship where an increase in one variable is accompanied by a predictable and consistent increase in the other.

Correlation values of -1 or 1 imply an exact linear relationship, however, the real value of correlation is in quantifying less than perfect relationships. Finding that two variables are correlated often informs a regression analysis which attempts to further describe this type of relationship though it is important to note that correlation does not imply causation (Minitab, 2012).

Important considerations:

- Strength - The larger the absolute value of the correlation coefficient, the stronger the linear relationship between the variables. A value of one indicates a perfect linear

relationship, and a value of zero indicates the absence of a linear relationship. For the purpose of this study, correlation coefficients greater than 0.8 are considered strong, less than 0.3 is considered weak, and between 0.3 and 0.8 is considered moderate with very little value to this study.

- Direction - The sign of the coefficient indicates the direction of the relationship. If both variables tend to increase or decrease together, the coefficient is positive. If one variable tends to increase as the other decreases, the coefficient is negative.
- Correlation does not necessarily imply causation. Only controlled experiments allow you to determine causality.

The correlation analysis was conducted using all 52 samples and includes three Slo-Corer results from a program that collected undisturbed cores of the sediment profile, in an effort to capture an undisturbed surface layer, representing the most recent sediment depositions. The three Slo-Corer samples included in this analysis were collected at three separate locations within Sydney Harbour.

The analysis was conducted using Minitab 16 and the results were tabulated in an excel spreadsheet, provided in APPENDIX 4. Conditional formatting was used to easily identify correlations with Pearson Correlation Coefficients greater than 0.8, which would be considered highly correlated relationships, and others that were lower than 0.3, to identify relationships with low correlation. Correlations between samples of the same sample matrix (e.g., South Tar Pond Sediments vs. North Tar Pond Sediments) were reviewed to confirm the expected high correlations and any potential anomalies.

3.6.4. Principal Component Analysis (PCA)

PCA is likely the most common statistical technique used in these assessments. It works by transforming the analytical data into what is called principal components, smaller uncorrelated variables, for analyzing the structure of the data sets (Wang et al., 2003). PCA can be used to summarize the data *covariance structure* in fewer dimensions. PCA was used to reduce the data set into a smaller number of uncorrelated variables. The goal of principal components analysis is to explain the maximum amount of variance with the fewest number of principal components.

Eigenvalue results are used to determine the number of principal components. Two techniques for selecting the principal components are to retain those with eigenvalues greater than 1, or analyze the scree plot. A commonly used approach is to retain components that cumulatively explain 90% of the variance. Scree plots present component numbers versus eigenvalues. Ideally, scree plots will present a steep curve followed by a nearly horizontal line. This qualitative determination would retain components within the steep curve of the plot.

Prior to PCA, the PAH input were normalized to remove the effect of widely varying concentrations between samples and between individual analytes, giving analytes equal weight in the PCA (Stout et al., 2003). Like other Fingerprint Analysis techniques, the primary object of PCA is to aid in the classification of PAH according to chemical similarities or differences, without any pre-classification as to their nature/source(s) (Stout et al., 2003).

Principal Components Analysis is commonly used as one step in a series of analyses. For example, you can use Principal Components to reduce the data set by reducing the number of PAH parameters included in a sample analysis, or by reducing the number of media samples that are required to assess environmental conditions.

A multivariate statistical method such as PCA can be utilized to evaluate environmental conditions with efficiency by identifying variables that express target conditions (e.g. similar PAH patterns) as much as possible. A Principal Components Analysis often uncovers unsuspected relationships, allowing you to interpret the data in a new way.

Ranjan et al. (2012) used PCA to apportion PAH sources in estuarine sediment samples. 66% of variance was explained by five principle components. Each of the five components typically derived from known sources such as diesel or coal combustion, providing direction on the potential source of impacts in each sample.

Data for the PCA analysis in this study was presented in a spreadsheet with 52 columns of sample locations and 19 rows of PAH parameter relative concentrations based on mass fraction. Each cell in the spreadsheet contains the individual normalized PAH concentration at each sample location and time. The first step was to review the scree plot to get an idea of how many principle components should be extracted in order to be interpreted meaningfully.

When reviewing the component matrix (what makes up a principal component), variables with high positive values (e.g., above 0.75) are considered to behave similarly. There is a general rule of thumb that a cut-off of 0.3 should be considered the threshold for contributing to the component in a valuable way. Variables with negative loadings indicate a negative contribution to the component, indicating that when other variables increase, this variable decreases. In summary, if four variables within a component behave similarly, any one of those variables could be assessed based on data from the other three variables.

3.6.5. Diagnostic Ratios

The purpose of plotting select Diagnostic Ratios is two-fold: firstly, to identify groupings of samples in the plot that have similar ratio values and therefore, potentially common PAH Fingerprints. Secondly, some Diagnostic Ratios are indicative of pyrogenic versus petrogenic origins. For example, the Fluoranthene / (Fluoranthene+Pyrene) ratio may indicate a pyrogenic source for the PAHs.

Ratios such as total Naphthalene / Total PAH and Chrysene / Phenanthrene are valuable as multi-source hydrocarbon identification and weathering indicators, respectively (Wang et al., 2003). When cautiously applied, a simple ratio such as lower molecular weight to higher molecular weight PAH can provide some insight as to the type of PAH present (Stout et al., 2003). PAHs are always emitted as mixtures, and the relative molecular concentration ratios are considered to be characteristic of a given emission source. Most diagnostic ratios involve pairs of PAHs with similar physiochemical properties, so they ought to undergo similar environmental fate processes (Tobiszewski and Namiesnik, 2012). Other ratios such as Fluoranthene/Pyrene and Anthracene/Phenanthrene can provide some indications of similarities and can be plotted against each other or against distance from a source (Stout et al., 2003).

A benefit of comparing diagnostic ratios of PAHs in environmental samples with suspected source materials is that differences in concentrations are not relevant. This self-normalizing effect on the data (ratios are comparable despite differences in concentrations) minimizes the potential influence of factors such as analytical instrument operations and the effects of various sample matrices (Wang et al., 2003).

A number of published articles on the use of Diagnostic Ratios for forensic PAH assessment were reviewed in preparation for this study. Based on the results observed in the published articles, the following plots for Diagnostic Ratios were selected to visually present the ratio information for the various matrix samples:

1. B(a)P / B(g,h,i)Pl vs. Flour/(Fluor/Pyrene)
2. Flour/(Fluor/Pyrene) vs. (Ideno(1,2,3) / (Ideno(1,2,3) + B(g,h,i)Pl)
3. Fluor / Pyrene vs. B(a)A / B(a)P)
4. Fluor / Pyrene vs. B(a)A / Chrysene
5. Fluor / Pyrene vs. Chrysene / B(a)P
6. Ant / (Ant + Phen) vs. B(a)A / (B(a)A + Chrysene)
7. Fluor / Pyrene vs. Phen / Ant

The ratios were calculated using the normalized mass fraction data set and plotted using Microsoft Excel. Clusters of samples were identified in each plot, and correlations between the PAH fingerprints in the matrix samples could be identified by samples that were clustered with one another. For example, in Figures 5-8 through 5-15, the ASTM Coal Tar Reference Material can be seen plotted within the Tar Ponds Sediments, due mainly to the fact that Tar Ponds Sediments are known to have been impacted with PAH from Coal Tar.

Not all Diagnostic Ratio plots are expected to provide clustering that is anticipated based on previous work using other fingerprint techniques. The value in such plots may be to potentially identify new relationships in the data, rather than to confirm previous findings. As shown in the Diagnostic Ratio plots provided herein, the interpretation of value in some plots may be difficult to identify and perhaps may not be of any value. Select plots are considered valuable based on the literature review and previous studies while other plots provide a visual interpretation of the data that may provide new insight into the sample relationships.

3.6.6. Mann Whitney Non-Parametric Test

The Mann-Whitney Non-Parametric Test determines if the null hypothesis, that the population medians are equal, is true. Significantly similar population medians suggest significantly similar PAH Fingerprints for the two samples compared in the test. This non-parametric test uses relative rankings rather than values, so it does not use parametric assumptions such as normality.

In other words, it does not require populations (sample results) to maintain a normal distribution, but the test does include two assumptions:

- Populations of data have the same shape (i.e., similar PAH parameter distribution); and,
- Populations are independent (i.e., study samples were collected across a large study area).

A number of sample pairings were selected for use in the Mann-Whitney test, including samples from within a given matrix (i.e., Tar Ponds Sediments) to confirm statistically equal sample medians, and therefore similar PAH Fingerprints, within that matrix:

- Tar Ponds Sediments vs. Tar Ponds Sediments
- Tar Ponds Sediments vs. ASTM Coal Tar Reference
- Harbour Sediments vs. Harbour Sediments (furthest south and north)

Other sample pairings for use in the Mann-Whitney test included comparing samples to identify similar population medians and therefore PAH Fingerprints. These sample pairings included:

- Upstream Sediments vs. Tar Ponds Sediments (x2)
- Upstream Sediments vs. Harbour Sediments
- Upstream Sediments vs. Coal Sediments
- Tar Ponds Sediments vs. Harbour Sediments (x4)
- Tar Ponds Sediments vs. Coal Sediments (x4)
- Harbour Sediments vs. Coal Sediments (x4)

Chapter 4 - Case Study

This section provides additional project and site information as it regards to this study. Figure 4-1 is a simple site plan to orient the site and put the approximate locations of the PAH sample data points into geographic perspective.

4.1. The Sydney Tar Ponds and Coke Ovens

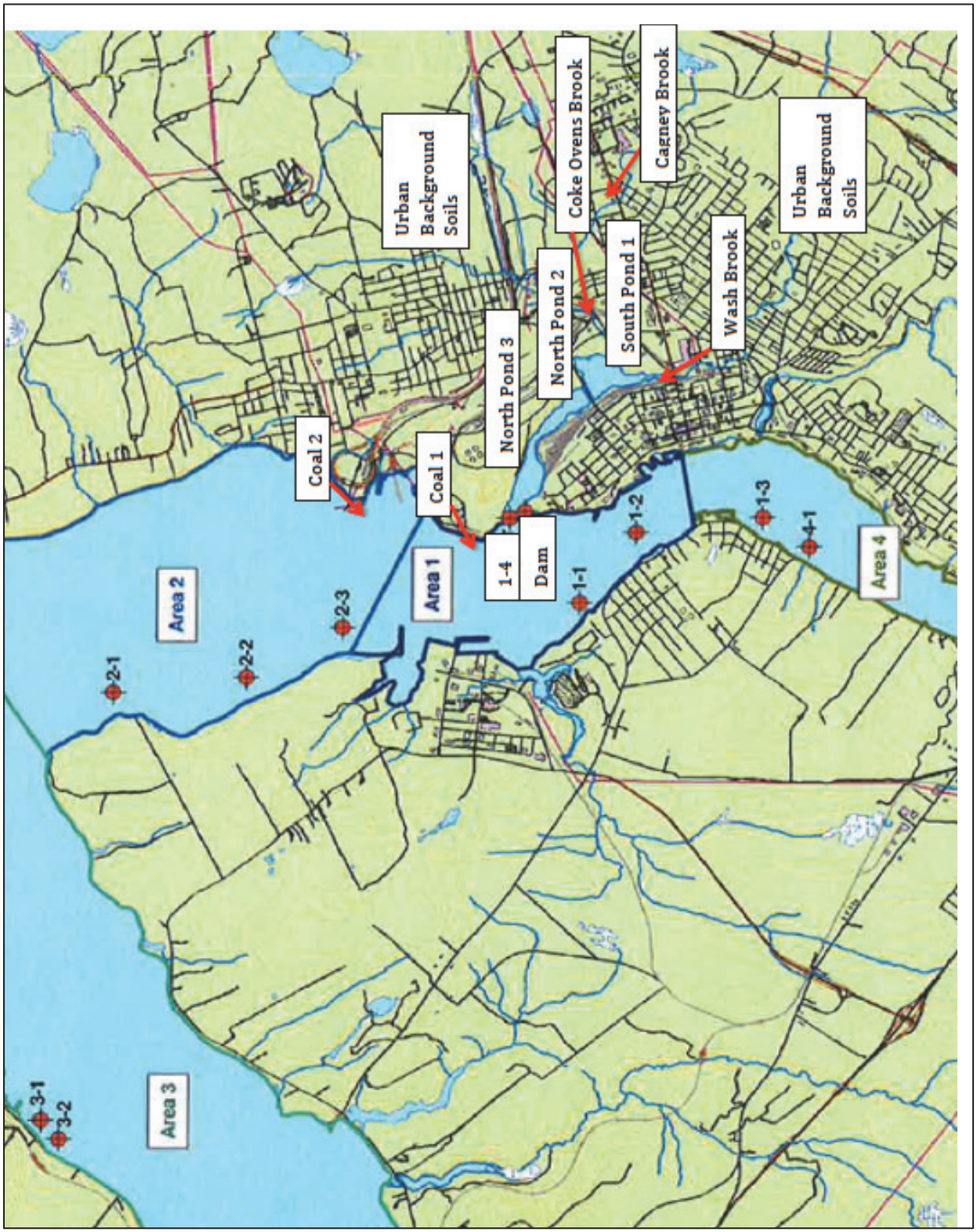
Nearly 100 years of steel and coke production left behind more than a million tonnes of contaminated soil and sediment within the Muggah Creek watershed. Environmental assessments in the area have included:

- North and South Tar Ponds;
- Former Coke Ovens property;
- Adjacent former landfill and active Solid Waste Management Facility;
- Upgradient surface waters;
- Sydney Harbour;
- Surrounding properties

The footprint of the Sydney Tar Ponds and former Coke Ovens site encompasses approximately 100 hectares of property within the Muggah Creek Watershed in the Cape Breton Regional Municipality (CBRM) of Nova Scotia. Extensive testing identified widespread contamination of soil, groundwater, surface water, and sediments due to long-term and historic industrial use of the property. In particular, Acres International (1988) summarized Total PAH data from pond sediments 0-0.6m in depth, and found that Total PAH concentration presents a generally decreasing trend with distance downstream from Coke Ovens Brook (the migration pathway for coke production bi-products from the Coke Ovens):

Area	Average Total PAH (mg/kg)
South Pond Wash Brook Arm	3,700
South Pond Discharge Point	12,000
North Pond Phase II	8,000
North Pond Phase III (open to harbour)	5,500

Figure 4-1 Site Plan and Approximate Sample Locations



Source: Dillon Consulting Limited (2010) for the Sydney Tar Ponds Agency.

In May 2004, a Memorandum of Agreement (MOA) jointly committed the Federal Government of Canada and the Province of NS to remediate contaminated areas of the Watershed with the intent of reducing/removing potential ecological and human health risks to the environment. The remediation project managed by the Sydney Tar Ponds Agency (STPA), was a complex undertaking consisting of many design and construction elements to be completed over several years.

An Environmental Effects Monitoring and Surface Water Compliance Monitoring (EEM/SWCM) Program was established to assess performance of construction/remedial measures and to verify environmental effects predictions made in the Environmental Impact Statement (EIS) for the remediation period. The Program was designed to assess changes (both positive and negative) to the surrounding environment that could be attributed to construction/remediation activities. In a general sense, as such trends can be attributed to the remediation activities, decreases in concentrations of parameter(s) of potential concern can be inferred as positive and increases as negative.

4.2. Solidification / Stabilization

Following a period of bench scale and "recipe" testing, S/S of contaminated sediment at the Sydney Tar Ponds began in the Fall of 2009. Work was conducted within Muggah Creek, the estuary outfall of Coke Ovens Brook, Wash Brook, combined municipal sewer overflow, and a history of potential industrial discharges. S/S was conducted in cells in three phases (South Pond, North Pond I and North Pond II). The S/S process creates a structurally enhanced, low permeability mass that immobilizes contaminants in place. The contractor conducting the S/S was a partnership of local contractor J&T vanZutphen Construction of Mabou, Nova Scotia, and ECC of Marlborough, Massachusetts.

Treated S/S cells are tested as per the performance criteria, developed by AECOM during bench and pilot scale testing, for:

- Hydraulic conductivity (permeability);
- SPLP (leachability); and
- Unconfined compressive strength.

Cells that did not meet the criteria were reworked. For example, 12 of 88 cells required rework in the Fall of 2009 (AECOM, 2010). AECOM developed all sampling and testing SOPs to ensure Quality Control testing by the contractor and Quality Assurance testing by an independent consultant (Stantec).

Europe has seen an increase in the use of Solidification/Stabilization risk management techniques due to an increasing avoidance of landfilling of contaminated materials. This was evident during proceedings at the 2010 International Solidification/Stabilization Technology Forum held in Sydney, Nova Scotia in 2010. However, there continues to be concern about the long-term stability of the immobilized contaminants over time (Hills et al., 2010).

4.3. Data Sources

The Sydney Tar Ponds Agency (STPA) provides public access to environmental assessment and monitoring reports at the following website: www.tarpondscleanup.ca (Environmental Reporting).

Most of the data included in this study was collected during the STPA EEM and the STPA granted its use in this study. Historical reports from previous assessment and monitoring programs were also obtained through the STPA public database.

4.4. Standard Reference Material SRM 1597a

SRM 1597 Complex Mixture of Polycyclic Aromatic Hydrocarbons from Coal Tar used multiple analytical techniques to characterize 34 certified, 46 reference and 12 information PAH concentrations in coal tar (Wise et al., 2010).

Standard concentrations for the 19 PAH compounds being used in this study, including the 16 US EPA priority pollutants, are presented in the study data set in **Appendix 2**.

4.5. Sample Data

4.5.1. Monitoring Program - Soil and Sediment Sampling

As part of the STPA EEM, on behalf of Dillon Consulting Limited, the author coordinated the collection of samples and data from various environmental media. Some of the samples that were collected during the EEM were used in this study, including:

- Upstream (Tributary) Sediments
- Harbour Grab Samples
- Harbour Sediment Traps
- Harbour Slo-Corer Sediments
- Coal Sediments

Previous studies at the Sydney Tar Ponds site were referenced for PAH results in the following environmental matrices:

- Tar Ponds Sediment
- Off-site Urban Background Soils

The total concentrations of PAHs are highly variable from one sample matrix to another (e.g. Tar Ponds Sediments compared to Urban Background Soils) as well as within specific matrix data sets (e.g., some Upstream Sediments are much more impacted than others). The objective of this study is to compare the composition, or fingerprint, of identified PAH impacts. It is not meant to assess environmental conditions within the study area. Data used in this study was normalized (or standardized) using both mass fraction and molar fraction, as described in 3.4, in order to develop comparable data sets.

4.5.2. Tar Ponds Sediments

Acres International (1988) collected data from borehole cores throughout the Tar Ponds at depths of 0-0.6m. This report had total PAH results of the impacted sediments and native sediments, below the impacted Tar Ponds. A total of 14 sample results, impacted with PAHs, were referenced from this report for the study. One sediment sample from the Wash Brook Arm, five samples from the South Pond, four samples from North Pond Phase I and four samples from North Pond Phase II.

The Tar Ponds Sediment sample results from this Acres International study were available for this thesis research project through publicly available information. Other Tar Ponds Sediment PAH analysis results may be publicly available now that the remediation project is complete, as each solidification/stabilization cell was analyzed for contaminants.

The PAH analysis results of the Tar Ponds Sediments from 1988 are considered representative because these results represent the profile of impacted sediments from 0-0.6m. PAH impacts below surface would not have been subject to degradation by atmospheric influences such as solar radiation and tidal action. PAH-laden sediments that might have emanated from the site during remediation would include these previously undisturbed sediments. Therefore, the PAH Fingerprints developed using the 1988 results should be considered comparable to PAH Fingerprints identified during the remediation project, which constitute the bulk of the recent data included in this study.

4.5.3. Upstream Surface Water Sediments

A total of 9 upstream sediment samples were used in the study. Samples from the Cagney Brook (upstream residential/commercial), Radar Base Brook (upstream forest) and Wash Brook (upstream residential/commercial) were included from October 2010, July 2011 and April 2012. Samples from Coke Ovens Brook and the DOMTAR area are included for reference purposes in some tests, as these and other surface water channels on site were excavated and relined with stone, preventing any sediment quality monitoring in these channels.

4.5.4. Harbour Sediment Grabs

Harbour Sediment Grab samples from 10 monitoring stations throughout Sydney Harbour and the North West Arm are included in the study for October 2010, July 2011 and July 2012. It should be noted that the sediment samples collected in July 2012 were following the dredging of Sydney Harbour and construction of a large in filled area within the harbour that filled in one of the previous monitoring stations.

Included in the Marine Sediment data set are two samples collected at stations that were not included in the EEM Program. Coal 1 and Coal 2 were collected at the sea floor beneath two coal handling facilities on the Sydney waterfront. Both of these sampling locations have significant industrial and coal handling history associated with them that is not directly related to the Sydney Tar Ponds.

4.5.5. Sediment Traps

Sediment traps were constructed using vertical PVC pipes at 5:1 length:diameter ratio, weighted to cement blocks for stability. 9 Sediment Traps were deployed across Sydney Harbour at the GPS recorded marine stations, which were used for various media sampling to provide consistent sampling points. Sediment Traps were deployed at several periods during the remediation project, including during the dredging of Sydney Harbour. One sample from 2009 is included in this study, three from 2010 and three from 2011, during the harbour dredging. The purpose of employing the Sediment Traps was to sample and analyze the most recently deposited harbour sediments, in order to assess potential positive or negative environmental effects associated with the remediation of the Tar Ponds. The Traps were designed to capture sediment as it was deposited, thereby providing the most recent sample possible of representative sediments.

4.5.6. Slo-Corer Harbour Sediments

During project meetings with regulators, sediment deposition rates were frequently discussed. In particular, the marine sediment-monitoring program that Dillon was conducting for the Sydney Tar Ponds was designed to monitor changes to sediment quality in Sydney Harbour during the remediation construction. To that end, it was important that the sediment-sampling program was capturing the most recently deposited sediment for laboratory analysis. The project team at Dillon was confident that the standard operating methods with an Ekman sediment grab (Wildco®) was retaining the surficial (0-1 cm) sediment layer in each sample collected. To confirm that, a Slo-Corer sampling unit was recommended and supplied by the Bedford Institute of Oceanography and deployed at the sediment monitoring stations in Sydney Harbour. Due to mechanical problems, only three of the monitoring stations were sampled with the Slo-Corer (1-2, 1-3 and 4-1). These sites could be considered inner harbour as opposed to the other monitoring stations.

The Slo-Corer is a hydraulically dampened gravity corer designed to collect sediment cores from the ocean floor, while maintaining an undisturbed sediment / water interface. This technique would prevent any surficial sediment from being washed off of the sample while raising the sampler to surface, thus ensuring that the most recently deposited sediment will be analyzed. The surficial sediment at 0-0.5 cm was retained from each core for analysis. Triplicate samples were collected and composited at each monitoring station.

In general, PAH concentrations in the Slo-Corer samples did not differ significantly from the Ekman sediment grab sample concentrations, and were within the previously observed range of concentrations. This suggests that any disturbance of the sediment water interface being introduced by the grab sampling technique was minimal. Considering the level of effort required to employ the Slo-Corer sampling and budget requirements, further use of the Slo-Corer was not considered warranted and the EEM program continued with the use of the Ekman sediment grab.

4.5.7. Urban Background Soil

A JDAC Urban Shallow Soil Report (2002) identified PAH contamination in shallow soil in areas outside of the project site. A total of 13 shallow soil sample PAH results were summarized for inclusion in the study. These samples were collected from five different background areas of Sydney in July and August 2001. None of these five areas are known to be impacted by industrial or commercial activity and many are from within residential areas.

4.6. Limitations

Some of the data being used in the study dates back to 1988. Not all of the analytical method records are included in the older reports so the consistency of the PAH analysis methods cannot be confirmed. The data set also includes several samples that vary in the PAH compounds included in the analytical report.

Chapter 5 - Results and Discussion

5.1. Chromatograms

Select sample chromatograms are provided in Appendix 4. Historic and reference chromatograms were not available for this study. Qualitative review of the three upstream sediments does not present any obvious similarities between the distributions of PAH parameters on the sample chromatograms. CB-SED presented six PAHs in the same elevated range (20,000-30,000 mg/kg), which set it apart from the other two samples. Due to the sample location, this PAH Fingerprint should represent off-site PAH influences from residential and commercial sources. The Coke Ovens Brook sample (COB-SED) presents a different PAH Fingerprint than Cagney Brook, suggesting the sediment impacts observed down gradient of the landfill are due to different sources of PAHs. Similarly, the DOMTAR-SED sample is different again, with many more PAHs observed, some at much higher concentrations, than the other two samples.

Sediment Traps collected newly deposited harbour sediments during their deployment in Sydney Harbour. One trap was located at the far-field reference point (3-2), in the Northwest Arm of Sydney Harbour. The second sediment trap result used in the study was collected at the nearest marine monitoring point to the Sydney Tar Ponds (1-4). Chromatograms for these samples present very similar PAH distributions patterns. However, the chromatograms for these sediment trap samples do not share the same qualitative similarities as the Coal Sediments, also from within Sydney Harbour.

Marine Sediment samples collected at the site located closest to the mouth of the Tar Ponds (MARSED-1-4) were reviewed from October 2010 and August 2011. Very few differences could be identified between the two sample chromatograms, with the exception of an increase in some PAH parameters over that period. This confirms a uniformity of the PAH Fingerprint at this location over time. Sample location MARSED-2-1 was approximately 1 km away from MARSED-1-4 on the opposite (West) side of Sydney Harbour, but also presents a very similar PAH Fingerprint as 1-4 on the chromatogram in 2010. This suggests that the PAH impacts in the shallow sediments in this region of the harbour are very similar and may have originated from the same source. A third harbour sediment sample, from the far-field reference point in the Northwest Arm of Sydney Harbour, was reviewed for comparison with the other two samples. While some similarities were identified, in general, some PAHs were much lower at 3-2 when

compared to other PAHs (e.g., Fluoranthene, Pyrene, Benzo(b)fluoranthene and Benzo(k)fluoranthene). These changes were not isolated to the lower molecular weight PAHs, which would suggest potential weathering and solution of lighter PAHs.

Chromatograms for Coal-1 and Coal-2 sediments presented very similar patterns of PAH distribution. PAH parameter concentrations in the Coal-1 sample, collected at the coal pier closer to the Tar Ponds, were generally >2x the concentrations observed in Coal-2, collected at the second coal pier, approximately 2 km north. Qualitatively, the similarities in the PAH distribution peaks is unmistakable.

5.2. Histograms

Histograms of representative soil and sediment samples were prepared to visually present the relative abundance of PAH parameters in different matrix samples. The following histograms have been prepared in several combinations and other qualitative presentations of the data are being considered. The following histograms are provided below:

- Upstream Sediments vs. Tar Ponds Sediments
- Harbour Sediment Grabs vs. Sediment Traps
- Standard Reference Material vs. Tar Ponds Sediments
- Standard Reference Material vs. Coal Sediments
- Harbour Sediments vs. Tar Ponds Sediment

Figure 5-1 - Histogram - Upstream Sediments vs. Tar Ponds Sediments

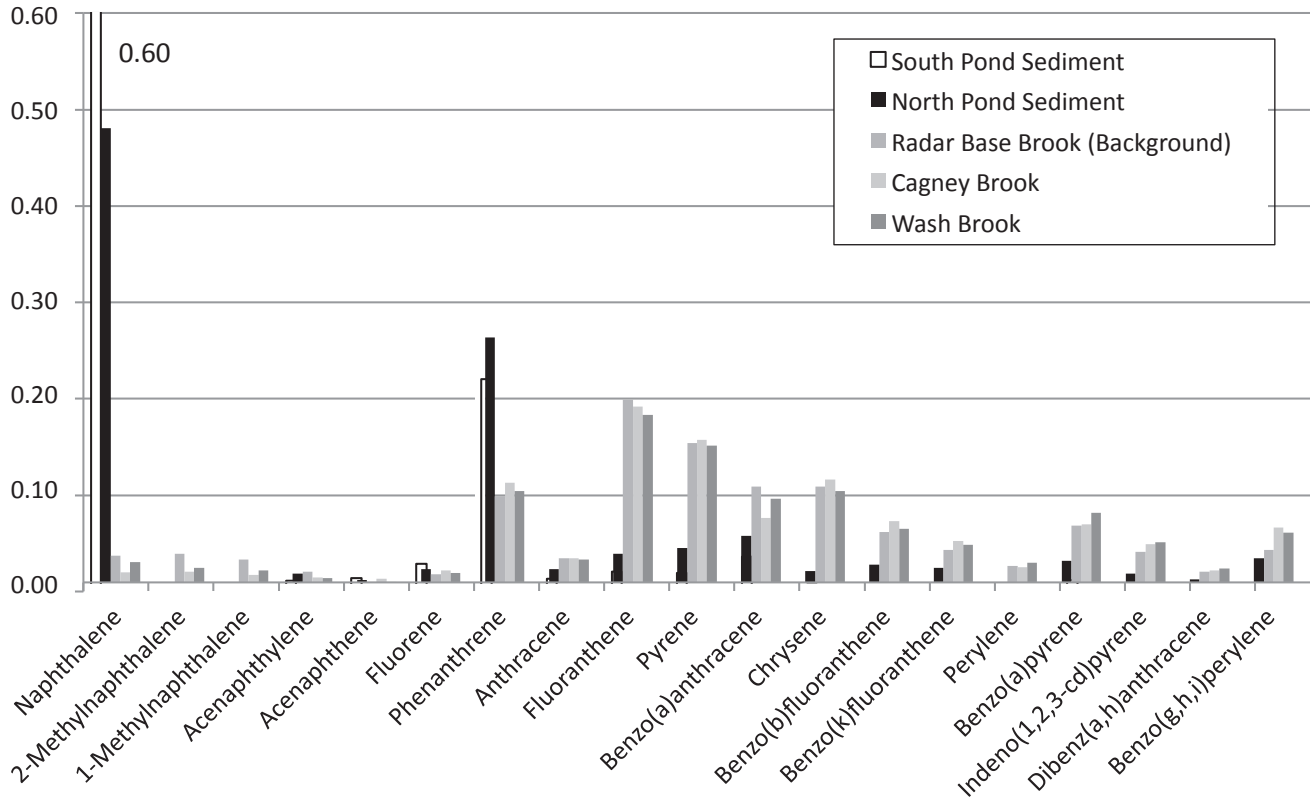


Figure 5-1 Histogram plots for Tar Ponds Sediments (South Pond and North Pond) as well as three of the Upstream Sediments. The Upstream Sediments include Radar Base Brook, which can be considered a background sample, as it is upstream of the site, Cagney Brook is within the site but is subject to potential commercial and residential impacts, whereas Wash Brook is within the vicinity of the Tar Ponds, and has a history of inputs from historic residential, commercial and light industrial wastewater. As shown in the histogram, PAHs with molecular weights higher than Anthracene (Fluoranthene to Benzo(g,h,i)perylene) are more prevalent than lighter PAHs in Upstream Sediments. Tar Ponds Sediments are obviously higher than the Upstream Sediments in the lighter PAHs such as Naphthalene and Phenanthrene, presenting obvious differences in the PAH Fingerprints of Upstream Sediment and Tar Ponds Sediments.

Figure 5-2 - Harbour Sediment Grabs vs. Sediment Traps

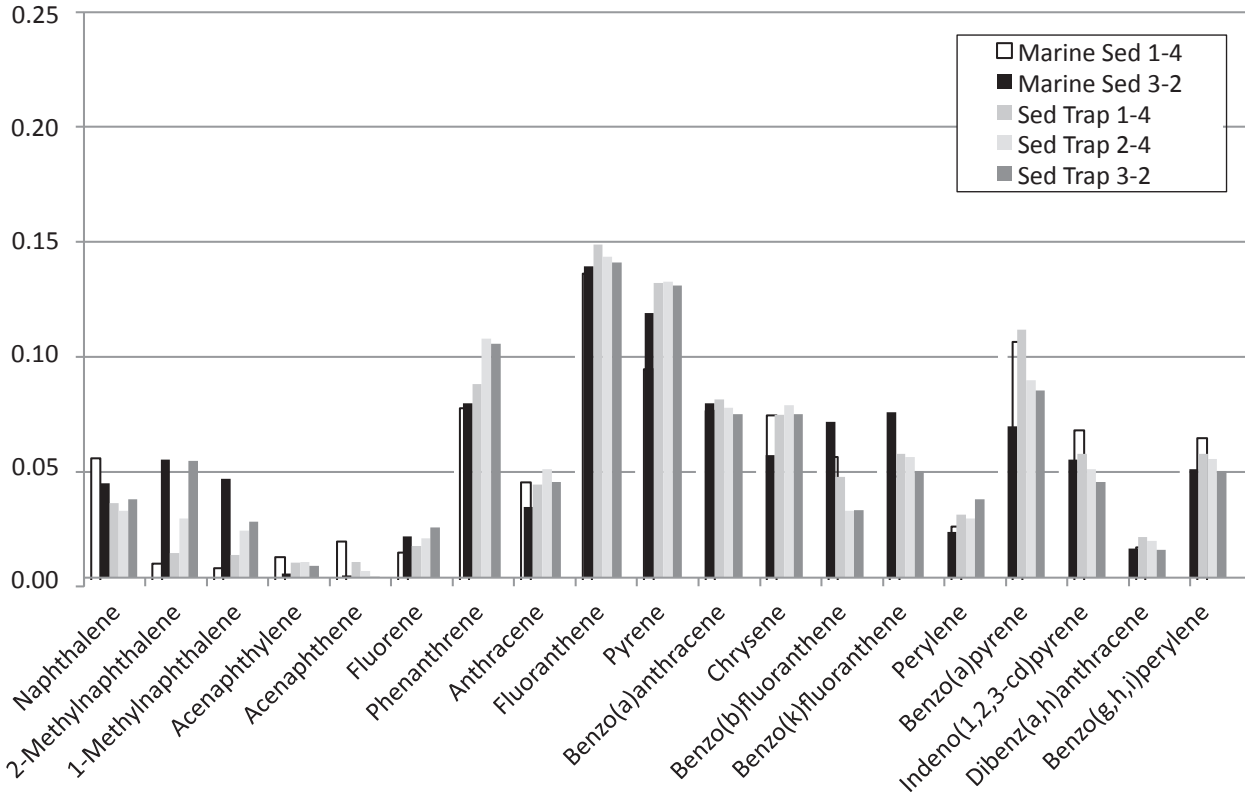


Figure 5-2, PAH Fingerprints found in Harbour Sediment samples at the mouth of Muggah Creek (1-4) as well as the far-field reference station (3-2), present similar distributions as the Sediment Grabs collected as the same sites, as well as 2-4. This histogram suggests a common PAH Fingerprint in Harbour Sediments throughout Sydney Harbour. This homogeneity suggests a potential source of PAHs that is capable of distributing impacts throughout the geographical study area.

Figure 5-3 - Standard Reference Material vs. Tar Ponds Sediments

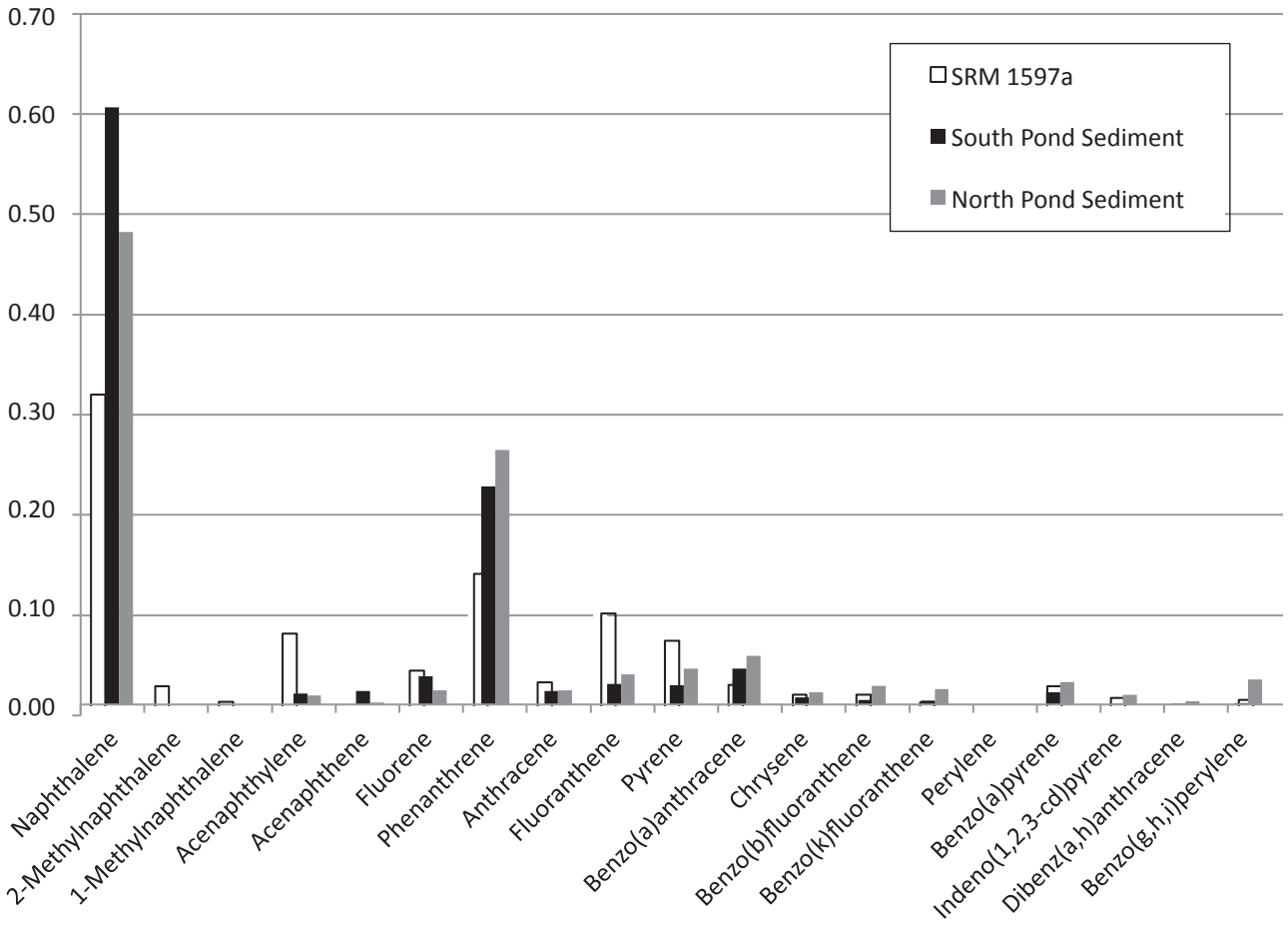


Figure 5-3 Histogram plot for Tar Ponds Sediments compared with the PAH Fingerprint of the ASTM Coal Tar Reference Material. Figure 5-3 is meant to present the similarities between the Reference Material and the Tar Ponds Sediments, confirming that the Sydney Tar Ponds were created primarily by Coal Tar by-products from the Coke Ovens.

Figure 5-4 - Standard Reference Material vs. Coal Sediments

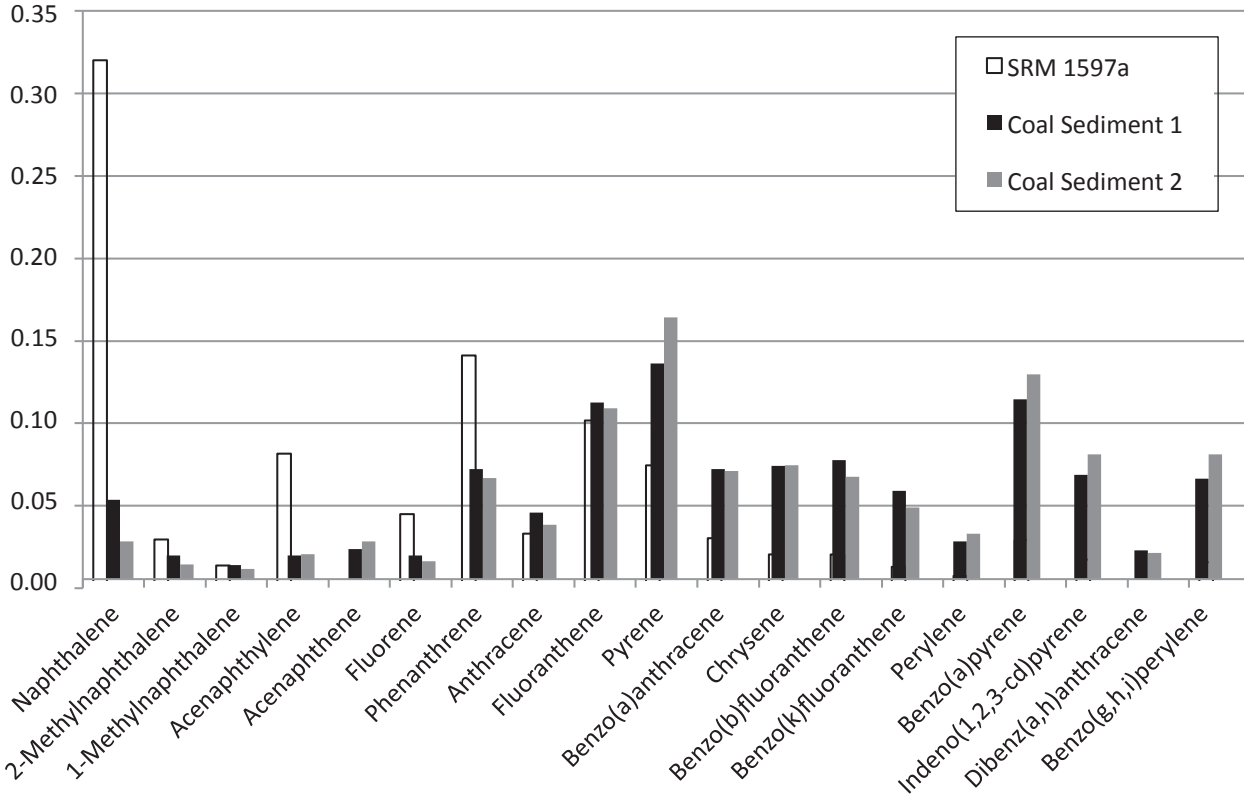


Figure 5-4 ASTM Coal Tar Reference Material plotted against the Coal Sediments found beneath the coal handling facilities in Sydney Harbour. In this histogram, the PAH Fingerprint in the ATSM Coal Tar Reference Material is higher in lighter molecular weight PAHs (e.g., Naphthalene, Acenapthylene, Phenanthrene) than the Coal Sediments found beneath the coal piers. Mass fractions of Anthracene and Fluoranthene are similar for the two sample media, however, higher molecular weight PAH predominate in the Coal Sediments rather than coal tar bi-products, this presents the qualitative differences between the Tar Ponds Sediments and the Coal Sediments.

Figure 5-5 - Harbour Sediments vs. Tar Ponds Sediments

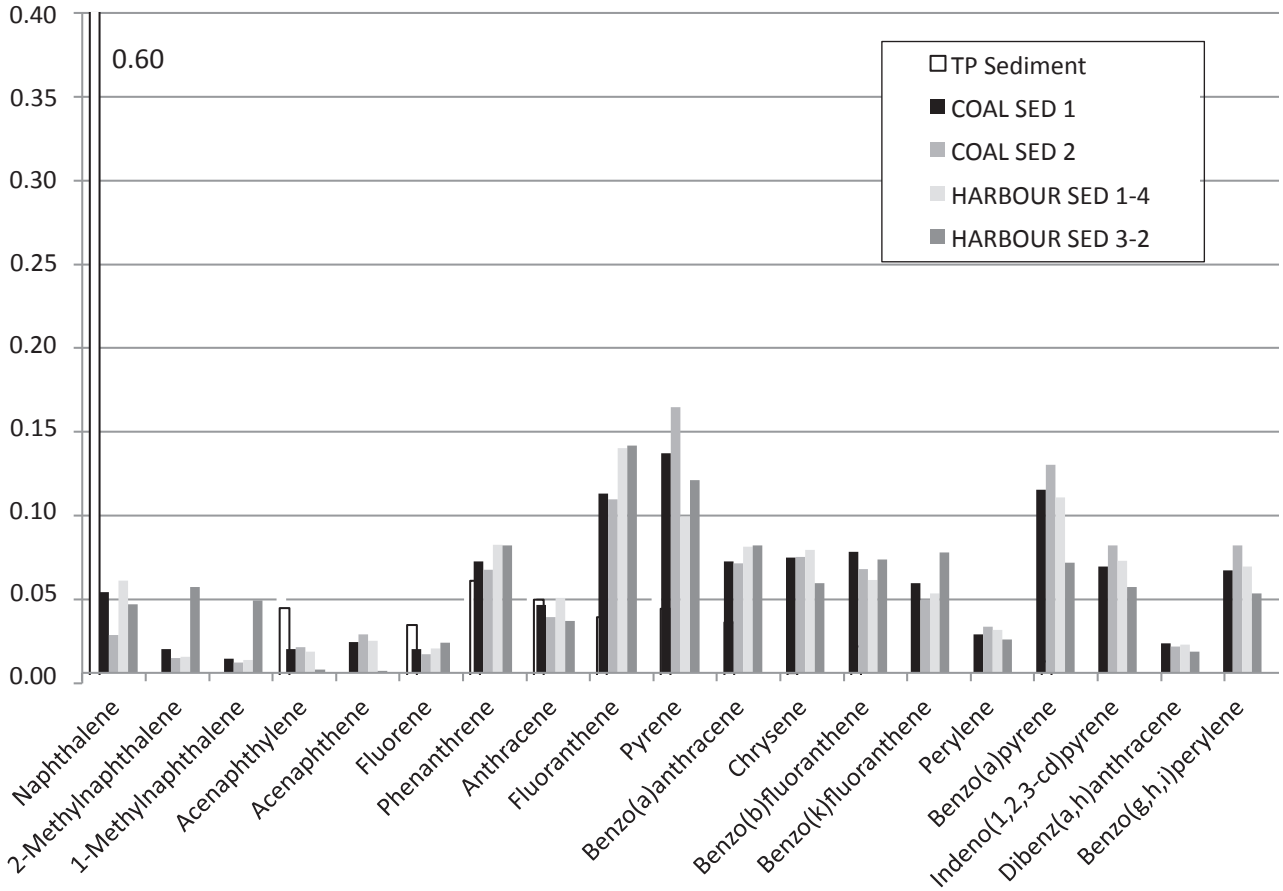


Figure 5-5 PAH Fingerprints of representative Tar Ponds Sediment, the two Coal Sediments and two representative Harbour Sediments (1-4 and 3-2). The Tar Ponds Sediments clearly show a predominance of light and moderate molecular weight PAH parameters. Whereas both the Coal Sediments and Harbour Sediments show a predominance of moderate and heavy molecular weight PAHs. Significant differences are observed in the PAH Fingerprints of the Tar Ponds Sediments and the Harbour Sediments while also presenting significant similarities between the Harbour Sediments and the Coal Sediments. These differences and similarities indicate that PAH impacts in Sydney Harbour sediments are due to coal handling activities at the coal piers and not due to discharges from the Sydney Tar Ponds during the remediation project.

5.3. Correlation Analysis

The results of the correlation analysis are presented in a spreadsheet in APPENDIX 5. The following sections describe the results of the correlation analysis, grouped together to present the "story" of how PAH Fingerprints in a given media relate to other media samples.

ASTM Coal Tar Reference Material

The Reference Material presents a high correlation (>0.8) with 8 of the 10 Tar Ponds Sediment samples. This supports the fact that the Sydney Tar Ponds PAH impacts are due primarily to coal tar by-products generated from the Coke Ovens. One of the two Tar Ponds samples that did not correlate well (0.51) with the reference material is considered anomalous and may include other sources of PAHs from the Steel Plant, whereas the second low correlation (0.55) was a sample located in the Wash Brook Arm of the Tar Ponds, an area subject to a history of other domestic effluents. This low correlation suggests another source of PAHs in this area of the Tar Ponds, potentially from an off-site source.

Urban Background Soil

The source of PAHs in these samples is considered to be a) ash/dust associated with a legacy of domestic coal use in the area, and b) atmospheric deposition associated with Steel Plant operations. In either case, the PAH Fingerprints are not expected to correlate well with the coal tar impacts in the Tar Ponds sediments. Not surprisingly, none of the 13 Urban Background Soil samples present a Pearson Correlation Coefficient higher than 0.69 with Tar Ponds sediments, with most correlations below 0.3. This suggests that there is very little to no relationship between the PAH Fingerprints found in the Urban Background Soil samples and the PAH Fingerprints identified in the Sydney Tar Ponds sediments. Similarly, the ASTM Standard did not show any significant correlations with Urban Background Soil, suggesting that the PAHs found in Urban Background Soil are not related to coal tar bi-products.

Harbour Sediment Traps

The Harbour Sediment Traps were deployed to capture new harbour sediments during their deployment upon the harbour bottom. The traps were a means of confirming the assessment of sediments deposited during a specific period, rather than the routine grab samples.

Of the seven sediment trap samples located throughout Sydney Harbour, none exhibited highly correlated relationships with the Tar Ponds sediments or the ASTM Reference Material. This suggests that PAHs identified in sediments deposited in Sydney Harbour during the remediation of the Sydney Tar Ponds do not present the same PAH Fingerprints as the Tar Ponds Sediments.

Conversely, 84% of the correlations between the PAH Fingerprints at seven Sediment Traps and the 13 Urban Background Soil samples were high (>0.8). This suggests a common source of PAHs for both sample media (e.g., coal dust from coal piers).

Harbour Sediment Grabs

Harbour Sediment Grabs were collected using a clamshell grab sampler and care was taken to subsample only the top 2 cm of sediment in each grab. This was an attempt to sample approximately 2 years of sediment deposition (sediment deposition rates were calculated to be between 0.4 and 0.8 cm/yr) (Dillon, 2010).

10 Harbour Sediment Grab samples at 5 locations throughout Sydney Harbour (5 in 2010 and 5 in 2012) were used in this correlation analysis. None of the 10 Harbour Sediment Grabs produced a Pearson Correlation Coefficient higher than 0.51 with the Tar Ponds Sediments. This supports the data from the Sediment Traps, suggesting that the PAH Fingerprints observed in the Harbour Sediments do not correlate with PAH Fingerprints observed in the Tar Ponds.

Also similar to the Sediment Traps, the majority of the Harbour Sediment grab samples present high correlations with Urban Background Soil, suggesting a likely common source of PAH for both media (e.g., coal). Not surprisingly, the PAH Fingerprints found in Harbour Sediment Grabs present high correlations (>0.8) with the Sediment Trap PAH Fingerprints. This supports the grab sampling technique as a means to assess recently deposited harbour sediments.

Harbour Sediment Slo-Corer

The Slo-Corer was another sampling method that was utilized to obtain the most representative "recent" sediments available on the harbour bottom. The purpose of obtaining these undisturbed recent depositions was to assess the potential impacts that the Sydney Tar Ponds Remediation was having on the Sydney Harbour. As seen with the Harbour Sediment Grabs and the Sediment Traps, the Slo-Corer PAH Fingerprints present high correlations with most Urban Background Soil samples, and low correlations with all Tar Ponds Sediments. Again, this suggests a common source of PAHs for Harbour Sediments and Urban Background Soils, but a different source of PAHs in the Sydney Tar Ponds sediments. Not surprisingly, all Slo-Corer PAH Fingerprints present very high correlations with the Harbour Sediment Grab samples and the Sediment Traps, confirming the consistency of the PAH Fingerprints in Harbour Sediments through time, location and sampling method.

Upstream Sediments

Two of the upstream channels (Cagney Brook and Wash Brook) were included in this study because of available sediments whereas other upstream tributaries of the Tar Ponds were relined (with rock) during the course of this project. Upstream Sediment samples were used for the study from sampling programs in 2010, 2011 and 2012.

None of the correlation relationships between the PAH Fingerprints in Upstream Sediments and the Tar Ponds are considered to be high (<0.63) with most being very low, suggesting the PAH impacts in these two streams are not related to the PAH impacts observed in the Tar Ponds.

Conversely, PAH Fingerprints are highly correlated between the Upstream Sediments, all Marine Sediments (Grab, Trap and Slo-Corer), Urban Background Soils as well as Coal Sediments. These high correlations between the PAH Fingerprints, as well as known coal handling activities at some of these locations, suggest a common, petrogenic source of PAHs in these samples.

Coal Sediments

One coal sediment sample was obtained from the harbour bottom, below the coal-handling pier next to the Tar Ponds. A second coal sediment sample was obtained below a second coal-handling pier, approximately 2 km north of the Tar Ponds. Both of these sites are active with stockpiles currently in place.

No significant correlations were observed between the PAH Fingerprints of the Coal Sediments and the Tar Ponds Sediments (maximum of 0.36). This suggests two independent sources of PAHs in these two sample matrices. 18 of 26 relationships between PAH Fingerprints in the Coal Sediments and Urban Background Soils were high (>0.8) with the remaining being moderate (>0.6). This suggests a common source of PAHs in these media (e.g., history of coal handling activity).

PAH Fingerprints in Harbour Sediments (Grab, Trap and Slo-Corer) present high or very high correlations to the Coal Sediments in 36 sample relationships. Only four of these Coal Sediment/Harbour Sediment relationships presented correlations that were less than 0.8, but were still greater than 0.69. These four Harbour Sediment samples were located at the project reference station (sample location 3-2), the furthest from the Tar Ponds and coal handling piers. The location of these samples on the North Sydney waterfront suggests additional potential sources of PAHs (e.g. urban storm discharge) in these particular samples. These results strongly suggest a strong relationship between the PAH Fingerprints found in the Harbour Sediments and the PAH Fingerprints found in the Coal Sediments.

Summary

For the interpretation of the Correlation Analysis, Pearson Coefficients greater than 0.8 were considered high, representing a strong relationship between the PAH Fingerprints of the samples. Correlations lower than 0.3 were considered to represent very little to no relationship between the PAH Fingerprints of the samples. Correlations for sample relationships that are between 0.3 and 0.8 were not considered to represent particularly strong or particularly weak relationships between variables, and therefore are not the focus of this analysis.

Strong correlations were identified for the following sample sets:

- ASTM Coal Tar Reference Material and Tar Ponds Sediments;
- Urban Background Soil and Upstream Sediments;
- Sediment Traps and Harbour Sediment Grabs (both special and temporal); and,
- Coal Sediments, Harbour Sediments (trap, grab and core) and Urban Background Soils.

These strong correlations between sample PAH Fingerprints indicate common origins for the PAHs in these samples. A high correlation between the Tar Ponds and the Reference Material confirms that the Tar Ponds impacts originated from Coal Tar. The high correlation between PAH Fingerprints in Urban Background Soils and the Upstream Sediments indicates that coal handling (residential in the urban soils and industrial in the upstream sediments of the Coke Ovens site) is likely the common origin of PAH impacts in these samples, not the Coke Ovens coal tar. High correlations between the PAH Fingerprints in various Harbour Sediment samples confirms homogeneity of the PAH impacts throughout the harbour in both space and time.

Most importantly, high correlations were identified for the PAH Fingerprints in Harbour Sediments of each type (core, grab and trap) and the Coal Sediments, collected at the coal handling piers. In addition, these Fingerprints present high correlations with Urban Background Soils, which confirm coal handling as the most likely source of these PAH impacts.

Low correlations were observed for the following sample sets:

- Sediment Traps and Tar Ponds Sediments;
- Urban Background Soil and Tar Ponds Sediments;
- Upstream Sediments and Tar Ponds Sediments; and,
- Coal Sediments and Tar Ponds Sediments.

Low correlations were identified between PAH Fingerprints in Tar Ponds Sediments and Harbour Sediments / Upstream Sediment / Urban Background Soil and the Coal Sediments. This indicates that the source of PAHs in the Sydney Tar Ponds is different from the source of PAHs identified at these other locations. Upstream, this suggests that the PAHs in shallow soil and the stream sediments are not impacted by coal tar like the Tar Ponds. Downstream, it is evident that the PAH impacts observed in Sydney Harbour Sediments, including the Coal Sediments at the coal piers, did not originate from the same source. Therefore, the PAH Fingerprints in Sydney

Harbour sediments used in this study, do not appear to be related to PAHs in the Sydney Tar Ponds, that may have discharged from the site during the remediation project.

5.4. Principal Components Analysis

The Principal Component Analysis was run several times using several different versions of the data set. Initially, a set of 10 samples was used for a preliminary analysis. Following that preliminary analysis, PCA was conducted using the full, original data set, which included a large number of surface water, marine water and groundwater samples. After waterborne PAHs were excluded from this study and the data set was focused down to soil and sediment samples only, the 52 remaining samples, and their PAH Fingerprints, were used for the PCA.

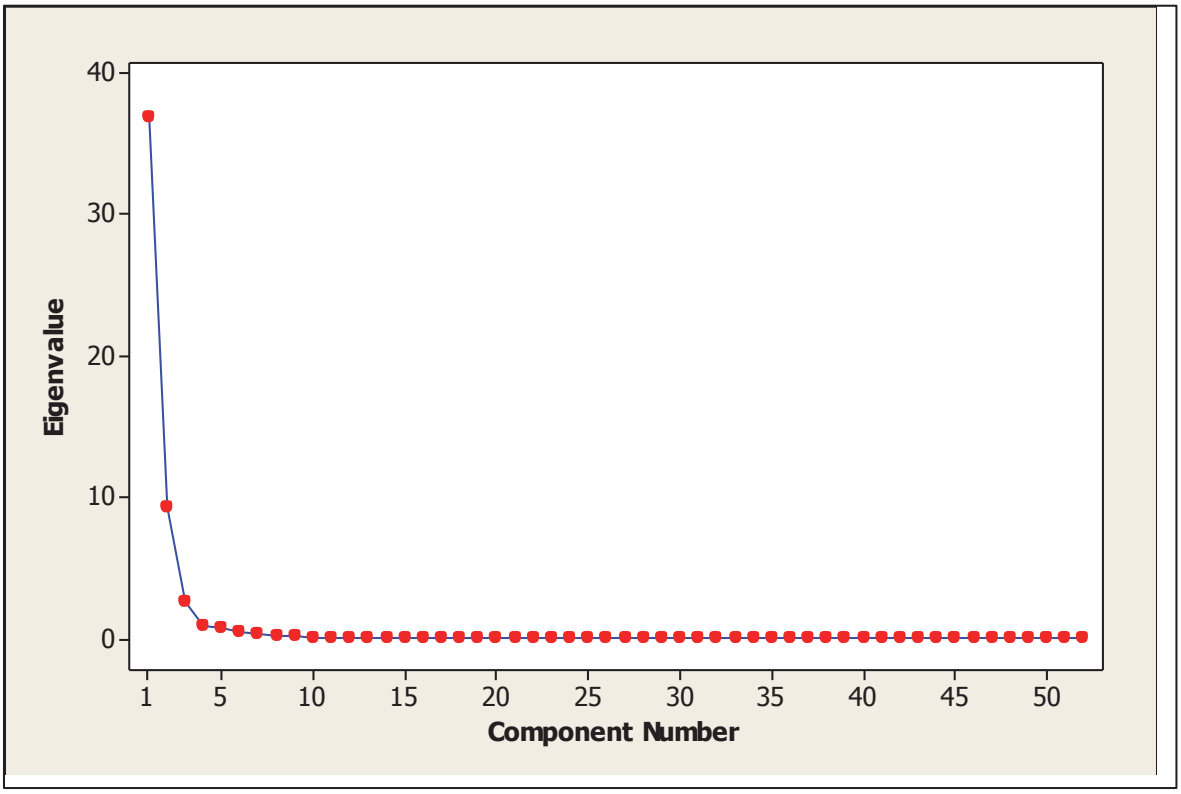
The results of the PCA are presented below. As shown in the Eigen analysis of the Correlation Matrix, the first Principal Component, Principal Component One (PC1) represents a proportion of 71% of the sample variance. Principal Component Two (PC2) is shown to represent 17.9% of the sample variance. Together, PC1 and PC2 represent a cumulative variance of 88.9%, which is enough cumulative variance to focus on these two Principal Components only.

Table 5-1 - Eigen Analysis of the Correlation Matrix

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9
Eigenvalue	36.904	9.298	2.597	0.944	0.728	0.490	0.316	0.272	0.145
Proportion	0.710	0.179	0.050	0.018	0.014	0.009	0.006	0.005	0.003
Cumulative	0.710	0.889	0.938	0.957	0.971	0.980	0.986	0.991	0.994
	PC10	PC11	PC12	PC13	PC14	PC15	PC16	PC17	PC18
Eigenvalue	0.085	0.070	0.058	0.031	0.028	0.019	0.011	0.004	0.003
Proportion	0.002	0.001	0.001	0.001	0.001	0.000	0.000	0.000	0.000
Cumulative	0.996	0.997	0.998	0.999	0.999	1.000	1.000	1.000	1.000
	PC19	PC20	PC21	PC22	PC23	PC24	PC25	PC26	PC27
Eigenvalue	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Proportion	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cumulative	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	PC28	PC29	PC30	PC31	PC32	PC33	PC34	PC35	PC36
Eigenvalue	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Proportion	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cumulative	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	PC37	PC38	PC39	PC40	PC41	PC42	PC43	PC44	PC45
Eigenvalue	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Proportion	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cumulative	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	PC45	PC46	PC47	PC48	PC49	PC50	PC51	PC52	PC53
Eigenvalue	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Proportion	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cumulative	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

As shown in the eigenvalues of the correlation matrix, the first two principal components represent 88.9% of the total variance and the other components can be considered insignificant. The first four principal components are presented in Table 5-2.

Figure 5-6 - Scree Plot of Principal Component Eigenvalues



An ideal scree plot normally contains a nearly vertical portion and a nearly horizontal portion. The components that are included in the vertical portion of the line, have the highest eigenvalues and represent most of the variance in the data. This way, the two or three Principal Components in this vertical portion can be shown to be the most representative of the data and focused on, rather than other components representing lower proportions of variance. In this case, the first two Principal Components are shown to have the highest eigenvalues and will be evaluated further.

Table 5-2 - Detailed Descriptions of Top Four Principal Components

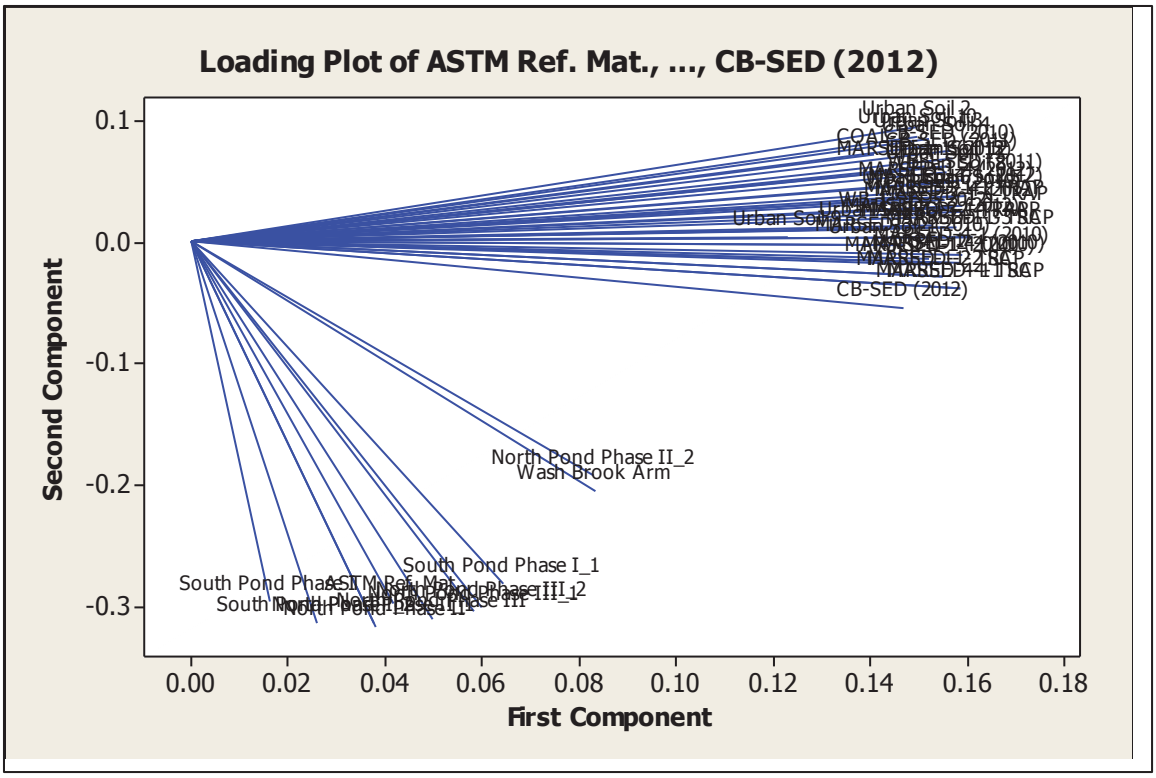
Variable	PC1	PC2	PC3	PC4
ASTM Ref. Mat.	0.042	-0.297	-0.111	-0.034
Wash Brook Arm	0.083	-0.205	0.343	0.035
South Pond Phase I	0.016	-0.296	-0.218	0.031
South Pond Phase I_1	0.064	-0.283	0.189	0.030
South Pond Phase I_2	0.026	-0.314	-0.122	0.015
North Pond Phase II	0.038	-0.317	-0.036	0.016
North Pond Phase II_1	0.038	-0.315	-0.076	0.021
North Pond Phase II_2	0.083	-0.193	0.360	0.038
North Pond Phase III	0.050	-0.312	0.003	0.023
North Pond Phase III_1	0.058	-0.304	0.065	0.025
North Pond Phase III_2	0.060	-0.302	0.086	0.006
Urban Soil 1	0.143	-0.003	0.289	-0.004
Urban Soil 2	0.150	0.094	0.049	0.059
Urban Soil 3	0.152	0.085	0.016	-0.034
Urban Soil 4	0.154	0.081	0.018	-0.019
Urban Soil 5	0.160	0.038	0.016	0.047
Urban Soil 6	0.149	0.038	0.214	-0.025
Urban Soil 7	0.141	0.011	0.302	-0.035
Urban Soil 8	0.157	0.049	0.076	-0.051
Urban Soil 9	0.123	0.004	-0.176	-0.508
Urban Soil 10	0.150	0.087	0.061	0.074
Urban Soil 11	0.156	0.058	0.133	-0.011
Urban Soil 12	0.156	0.062	0.057	-0.083
Urban Soil 13	0.155	0.062	0.103	-0.022
MARSED-1-1 TRAP	0.159	0.030	-0.002	0.135
MARSED-1-2 TRAP	0.155	-0.029	-0.167	0.096
MARSED-1-3 TRAP	0.161	0.004	-0.106	0.048
MARSED-1-4 TRAP	0.159	0.025	-0.051	0.132
MARSED-2-4 TRAP	0.158	0.012	0.031	-0.025
MARSED-3-1 TRAP	0.155	0.012	-0.074	-0.243
MARSED-4-1 TRAP	0.159	-0.039	-0.057	-0.041
MARSED-1-1 (2010)	0.153	-0.018	-0.187	0.085
MARSED-1-1 (2012)	0.151	0.062	-0.107	0.236
MARSED 1-4 (2010)	0.156	-0.018	-0.129	0.089
MARSED-1-4 (2012)	0.156	0.043	-0.096	0.222
MARSED 2-4 (2010)	0.158	-0.016	-0.105	-0.103
MARSED-2-4 (2012)	0.157	0.028	0.067	0.112
MARSED-3-2 (2010)	0.147	-0.002	-0.110	-0.389
MARSED-3-2 (2012)	0.153	0.014	0.026	-0.131
MARSED-4-1 (2010)	0.159	-0.010	-0.132	0.000
MARSED-4-1 (2012)	0.158	0.038	-0.059	0.150
COAL-1	0.152	-0.014	-0.157	0.207
COAL-2	0.141	0.072	-0.112	0.255
MARSED-4-1 SC	0.159	-0.039	-0.057	-0.041
MARSED-1-3 SC	0.161	0.004	-0.106	0.048
MARSED-1-2 SC	0.155	-0.029	-0.167	0.096
WB-1-SED (2010)	0.155	0.035	0.092	-0.206
WB-1-SED (2011)	0.160	0.051	0.005	-0.037
WB-1-SED (2012)	0.150	0.020	0.226	0.017
CB-SED (2010)	0.157	0.075	0.046	0.041
CB-SED (2011)	0.157	0.069	0.046	-0.020
CB-SED (2012)	0.147	-0.055	-0.109	-0.316

As seen within the component matrix in Table 5-2, none of the variables in PC1 have component loadings greater than 0.3 (considered to be a rule-of-thumb level of statistical significance for this test). Most variables have loadings around 0.15, with the exception of Tar Ponds Sediments and the Coal Tar Reference Material. This suggests that while PC1 does not share a strong correlation with any particular samples, all samples outside of the Tar Ponds (and the Reference Material) behave similarly in relation to one another. From this, it can be interpreted that the PAH Fingerprints in sediments that are known to be impacted by coal tar (Tar Ponds Sediments and Reference Material) behave similar to one another, but differently from all other samples in the study, suggesting two different sources of PAHs.

The second principal component, PC2, contains some variables with loadings between -0.20 and -0.32, which are still considered low, but are more significant than the component loadings in PC1. The second component has samples from Tar Ponds Sediments and the Coal Tar Reference Material with greater loadings, while all other samples had loadings less than 0.09. This suggests that PC2 behaves more like the PAH Fingerprints in the Tar Ponds Sediments, and not like the other sample media. This is the opposite of PC1.

The differences between PC1 and PC2 and the similarities between the samples within the components, supports that PAH Fingerprints found in Harbour Sediments, Upstream Sediments, Urban Background Soil and Coal Sediments are similar, but significantly different from PAH Fingerprints found in coal-tar impacts at the Sydney Tar Ponds.

Figure 5-7 - Loading Plot of Principal Components 1 and 2

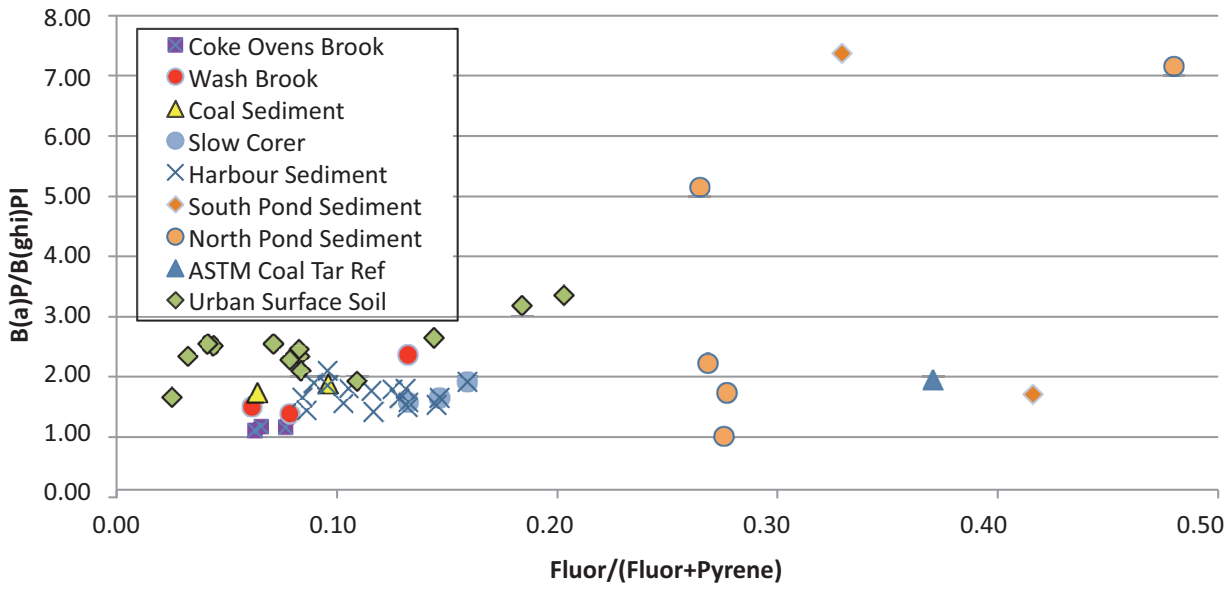


The loading plot is an excellent visual presentation of the way the two principal components that represent 88.9% of the variance in the sample data set, are primarily represented by different sample media. One cluster of samples is obvious with low loadings for the first component and negative loadings for the second component. This cluster represents PAH Fingerprints in samples collected from Tar Ponds Sediments. A separate cluster of samples has higher first component loadings, and positive second component loadings. This cluster represents all other sample media in the study. These findings suggest the each cluster of PÂH Fingerprints behave differently, but within each cluster, the PAH Fingerprints behave similarly. In other words, the PAH Fingerprints in the Tar Ponds Sediments behave differently than the PAH Fingerprints found in the Harbour Sediments, Upstream Sediments, Urban Background Soil and Coal Sediments.

5.5. Diagnostic Ratios

As described in Section 3.6.5, diagnostic ratios were selected from a number of published forensic PAH analysis studies. Following the review of numerous studies using diagnostic ratios as a forensic tool, seven diagnostic ratio plots were selected for use in this study. The diagnostic ratios were plotted with one another to visually present the PAH parameter ratios in the sample media in relation to one another. All plots are referenced from published studies; however, some were selected for reliability whereas others were selected for more evaluation purposes. The select plots are presented below with an interpretation of the information provided with the plot.

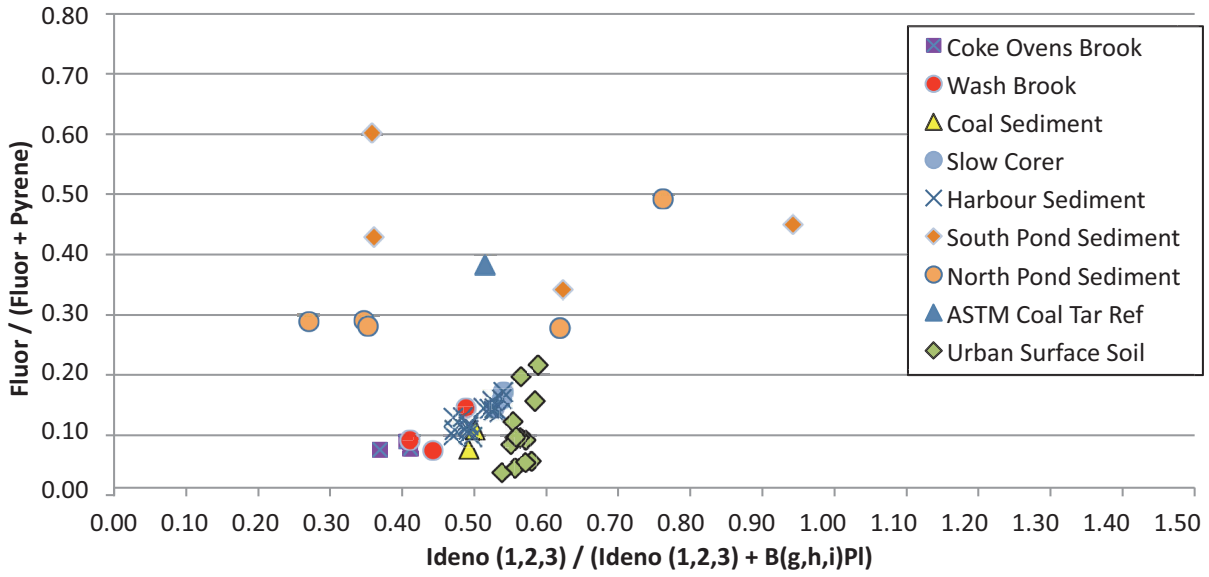
Figure 5-8 - B(a)P / B(g,h,i)Pl vs. Flour / (Fluor / Pyrene)



In Figure 5-8**,** the South Pond and North Pond Sediments, as well as the Coal Tar Reference Material, are clearly separated from the rest of the samples with higher Fluoranthene / (Fluoranthene + Pyrene) ratios. This ratio suggests a pyrogenic source for these PAH Fingerprints. Other samples present this ratio at less than 0.25, but it is important to note that Coal Sediment ratios are plotted amongst Harbour Sediment samples suggesting similar PAH Fingerprints and therefore, similar sources, different from the Sydney Tar Ponds. Coke Ovens Brook has the lowest B(a)P/Benzo(g,h,i)Perylene ratios, with the exception of Tar Ponds Sediments. Marine Sediment ratios are in the same ranges as the Coal Sediment ratios. The

ASTM Coal Tar Reference Material is in the same ranges as the Tar Ponds Sediments, reaffirming the source of PAH in the Tar Ponds, Coal Tar and similar bi-products of the Coke making process.

Figure 5-9 – Flour / (Fluor / Pyrene) vs. Ideno(1,2,3) / (Ideno(1,2,3) + B(g,h,i)Pl)



In Figure 5-9, South Pond and North Pond sediments present distinctly high Fluor/(Fluor+Pyrene) ratios, as well as the ASTM Coal Tar Reference Material, suggesting some similarities in these PAH Fingerprints. The Coal Sediment ratios are very similar to the ratios presented for Harbour Sediment, Urban Surface Soil and Wash Brook Sediment. This suggests that the significance of these ratios is common between the coal in the Coal Sediment samples, Harbour Sediments and urban areas of Sydney. Considering the history and legacy of coal in Industrial Cape Breton, these results suggest the PAH impacts observed in the Harbour Sediments are more likely to have originated from coal than from the Sydney Tar Ponds.

Figure 5-10 – Fluor / Pyrene vs. B(a)A / B(a)P

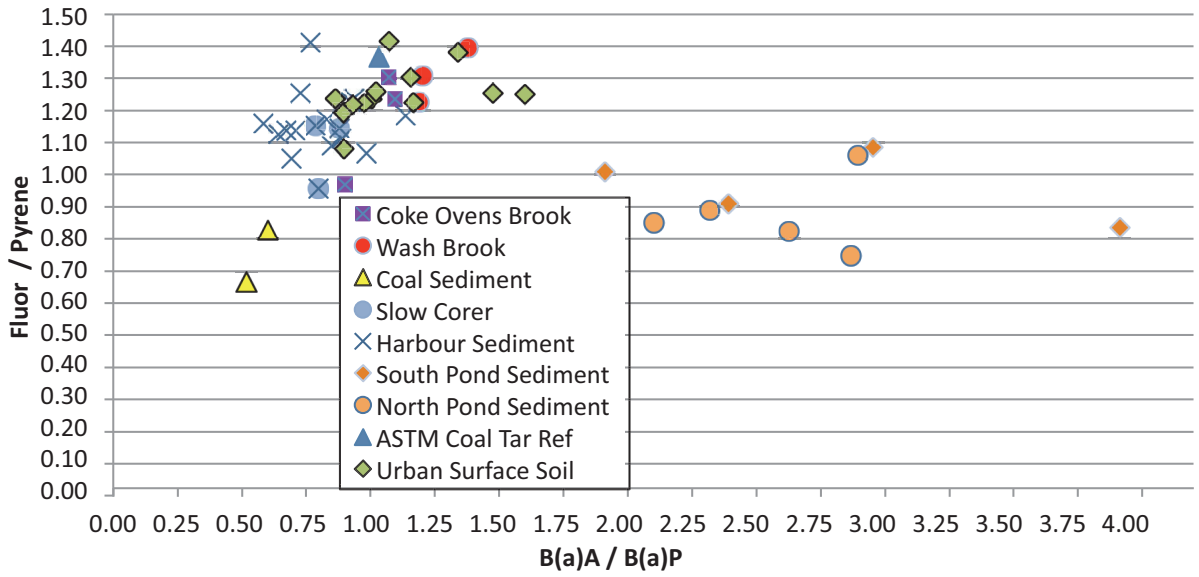
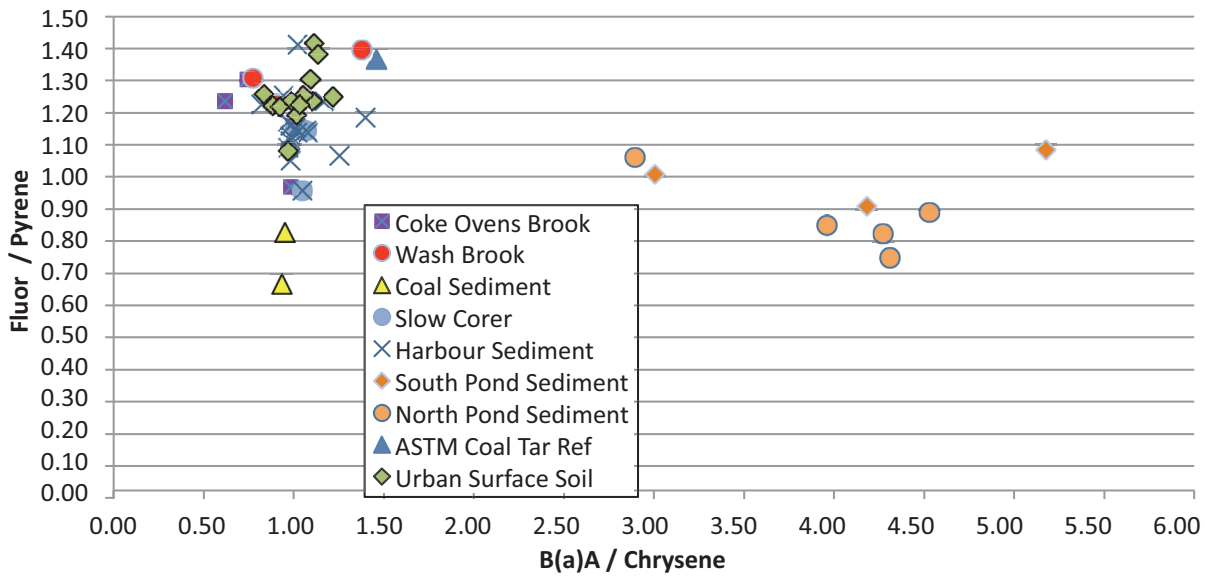


Figure 5-10. The South Pond and North Pond Sediments present distinctly higher B(a)A/B(a)P ratios than other samples. The B(a)A / B(a)P ratio may be a potential indicator of a pyrogenic source, supporting the grouping of Tar Ponds Sediments at higher ratio values. However, the Coal Tar Reference Material is not grouped among the Tar Ponds samples but is instead, grouped among the Urban Surface Soil samples and Upstream Sediments. Also surprising are the Coal Sediment samples, which are lower than most samples for both of the ratios plotted here. While the grouping of some samples is expected, the plotting of the Reference Material and the Coal Sediments are surprising and therefore, the value in these particular ratios is not recognized.

Figure 5-11 – Fluor / Pyrene vs. B(a)A / Chrysene



In Figure 5-11**,** the results of this diagnostic ratio plot are similar to Figure 14. Chrysene was substituted for Benzo(a)pyrene, which did not affect the ratio plots significantly. Tar Ponds Sediments are plotted with higher B(a)A/Chrysene ratios with relatively stable Fluoranthene/Pyrene ratios. However, the Coal Tar Reference Material ratios are not in line with the Tar Ponds Sediments, and the Coal Sediments are not plotted amongst the Harbour Sediments as anticipated. Like Figure 14, the value in this particular plot is difficult to recognize.

Figure 5-12 – Fluor / Pyrene vs. Chrysene / B(a)P

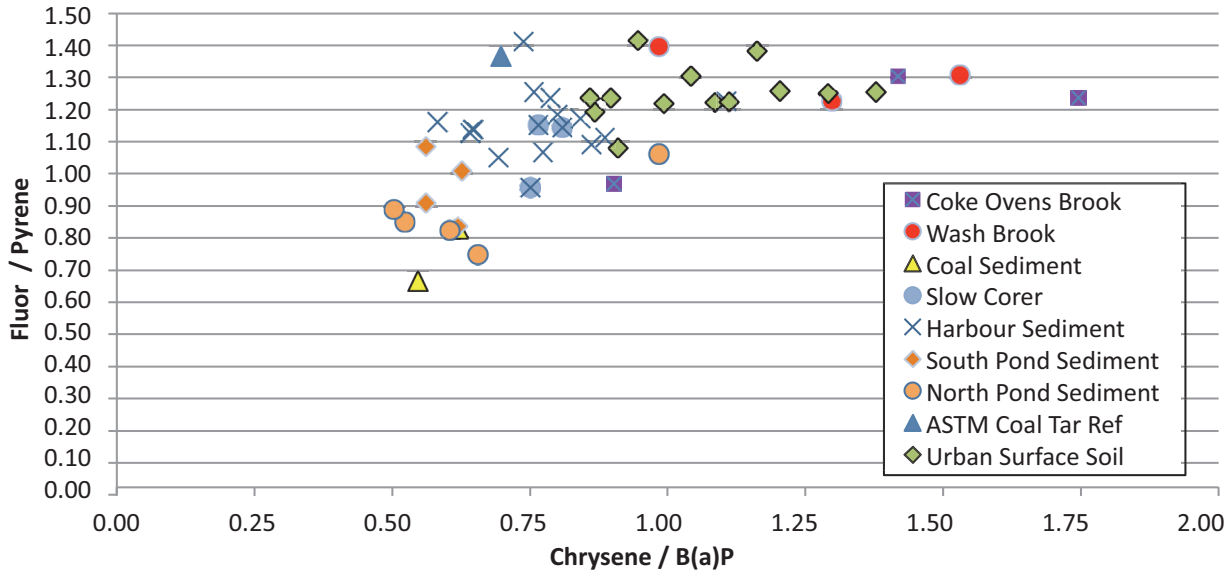
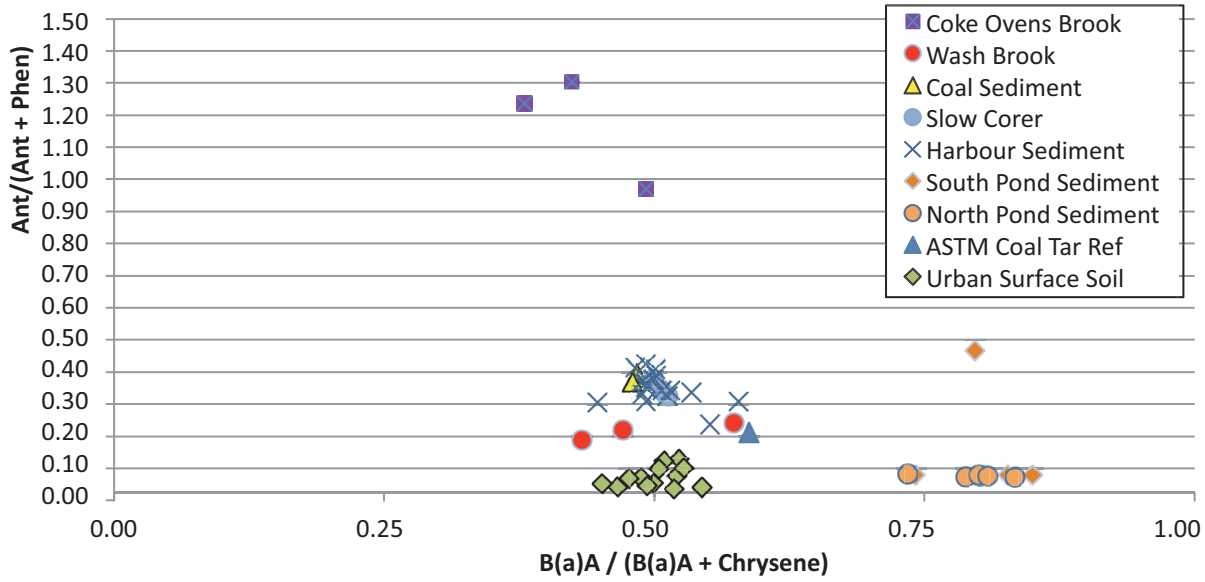


Figure 5-12 distributions show the South Pond and North Pond Sediments, as well as the Coal Sediments, have the lowest values of the plotted ratios. The Chrysene/B(a)P ratio appears to increase with the following order: Tar Ponds Sediment/Coal Sediment/Harbour Sediment/Urban Surface Soil/Wash Brook/Coke Ovens Brook. Once again, the value of this plot is unclear as it groups the Coal Sediments in with the Tar Ponds Sediments and does not plot the Coal Tar Reference Material with the Tar Ponds Sediments.

Figure 5-13 – Ant / (Ant + Phen) vs. B(a)A / (B(a)A + Chrysene)



In Figure 5-13, the Tar Ponds sediments are obviously higher in the B(a)A/(B(a)A + Chrysene) ratios. Fang et al (2003) found that B(a)A / (B(a)A+Chrysene) was a good indicator of pyrogenic pollution emission sources. Ratio values in the Tar Ponds samples are noticeably higher than other samples, suggesting the source of the PAH Fingerprints in the Tar Pons may not be the same as other media samples. Coke Ovens Brook sediments were noticeably higher in the Ant/(Ant+Phe) ratios, suggesting a source of PAHs in these samples that is not influencing the other sample media in this study (e.g., upstream solid waste facility). The Urban Soil samples and the Tar Ponds Sediments presented the lowest Ant/(Ant+Phe) ratios, suggesting some level of similarity with this ratio, but not enough similarity to cluster the samples together. The Coal Sediments and Harbour Sediments ratios are very similar, but clustered between the ranges of other samples.

Figure 5-14 - Fluor / Pyrene vs. Phen / Ant

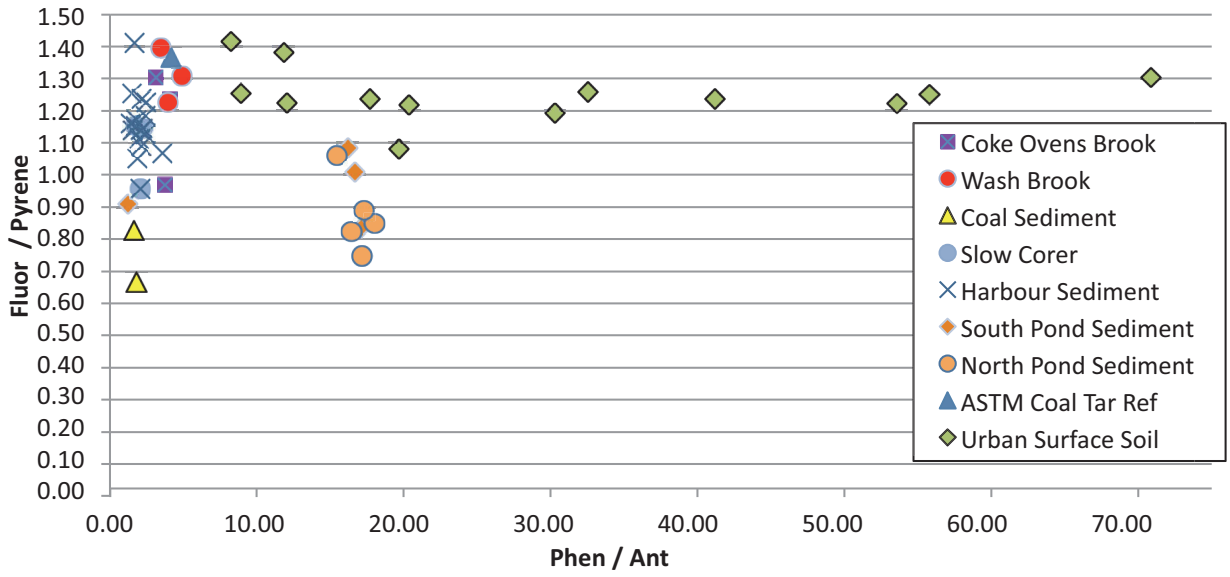


Figure 5-14. Phenanthrene/Anthracene and Fluoranthene/Pyrene are frequently used to indicate a potential dominance of petrogenic PAH impacts. A Phenanthrene/Anthracene ratio greater than 10 combined with a low Fluoranthene/Pyrene ratio (<1) is generally considered indicative of petrogenic PAH impacts (Fabbri et al., 2003). However, this suggests a petrogenic source for most Tar Ponds samples, whereas the source of the Tar Ponds is pyrogenic in nature (coke production). So the findings of Fibbri et al. (2003) are not supported in this plot. It is unclear what a wide range of Phenanthrene/Anthracene ratios in the Urban Background Soil might suggest, however these samples are within the same range of Fluoranthene/Pyrene ratios as the Harbour Sediments and Upstream Sediments. Coal Sediments were not clustered with Harbour Sediments as expected, and had lower P/A ratios and similar F/P ratios as the Tar Ponds.

Figure 5-15 – Chrysene / Phen vs. Naphthalene / Total PAH

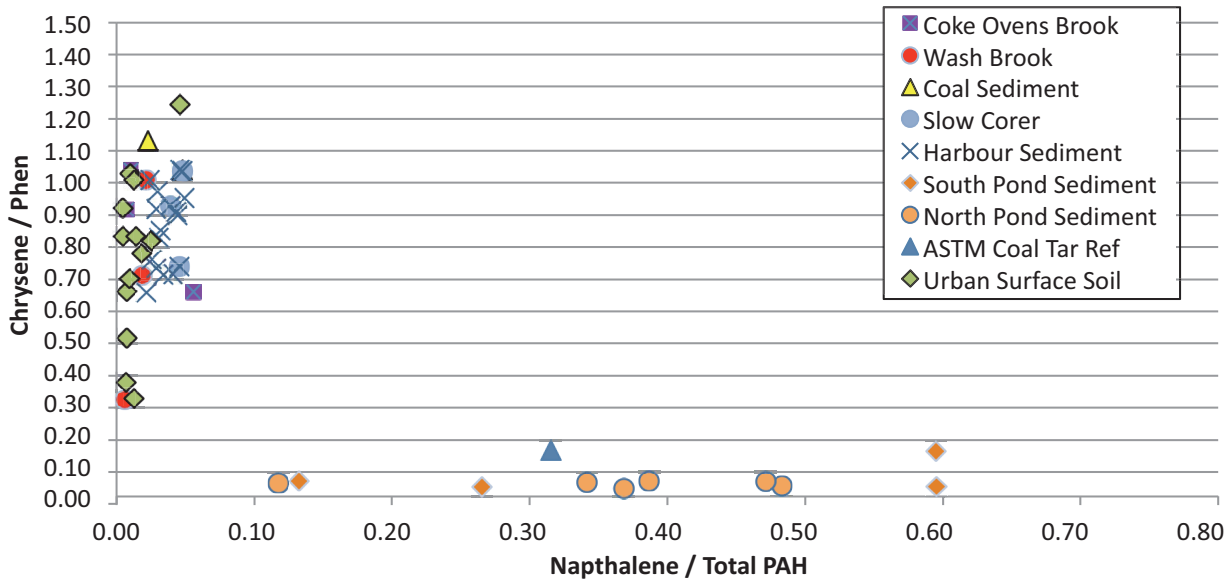


Figure 5-15. Wang et al. (2003) suggest the Chrysene / Phenanthrene ratios can be used as a weathering indicator. The Tar Ponds Sediments have noticeably lower values of this ratio, as well as the Coal Tar Reference Material. This may suggest that the samples collected from the Tar Ponds Sediments were less weathered than the PAH Fingerprints found in other sample media. Naphthalene / Total PAH ratios vary widely in Tar Ponds Sediments samples, as compared to the small range of ratio values elsewhere in the study area. This finding may suggest that a variety of source materials contributed to these PAH Fingerprints (e.g. varying waste streams from the Coke Ovens, other periodic dumping etc.).

5.6. Mann Whitney Non-Parametric Test

The Mann-Whitney Non-Parametric Test was run on a number of sample pairings to assess if the population medians were significantly equal, and therefore, the populations themselves (i.e., the PAH Fingerprints) were significantly similar. Results of the Mann Whitney tests are provided in Appendix 6. Two samples from within the Tar Ponds Sediments were tested and were found to have significantly equal population medians and therefore, the PAH Fingerprints of those samples are considered to be similar. A similar result was observed for a Tar Ponds Sediment sample and the Coal Tar Reference Material, once again indicating PAH Fingerprints for these samples and a common source of PAH impacts. A third similar test was conducted on Harbour Sediment samples from the southernmost and northernmost points of the study area. Again, the population medians of these samples were found to be significantly equal and therefore, the PAH Fingerprints of these samples are considered similar. These pairings support the validity of this test.

The Mann Whitney test for the following sample pairings identified significantly equal population medians and therefore, the populations themselves (i.e. sample PAH Fingerprints) are considered significantly similar:

- Upstream Sediments and Harbour Sediments;
- Upstream Sediments and Coal Sediments;
- Harbour Sediments (x4) and Coal Sediments (x2);

The identification of significantly similar populations (PAH Fingerprints) for these samples clearly indicates a similarity in the distribution of PAHs in the Upstream Sediments, the Coal Sediments and the Harbour Sediments. This indicates that coal-related impacts are most likely the common source for the PAHs observed and are therefore, not related to PAHs associated with coal tar impacts (i.e., Tar Ponds Sediments). Eight iterations of the test were conducted on four Harbour Sediment samples and two Coal Sediment samples, with each iteration resulting in significantly equal medians and significantly similar PAH Fingerprints. Once again, this supports previous findings that the PAH Fingerprints observed in the Harbour Sediments are more similar to the coal dust impacts at the loading piers than the PAH Fingerprints found in the Sydney Tar Ponds Sediments.

Conversely, the following sample pairings were found to have significantly different population medians and therefore, the PAH Fingerprints of the following samples are not considered similar using this test:

- Upstream Sediment and Tar Ponds Sediments;
- Tar Ponds Sediments (x4) and Coal Sediments (x2);
- Tar Ponds Sediments (x4) and Harbour Sediments (x4);

Sediment samples from the upgradient streams were paired with Tar Ponds Sediments and were found to have different population medians and therefore, different PAH profiles. Then, four Tar Ponds Sediment samples were paired with two Coal Sediment samples and in each of the 8 tests, the population medians were found to be significantly different and therefore, the PAH Fingerprints of the Tar Ponds Sediments are considered to be significantly different from the PAH Fingerprints of the Coal Sediments. Similarly, a total of 16 tests were run for Tar Ponds Sediments paired with Harbour Sediments and in each case, the population median was found to be significantly different and therefore, the PAH Fingerprints for the Tar Ponds Sediments are considered to be significantly different from the PAH Fingerprints for Sydney Harbour Sediments.

Chapter 6 - Conclusions and Recommendations

6.1. Fingerprint Technique Summaries

6.1.1. Chromatograms

There was some value in this qualitative analysis of PAH chromatograms, however, other than fairly obvious visual similarities in the Harbour Sediment chromatogram plots, any correlations between PAH Fingerprints at different locations within the study area are difficult to identify using chromatograms alone. For the purposes of this study, the review of the chromatograms did not support nor reject the project hypothesis.

6.1.2. Histograms

Plotting of PAH Fingerprints in histograms was an excellent qualitative analysis of PAH distributions in the various sample media included in the study. Qualitative analysis of the plots confirm similarities between PAH Fingerprints in samples of the same media (e.g., Sydney Harbour Sediments were similar throughout the Harbour). The results also confirm qualitative similarities between the Coal Tar Reference Material and the Tar Ponds Sediments, supporting the fact that the Tar Ponds are due in large part, to the historic discharge of bi-products from the Coke Ovens. These observations confirmed the value in comparing the PAH Histograms for samples as a Fingerprint Technique.

Histograms of many samples did not present observed similarities, suggesting different sources of PAHs in some samples. For example, the Coal Sediments collected from beneath the coal piers in Sydney Harbour do not present PAH Histograms similar to the ASTM Coal Tar Reference Material and Tar Ponds Sediments. This indicates that the sediments collected from beneath the coal piers are not impacted by coal tar bi-products and are instead impacted by coal dust. Conversely, similarities between the PAH Histograms of Harbour Sediments and Coal Sediments were evident during the assessment. Both sample sets tend to be predominantly moderate to heavy molecular weight PAHs, whereas the Tar Ponds Sediments are predominantly lighter to moderate molecular weight PAHs. These results suggest the PAHs in Harbour Sediments and Coal Sediments originate at the same source, which is not the Sydney Tar Ponds Sediments.

6.1.3. Correlation Analysis

Strong correlations were identified for the following sample sets:

- ASTM Coal Tar Reference Material and Tar Ponds Sediments;
- Urban Background Soil and Upstream Sediments;
- Sediment Traps and Harbour Sediment Grabs (both special and temporal); and,
- Coal Sediments, Harbour Sediments (trap, grab and core) and Urban Background Soils.

These strong correlations between sample PAH Fingerprints indicate common origins for the PAHs in these samples.

Low correlations were observed for the following sample sets:

- Sediment Traps and Tar Ponds Sediments;
- Urban Background Soil and Tar Ponds Sediments;
- Upstream Sediments and Tar Ponds Sediments; and,
- Coal Sediments and Tar Ponds Sediments.

Low correlations were identified between PAH Fingerprints in Tar Ponds Sediments and Harbour Sediments / Upstream Sediment / Urban Background Soil and the Coal Sediments. This indicates that the source of PAHs in the Sydney Tar Ponds is different from the source of PAHs identified at these other locations.

6.1.4. Principal Component Analysis

Interpreting the variable loadings in the Principal Components suggests that PC1 represents the behavior of PAH Fingerprints in all other samples more so than Tar Ponds Sediments. Conversely, PC2 has sample loadings that are greater for Tar Ponds Sediments, and noticeably lower for all other sample media. This suggests that PC2 represents the behavior of PAH profiles in Tar Ponds sediments moreso than other sample media. The fact that one principal component represents Tar Ponds Sediments and another represents all other PAH Fingerprints included in the study, strongly suggests that the PAH profiles found in the Tar Ponds are not similar to the Harbour Sediments, Upstream Sediments, Urban Background Soil and Coal Sediments. It therefore suggests that other media samples included in this study have been impacted by PAH from a source other than the Sydney Tar Ponds.

6.1.5. Diagnostic Ratios

Of the eight Diagnostic Ratio plots prepared during this study, Tar Ponds Sediment samples are generally plotted in clusters, including the ASTM Coal Tar Reference Material. A variety of PAH parameters were used in these ratio plots, so the clustering of samples observed suggests similarities in the PAH Fingerprints of the Tar Ponds Sediments and Reference Material. The clustering also suggests different PAH Fingerprints for all other samples included in the study.

Not all ratio plots provided groupings of samples as anticipated and it was difficult to determine meaning behind some plots. However, many of the plots clearly presented clusters of samples that confirm similarities in the PAH Fingerprints between these samples.

6.1.6. Mann-Whitney Non-Parametric Test

The Mann Whitney Non-Parametric test was a very useful check to compare sample pairings from the same media to confirm similarities of PAH Fingerprints, but also from different media to assess similar PAH Fingerprints to significantly different PAH Fingerprints. Results of the Non-Parametric tests support the findings of the other PAH Fingerprint techniques, in identifying similar PAH Fingerprints within the same media, between the Reference Material and the Tar Ponds Sediments, as well as between the Upstream Sediment, the Harbour Sediments, the Urban Background Soil and the Coal Sediments. The results of the Mann Whitney Non-Parametric Tests indicate different sources of PAHs for the Sydney Tar Ponds and Sydney Harbour Sediments.

6.1.7. Summary

Results of the Forensic PAH Assessment have generally identified similar PAH Fingerprints for a number of samples that have been, or are likely to have been, exposed to coal-handling activities. While no single source can be confirmed for these samples, PAH Fingerprints appear to be similar in samples related to coal exposure. In contrast, Sydney Tar Ponds Sediments do not present PAH Fingerprints that are similar to the other media included in the study, confirming that the PAH impacts observed in Sydney Harbour Sediments, Upstream Sediments and Urban Background Soils are not due to PAHs in the Sydney Tar Ponds. These other samples have PAH Fingerprints that are much more similar to the Coal Sediment samples collected from beneath the loading piers, suggesting that coal-handling activities, both domestic in Sydney and

industrial at the Coke Ovens and on Sydney Harbour, are the likely source of PAH impacts observed in the sediments of Sydney Harbour.

There is sufficient evidence to reject the study hypothesis. The PAH Fingerprints in Sydney Harbour Sediments are not similar to those found in the Sydney Tar Ponds, and are therefore from another source. The PAH Fingerprint found in coal laden sediments below the coal handling facilities, closely matches the PAH Fingerprints in the Harbour Sediments, suggesting these impacts originate from a common source, which is most likely coal dust that is generated during coal handling activities at the two facilities.

6.2. Research Contribution

One of the significant findings discovered early on in this study was the validity of ½ RDL as a suitable substitute for non-detect data. There is value in sample results that are below the reportable detection limit and the methods evaluated herein confirmed that using ½ of the RDL value is a suitable method for using non-detect results in a statistical analysis.

This study was conducted using Mass Fractions of PAH compounds in the data set samples. Following the completion of the forensic assessment, it was recognized that Molar Fractions would be a more representative method for determining abundance of each PAH compound in samples. Using the molar factions takes into account the molecular mass of each compound and determines the abundance of each compound by moles rather than mass. In an effort to avoid repeating all of the forensic assessments, several trials were conducted to determine if a significant difference in the findings would result from using Molar Fractions instead. Based on the results of this work, Mass Fractions of PAH compounds in samples can be used to conduct a forensic investigation of PAH Fingerprints.

This study was set up to confirm that the PAHs observed in shallow sediment in Sydney Harbour are in fact, related to PAHs observed in the Sydney Tar Ponds. The idea behind this was that environmental controls were established prior to, and during, the remediation project, to reduce any potential release of contaminated sediments into the marine environment. This evolved into an assessment known as Source Apportionment. Based on the characteristics of the PAH Fingerprints of the samples included in the study, the source of PAHs in the Harbour Sediments has been identified as coal dust, likely generated at the two coal piers on Sydney Harbour. Using

the PAH Fingerprint techniques will allow other researchers to confirm similarities between source PAHs and environmental samples, thereby confirming a release point or in this case, rejecting the null hypothesis and identifying another source of PAHs.

The work conducted in this study presents effective methods of determining relationships between PAH impacts identified in various soil and sediment samples. While the media samples varied spatially, temporally and even physically, the PAH Fingerprints in each media allowed for a comparison of PAH distribution in each sample and identified relationships between some while confirming that other samples did not appear to be related. This research will assist other researchers in identifying relationships between PAH impacts and identifying potential sources of those impacts.

6.3. Recommendations for Future Study

There are several routes that this study could follow for additional research. Additional data could be added to the study, including:

- Tar Ponds Sediments sampled during the Remediation Project;
- Deeper sediments cored from the bottom of Sydney Harbour to represent deposits that occurred during the periods of high contamination discharge from the Coke Ovens into Muggah Creek; and,
- A comparison of PAH profiles in coals mined in Cape Breton as compared to coals that are currently being imported from other countries.

Another research topic that was not identified in this study is water. PAH Fingerprints in surface water and groundwater throughout the site could be included in a study to identify similarities between PAH contaminants and potentially identify common sources of PAHs using Fingerprint Techniques.

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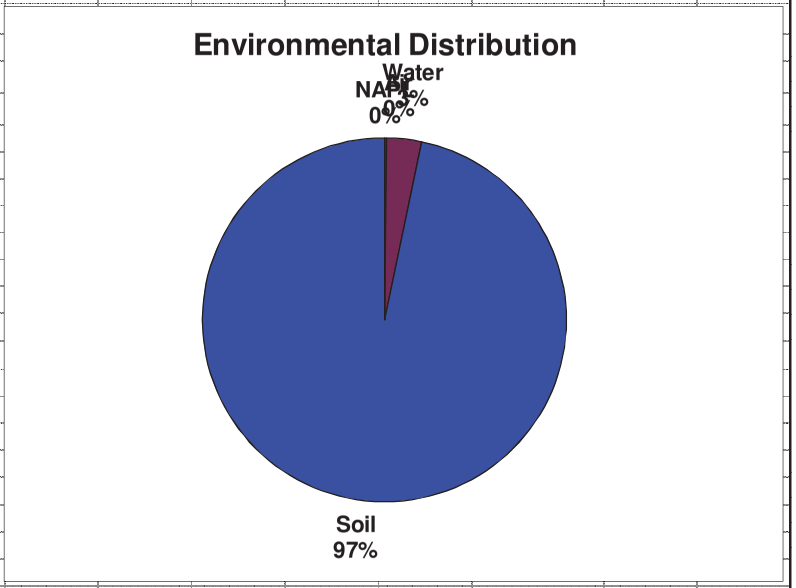
Appendix 1 – Fugacity Environmental Fate Modeling

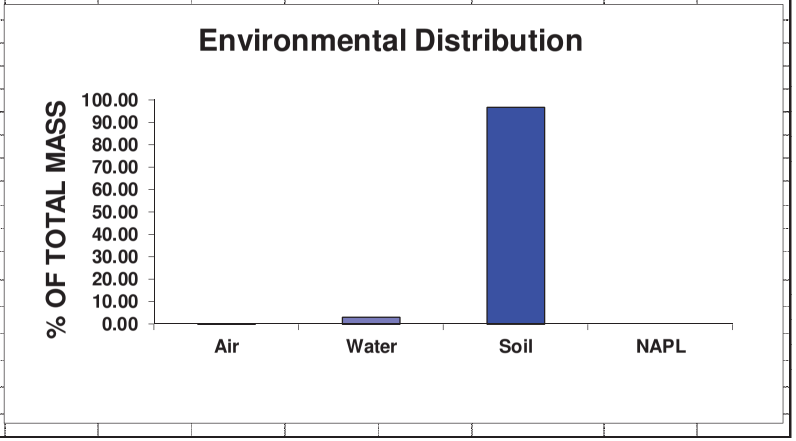
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Naphthalene
Enter the molecular weight:	128.2
Enter water solubility (mg/L):	3.10E+01
Enter vapor Pressure (mmHg):	2.34E-01
Enter Henry's law constant (atm*m^3/mol):	1.27E-03
Enter Log Kow:	3.3
Enter Log Koc	3.11
*bold items are not directly used in the fugacity calculation	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	6.61E-05	**0.17**
Water	1.25E-03	**3.13**
Soil	1.93E-02	**96.71**
NAPL	0.00E+00	**0.00**
	Sum=	100.0

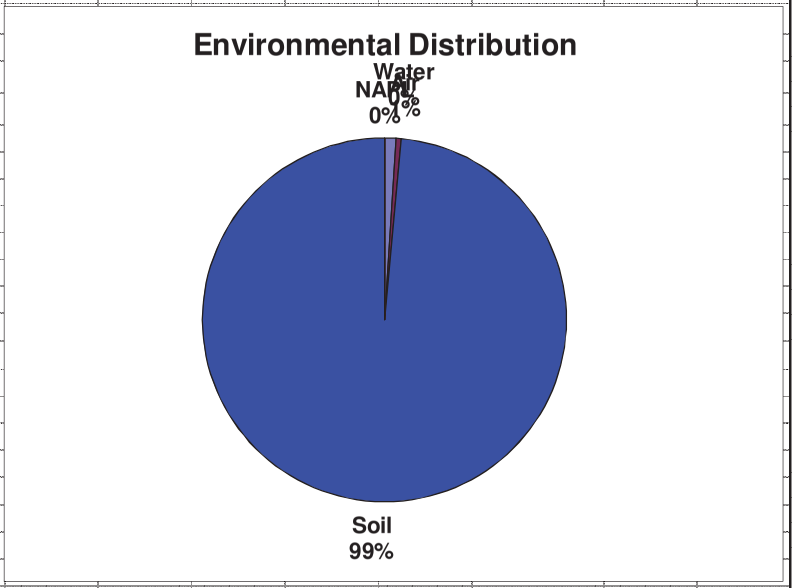


Instructions for using the "Fugacity Calculator"

1-Find the chemical that you are interested in under the "Chemical Data" tab
2-Copy the selected data and return to the "Fugacity-level 1" tab
3-Paste the data into the "chemical characteristics" area and view your results
4-Modifications can be made to the "site characterisitcs" inputs to better represent a specific site
5-Mouse over cells with red corners to view notes about specific parameters

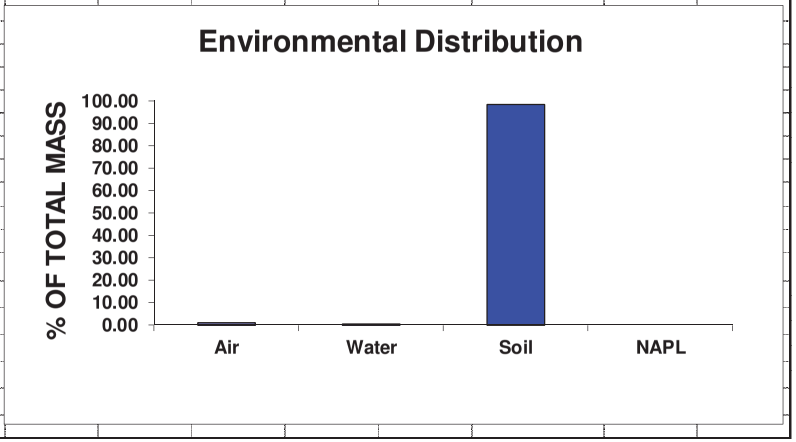
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	2-Methyl naphthalene
Enter the molecular weight:	142.2
Enter water solubility (mg/L):	2.54E+01
Enter vapor Pressure (mmHg):	6.80E-02
Enter Henry's law constant (atm*m^3/mol):	5.06E-02
Enter Log Kow:	3.86
Enter Log Koc	3.93
*bold items are not directly used in the fugacity calculation	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	4.06E-04	**1.01**
Water	1.93E-04	**0.48**
Soil	1.97E-02	**98.50**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



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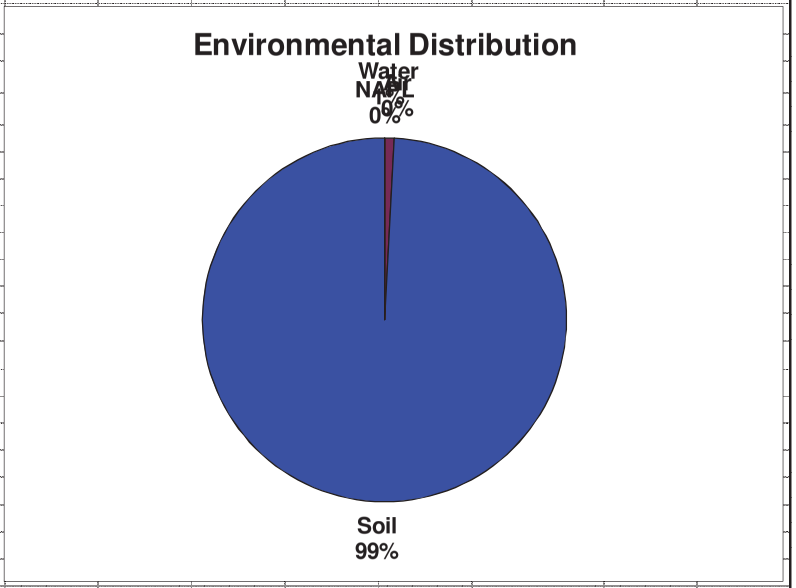
3-Paste the data into the "chemical characteristics" area and view your results
4-Modifications can be made to the "site characterisitcs" inputs to better represent a specific site
5-Mouse over cells with red corners to view notes about specific parameters

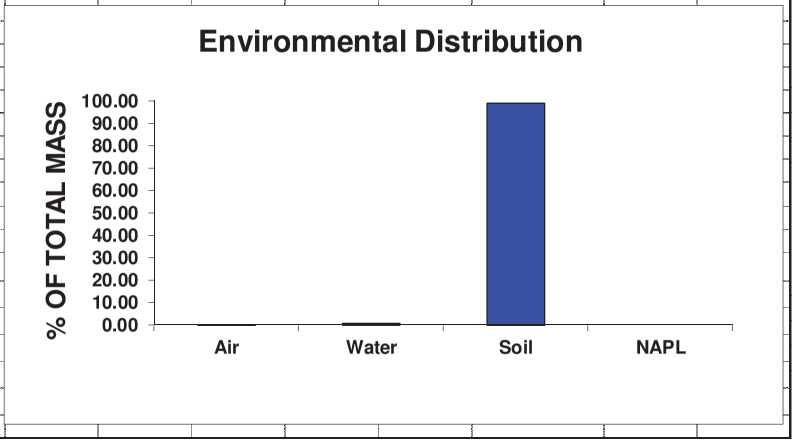
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Acenaphthene
Enter the molecular weight:	154.21
Enter water solubility (mg/L):	3.88E+00
Enter vapor Pressure (mmHg):	2.31E-02
Enter Henry's law constant (atm*m^3/mol):	1.20E-03
Enter Log Kow:	3.92
Enter Log Koc	3.7
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	1.65E-05	**0.04**
Water	3.30E-04	**0.82**
Soil	1.98E-02	**99.13**
NAPL	0.00E+00	**0.00**
	Sum=	100.0

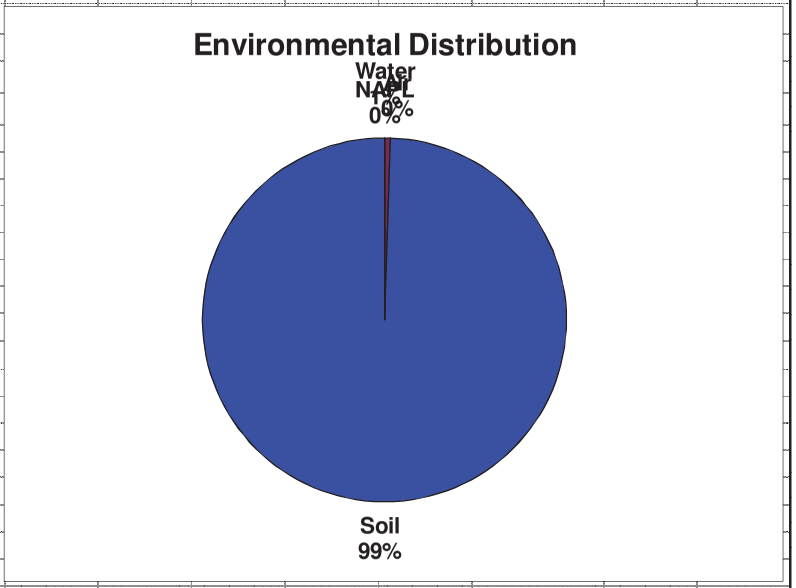


Instructions for using the "Fugacity Calculator"

1-Find the chemical that you are interested in under the "Chemical Data" tab
2-Copy the selected data and return to the "Fugacity-level 1" tab
3-Paste the data into the "chemical characteristics" area and view your results
4-Modifications can be made to the "site characterisitcs" inputs to better represent a specific site
5-Mouse over cells with red corners to view notes about specific parameters

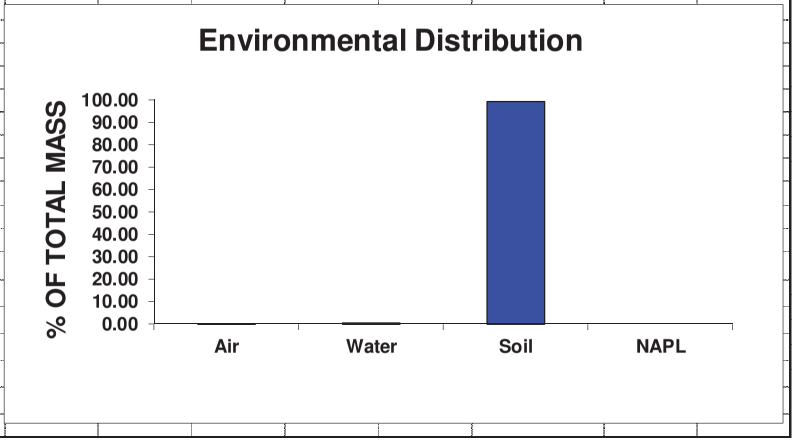
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Fluorene
Enter the molecular weight:	166.22
Enter water solubility (mg/L):	1.90E+00
Enter vapor Pressure (mmHg):	6.67E-04
Enter Henry's law constant (atm*m^3/mol):	7.65E-05
Enter Log Kow:	4.18
Enter Log Koc	3.9
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	6.64E-07	**0.00**
Water	2.09E-04	**0.52**
Soil	1.99E-02	**99.48**
NAPL	0.00E+00	**0.00**
	Sum=	100.0

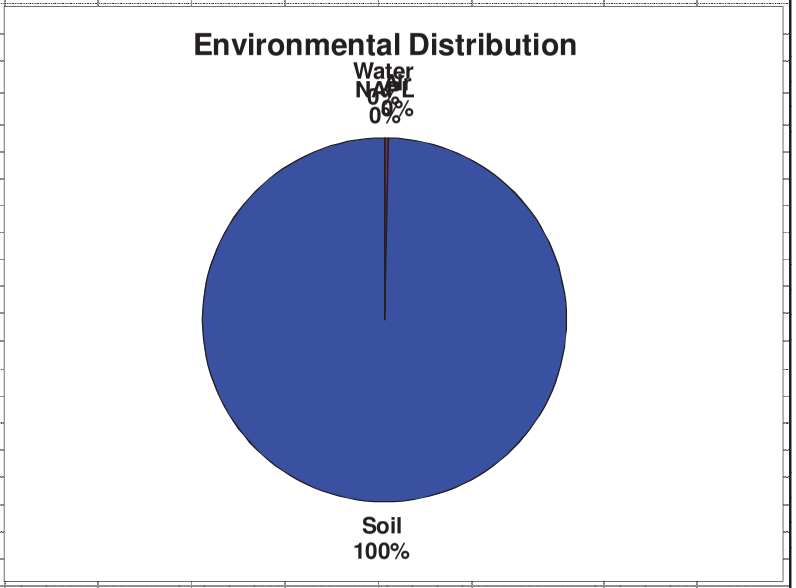


Instructions for using the "Fugacity Calculator"

1-Find the chemical that you are interested in under the "Chemical Data" tab
2-Copy the selected data and return to the "Fugacity-level 1" tab
3-Paste the data into the "chemical characteristics" area and view your results
4-Modifications can be made to the "site characterisitcs" inputs to better represent a specific site
5-Mouse over cells with red corners to view notes about specific parameters

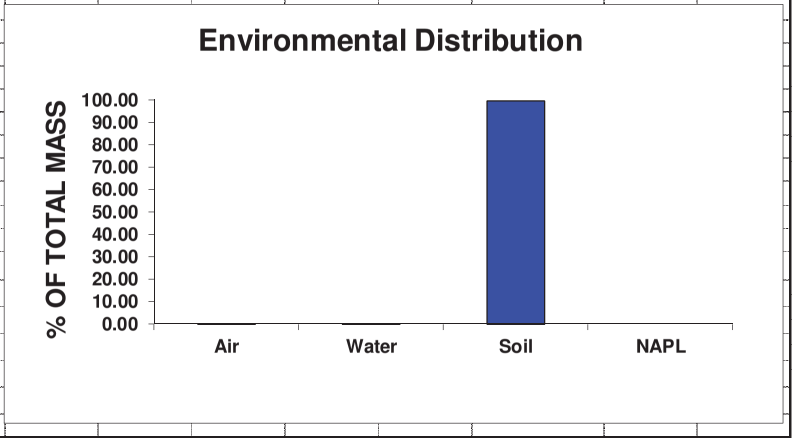
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Phenanthrene
Enter the molecular weight:	178.2
Enter water solubility (mg/L):	1.18E+00
Enter vapor Pressure (mmHg):	2.01E-04
Enter Henry's law constant (atm*m^3/mol):	3.98E-05
Enter Log Kow:	4.46
Enter Log Koc	4.1
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	2.18E-07	**0.00**
Water	1.32E-04	**0.33**
Soil	1.99E-02	**99.67**
NAPL	0.00E+00	**0.00**
	Sum=	100.0

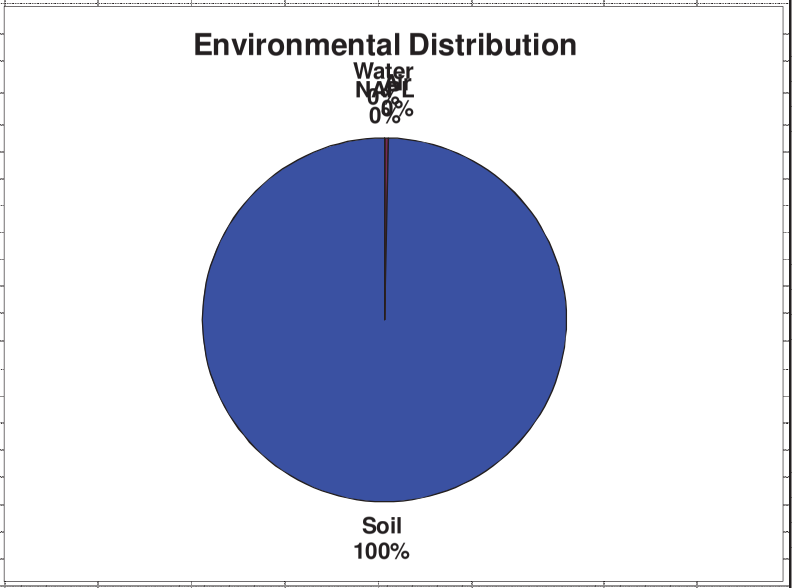


Instructions for using the "Fugacity Calculator"

1-Find the chemical that you are interested in under the "Chemical Data" tab
2-Copy the selected data and return to the "Fugacity-level 1" tab
3-Paste the data into the "chemical characteristics" area and view your results
4-Modifications can be made to the "site characterisitcs" inputs to better represent a specific site
5-Mouse over cells with red corners to view notes about specific parameters

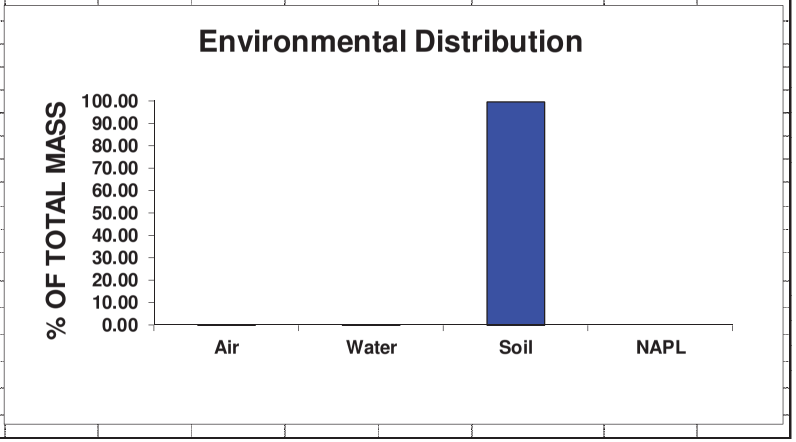
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Anthracene
Enter the molecular weight:	178.2
Enter water solubility (mg/L):	7.50E-02
Enter vapor Pressure (mmHg):	1.08E-05
Enter Henry's law constant (atm*m^3/mol):	3.38E-05
Enter Log Kow:	4.45
Enter Log Koc	4.1
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	1.85E-07	**0.00**
Water	1.32E-04	**0.33**
Soil	1.99E-02	**99.67**
NAPL	0.00E+00	**0.00**
	Sum=	100.0

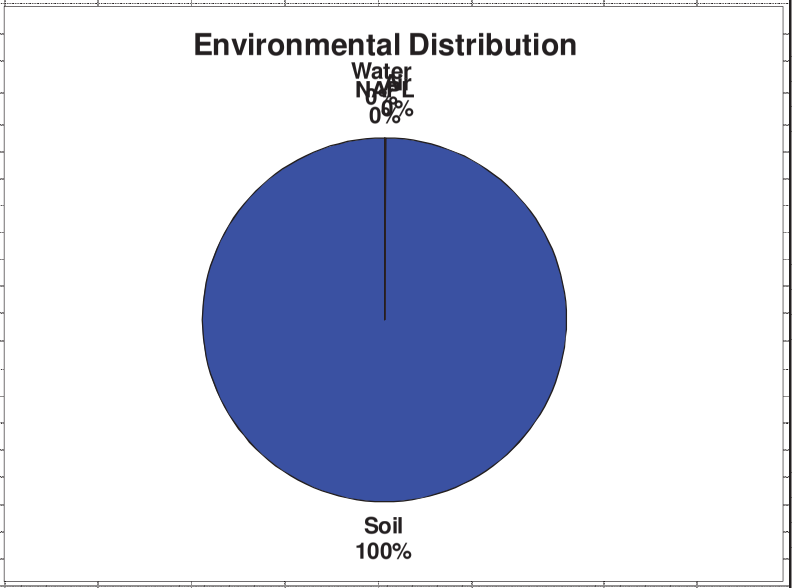


Instructions for using the "Fugacity Calculator"

1-Find the chemical that you are interested in under the "Chemical Data" tab
2-Copy the selected data and return to the "Fugacity-level 1" tab
3-Paste the data into the "chemical characteristics" area and view your results
4-Modifications can be made to the "site characterisitcs" inputs to better represent a specific site
5-Mouse over cells with red corners to view notes about specific parameters

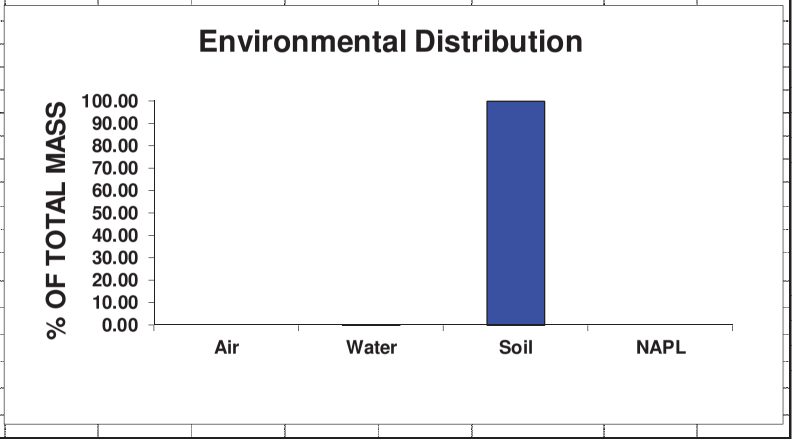
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Fluoranthene
Enter the molecular weight:	202.26
Enter water solubility (mg/L):	2.65E-01
Enter vapor Pressure (mmHg):	1.00E-02
Enter Henry's law constant (atm*m^3/mol):	6.50E-06
Enter Log Kow:	4.9
Enter Log Koc	4.58
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	1.18E-08	**0.00**
Water	4.38E-05	**0.11**
Soil	2.00E-02	**99.89**
NAPL	0.00E+00	**0.00**
	Sum=	100.0

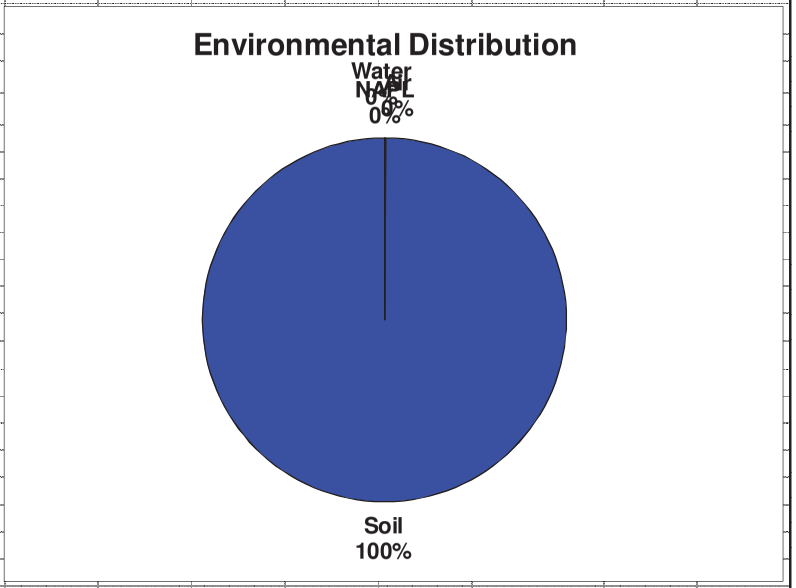


Instructions for using the "Fugacity Calculator"

1-Find the chemical that you are interested in under the "Chemical Data" tab
2-Copy the selected data and return to the "Fugacity-level 1" tab
3-Paste the data into the "chemical characteristics" area and view your results
4-Modifications can be made to the "site characterisitcs" inputs to better represent a specific site
5-Mouse over cells with red corners to view notes about specific parameters

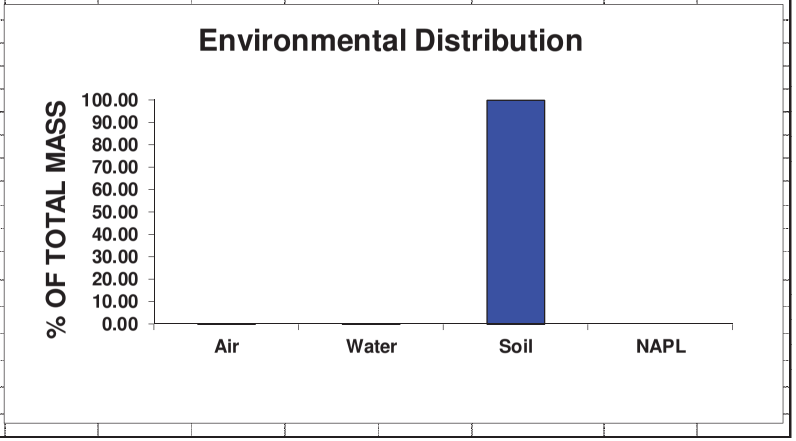
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Pyrene
Enter the molecular weight:	202.3
Enter water solubility (mg/L):	1.48E-01
Enter vapor Pressure (mmHg):	6.67E-06
Enter Henry's law constant (atm*m^3/mol):	1.20E-05
Enter Log Kow:	4.88
Enter Log Koc	4.58
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	2.19E-08	**0.00**
Water	4.38E-05	**0.11**
Soil	2.00E-02	**99.89**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



Instructions for using the "Fugacity Calculator"

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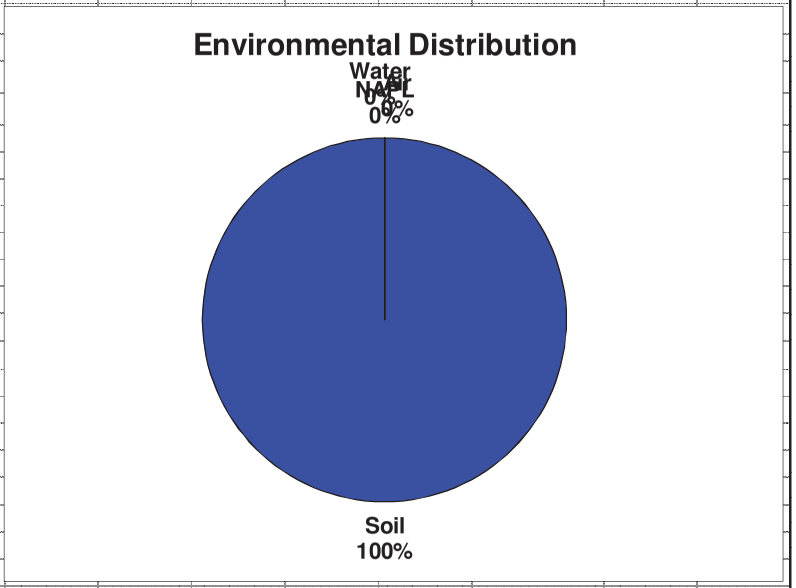
5-Mouse over cells with red corners to view notes about specific parameters

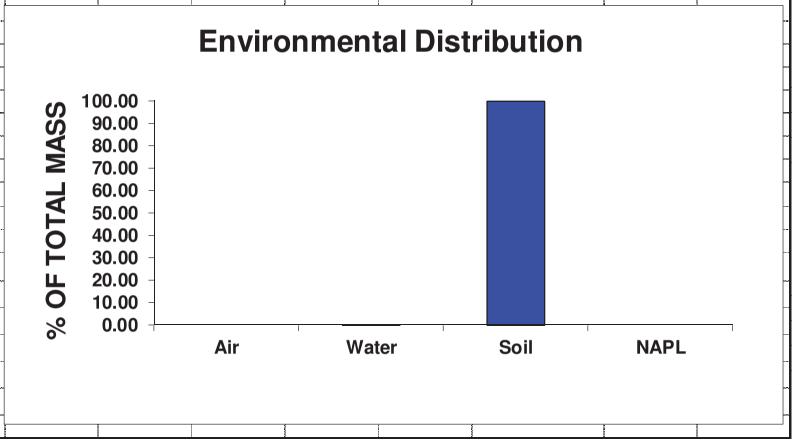
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Benzo(a)anthracene
Enter the molecular weight:	228.3
Enter water solubility (mg/L):	1.40E-02
Enter vapor Pressure (mmHg):	1.16E-09
Enter Henry's law constant (atm*m^3/mol):	4.50E-06
Enter Log Kow:	5.61
Enter Log Koc	6.14
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	2.26E-10	**0.00**
Water	1.21E-06	**0.00**
Soil	2.00E-02	**100.00**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



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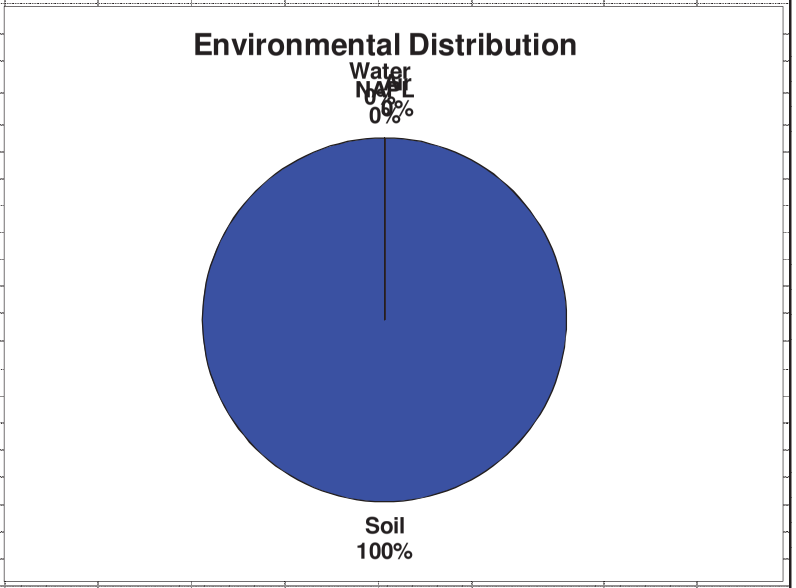
3-Paste the data into the "chemical characteristics" area and view your results
4-Modifications can be made to the "site characterisitcs" inputs to better represent a specific site
5-Mouse over cells with red corners to view notes about specific parameters

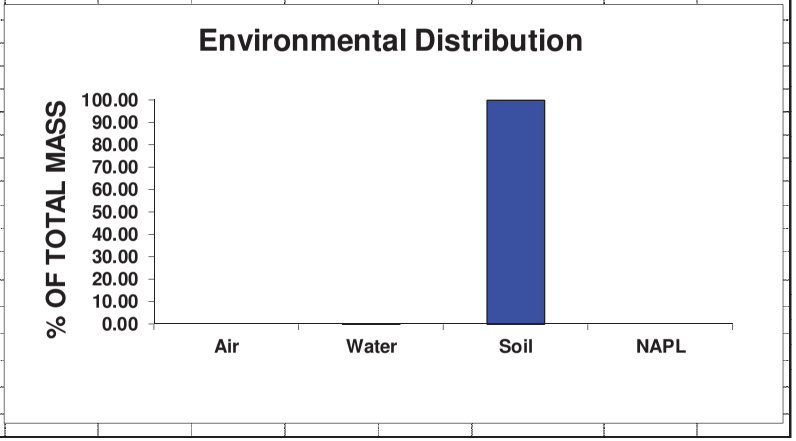
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Chrysene
Enter the molecular weight:	228.29
Enter water solubility (mg/L):	6.00E-03
Enter vapor Pressure (mmHg):	6.30E-09
Enter Henry's law constant (atm*m^3/mol):	1.05E-06
Enter Log Kow:	5.61
Enter Log Koc	5.3
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	3.65E-10	**0.00**
Water	8.35E-06	**0.02**
Soil	2.00E-02	**99.98**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



Instructions for using the "Fugacity Calculator"

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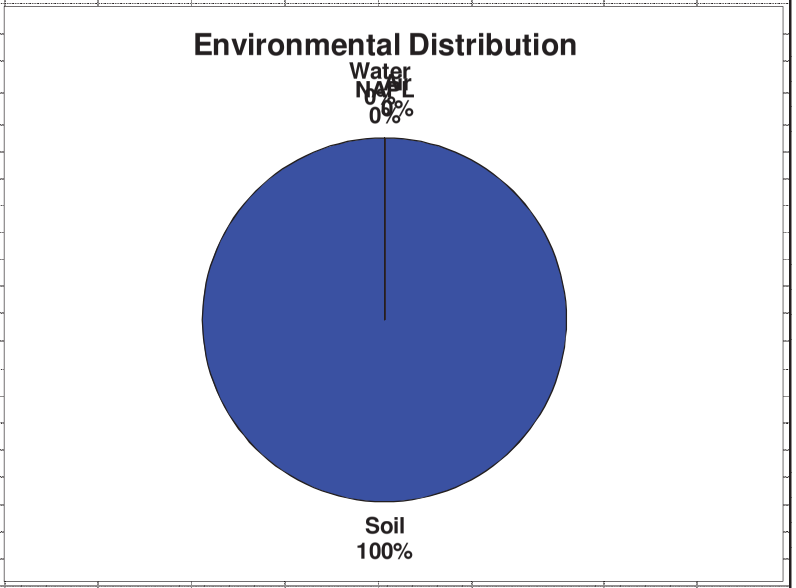
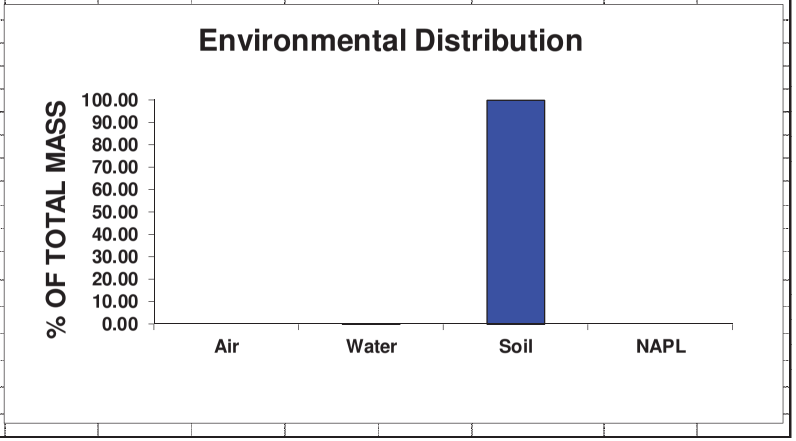
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Benzo(b)fluoranthene
Enter the molecular weight:	252.31
Enter water solubility (mg/L):	1.40E-02
Enter vapor Pressure (mmHg):	5.00E-07
Enter Henry's law constant (atm*m^3/mol):	1.19E-05
Enter Log Kow:	6.57
Enter Log Koc	5.74
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	1.50E-09	**0.00**
Water	3.03E-06	**0.01**
Soil	2.00E-02	**99.99**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



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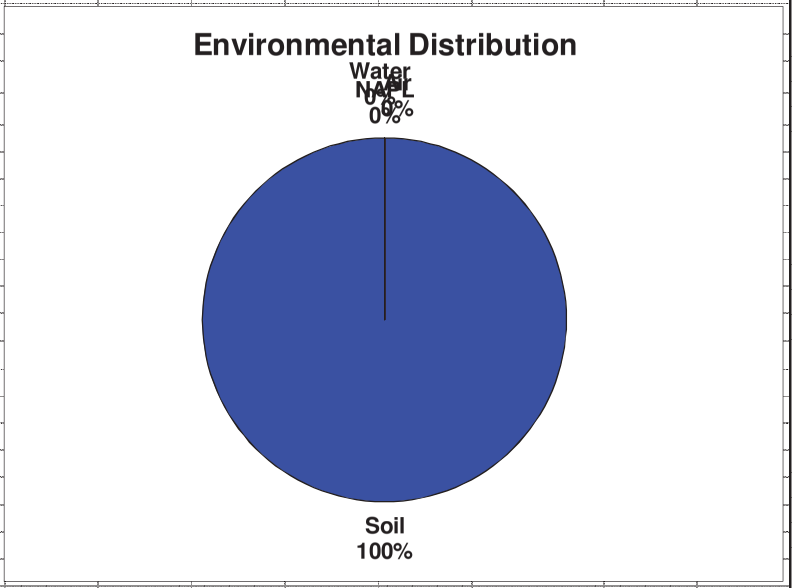
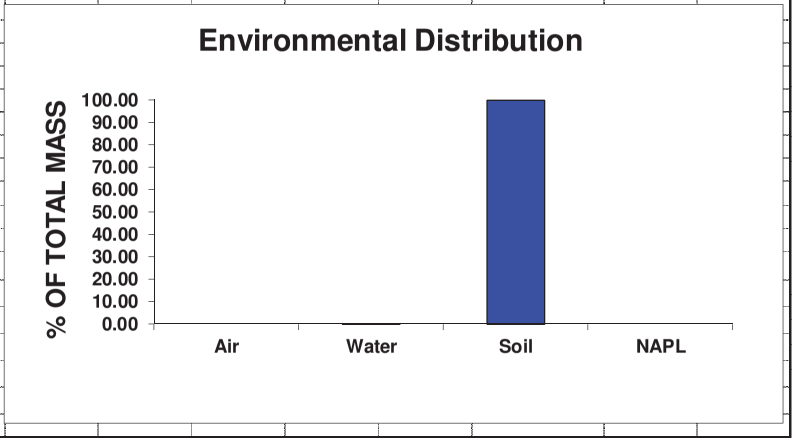
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Benzo(k)fluoranthene
Enter the molecular weight:	252.31
Enter water solubility (mg/L):	4.30E-03
Enter vapor Pressure (mmHg):	9.59E-11
Enter Henry's law constant (atm*m^3/mol):	9.94E-05
Enter Log Kow:	6.06
Enter Log Koc	5.74
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	1.25E-08	**0.00**
Water	3.03E-06	**0.01**
Soil	2.00E-02	**99.99**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



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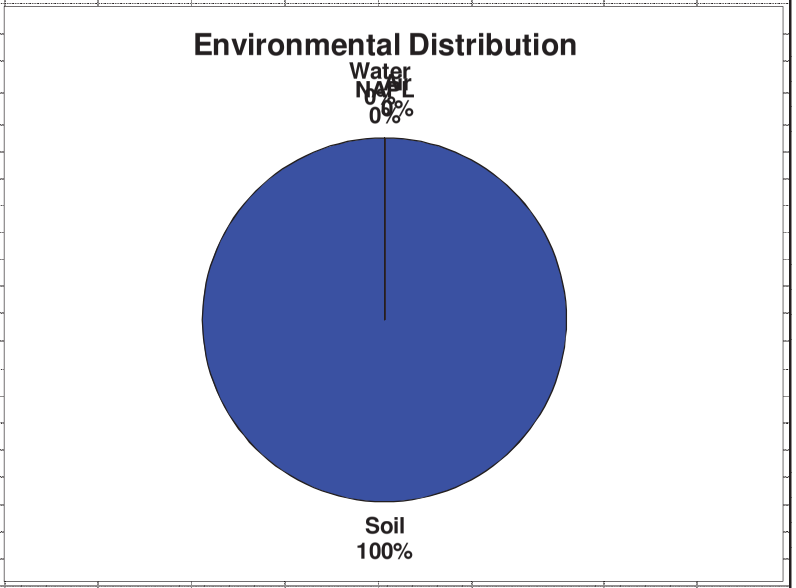
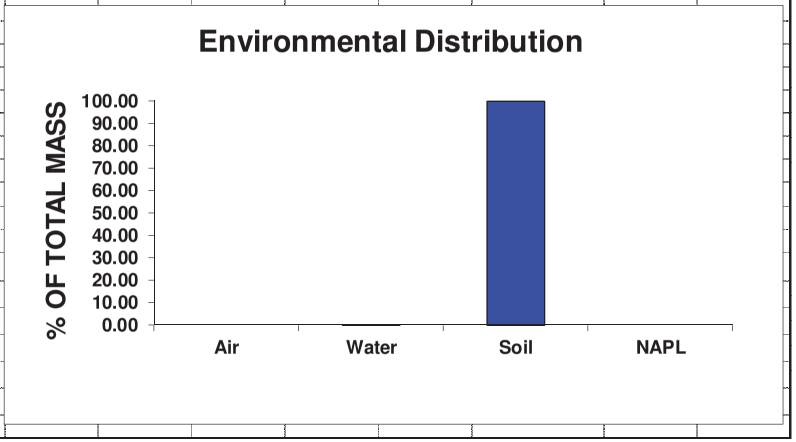
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Benzo(a)pyrene
Enter the molecular weight:	252.3
Enter water solubility (mg/L):	3.80E-03
Enter vapor Pressure (mmHg):	5.49E-09
Enter Henry's law constant (atm*m^3/mol):	1.80E-05
Enter Log Kow:	6.06
Enter Log Koc	6.74
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	2.27E-10	**0.00**
Water	3.03E-07	**0.00**
Soil	2.00E-02	**100.00**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



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LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Indeno(1,2,3-cd)pyrene
Enter the molecular weight:	276.34
Enter water solubility (mg/L):	5.30E-04
Enter vapor Pressure (mmHg):	1.00E-10
Enter Henry's law constant (atm*m^3/mol):	6.95E-08
Enter Log Kow:	6.5
Enter Log Koc	6.2
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00

RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	3.04E-12	**0.00**
Water	1.05E-06	**0.00**
Soil	2.00E-02	**100.00**
NAPL	0.00E+00	**0.00**
	Sum=	100.0

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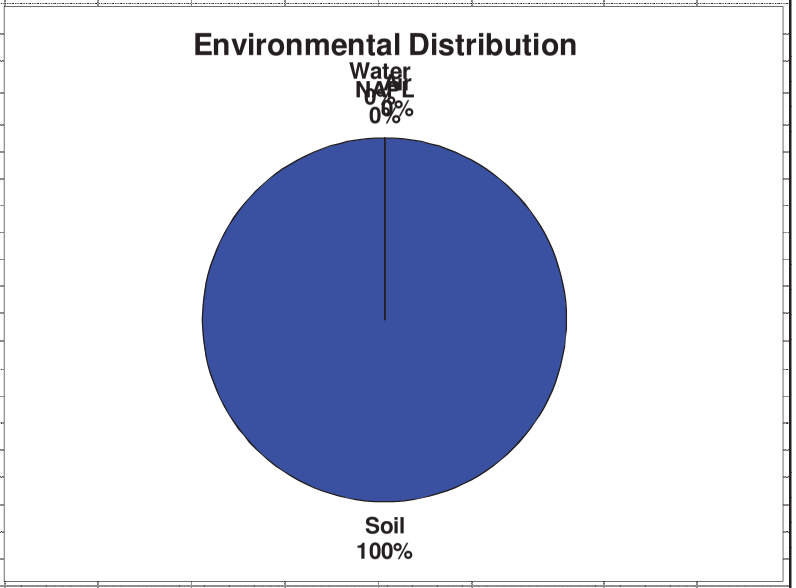
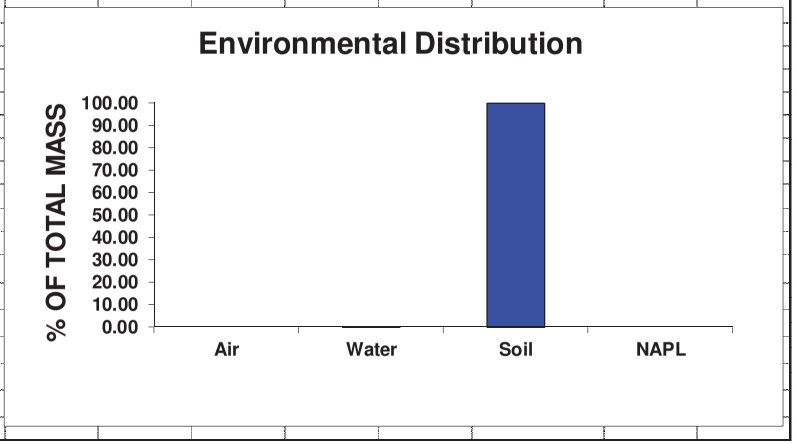
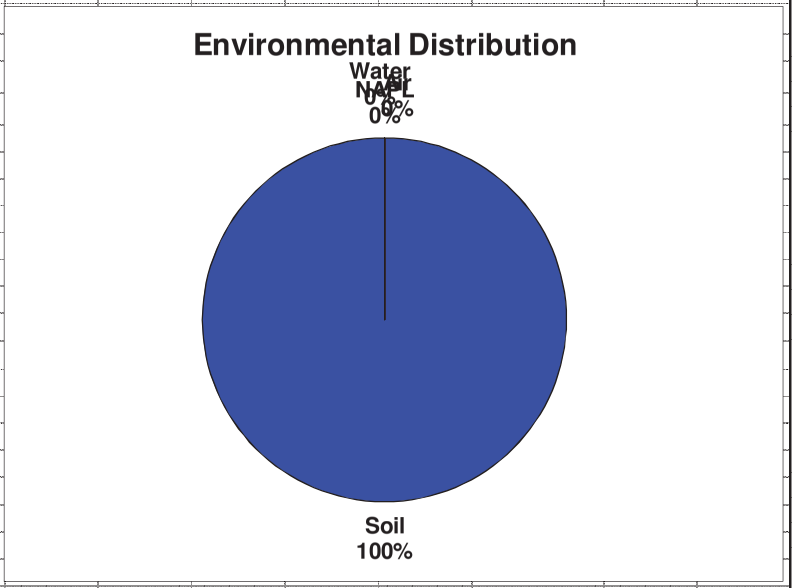




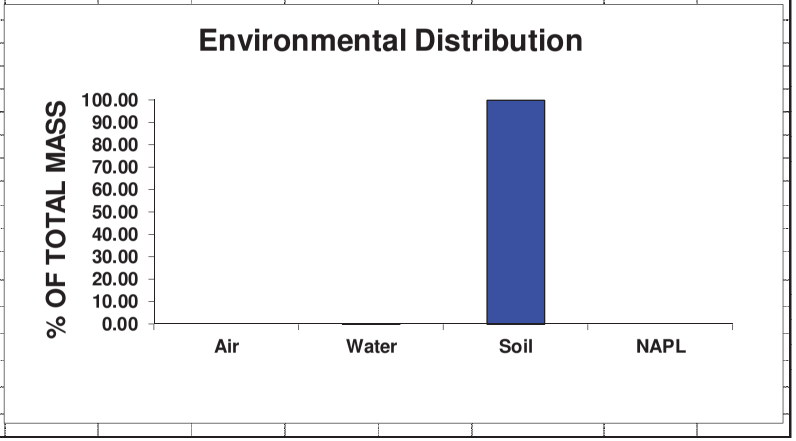
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	dibenz(a,h)anthracene
Enter the molecular weight:	278.35
Enter water solubility (mg/L):	2.50E-03
Enter vapor Pressure (mmHg):	1.00E-10
Enter Henry's law constant (atm*m^3/mol):	7.33E-08
Enter Log Kow:	6.8
Enter Log Koc	6.52
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	1.53E-12	**0.00**
Water	5.03E-07	**0.00**
Soil	2.00E-02	**100.00**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



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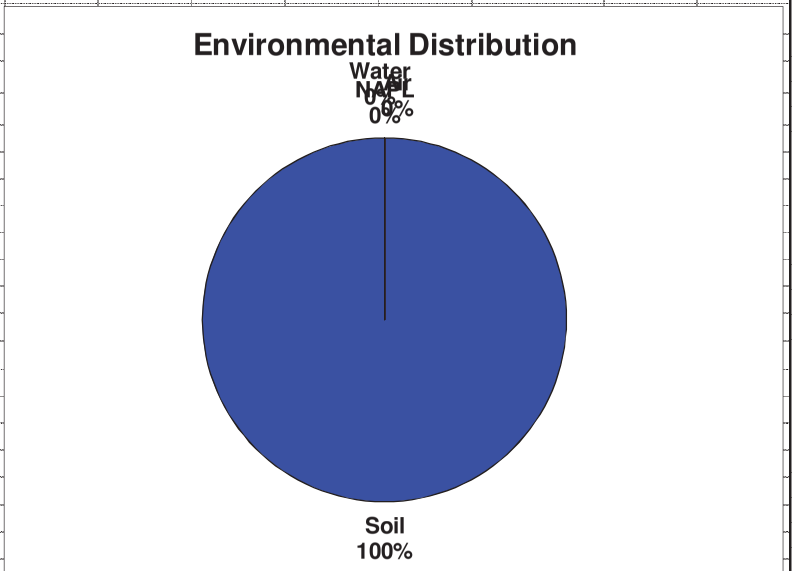
5-Mouse over cells with red corners to view notes about specific parameters

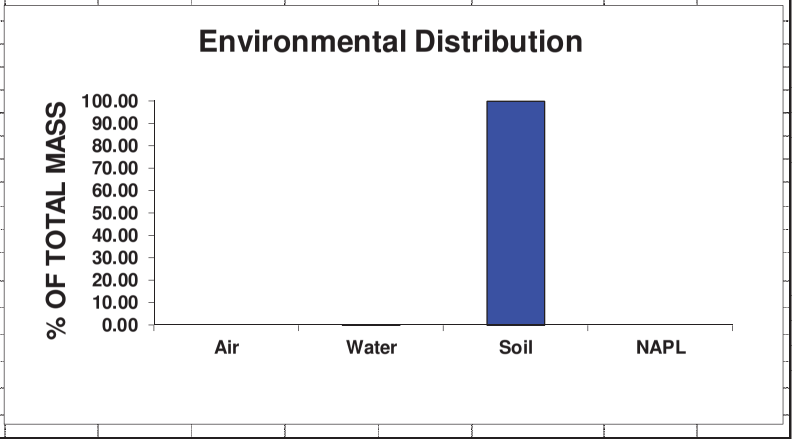
LEVEL 1 FUGACITY CALCULATOR-VERSION 1.2-by Karl Nieman (k.nieman@usu.edu)

CHEMICAL CHARACTERISTICS	
(copy and paste from chemical data tab)	
Enter the compound name:	Benzo(ghi)perylene
Enter the molecular weight:	276.34
Enter water solubility (mg/L):	2.60E-04
Enter vapor Pressure (mmHg):	1.00E-10
Enter Henry's law constant (atm*m^3/mol):	5.34E-08
Enter Log Kow:	6.51
Enter Log Koc	6.2
***bold items are not directly used in the fugacity calculation**	
SITE CHARACTERISTICS	
Enter the following:	
Volume of air (m^3):	25
Volume of Water(m^3):	25
Volume of Soil(m^3):	50
Volume of NAPL(m^3):	0
total volume (m^3) is :	**100**
Enter the % organic carbon in the soil phase:	0.5
Enter the Soil Phase Density (Kg/m^3):	2400
Enter the total mass of the compound in the system (g):	1.00E+00



RESULTS

Compartment	Concentration (mg/L)	% distrubution
Air	2.34E-12	**0.00**
Water	1.05E-06	**0.00**
Soil	2.00E-02	**100.00**
NAPL	0.00E+00	**0.00**
	Sum=	100.0



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Appendix 2 – Study Data Set

Appendix 2 - Table 1 Raw Sample Data PAHs in Soil/Sediment (mg/kg)		Acenaphthene	Acenaphthylene	Anthracene	Benzo(a)anthracene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(g,h,i)perylene	Benzo(k)fluoranthene	Chrysene	Dibenz(a,h)anthracene	Fluoranthene	Fluorene	Indeno(1,2,3-cd)pyrene	1-Methylnaphthalene	2-Methylnaphthalene	Naphthalene	Perylene	Phenanthrene	Pyrene	Total PAH
	Number of Rings	3	3	3	4	5	4+	6	4+	4	5	3+	2+	5+	2	2	2	5	3	4	
	Molecular Weight	154	152	178	228	252	252	276	252	228	278	202	166	276	142	142	128	252	178	202	
	ASTM Ref. Mat.	7.63	263	107	98.1	93.5	66.1	50.5	41.2	66.2	6.93	327	145	55.5	43.9	95	1030		454	240	3215.16
Tar Ponds Sediments	Wash Brook Arm	55.05	49.81	98.12	251.66	129.58	116.84	17.60	97.74	82.39	17.23	237.81	119.47	30.33			498.46		1660.16	237.81	3700.06
	South Pond Phase I	88.82	1321.23	1460.02	1085.30	446.89	693.93	8.33	30.53	255.36	0.00	1179.67	1049.21	188.75			16640.32		1779.22	1310.13	27537.72
	South Pond Phase I	52.61	208.24	260.85	809.94	203.86	163.30	127.14	137.00	128.23	30.69	401.14	356.20	73.43			2938.38		4526.48	486.62	10904.10
	South Pond Phase I	252.57	206.48	247.04	669.23	223.08	88.49	25.81	73.74	127.21	7.37	381.63	529.11	14.75			11122.44		4057.76	353.97	18380.69
	North Pond Phase II	65.22	32.07	105.98	159.79	54.35	57.61	7.61	79.89	54.35	15.76	151.64	136.96	26.09			2651.19		1661.48	144.03	5404.02
	North Pond Phase II	27.00	109.16	164.33	571.64	267.63	217.15	294.62	181.94	142.03	37.56	354.49	164.33	111.51			5584.94		3010.80	422.57	11661.70
	North Pond Phase II	37.58	230.28	251.47	847.88	290.98	231.24	178.25	176.32	193.66	28.91	505.84	269.78	97.31			1140.78		4387.78	687.94	9555.99
	North Pond Phase III	6.65	18.22	53.50	194.63	72.88	65.36	34.13	54.95	44.83	5.49	104.11	48.01	19.09			1128.46		894.50	128.12	2872.91
	North Pond Phase III	19.62	41.94	133.93	479.57	203.60	88.61	39.91	73.73	104.17	16.23	294.23	123.10	67.64			2327.49		2355.90	334.82	6704.48
	North Pond Phase III	20.64	9.56	78.73	204.09	10.70	5.73	0.00	0.00	36.69	0.00	195.30	56.18	0.00			1428.28		1529.56	241.17	3816.65
Urban Background Soil	Urban Soil 1	1.87	0.03	0.86	2.54	2.33	2.91	0.75	1.02	2.24	0.27	6.50	1.06	1.01	0.24	0.33	0.47	-	7.21	4.60	36.24
	Urban Soil 2	0.14	0.11	0.03	0.46	0.45	0.58	0.20	0.22	0.41	0.08	0.80	0.06	0.26	0.03	0.03	0.03	-	0.45	0.65	4.97
	Urban Soil 3	0.31	0.29	0.03	1.25	1.26	1.91	0.56	0.70	1.39	0.20	2.51	0.07	0.73	0.14	0.22	0.15	-	1.36	2.06	15.14
	Urban Soil 4	0.59	0.38	0.03	2.00	1.70	1.40	0.70	1.40	1.80	0.14	3.90	0.14	1.00	0.18	0.18	0.27	0.31	1.80	3.00	20.92
	Urban Soil 5	1.40	1.80	0.39	10.00	11.00	8.20	6.00	8.20	9.70	1.30	19.00	2.00	7.70	0.77	0.97	3.10	2.60	12.00	16.00	122.13
	Urban Soil 6	8.60	1.70	3.10	15.00	10.00	8.00	3.90	8.00	14.00	1.10	35.00	4.80	5.70	1.50	1.20	1.40	1.90	28.00	28.00	180.90
	Urban Soil 7	2.10	0.28	0.60	3.00	2.20	1.50	0.67	1.50	2.60	0.15	6.90	1.30	1.00	0.48	0.33	0.27	0.30	7.20	5.00	37.38
	Urban Soil 8	1.10	0.59	0.13	2.80	2.70	2.30	1.10	2.30	3.30	0.21	7.40	0.46	1.40	0.37	0.36	0.70	0.39	4.30	5.90	37.81
	Urban Soil 9	0.15	0.14	0.03	0.61	0.67	0.97	0.43	0.36	0.62	0.14	1.03	0.03	0.52	0.39	0.61	0.40	-	0.50	0.96	8.55
	Urban Soil 10	0.67	0.69	0.07	2.42	2.76	3.72	1.26	1.32	2.41	0.40	4.67	0.33	1.74	0.10	0.11	0.14	-	2.93	3.79	29.53
	Urban Soil 11	2.12	0.31	0.66	5.50	4.64	6.00	1.96	2.32	5.24	0.74	11.00	0.83	2.62	0.38	0.63	0.49	-	8.07	9.02	62.53
	Urban Soil 12	1.30	0.12	0.09	5.20	3.20	3.10	1.30	3.10	4.20	0.38	9.10	0.32	1.80	0.54	0.65	0.68	0.69	5.10	7.30	48.17
	Urban Soil 13	0.69	0.32	0.16	2.14	2.26	3.16	1.13	1.08	2.28	0.38	4.54	0.35	1.48	0.28	0.38	0.26	-	3.31	3.74	27.94
Harbour Sediment Traps	MARSED-1-1 TRAP	0.04	0.01	0.13	0.42	0.42	0.38	0.32	0.45	0.33	0.07	0.70	0.09	0.31	0.19	0.21	0.19	0.12	0.47	0.66	5.51
	MARSED-1-2 TRAP	0.58	0.25	2.10	3.40	4.20	3.60	2.30	3.80	3.20	0.85	5.40	1.10	2.80	1.10	1.50	2.30	0.99	4.40	5.70	49.57
	MARSED-1-3 TRAP	0.23	0.11	1.10	2.50	2.80	2.70	1.90	2.20	2.30	0.62	4.10	0.56	2.20	0.47	0.63	1.30	0.77	2.50	3.60	32.59
	MARSED-1-4 TRAP	0.35	0.23	1.90	3.60	4.50	3.90	2.90	3.90	3.50	1.00	5.50	0.84	3.50	0.75	1.00	2.40	1.30	3.40	4.80	49.27
	MARSED-2-4 TRAP	0.19	0.19	1.20	2.30	3.20	1.30	1.60	1.60	2.10	0.52	4.30	0.41	1.60	0.29	0.32	0.96	0.81	2.50	3.80	29.19
	MARSED-3-1 TRAP	0.14	0.15	0.82	1.50	2.30	0.90	1.30	1.20	1.50	0.45	2.80	0.27	1.20	0.21	0.29	0.53	0.47	2.00	2.50	20.53
	MARSED-4-1 TRAP	0.08	0.06	0.44	0.69	0.80	0.27	0.48	0.49	0.70	0.15	1.30	0.16	0.44	0.19	0.24	0.27	0.24	0.97	1.20	9.17
Harbour Sediment Grabs	MARSED-1-1 (2010)	0.30	0.21	1.60	3.10	4.40	3.90	2.60	3.70	3.10	0.87	4.80	0.67	3.10	0.72	0.98	2.10	1.20	3.00	4.60	44.95
	MARSED-1-1 (2012)	0.53	0.35	3.20	5.30	6.80	5.30	4.00	6.10	5.10	1.30	11.00	1.20	4.50	0.85	1.20	3.80	1.90	5.40	7.80	75.63
	MARSED 1-4 (2010)	0.21	0.11	1.00	1.80	2.00	1.50	1.30	2.00	1.80	0.40	3.10	0.42	1.50	0.60	0.82	1.10	0.55	2.00	2.80	25.01
	MARSED-1-4 (2012)	0.03	0.01	0.15	0.37	0.32	0.33	0.23	0.35	0.26	0.06	0.66	0.09	0.25	0.21	0.25	0.20	0.10	0.37	0.56	4.79
	MARSED 2-4 (2010)	0.16	0.08	0.83	1.90	2.00	1.90	1.40	1.90	1.60	0.44	3.20	0.45	1.60	0.40	0.54	1.10	0.59	1.80	2.60	24.49
	MARSED-2-4 (2012)	0.15	0.33	1.10	1.60	2.70	2.30	1.50	1.20	1.60	0.43	3.00	0.26	1.50	0.33	0.10	0.58	0.66	1.60	2.60	23.54
	MARSED-3-2 (2010)	0.29	0.67	1.80	2.80	4.10	3.70	2.40	2.30	2.70	0.79	5.10	0.54	2.40	0.46	0.19	1.20	0.97	2.80	4.50	39.71
	MARSED-3-2 (2012)	0.12	0.15	0.60	0.70	0.83	0.70	0.57	0.41	0.71	0.16	1.40	0.14	0.57	0.20	0.08	0.22	0.19	1.10	1.20	10.05
	MARSED-4-1 (2010)	0.02	0.02	0.09	0.15	0.16	0.10	0.12	0.07	0.18	0.03	0.33	0.03	0.11	0.11	0.03	0.07	0.07	0.22	0.27	2.18
	MARSED-4-1 (2012)	0.11	0.16	0.72	0.96	1.30	1.10	0.83	0.56	1.00	0.23	2.00	0.15	0.85	0.22	0.08	0.40	0.31	1.10	1.60	13.68
Coal Sediment	COAL-1	0.52	1.30	3.70	6.10	10.00	6.60	5.60	4.90	6.30	1.60	9.80	1.30	5.80	0.78	1.30	4.40	2.10	6.10	12.00	90.20
	COAL-2	0.65	2.20	4.80	9.50	18.00	9.00	11.00	6.30	10.00	2.30	15.00	1.60	11.00	0.90	1.30	3.30	4.00	8.90	23.00	142.75
Slo-Corer Sediments	MARSED-4-1 SC	0.58	0.25	2.10	3.40	4.20	3.60	2.30	3.80	3.20	0.85	5.40	1.10	2.80	1.10	1.50	2.30	0.99	4.40	5.70	49.57
	MARSED-1-3 SC	0.23	0.11	1.10	2.50	2.80	2.70	1.90	2.20	2.30	0.62	4.10	0.56	2.20	0.47	0.63	1.30	0.77	2.50	3.60	32.59
	MARSED-1-2 SC	0.35	0.23	1.90	3.60	4.50	3.90	2.90	3.90	3.50	1.00	5.50	0.84	3.50	0.75	1.00	2.40	1.30	3.40	4.80	49.27
Upstream Sediments	WB-1-SED (2010)	0.02	0.01	0.04	0.11	0.09	0.09	0.07	0.04	0.14	0.02	0.30	0.02	0.05	0.05	0.05	0.03	0.03	0.20	0.23	1.59
	WB-1-SED (2011)	0.02	0.02	0.17	0.37	0.34	0.48	0.32	0.22	0.49	0.07	0.91	0.05	0.23	0.03	0.03	0.04	0.11	0.54	0.70	5.14
	WB-1-SED (2012)	0.01	0.01	0.03	0.11	0.09	0.07	0.07	0.05	0.12	0.02	0.22	0.01	0.05	0.02	0.02	0.03	0.03	0.12	0.18	1.25
	CB-SED (2010)	0.10	0.04	0.22	0.59	0.53	0.56	0.50	0.38	0.94	0.11	1.60	0.11	0.35	0.07	0.10	0.09	0.14	0.91	1.30	8.64
	CB-SED (2011)	0.54	0.08	1.40	2.10	1.50	1.60	0.66	1.60	1.50	0.14	5.30	0.59	0.65	0.17	0.12	0.17	0.35	4.90	3.80	27.17
	CB-SED (2012)	0.01	0.02	0.05	0.11	0.12	0.16	0.12	0.15	0.11	0.02	0.24	0.02	0.07	0.09	0.07	0.11	0.05	0.17	0.25	1.94

Appendix 2 - Table 2 Normalized Data Set Mass Fractions		Naphthalene	2-Methylnaphthalene	1-Methylnaphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Perylene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene	Dibenz(a,h)anthracene	Benzo(g,h,i)perylene
	ASTM Ref. Mat.	0.32	0.03	0.01	0.08	0.00	0.05	0.14	0.03	0.10	0.07	0.03	0.02	0.02	0.01	0.01	0.03	0.02	0.00	0.02
Tar Ponds Sediments	Wash Brook Arm	0.13	0.00	0.00	0.01	0.01	0.03	0.45	0.03	0.06	0.06	0.07	0.02	0.03	0.03	0.00	0.04	0.01	0.00	0.00
	South Pond Phase I	0.60	0.00	0.00	0.05	0.00	0.04	0.06	0.05	0.04	0.05	0.04	0.01	0.03	0.00	0.00	0.02	0.01	0.00	0.00
	South Pond Phase I	0.27	0.00	0.00	0.02	0.00	0.03	0.42	0.02	0.04	0.04	0.07	0.01	0.01	0.01	0.00	0.02	0.01	0.00	0.01
	South Pond Phase I	0.61	0.00	0.00	0.01	0.01	0.03	0.22	0.01	0.02	0.02	0.04	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	North Pond Phase II	0.49	0.00	0.00	0.01	0.01	0.03	0.31	0.02	0.03	0.03	0.03	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00
	North Pond Phase II	0.48	0.00	0.00	0.01	0.00	0.01	0.26	0.01	0.03	0.04	0.05	0.01	0.02	0.02	0.00	0.02	0.01	0.00	0.03
	North Pond Phase II	0.12	0.00	0.00	0.02	0.00	0.03	0.46	0.03	0.05	0.07	0.09	0.02	0.02	0.02	0.00	0.03	0.01	0.00	0.02
	North Pond Phase III	0.39	0.00	0.00	0.01	0.00	0.02	0.31	0.02	0.04	0.04	0.07	0.02	0.02	0.02	0.00	0.03	0.01	0.00	0.01
	North Pond Phase III	0.35	0.00	0.00	0.01	0.00	0.02	0.35	0.02	0.04	0.05	0.07	0.02	0.01	0.01	0.00	0.03	0.01	0.00	0.01
	North Pond Phase III	0.37	0.00	0.00	0.00	0.01	0.01	0.40	0.02	0.05	0.06	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Urban Background Soil	Urban Soil 1	0.01	0.01	0.01	0.00	0.05	0.03	0.20	0.02	0.18	0.13	0.07	0.06	0.08	0.03	0.00	0.06	0.03	0.01	0.02
	Urban Soil 2	0.01	0.01	0.01	0.02	0.03	0.01	0.09	0.01	0.16	0.13	0.09	0.08	0.12	0.05	0.00	0.09	0.05	0.02	0.04
	Urban Soil 3	0.01	0.01	0.01	0.02	0.02	0.00	0.09	0.00	0.17	0.14	0.08	0.09	0.13	0.05	0.00	0.08	0.05	0.01	0.04
	Urban Soil 4	0.01	0.01	0.01	0.02	0.03	0.01	0.09	0.00	0.19	0.14	0.10	0.09	0.07	0.07	0.01	0.08	0.05	0.01	0.03
	Urban Soil 5	0.03	0.01	0.01	0.01	0.01	0.02	0.10	0.00	0.16	0.13	0.08	0.08	0.07	0.07	0.02	0.09	0.06	0.01	0.05
	Urban Soil 6	0.01	0.01	0.01	0.01	0.05	0.03	0.15	0.02	0.19	0.15	0.08	0.08	0.04	0.04	0.01	0.06	0.03	0.01	0.02
	Urban Soil 7	0.01	0.01	0.01	0.01	0.06	0.03	0.19	0.02	0.18	0.13	0.08	0.07	0.04	0.04	0.01	0.06	0.03	0.00	0.02
	Urban Soil 8	0.02	0.01	0.01	0.02	0.03	0.01	0.11	0.00	0.20	0.16	0.07	0.09	0.06	0.06	0.01	0.07	0.04	0.01	0.03
	Urban Soil 9	0.05	0.07	0.05	0.02	0.02	0.00	0.06	0.00	0.12	0.11	0.07	0.07	0.11	0.04	0.00	0.08	0.06	0.02	0.05
	Urban Soil 10	0.00	0.00	0.00	0.02	0.02	0.01	0.10	0.00	0.16	0.13	0.08	0.08	0.13	0.04	0.00	0.09	0.06	0.01	0.04
	Urban Soil 11	0.01	0.01	0.01	0.00	0.03	0.01	0.13	0.01	0.18	0.14	0.09	0.08	0.10	0.04	0.00	0.07	0.04	0.01	0.03
	Urban Soil 12	0.01	0.01	0.01	0.00	0.03	0.01	0.11	0.00	0.19	0.15	0.11	0.09	0.06	0.06	0.01	0.07	0.04	0.01	0.03
	Urban Soil 13	0.01	0.01	0.01	0.01	0.02	0.01	0.12	0.01	0.16	0.13	0.08	0.08	0.11	0.04	0.00	0.08	0.05	0.01	0.04
Harbour Sediment Traps	MARSED-1-1 TRAP	0.03	0.04	0.03	0.00	0.00	0.02	0.09	0.02	0.13	0.12	0.08	0.06	0.07	0.08	0.02	0.08	0.06	0.01	0.06
	MARSED-1-2 TRAP	0.05	0.03	0.02	0.01	0.02	0.02	0.09	0.04	0.11	0.11	0.07	0.06	0.07	0.08	0.02	0.08	0.06	0.02	0.05
	MARSED-1-3 TRAP	0.04	0.02	0.01	0.00	0.01	0.02	0.08	0.03	0.13	0.11	0.08	0.07	0.08	0.07	0.02	0.09	0.07	0.02	0.06
	MARSED-1-4 TRAP	0.05	0.02	0.02	0.00	0.01	0.02	0.07	0.04	0.11	0.10	0.07	0.07	0.08	0.08	0.03	0.09	0.07	0.02	0.06
	MARSED-2-4 TRAP	0.03	0.01	0.01	0.01	0.01	0.01	0.09	0.04	0.15	0.13	0.08	0.07	0.04	0.05	0.03	0.11	0.05	0.02	0.05
	MARSED-3-1 TRAP	0.03	0.01	0.01	0.01	0.01	0.01	0.10	0.04	0.14	0.12	0.07	0.07	0.04	0.06	0.02	0.11	0.06	0.02	0.06
	MARSED-4-1 TRAP	0.03	0.03	0.02	0.01	0.00	0.02	0.11	0.05	0.14	0.13	0.08	0.08	0.03	0.05	0.03	0.09	0.05	0.02	0.05
Harbour Sediment Grabs	MARSED-1-1 (2010)	0.05	0.02	0.02	0.00	0.01	0.01	0.07	0.04	0.11	0.10	0.07	0.07	0.09	0.08	0.03	0.10	0.07	0.02	0.06
	MARSED-1-1 (2012)	0.05	0.02	0.01	0.00	0.02	0.02	0.07	0.04	0.15	0.10	0.07	0.07	0.07	0.08	0.03	0.09	0.06	0.02	0.05
	MARSED 1-4 (2010)	0.04	0.03	0.02	0.00	0.01	0.02	0.08	0.04	0.12	0.11	0.07	0.07	0.06	0.08	0.02	0.08	0.06	0.02	0.05
	MARSED-1-4 (2012)	0.04	0.05	0.04	0.00	0.00	0.02	0.08	0.03	0.14	0.12	0.08	0.05	0.07	0.07	0.02	0.07	0.05	0.01	0.05
	MARSED 2-4 (2010)	0.04	0.02	0.02	0.00	0.01	0.02	0.07	0.03	0.13	0.11	0.08	0.07	0.08	0.08	0.02	0.08	0.07	0.02	0.06
	MARSED-2-4 (2012)	0.02	0.00	0.01	0.01	0.01	0.01	0.07	0.05	0.13	0.11	0.07	0.07	0.10	0.05	0.03	0.11	0.06	0.02	0.06
	MARSED-3-2 (2010)	0.03	0.00	0.01	0.02	0.01	0.01	0.07	0.05	0.13	0.11	0.07	0.07	0.09	0.06	0.02	0.10	0.06	0.02	0.06
	MARSED-3-2 (2012)	0.02	0.01	0.02	0.01	0.00	0.01	0.11	0.06	0.14	0.12	0.07	0.07	0.07	0.04	0.02	0.08	0.06	0.02	0.06
	MARSED-4-1 (2010)	0.03	0.01	0.05	0.01	0.00	0.01	0.10	0.04	0.15	0.12	0.07	0.08	0.05	0.03	0.03	0.07	0.05	0.01	0.06
	MARSED-4-1 (2012)	0.03	0.01	0.02	0.01	0.00	0.01	0.08	0.05	0.15	0.12	0.07	0.07	0.08	0.04	0.02	0.10	0.06	0.02	0.06
Coal Sediment	COAL-1	0.05	0.01	0.01	0.01	0.02	0.01	0.07	0.04	0.11	0.13	0.07	0.07	0.07	0.05	0.02	0.11	0.06	0.02	0.06
	COAL-2	0.02	0.01	0.01	0.02	0.02	0.01	0.06	0.03	0.11	0.16	0.07	0.07	0.06	0.04	0.03	0.13	0.08	0.02	0.08
Slo-Corer Sediments	MARSED-4-1 SC	0.05	0.03	0.02	0.01	0.02	0.02	0.09	0.04	0.11	0.11	0.07	0.06	0.07	0.08	0.02	0.08	0.06	0.02	0.05
	MARSED-1-3 SC	0.04	0.02	0.01	0.00	0.01	0.02	0.08	0.03	0.13	0.11	0.08	0.07	0.08	0.07	0.02	0.09	0.07	0.02	0.06
	MARSED-1-2 SC	0.05	0.02	0.02	0.00	0.01	0.02	0.07	0.04	0.11	0.10	0.07	0.07	0.08	0.08	0.03	0.09	0.07	0.02	0.06
Upstream Sediments	WB-1-SED (2010)	0.02	0.03	0.03	0.01	0.00	0.01	0.13	0.03	0.19	0.14	0.07	0.09	0.06	0.03	0.02	0.06	0.03	0.01	0.04
	WB-1-SED (2011)	0.01	0.01	0.01	0.00	0.00	0.01	0.11	0.03	0.18	0.14	0.07	0.10	0.09	0.04	0.02	0.07	0.04	0.01	0.06
	WB-1-SED (2012)	0.02	0.02	0.01	0.00	0.00	0.01	0.10	0.02	0.18	0.14	0.09	0.10	0.06	0.04	0.02	0.07	0.04	0.01	0.05
	CB-SED (2010)	0.01	0.01	0.01	0.00	0.00	0.01	0.11	0.03	0.19	0.15	0.07	0.11	0.06	0.04	0.02	0.06	0.04	0.01	0.06
	CB-SED (2011)	0.01	0.00	0.01	0.00	0.02	0.02	0.18	0.05	0.20	0.14	0.08	0.06	0.06	0.06	0.01	0.06	0.02	0.01	0.02
	CB-SED (2012)	0.06	0.04	0.05	0.01	0.00	0.01	0.09	0.02	0.12	0.13	0.06	0.06	0.08	0.08	0.03	0.06	0.04	0.01	0.06

Appendix 2 - Table 3 Normalized Data Set Molar Fractions		Naphthalene	2-Methylnaphthalene	1-Methylnaphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo(a)anthracene	Chrysene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Perylene	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene	Dibenz(a,h)anthracene	Benzo(g,h,i)perylene
	ASTM Ref. Mat.	0.41	0.03	0.02	0.09	0.00	0.04	0.13	0.03	0.08	0.06	0.02	0.01	0.01	0.01	0.00	0.02	0.01	0.00	0.01
Tar Ponds Sediments	Wash Brook Arm	0.19	0.00	0.00	0.02	0.02	0.03	0.45	0.03	0.06	0.06	0.05	0.02	0.02	0.02	0.00	0.02	0.01	0.00	0.00
	South Pond Phase I	0.69	0.00	0.00	0.05	0.00	0.03	0.05	0.04	0.03	0.03	0.03	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00
	South Pond Phase I	0.35	0.00	0.00	0.02	0.01	0.03	0.39	0.02	0.03	0.04	0.05	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.01
	South Pond Phase I	0.69	0.00	0.00	0.01	0.01	0.03	0.18	0.01	0.01	0.01	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	North Pond Phase II	0.58	0.00	0.00	0.01	0.01	0.02	0.26	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00
	North Pond Phase II	0.59	0.00	0.00	0.01	0.00	0.01	0.23	0.01	0.02	0.03	0.03	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.01
	North Pond Phase II	0.17	0.00	0.00	0.03	0.00	0.03	0.47	0.03	0.05	0.06	0.07	0.02	0.02	0.01	0.00	0.02	0.01	0.00	0.01
	North Pond Phase III	0.50	0.00	0.00	0.01	0.00	0.02	0.28	0.02	0.03	0.04	0.05	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.01
	North Pond Phase III	0.44	0.00	0.00	0.01	0.00	0.02	0.32	0.02	0.04	0.04	0.05	0.01	0.01	0.01	0.00	0.02	0.01	0.00	0.00
	North Pond Phase III	0.46	0.00	0.00	0.00	0.01	0.01	0.36	0.02	0.04	0.05	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Urban Backgroun d Soil	Urban Soil 1	0.02	0.01	0.01	0.00	0.07	0.04	0.23	0.03	0.18	0.13	0.06	0.05	0.06	0.02	0.00	0.05	0.02	0.01	0.02
	Urban Soil 2	0.01	0.01	0.01	0.03	0.04	0.02	0.11	0.01	0.17	0.14	0.09	0.08	0.10	0.04	0.00	0.08	0.04	0.01	0.03
	Urban Soil 3	0.02	0.02	0.01	0.03	0.03	0.01	0.11	0.00	0.18	0.14	0.08	0.09	0.11	0.04	0.00	0.07	0.04	0.01	0.03
	Urban Soil 4	0.02	0.01	0.01	0.03	0.04	0.01	0.10	0.00	0.20	0.15	0.09	0.08	0.06	0.06	0.01	0.07	0.04	0.01	0.03
	Urban Soil 5	0.04	0.01	0.01	0.02	0.02	0.02	0.12	0.00	0.16	0.14	0.08	0.07	0.06	0.06	0.02	0.08	0.05	0.01	0.04
	Urban Soil 6	0.01	0.01	0.01	0.01	0.06	0.03	0.18	0.02	0.19	0.16	0.07	0.07	0.04	0.04	0.01	0.04	0.02	0.00	0.02
	Urban Soil 7	0.01	0.01	0.02	0.01	0.07	0.04	0.22	0.02	0.18	0.13	0.07	0.06	0.03	0.03	0.01	0.05	0.02	0.00	0.01
	Urban Soil 8	0.03	0.01	0.01	0.02	0.04	0.02	0.13	0.00	0.20	0.16	0.07	0.08	0.05	0.05	0.01	0.06	0.03	0.00	0.02
	Urban Soil 9	0.07	0.10	0.06	0.02	0.02	0.00	0.07	0.00	0.12	0.11	0.06	0.06	0.09	0.03	0.00	0.06	0.04	0.01	0.04
	Urban Soil 10	0.01	0.01	0.01	0.03	0.03	0.01	0.12	0.00	0.17	0.14	0.08	0.08	0.11	0.04	0.00	0.08	0.05	0.01	0.03
	Urban Soil 11	0.01	0.01	0.01	0.01	0.05	0.02	0.15	0.01	0.18	0.15	0.08	0.08	0.08	0.03	0.00	0.06	0.03	0.01	0.02
	Urban Soil 12	0.02	0.02	0.02	0.00	0.04	0.01	0.13	0.00	0.20	0.16	0.10	0.08	0.05	0.05	0.01	0.06	0.03	0.01	0.02
	Urban Soil 13	0.02	0.02	0.02	0.02	0.03	0.02	0.14	0.01	0.17	0.14	0.07	0.08	0.10	0.03	0.00	0.07	0.04	0.01	0.03
Harbour Sediment Traps	MARSED-1-1 TRAP	0.06	0.06	0.05	0.00	0.00	0.02	0.10	0.03	0.13	0.12	0.07	0.05	0.06	0.07	0.02	0.06	0.04	0.01	0.04
	MARSED-1-2 TRAP	0.07	0.04	0.03	0.01	0.03	0.03	0.10	0.05	0.11	0.12	0.06	0.06	0.06	0.06	0.02	0.07	0.04	0.01	0.03
	MARSED-1-3 TRAP	0.07	0.03	0.02	0.00	0.01	0.02	0.09	0.04	0.13	0.12	0.07	0.07	0.07	0.06	0.02	0.07	0.05	0.01	0.04
	MARSED-1-4 TRAP	0.08	0.03	0.02	0.01	0.02	0.02	0.08	0.05	0.12	0.10	0.07	0.07	0.07	0.07	0.02	0.08	0.05	0.02	0.04
	MARSED-2-4 TRAP	0.05	0.02	0.01	0.01	0.01	0.02	0.10	0.05	0.15	0.14	0.07	0.07	0.04	0.05	0.02	0.09	0.04	0.01	0.04
	MARSED-3-1 TRAP	0.04	0.02	0.02	0.01	0.01	0.02	0.12	0.05	0.14	0.13	0.07	0.07	0.04	0.05	0.02	0.09	0.05	0.02	0.05
	MARSED-4-1 TRAP	0.05	0.04	0.03	0.01	0.00	0.02	0.12	0.06	0.15	0.13	0.07	0.07	0.02	0.04	0.02	0.07	0.04	0.01	0.04
Harbour Sediment Grabs	MARSED-1-1 (2010)	0.08	0.03	0.02	0.01	0.01	0.02	0.08	0.04	0.11	0.11	0.06	0.06	0.07	0.07	0.02	0.08	0.05	0.01	0.04
	MARSED-1-1 (2012)	0.08	0.02	0.02	0.01	0.03	0.02	0.08	0.05	0.15	0.11	0.06	0.06	0.06	0.07	0.02	0.07	0.04	0.01	0.04
	MARSED 1-4 (2010)	0.07	0.05	0.04	0.01	0.01	0.02	0.09	0.05	0.13	0.12	0.07	0.07	0.05	0.07	0.02	0.07	0.05	0.01	0.04
	MARSED-1-4 (2012)	0.07	0.08	0.06	0.00	0.00	0.02	0.09	0.04	0.14	0.12	0.07	0.05	0.06	0.06	0.02	0.05	0.04	0.01	0.04
	MARSED 2-4 (2010)	0.07	0.03	0.02	0.00	0.01	0.02	0.09	0.04	0.14	0.11	0.07	0.06	0.06	0.06	0.02	0.07	0.05	0.01	0.04
	MARSED-2-4 (2012)	0.04	0.01	0.02	0.02	0.01	0.01	0.08	0.06	0.14	0.12	0.06	0.06	0.08	0.04	0.02	0.10	0.05	0.01	0.05
	MARSED-3-2 (2010)	0.05	0.01	0.02	0.02	0.01	0.02	0.08	0.05	0.14	0.12	0.07	0.06	0.08	0.05	0.02	0.09	0.05	0.02	0.05
	MARSED-3-2 (2012)	0.04	0.01	0.03	0.02	0.01	0.02	0.13	0.07	0.15	0.12	0.06	0.07	0.06	0.03	0.02	0.07	0.04	0.01	0.04
	MARSED-4-1 (2010)	0.05	0.02	0.07	0.01	0.00	0.01	0.12	0.05	0.16	0.13	0.06	0.08	0.04	0.03	0.02	0.06	0.04	0.01	0.04
	MARSED-4-1 (2012)	0.05	0.01	0.02	0.02	0.01	0.01	0.10	0.06	0.15	0.12	0.07	0.07	0.07	0.03	0.02	0.08	0.05	0.01	0.05
Coal Sediment	COAL-1	0.08	0.02	0.01	0.02	0.03	0.02	0.08	0.05	0.11	0.14	0.06	0.06	0.06	0.04	0.02	0.09	0.05	0.01	0.05
	COAL-2	0.04	0.01	0.01	0.02	0.03	0.01	0.07	0.04	0.11	0.17	0.06	0.07	0.05	0.04	0.02	0.11	0.06	0.01	0.06
Slo-Corer Sediments	MARSED-4-1 SC	0.07	0.04	0.03	0.01	0.03	0.03	0.10	0.05	0.11	0.12	0.06	0.06	0.06	0.06	0.02	0.07	0.04	0.01	0.03
	MARSED-1-3 SC	0.07	0.03	0.02	0.00	0.01	0.02	0.09	0.04	0.13	0.12	0.07	0.07	0.07	0.06	0.02	0.07	0.05	0.01	0.04
	MARSED-1-2 SC	0.08	0.03	0.02	0.01	0.02	0.02	0.08	0.05	0.12	0.10	0.07	0.07	0.07	0.07	0.02	0.08	0.05	0.02	0.04
Upstream Sediments	WB-1-SED (2010)	0.03	0.05	0.05	0.01	0.00	0.02	0.15	0.03	0.19	0.15	0.06	0.08	0.05	0.02	0.02	0.05	0.02	0.01	0.03
	WB-1-SED (2011)	0.01	0.01	0.01	0.01	0.00	0.01	0.13	0.04	0.19	0.15	0.07	0.09	0.08	0.04	0.02	0.06	0.04	0.01	0.05
	WB-1-SED (2012)	0.04	0.02	0.02	0.01	0.00	0.01	0.12	0.03	0.19	0.15	0.08	0.09	0.05	0.03	0.02	0.06	0.03	0.01	0.04
	CB-SED (2010)	0.02	0.02	0.01	0.01	0.00	0.02	0.13	0.03	0.20	0.16	0.06	0.10	0.06	0.04	0.01	0.05	0.03	0.01	0.04
	CB-SED (2011)	0.01	0.01	0.01	0.00	0.03	0.03	0.21	0.06	0.20	0.14	0.07	0.05	0.05	0.05	0.01	0.04	0.02	0.00	0.02
	CB-SED (2012)	0.09	0.05	0.07	0.01	0.00	0.01	0.10	0.03	0.12	0.13	0.05	0.05	0.07	0.06	0.02	0.05	0.03	0.01	0.05

Appendix 3 – Robust Method of Substituting Data for Non-Detect Results

Appendix 3

March 23, 2012 – Censored data exercise

STPA data up to January 31, 2012 was summarized in a modified table. Most parameters with more than 70% of sample results below detection limits were removed from the working table. Some exceptions such as PAH parameters, aluminum and lead were not removed. The total number of samples as of January 30, 2012 is 246. The following is a list of parameters included in the working table:

Sample Date	
Time	
Tidal Direction	
Na	246
K	246
Ca	246
Mg	246
ALK	246
SO4	244
Cl	246
NH3	179
TURB	221
COND	246
pH	246
HARD	246
BICARB ALK	246
TSS	222
TDS	246
Anion Sum	246
Ion Bal_	246
Langelier Index (@20C)	246

Sat_ pH (@20C)	246
Sat_ pH (@4C)	246
Al	152
Ba	240
B	231
Cd	163
Cr	179
Cu	205
Pb	142
Li	245
Sr	246
U	233
Z	208
Acenaphthene	223
Acenaphthylene	167
Anthracene	182
Fluoranthene	244
Fluorene	214
Phenanthrene	236
Pyrene	241
No. of PAHs Detected	246
Total PAH Conc.	246

CHROMIUM

For the first trial, chromium was used for a run of the Robust Method of using censored data. The original data set included 163 of 246 data points (the remainder were ND). Using only outflow data, 87 of 121 data points were detected concentrations. The remaining ND values were replaced with discreet values below the detection limit, ranging from 0.65 to 0.99 (original RDL was 1 which was later raised to 10 due to dilutions). Normal scores were computed for all

of the concentrations (including modified NDs). A linear regression equation was then developed using only the above-limit observations where the log10 of the concentration as the y variable and the normal scores are the x variables.

Regression Analysis: Log 10 Detects Only versus Modifed Normal Scores

The regression equation is

Log 10 Detects Only = 1.22 + 0.580 Modifed Normal Scores

87 cases used, 34 cases contain missing values

Predictor	Coef	SE Coef	T	P
Constant	1.22250	0.00989	123.57	0.000
Modifed Normal Scores	0.58024	0.01176	49.35	0.000

S = 0.0769294 R-Sq = 96.6% R-Sq(adj) = 96.6%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	14.413	14.413	2435.38	0.000
Residual Error	85	0.503	0.006		
Total	86	14.916			

Unusual Observations

Obs	Modifed Normal Scores	Log 10 Detects Only	Fit	SE Fit	Residual	St Resid
1	-1.68	*	0.24718	0.02654	*	* X
2	-1.60	*	0.29328	0.02565	*	* X
3	-1.53	*	0.33416	0.02487	*	* X
4	-1.47	*	0.37106	0.02417	*	* X
5	-1.41	*	0.40480	0.02353	*	* X
6	-1.36	*	0.43598	0.02294	*	* X
10	-0.54	0.70757	0.90785	0.01443	-0.20028	-2.65R
17	-1.31	*	0.46505	0.02239	*	* X
18	-1.26	*	0.49233	0.02187	*	* X

20	2.21	2.56820	2.50736	0.02216	0.06085	0.83 X
29	-1.21	*	0.51808	0.02139	*	* X
31	-1.17	*	0.54252	0.02094	*	* X
32	-1.13	*	0.56580	0.02050	*	* X
36	2.57	2.64345	2.71097	0.02604	-0.06752	-0.93 X
98	-1.77	*	0.19394	0.02757	*	* X
102	-1.88	*	0.13031	0.02880	*	* X
106	-2.02	*	0.04994	0.03037	*	* X
114	-2.21	*	-0.06236	0.03256	*	* X
116	-0.57	0.38021	0.89386	0.01466	-0.51365	-6.80R
120	-2.57	*	-0.26598	0.03657	*	* X

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large leverage.

Using this regression equation, estimates for the below limit data were extrapolated from the normal scores for the below-limit data (assumed numbers below RDLs). Extrapolated estimates are then retransformed into units of concentration, combined with above-limit actual concentration data, and summary statistics can be computed. This data set now includes all of the actual detected concentrations and estimates for the values below detection, based on the distribution of the detected data.

MTB > Describe 'Cr Outflow with ND Estimators'.

Descriptive Statistics: Cr Outflow with ND Estimators

Variable	N	N*	Mean	SE Mean	StDev	Minimum	Q1	Median
Cr Outflow with ND Estim	121	0	39.14	6.07	66.75	0.54	6.11	16.00

Variable	Q3	Maximum
Cr Outflow with ND Estim	39.00	440.00

It can be seen that the mean concentration for Chromium during outflowing conditions since the beginning of the project is 39.14 ug/L. The standard deviation of the mean is 66.75 which is very

high. This implies a large variability of concentrations of chromium. There appears to be little value in this exercise.

When considering the correlation analysis, these ND estimates cannot be used for correlation. They are only to be used for the assessment of summary statistics based on data distribution. They cannot be used for correlation because of the arbitrary values used to develop the normal scores.

Let's do the exercise for two more parameters and see where we go from there.

Cadmium, Copper, Lead, Zinc, Acenapthene, Acenapthylene and Anthracene

Data was copied into Minitab for outflow only up to January 30, 2012. ND values for the parameters were arbitrarily substituted using the following:

Cadmium: 0.05-0.16

Copper: 0.5-19

Lead: 0.5-9

Zinc: 2-49

Acenapthene: 0.001-0.009

Acenapthylene: 0.001-0.009

Anthracene: 0.001-0.009

Following the same procedure as done previously for Cr, the regression analyses are as follows:

Regression Analysis: Log10 Cd versus NScore Cd

The regression equation is

Log10 Cd = - 0.692 + 0.408 NScore Cd

78 cases used, 43 cases contain missing values

Predictor	Coef	SE Coef	T	P
Constant	-0.69154	0.01910	-36.20	0.000
NScore Cd	0.40814	0.01907	21.41	0.000

S = 0.149335 R-Sq = 85.8% R-Sq(adj) = 85.6%

Analysis of Variance

Source DF SS MS F P

Regression 1 10.219 10.219 458.25 0.000

Residual Error 76 1.695 0.022

Total 77 11.914

Unusual Observations

Obs	NScore Cd	Log10 Cd	Fit	SE Fit	Residual	St Resid
1	-2.57	-1.4949	-1.7385	0.0602	0.2437	1.78 X
2	-1.95	*	-1.4861	0.0490	*	* X
3	-1.77	-1.2676	-1.4150	0.0459	0.1474	1.04 X
4	-2.21	-1.3565	-1.5953	0.0538	0.2388	1.71 X
5	-1.53	*	-1.3164	0.0417	*	* X
7	-1.68	-1.2518	-1.3776	0.0443	0.1258	0.88 X
56	2.57	1.5441	0.3555	0.0434	1.1886	8.32RX
69	-1.53	*	-1.3164	0.0417	*	* X
75	-1.95	*	-1.4861	0.0490	*	* X
79	-1.53	*	-1.3164	0.0417	*	* X

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large leverage.

Regression Analysis: Log10 Cu versus NScore Cu

The regression equation is

Log10 Cu = 2.17 + 0.650 NScore Cu

103 cases used, 18 cases contain missing values

Predictor Coef SE Coef T P

Constant 2.17375 0.01172 185.44 0.000

NScore Cu 0.65036 0.01376 47.28 0.000

S = 0.113391 R-Sq = 95.7% R-Sq(adj) = 95.6%

Analysis of Variance

Source DF SS MS F P

Regression 1 28.743 28.743 2235.49 0.000

Residual Error 101 1.299 0.013

Total 102 30.042

Unusual Observations

Obs	NScore	Cu	Log10 Cu	Fit	SE Fit	Residual	St Resid
1	-1.47	0.7076	1.2194	0.0262	-0.5118	-4.64	R
2	-2.57	*	0.5054	0.0404	*	*	X
3	-2.21	*	0.7336	0.0358	*	*	X
4	-2.02	*	0.8595	0.0333	*	*	X
7	-1.31	0.8388	1.3248	0.0242	-0.4859	-4.39	R
18	-1.36	0.7993	1.2922	0.0248	-0.4929	-4.45	R
31	-1.88	*	0.9496	0.0315	*	*	X
35	-1.77	*	1.0209	0.0301	*	*	X
36	2.57	3.4150	3.8421	0.0336	-0.4271	-3.94	RX
42	-1.68	*	1.0806	0.0289	*	*	X
44	-1.60	*	1.1322	0.0279	*	*	X
89	2.21	3.3617	3.6139	0.0291	-0.2522	-2.30	RX

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large leverage.

MTB > Regress 'Log10 Pb' 1 'NScore Pb';

SUBC> Constant;

SUBC> Brief 2.

Regression Analysis: Log10 Pb versus NScore Pb

The regression equation is

Log10 Pb = 1.08 + 0.684 NScore Pb

66 cases used, 55 cases contain missing values

Predictor	Coef	SE Coef	T	P
Constant	1.08472	0.01702	63.73	0.000
NScore Pb	0.68354	0.01732	39.47	0.000

S = 0.103372 R-Sq = 96.1% R-Sq(adj) = 96.0%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	16.651	16.651	1558.21	0.000
Residual Error	64	0.684	0.011		
Total	65	17.334			

Unusual Observations

Obs	NScore	Pb	Log10 Pb	Fit	SE Fit	Residual	St Resid	
1	-2.11	*	-0.3560	0.0495	*	*		X
2	-1.28	0.0792	0.2087	0.0358	-0.1295	-1.34		X
3	-1.77	*	-0.1269	0.0439	*	*		X
4	-1.28	0.0792	0.2087	0.0358	-0.1295	-1.34		X
7	-1.21	0.1761	0.2549	0.0347	-0.0788	-0.81		X
36	2.57	2.3979	2.8382	0.0355	-0.4402	-4.53	R	X
47	-1.07	*	0.3501	0.0325	*	*		X
48	-1.50	*	0.0605	0.0394	*	*		X
49	-2.11	*	-0.3560	0.0495	*	*		X
50	-1.50	*	0.0605	0.0394	*	*		X
51	-1.07	*	0.3501	0.0325	*	*		X
66	-1.07	*	0.3501	0.0325	*	*		X
67	-1.50	*	0.0605	0.0394	*	*		X
68	-2.11	*	-0.3560	0.0495	*	*		X
69	-1.50	*	0.0605	0.0394	*	*		X
71	-1.07	*	0.3501	0.0325	*	*		X
85	-1.07	*	0.3501	0.0325	*	*		X
98	2.21	2.3802	2.5983	0.0299	-0.2181	-2.20	R	
106	-1.50	*	0.0605	0.0394	*	*		X
112	-2.11	*	-0.3560	0.0495	*	*		X
113	-1.50	*	0.0605	0.0394	*	*		X
121	-1.07	*	0.3501	0.0325	*	*		X

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large leverage.

MTB > Regress 'Log10Z' 1 'NScore Z';

SUBC> Constant;

SUBC> Brief 2.

Regression Analysis: Log10Z versus NScore Z

The regression equation is

Log10Z = 2.40 + 0.527 NScore Z

106 cases used, 15 cases contain missing values

Predictor	Coef	SE Coef	T	P
Constant	2.40302	0.01535	156.53	0.000
NScore Z	0.52676	0.01716	30.69	0.000

S = 0.154040 R-Sq = 90.1% R-Sq(adj) = 90.0%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	22.356	22.356	942.15	0.000
Residual Error	104	2.468	0.024		
Total	105	24.824			

Unusual Observations

Obs	NScore Z	Log10Z	Fit	SE Fit	Residual	St Resid
1	-2.57	*	1.0517	0.0498	*	* X
2	-1.64	1.0000	1.5392	0.0349	-0.5392	-3.59R
3	-1.88	0.9138	1.4115	0.0387	-0.4977	-3.34RX
4	-1.77	0.9912	1.4693	0.0370	-0.4780	-3.20RX
7	-2.02	0.8921	1.3385	0.0409	-0.4465	-3.01RX
13	2.21	3.3222	3.5694	0.0377	-0.2472	-1.66 X
31	-2.21	*	1.2366	0.0441	*	* X
36	2.57	3.4624	3.7543	0.0433	-0.2919	-1.97 X

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large leverage.

MTB > Regress 'Log10 Acenapthene' 1 'NScore Acenapthene';

SUBC> Constant;

SUBC> Brief 2.

Regression Analysis: Log10 Acenapthene versus NScore Acenapthene

The regression equation is

Log10 Acenapthene = - 1.48 + 0.393 NScore Acenapthene

112 cases used, 9 cases contain missing values

Predictor	Coef	SE Coef	T	P
Constant	-1.48456	0.00349	-425.06	0.000
NScore Acenapthene	0.393078	0.004049	97.08	0.000

S = 0.0363821 R-Sq = 98.8% R-Sq(adj) = 98.8%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	12.475	12.475	9424.97	0.000
Residual Error	110	0.146	0.001		
Total	111	12.621			

Unusual Observations

Obs	NScore Acenapthene	Log10 Acenapthene	Fit	SE Fit	Residual	St Resid
2	2.57	-0.44370	-0.47621	0.01036	0.03251	0.93 X
4	2.02	-0.60206	-0.69022	0.00831	0.08816	2.49R
6	-2.57	*	-2.49292	0.01153	*	* X
37	-2.21	*	-2.35498	0.01018	*	* X
86	-2.02	*	-2.27890	0.00945	*	* X
97	-1.88	*	-2.22446	0.00893	*	* X
101	1.77	-0.88606	-0.78778	0.00741	-0.09828	-2.76R
112	-1.77	*	-2.18135	0.00852	*	* X
116	2.21	-0.46852	-0.61415	0.00903	0.14563	4.13RX
119	1.68	-0.92082	-0.82384	0.00708	-0.09698	-2.72R

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large leverage.

MTB > Regress 'Log10 Acenaphylene' 1 'NScore Acenaphylene';

SUBC> Constant;

SUBC> Brief 2.

Regression Analysis: Log10 Acenaphylene versus NScore Acenaphylene

The regression equation is

Log10 Acenaphylene = - 1.74 + 0.461 NScore Acenaphylene

96 cases used, 25 cases contain missing values

Predictor	Coef	SE Coef	T	P
Constant	-1.73812	0.00302	-575.40	0.000
NScore Acenaphylene	0.461342	0.003692	124.94	0.000

S = 0.0266318 R-Sq = 99.4% R-Sq(adj) = 99.4%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	11.071	11.071	15610.07	0.000
Residual Error	94	0.067	0.001		
Total	95	11.138			

Unusual Observations

Obs	NScore Acenaphylene	Log10 Acenaphylene	Fit	SE Fit	Residual	St Resid
2	2.11	-0.82391	-0.76572	0.00701	-0.05819	-2.26RX
3	-2.35	*	-2.82426	0.01037	*	* X
5	-1.88	*	-2.60650	0.00870	*	* X
6	-1.60	*	-2.47693	0.00773	*	* X
14	-1.41	*	-2.38826	0.00707	*	* X
17	2.11	-0.82391	-0.76572	0.00701	-0.05819	-2.26RX
85	-1.41	*	-2.38826	0.00707	*	* X

86	-1.60	*	-2.47693	0.00773	*	* X
87	-1.88	*	-2.60650	0.00870	*	* X
96	-2.35	*	-2.82426	0.01037	*	* X
97	-1.88	*	-2.60650	0.00870	*	* X
105	-1.60	*	-2.47693	0.00773	*	* X
111	-1.41	*	-2.38826	0.00707	*	* X
116	2.57	-0.56864	-0.55465	0.00860	-0.01399	-0.56 X

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large leverage.

MTB > Regress 'Log10 Anthracene' 1 'NScore Anthracene';

SUBC> Constant;

SUBC> Brief 2.

Regression Analysis: Log10 Anthracene versus NScore Anthracene

The regression equation is

Log10 Anthracene = - 1.72 + 0.496 NScore Anthracene

98 cases used, 23 cases contain missing values

Predictor	Coef	SE Coef	T	P
Constant	-1.71855	0.00362	-475.23	0.000
NScore Anthracene	0.496338	0.004415	112.41	0.000

S = 0.0327066 R-Sq = 99.2% R-Sq(adj) = 99.2%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	1	13.517	13.517	12635.99	0.000
Residual Error	96	0.103	0.001		
Total	97	13.620			

Unusual Observations

Obs	NScore Anthracene	Log10 Anthracene	Fit	SE Fit	Residual	St Resid
6	-2.35	*	-2.88709	0.01232	*	* X

18	2.21	-0.53760	-0.61948	0.00894	0.08188	2.60RX
19	-1.88	*	-2.65281	0.01032	*	* X
25	-1.60	*	-2.51341	0.00916	*	* X
34	-1.41	*	-2.41801	0.00837	*	* X
84	-1.41	*	-2.41801	0.00837	*	* X
85	-1.60	*	-2.51341	0.00916	*	* X
86	-1.88	*	-2.65281	0.01032	*	* X
96	-2.35	*	-2.88709	0.01232	*	* X
97	-1.88	*	-2.65281	0.01032	*	* X
107	2.02	-0.65758	-0.71554	0.00815	0.05796	1.83 X
112	-1.60	*	-2.51341	0.00916	*	* X
113	-1.41	*	-2.41801	0.00837	*	* X
116	2.57	-0.30980	-0.44530	0.01040	0.13550	4.37RX

R denotes an observation with a large standardized residual.

X denotes an observation whose X value gives it large leverage.

Summary Statistics

Following the extrapolation of values less than detection limits based on the distribution of the detected concentrations, which are summarized in Table 1A, summary statistics were calculated for all of the selected paramters:

Descriptive Statistics: Cr, Cd, Cu, Pb, Zn, Acenapthene, Acenapthylen, ...

Variable	N	N*	Mean	SE Mean	StDev	Minimum	Q1	Median
Cr	121	0	39.14	6.07	66.75	0.54	6.11	16.00
Cd	121	0	0.569	0.288	3.170	0.032	0.106	0.200
Cu	121	0	367.3	46.4	510.5	3.2	59.0	170.0
Pb	121	0	34.02	4.61	50.72	0.43	3.79	11.00
Zn	121	0	444.5	40.6	446.7	7.8	105.0	370.0
Acenapthene	121	0	0.04891	0.00497	0.05463	0.00325	0.02000	0.03000
Acenapthylene	121	0	0.03075	0.00336	0.03693	0.00150	0.01000	0.02000

Antrhracene 121 0 0.03671 0.00542 0.05963 0.00129 0.01000 0.02000

Variable	Q3	Maximum
Cr	39.00	440.00
Cd	0.335	35.000
Cu	440.0	2600.0
Pb	45.50	250.00
Zn	615.0	2900.0
Acenapthene	0.06000	0.36000
Acenapthylene	0.04000	0.27000
Antrhracene	0.04000	0.49000

A review of the summary statistics shows that for each of the parameters, the standard deviation is greater than the calculation of the mean. It is therefore difficult to see the value in these summary statistics.

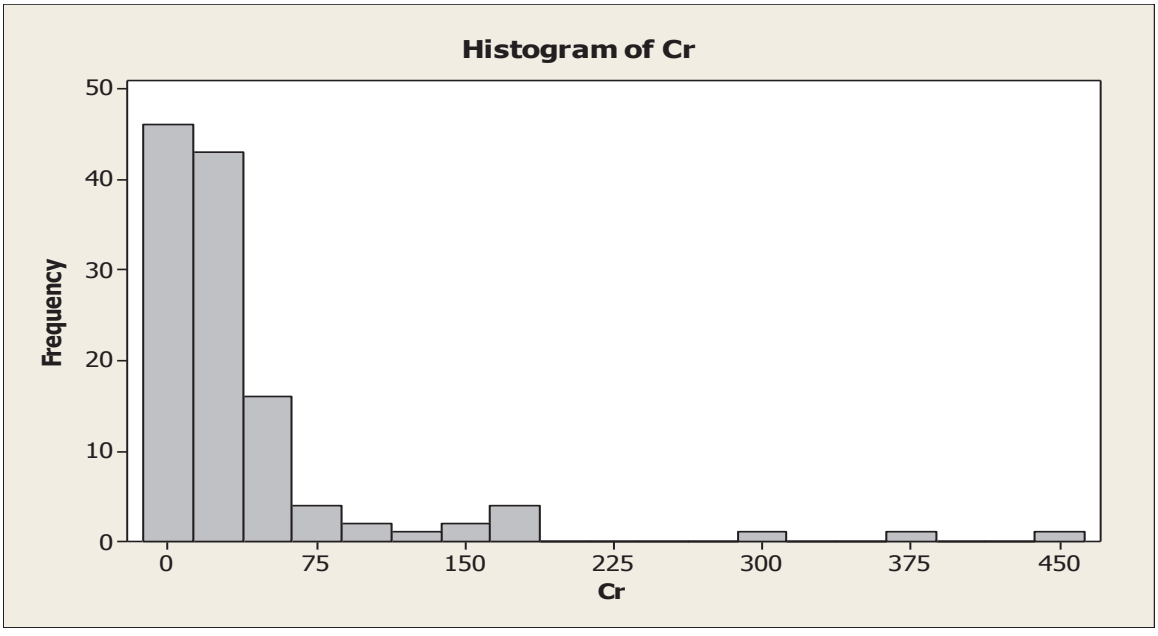
Comparing the use of the derived ND values with the use of 0 for NDs, ½ RDL for NDs, RDL for NDs and omission of NDs when calculating the means:

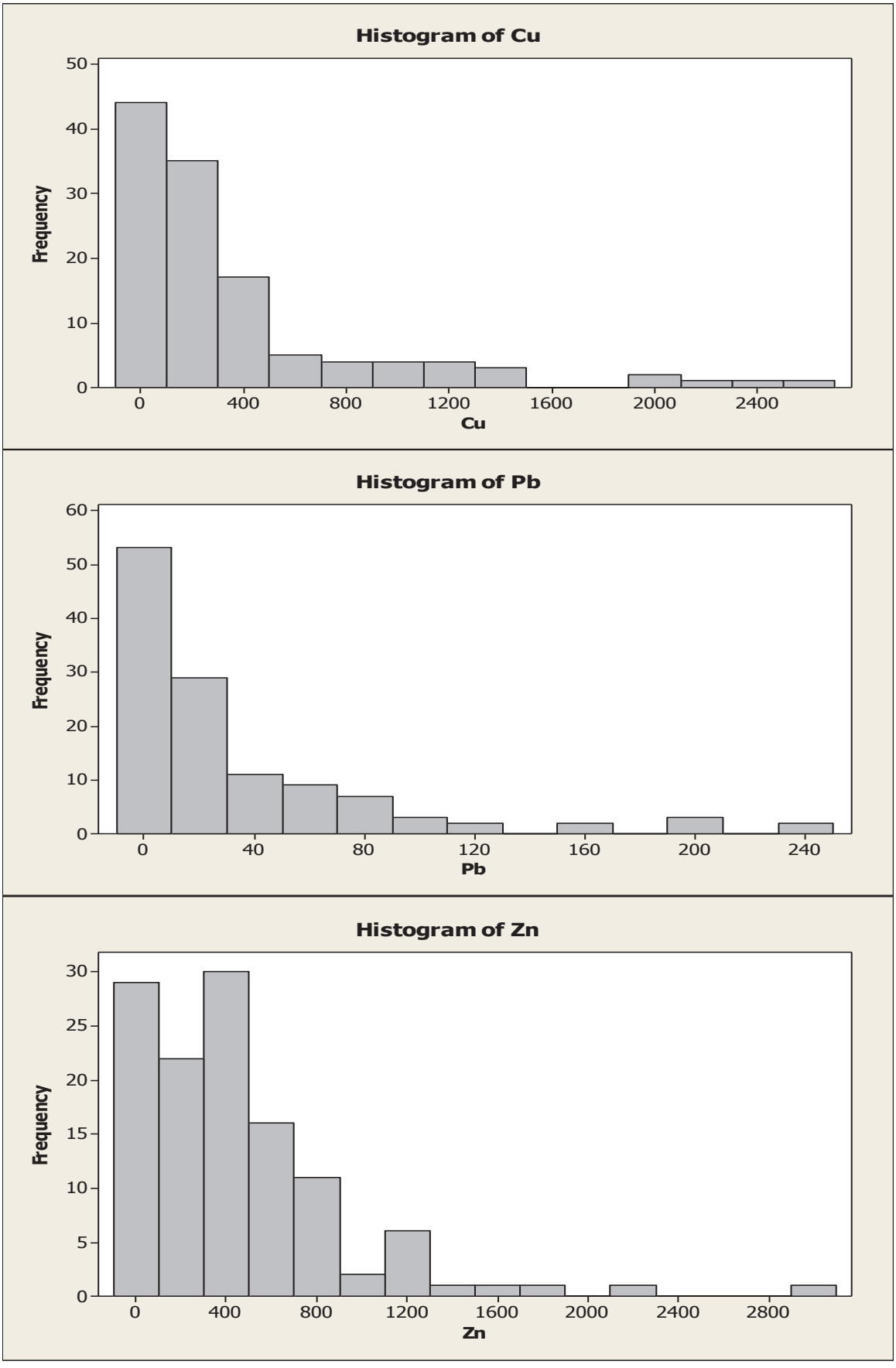
Mean Concentrations	Cadmium	Chromium	Copper	Lead	Zinc	Acenaphthene	Acenaphthylene	Anthracene
Calculated	0.57	39.14	367.30	34.02	444.50	0.049	0.031	0.037
Exclude NDs	0.83	52.87	428.09	58.28	500.37	0.052	0.038	0.044
ND=Zero	0.53	38.01	364.41	31.79	438.34	0.048	0.030	0.036
ND=1/2 RDL	0.56	39.14	365.67	33.96	441.25	0.049	0.031	0.037
ND=RDL	0.59	40.26	366.49	36.14	444.16	0.049	0.032	0.038

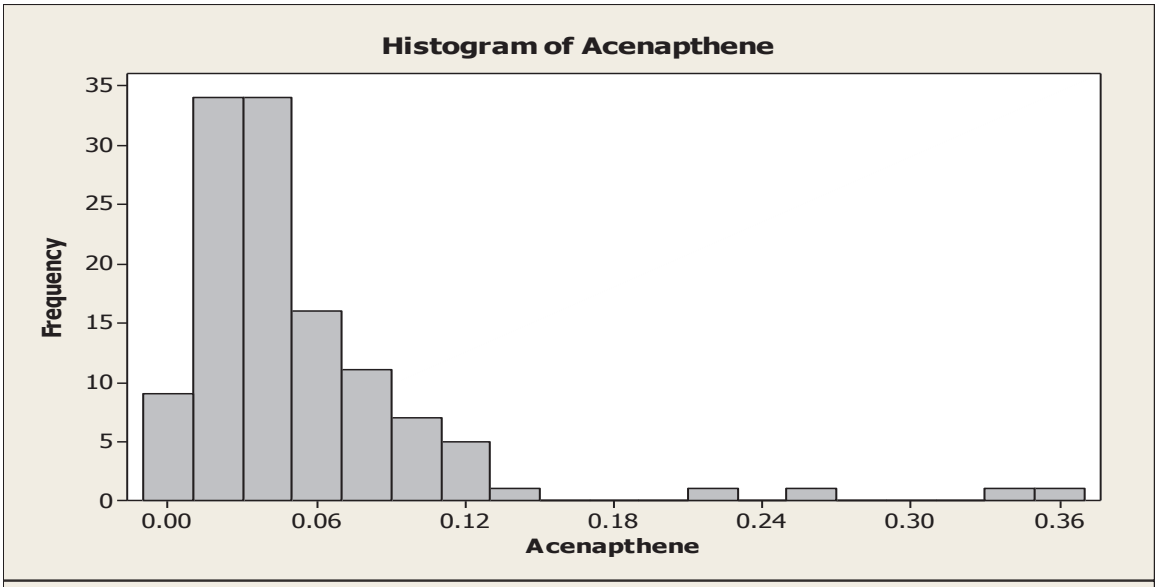
Understandably, the mean calculated using ND values based on the distribution of detected concentrations is greater than means calculated with zero substituted for ND values. Using ½ of the RDL as a substitution resulted in similar means. Even using the RDL in place of ND values did not always result in higher calculated means, as can be seen with copper, zinc and acenapthene which were lower or equal when the RDL was substituted. On the other hand, exclusion of ND values results in much higher mean calculations for all parameters, indicating this is the least desirable method of substitution.

Of the methods considered, using ½ of the RDL value for NDs to calculate mean values is the most comparable to the results of the Robust Method. Considering the amount of effort required to use the Robust Method (5 hours for the work completed today), using ½ RDL as a substitution could be considered an acceptable approach to using NDs in statistical analysis.

The following histograms were developed to show how the distribution of the detected samples would have generated enough information to extrapolate date below the RDLs:




Histogram of Cu
Frequency
Cu
0
400
800
1200
1600
2000
2400
0
10
20
30
40
50
Histogram of Pb
Frequency
Pb
0
40
80
120
160
200
240
0
10
20
30
40
50
60
Histogram of Zn
Frequency
Zn
0
400
800
1200
1600
2000
2400
2800
0
5
10
15
20
25
30


Histogram of Acenapthene
Frequency
Acenapthene
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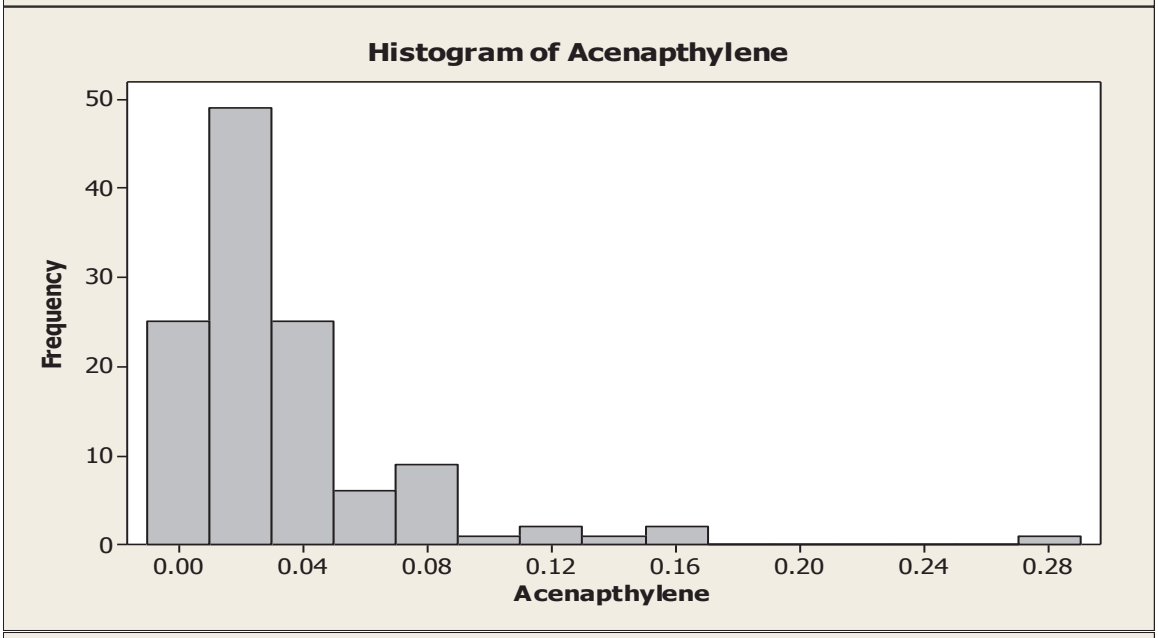
5
10
15
20
25
30
35
0.00
0.06
0.12
0.18
0.24
0.30
0.36


Histogram of Acenapthylene
Frequency
Acenapthylene
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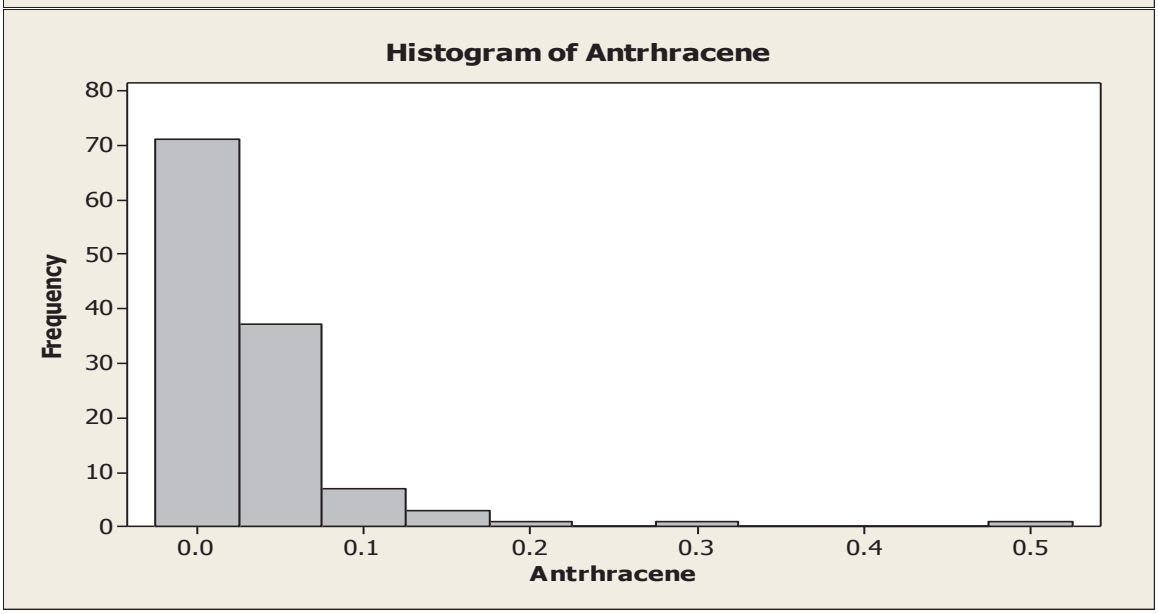
30
40
50
0.00
0.04
0.08
0.12
0.16
0.20
0.24
0.28


Histogram of Antrhracene
Frequency
Antrhracene
0
10
20
30
40
50
60
70
80
0.0
0.1
0.2
0.3
0.4
0.5

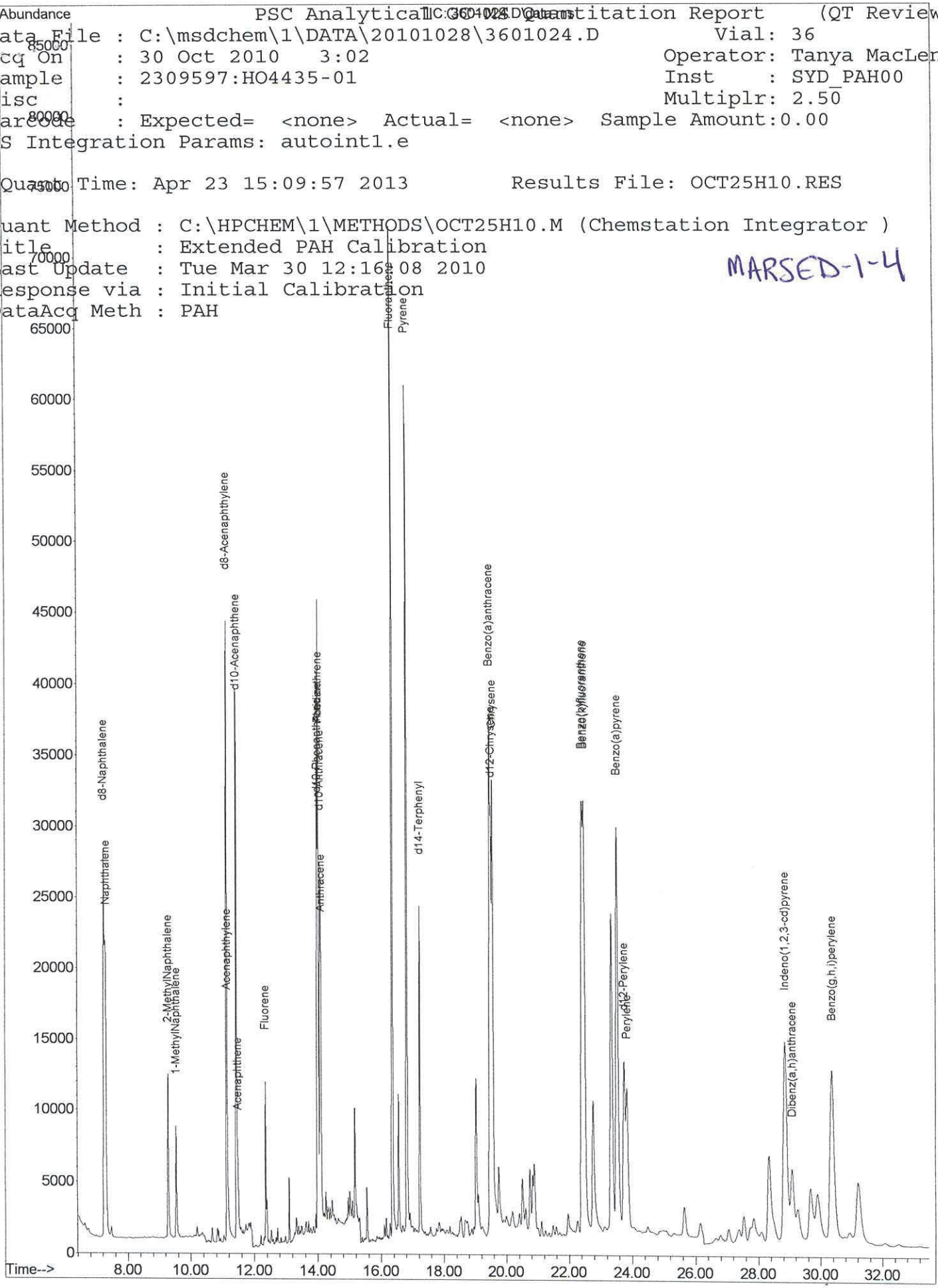
Appendix 4 – Sample Chromatograms

Data File : C:\msdchem\1\DATA\20101028\3601024.D Vial: 36
Acq On : 30 Oct 2010 3:02 Operator: Tanya MacLennan
Sample : 2309597:HO4435-01 Inst : SYD_PAH00
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: autoint1.e

Quant Time: Apr 23 15:09:57 2013 Results File: OCT25H10.RES

Quant Method : C:\HPCHEM\1\METHODS\OCT25H10.M (Chemstation Integrator)
Title : Extended PAH Calibration
Last Update : Tue Mar 30 12:16:08 2010
Response via : Initial Calibration
DataAcq Meth : PAH

MARSED-1-4



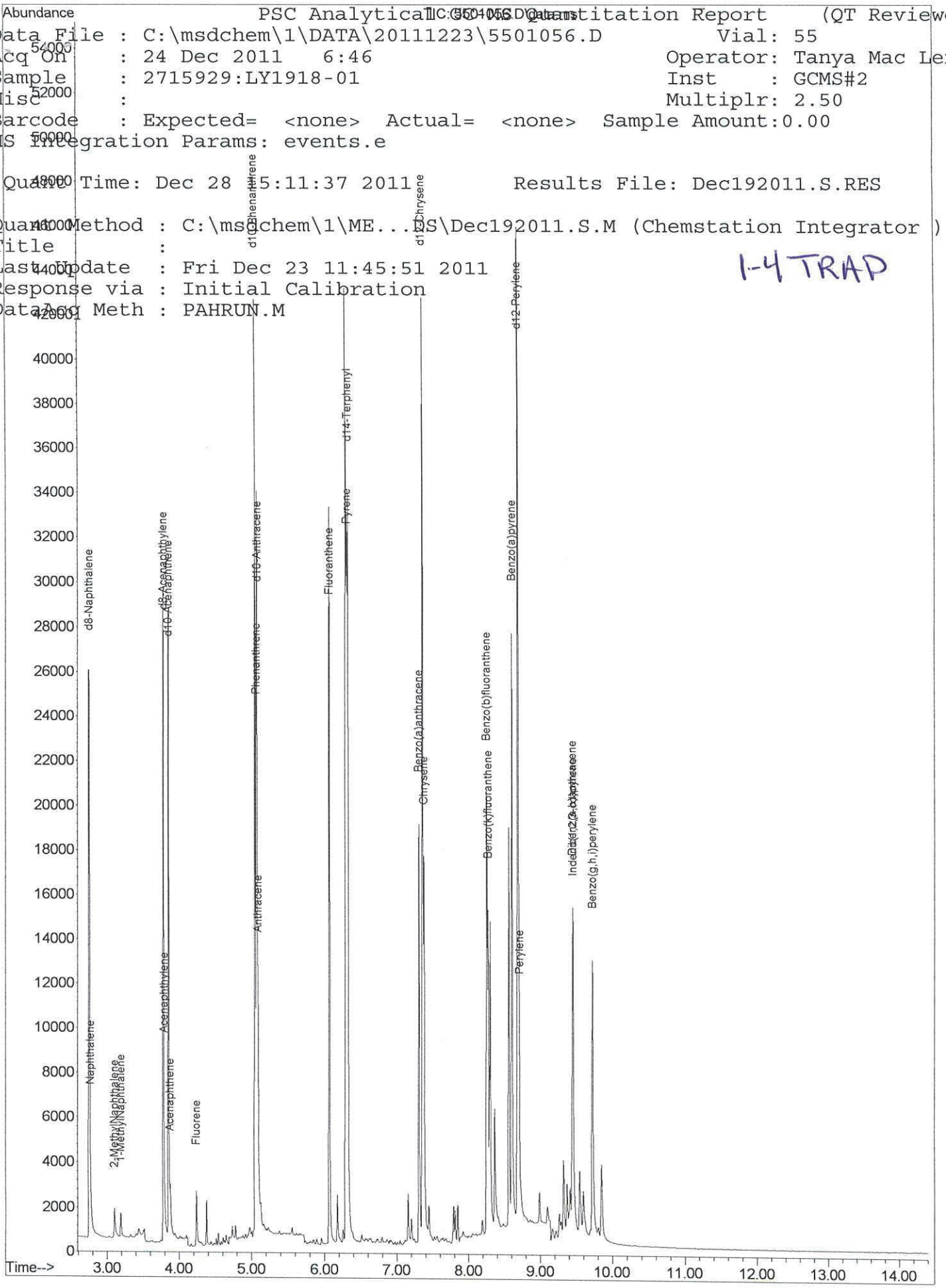
PSC Analytical GC-MS Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20111223\5501056.D Vial: 55
Acq On : 24 Dec 2011 6:46 Operator: Tanya Mac Lenna
Sample : 2715929:LY1918-01 Inst : GCMS#2
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: events.e

Quant Time: Dec 28 15:11:37 2011 Results File: Dec192011.S.RES

Quant Method : C:\msdchem\1\ME...LS\Dec192011.S.M (Chemstation Integrator)
Title :
Last Update : Fri Dec 23 11:45:51 2011
Response via : Initial Calibration
DataAcq Meth : PAHRUN.M

1-4 TRAD

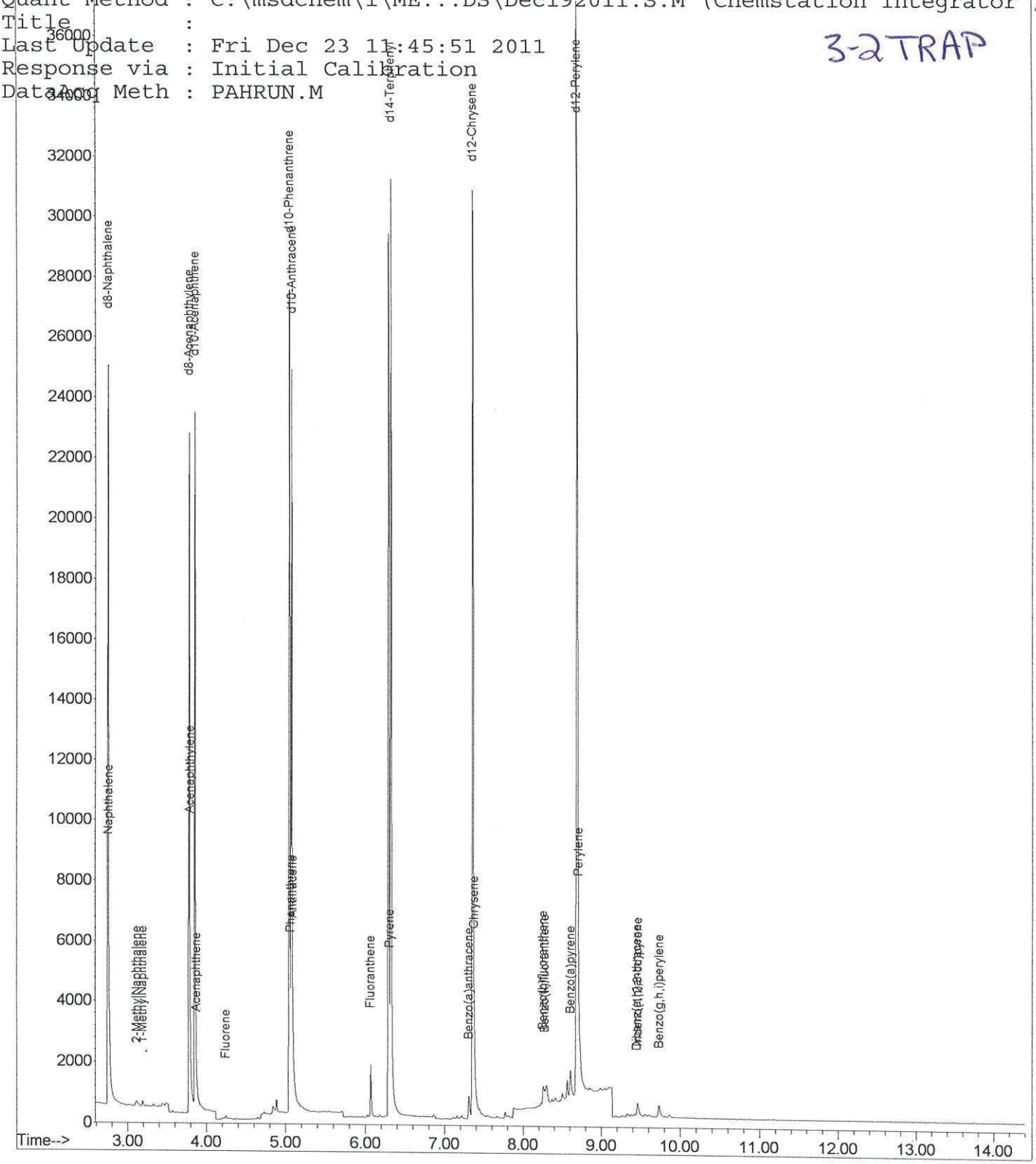


Data File : C:\msdchem\1\DATA\20111223\5301054.D Vial: 53
Acq On : 24 Dec 2011 5:58 Operator: Tanya Mac Lenna
Sample : 2715929:LY0789-01 Inst : GCMS#2
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: events.e

Quant Time: Dec 28 15:09:53 2011 Results File: Dec192011.S.RES

Quant Method : C:\msdchem\1\ME...DS\Dec192011.S.M (Chemstation Integrator)
Title :
Last Update : Fri Dec 23 11:45:51 2011
Response via : Initial Calibration
Data Acq Meth : PAHRUN.M

3-2 TRAP



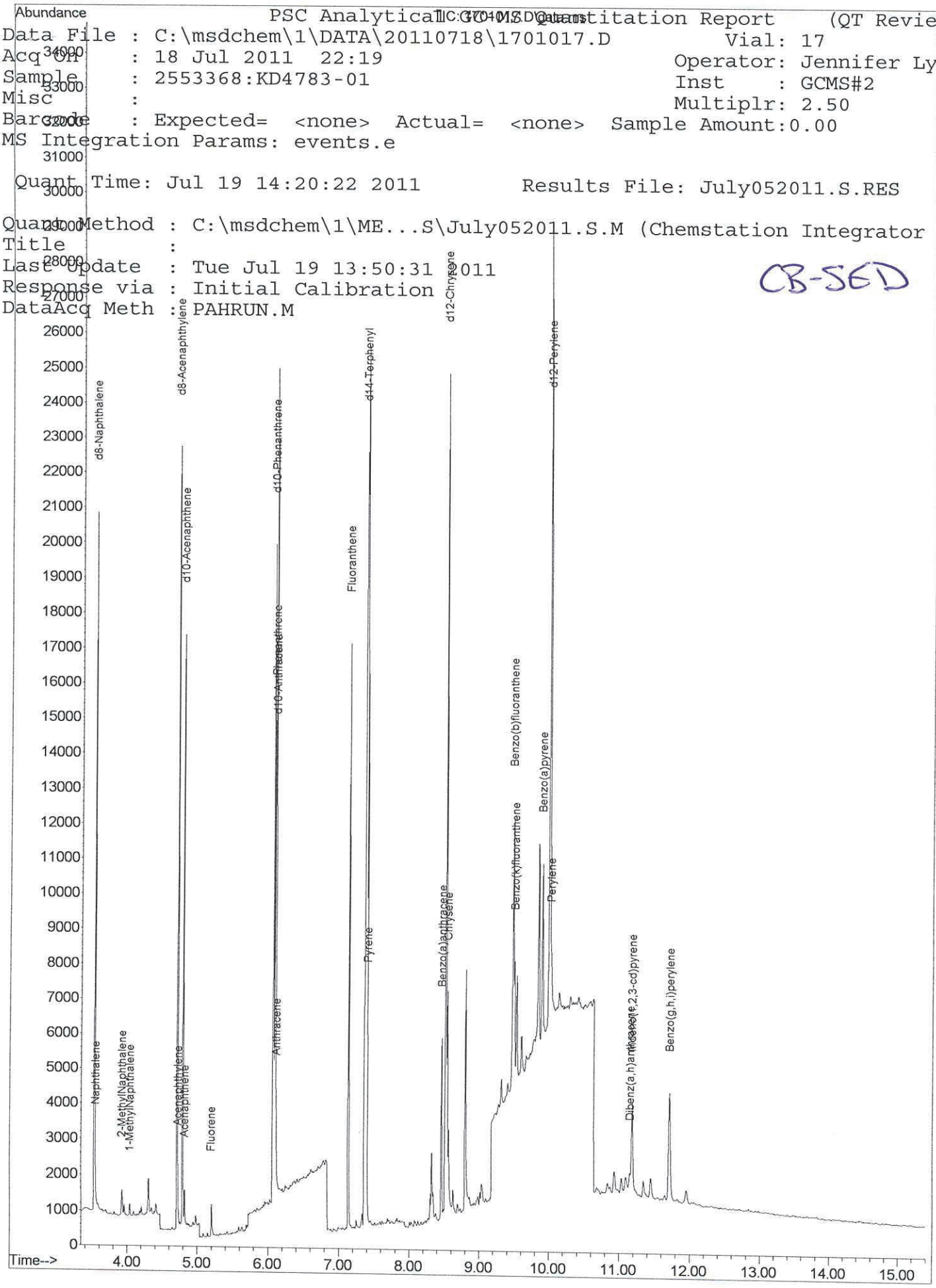
PSC Analytical GC-MS Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20110718\1701017.D Vial: 17
Acq On : 18 Jul 2011 22:19 Operator: Jennifer Lynk
Sample : 2553368:KD4783-01 Inst : GCMS#2
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: events.e

Quant Time: Jul 19 14:20:22 2011 Results File: July052011.S.RES

Quant Method : C:\msdchem\1\ME...S\July052011.S.M (Chemstation Integrator)
Title :
Last Update : Tue Jul 19 13:50:31 2011
Response via : Initial Calibration
DataAcq Meth : PAHRUN.M

CB-SED



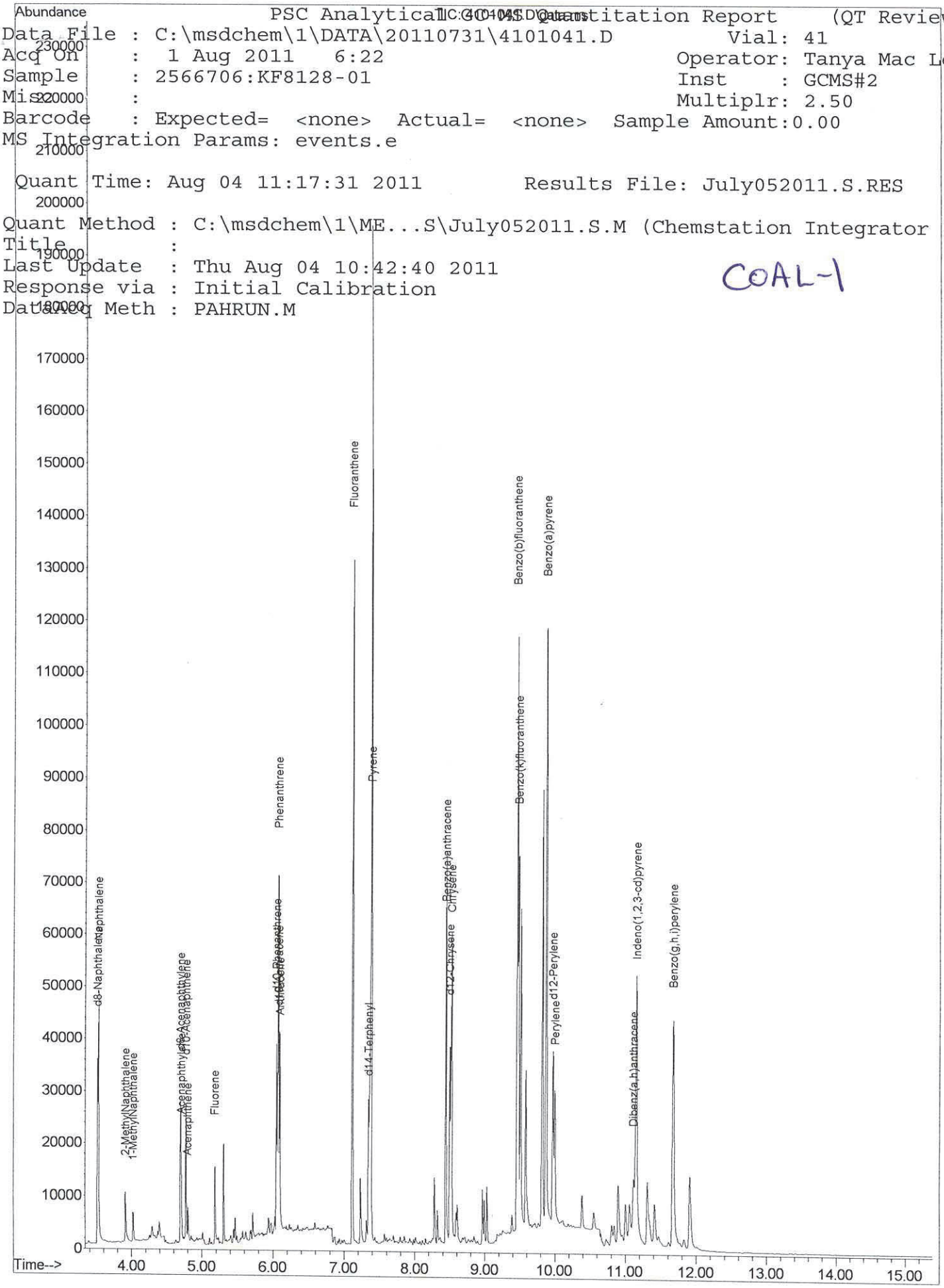
April152013.M Thu May 09 13:29:28 2013

Data File : C:\msdchem\1\DATA\20110731\4101041.D Vial: 41
Acq On : 1 Aug 2011 6:22 Operator: Tanya Mac Lenna
Sample : 2566706:KF8128-01 Inst : GCMS#2
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: events.e

Quant Time: Aug 04 11:17:31 2011 Results File: July052011.S.RES

Quant Method : C:\msdchem\1\ME...S\July052011.S.M (Chemstation Integrator)
Title :
Last Update : Thu Aug 04 10:42:40 2011
Response via : Initial Calibration
DataAcq Meth : PAHRUN.M

COAL-1



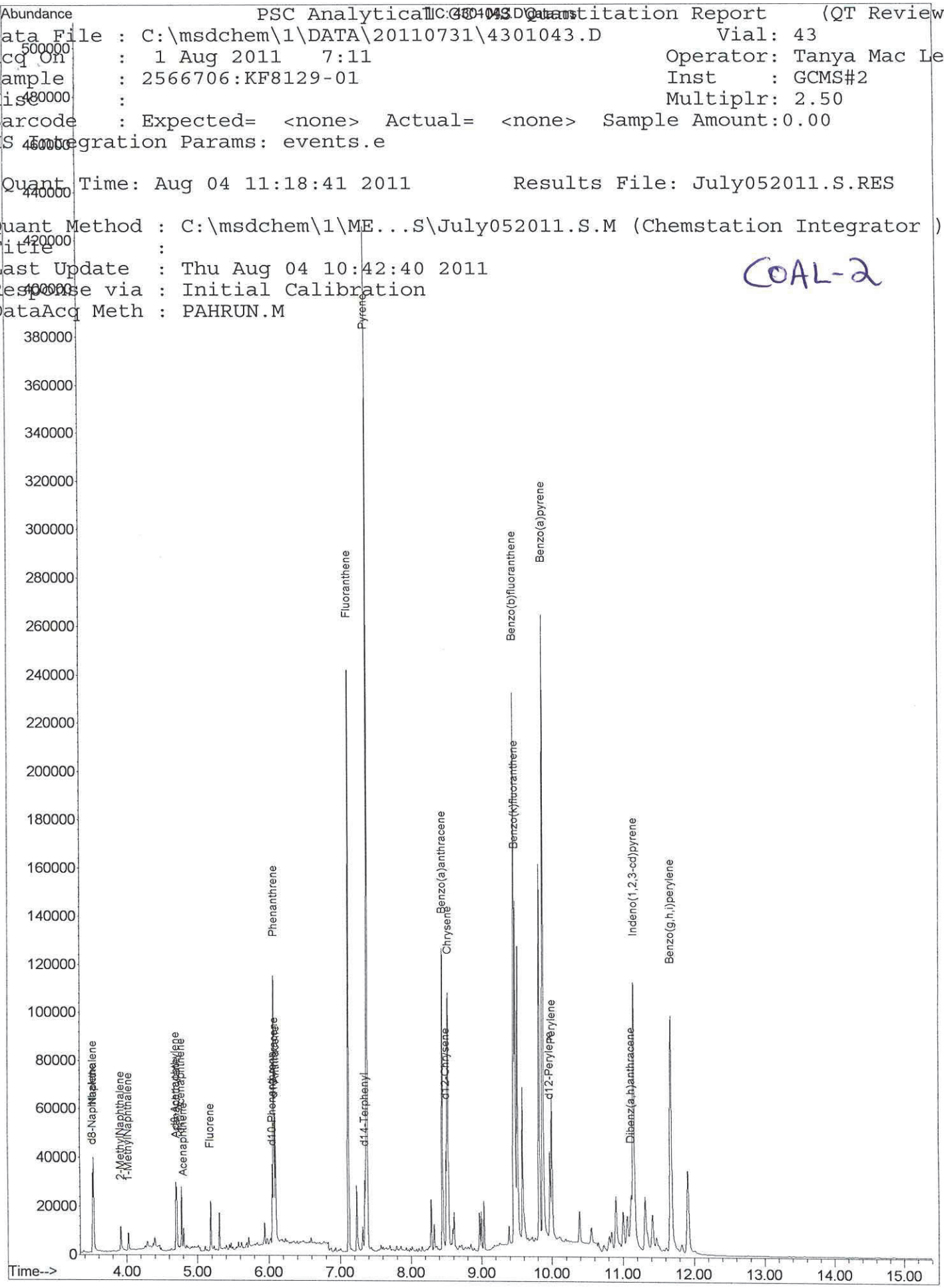
PSC Analytical TIC: 4301043.D Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20110731\4301043.D Vial: 43
Acq On : 1 Aug 2011 7:11 Operator: Tanya Mac Lenna
Sample : 2566706:KF8129-01 Inst : GCMS#2
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: events.e

Quant Time: Aug 04 11:18:41 2011 Results File: July052011.S.RES

Quant Method : C:\msdchem\1\ME...S\July052011.S.M (Chemstation Integrator)
Title :
Last Update : Thu Aug 04 10:42:40 2011
Response via : Initial Calibration
DataAcq Meth : PAHRUN.M

COAL-2



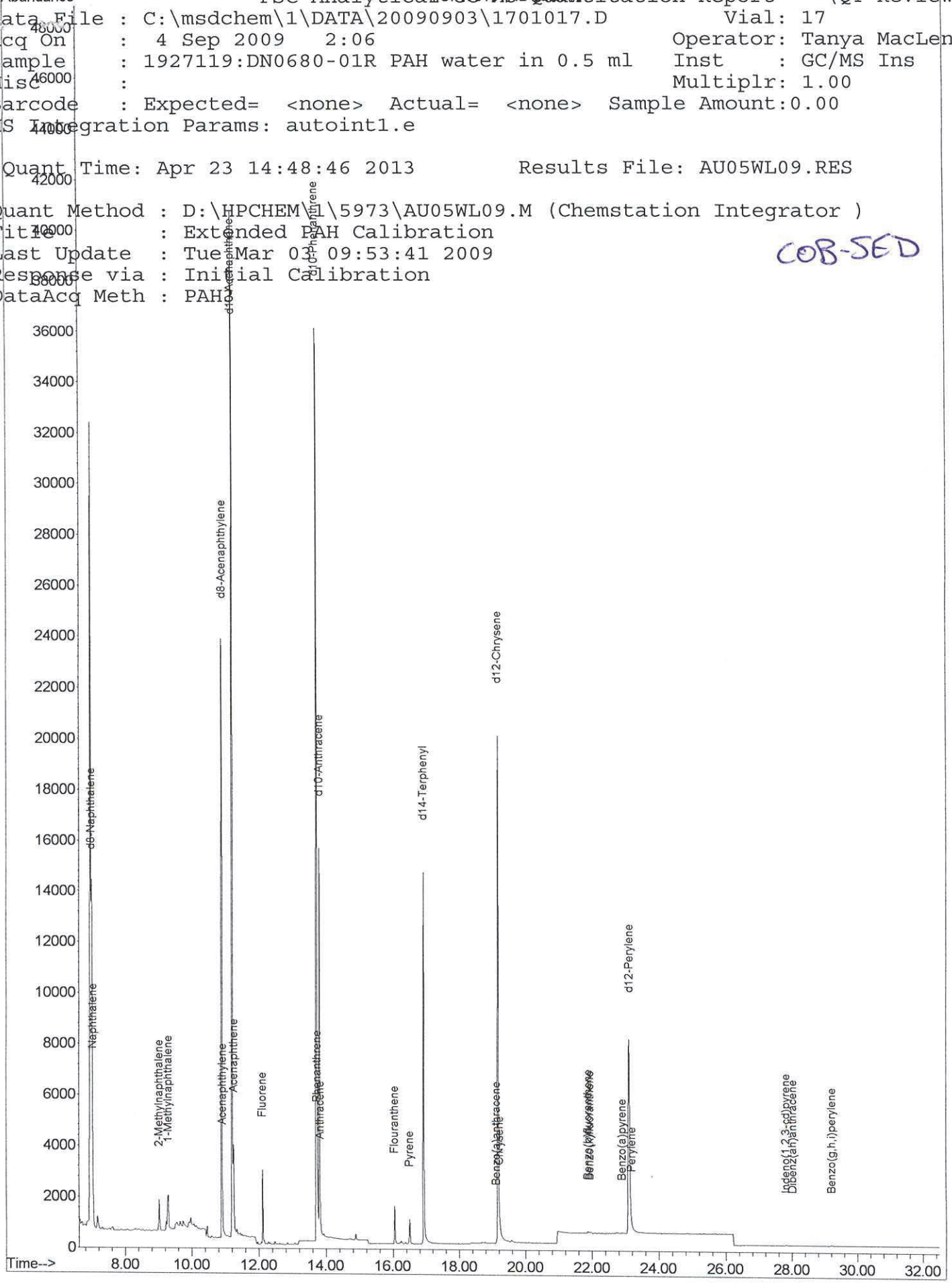
PSC Analytical GC-MS Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20090903\1701017.D Vial: 17
Acq On : 4 Sep 2009 2:06 Operator: Tanya MacLennan
Sample : 1927119:DN0680-01R PAH water in 0.5 ml Inst : GC/MS Ins
Misc : Multiplr: 1.00
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: autoint1.e

Quant Time: Apr 23 14:48:46 2013 Results File: AU05WL09.RES

Quant Method : D:\HPCHEM\1\5973\AU05WL09.M (Chemstation Integrator)
Title : Extended PAH Calibration
Last Update : Tue Mar 03 09:53:41 2009
Response via : Initial Calibration
DataAcq Meth : PAH3

COB-SED



April152013.M Tue Apr 23 14:50:47 2013 Page: 2

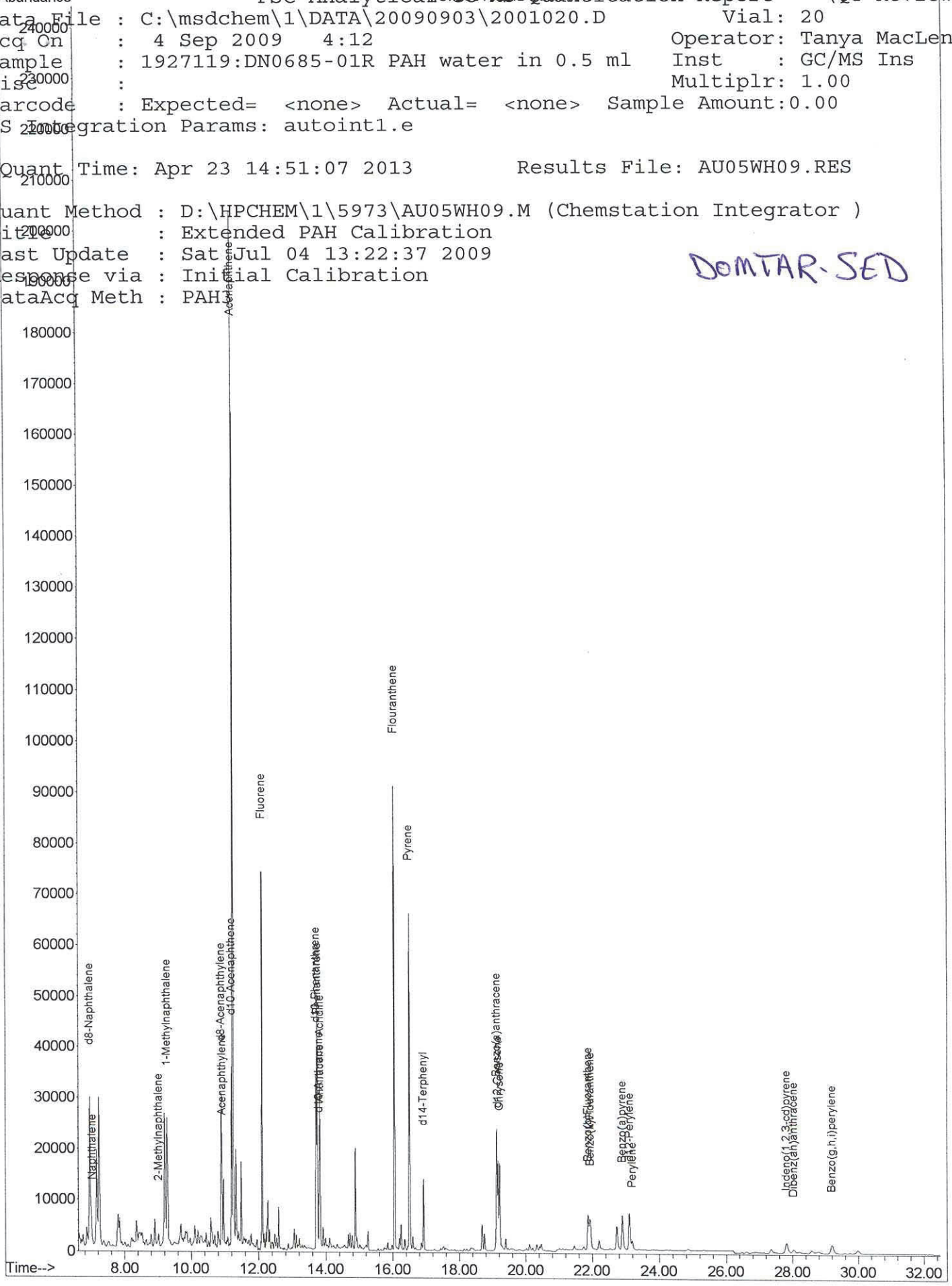
PSC Analytical 2001020.D Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20090903\2001020.D Vial: 20
Acq On : 4 Sep 2009 4:12 Operator: Tanya MacLennan
Sample : 1927119:DN0685-01R PAH water in 0.5 ml Inst : GC/MS Ins
Misc : Multiplr: 1.00
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: autoint1.e

Quant Time: Apr 23 14:51:07 2013 Results File: AU05WH09.RES

Quant Method : D:\HPCHEM\1\5973\AU05WH09.M (Chemstation Integrator)
Title : Extended PAH Calibration
Last Update : Sat Jul 04 13:22:37 2009
Response via : Initial Calibration
DataAcq Meth : PAH

DOMTAR-SED



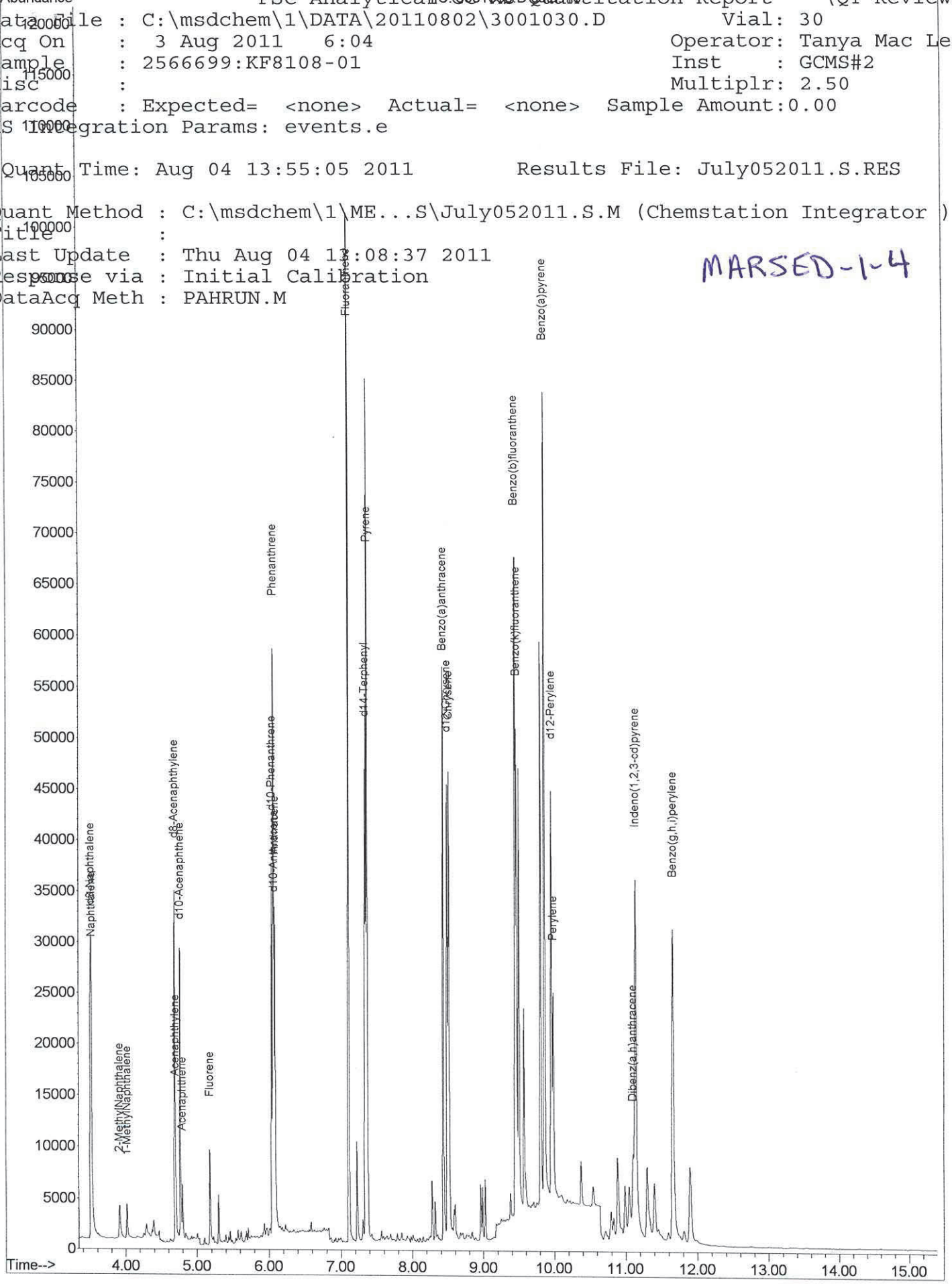
PSC Analytical GC-MS Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20110802\3001030.D Vial: 30
Acq On : 3 Aug 2011 6:04 Operator: Tanya Mac Lenna
Sample : 2566699:KF8108-01 Inst : GCMS#2
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: events.e

Quant Time: Aug 04 13:55:05 2011 Results File: July052011.S.RES

Quant Method : C:\msdchem\1\ME...S\July052011.S.M (Chemstation Integrator)
Title :
Last Update : Thu Aug 04 13:08:37 2011
Response via : Initial Calibration
DataAcq Meth : PAHRUN.M

MARSED-1-4



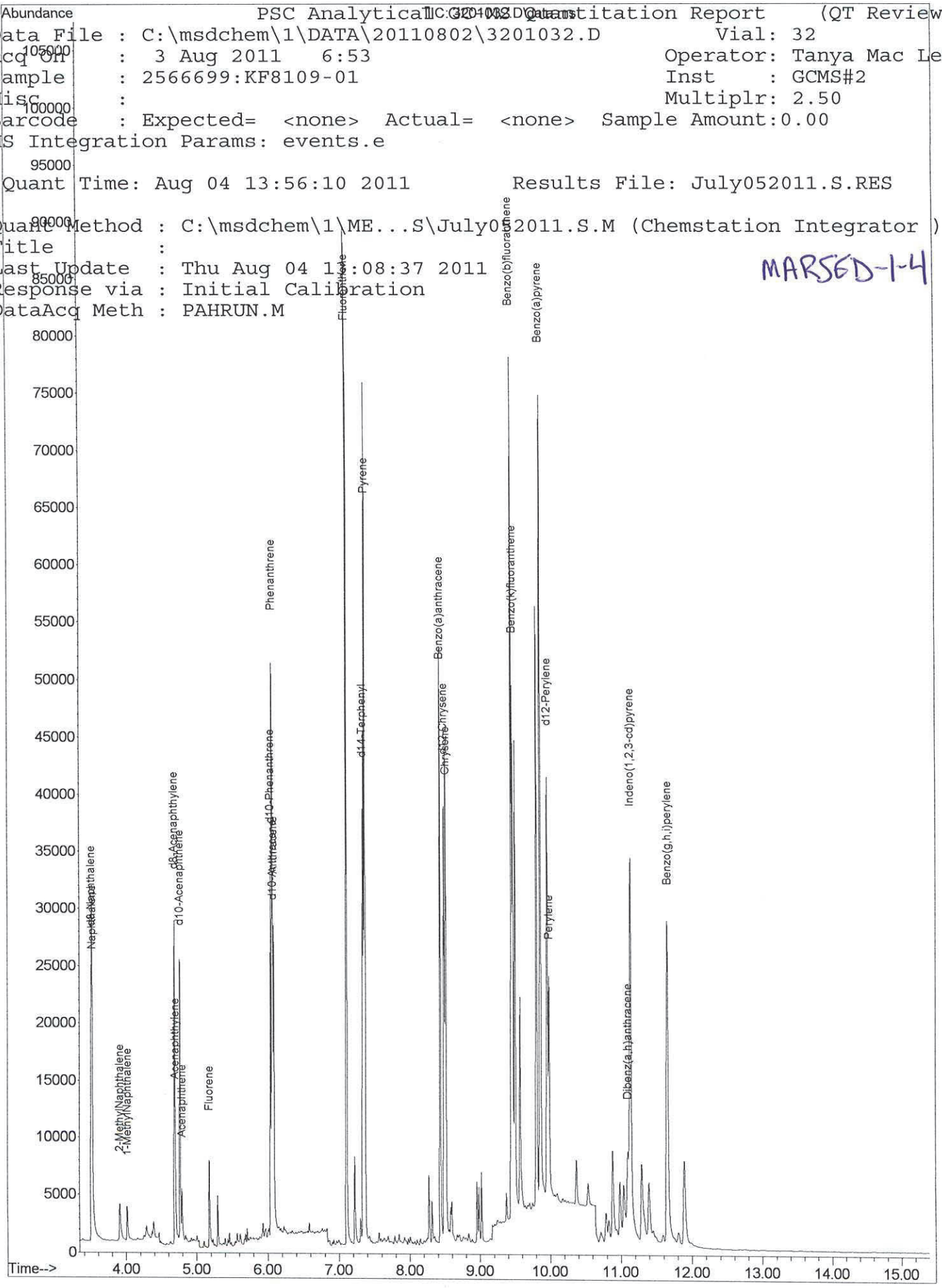
PSC Analytical TIC: 3201032.D Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20110802\3201032.D Vial: 32
Acq On : 3 Aug 2011 6:53 Operator: Tanya Mac Lenna
Sample : 2566699:KF8109-01 Inst : GCMS#2
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: events.e

Quant Time: Aug 04 13:56:10 2011 Results File: July052011.S.RES

Quant Method : C:\msdchem\1\ME...S\July052011.S.M (Chemstation Integrator)
Title :
Last Update : Thu Aug 04 13:08:37 2011
Response via : Initial Calibration
DataAcq Meth : PAHRUN.M

MARSED-1-4



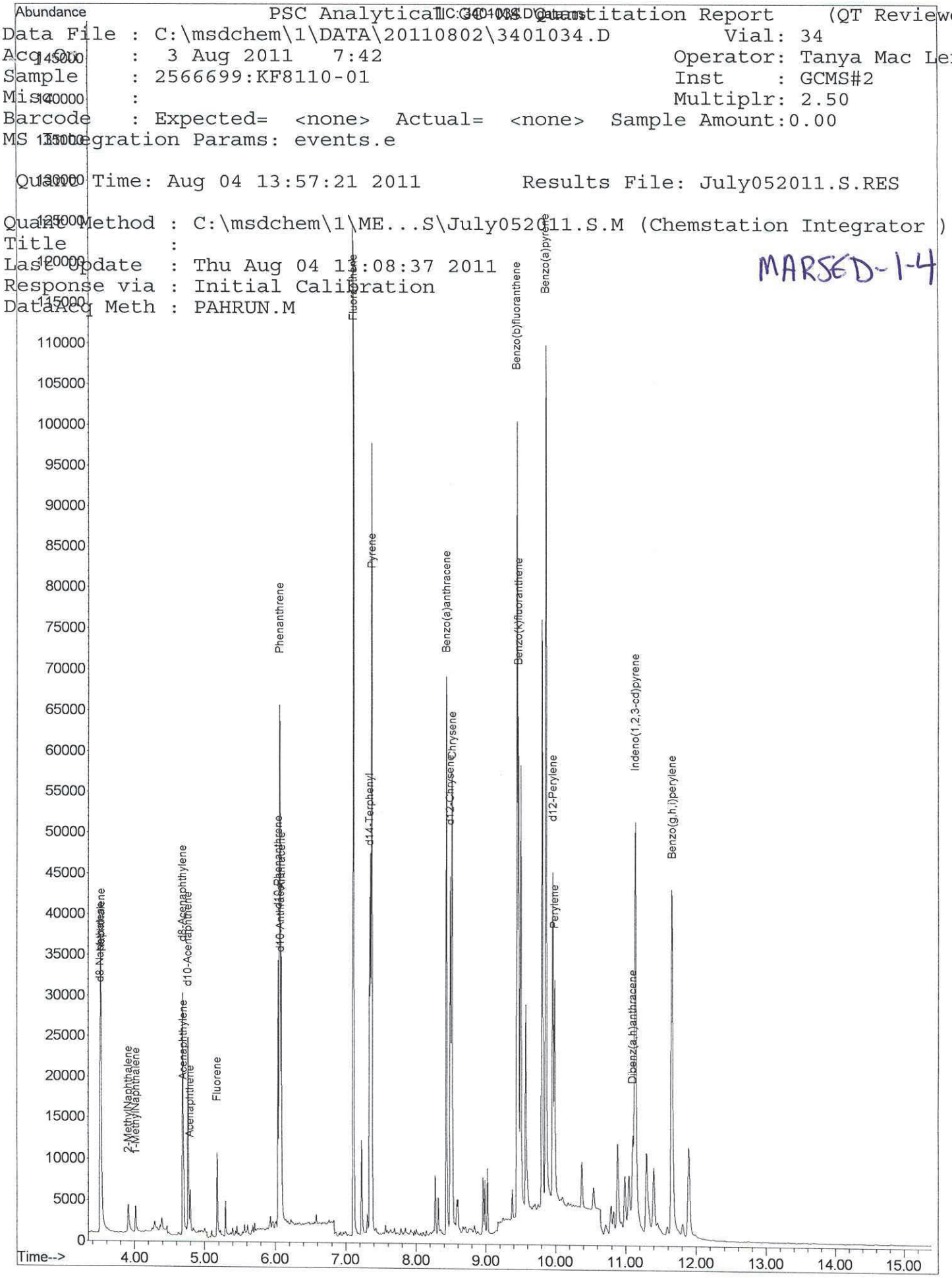
PSC Analytical TIC: 3401034.D Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20110802\3401034.D Vial: 34
Acq On : 3 Aug 2011 7:42 Operator: Tanya Mac Lenna
Sample : 2566699:KF8110-01 Inst : GCMS#2
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: events.e

Quant Time: Aug 04 13:57:21 2011 Results File: July052011.S.RES

Quant Method : C:\msdchem\1\ME...S\July052011.S.M (Chemstation Integrator)
Title :
Last Update : Thu Aug 04 14:08:37 2011
Response via : Initial Calibration
DataAcq Meth : PAHRUN.M

MARSED-1-4



PSC Analytical TIC: 3001018.D (Quant)

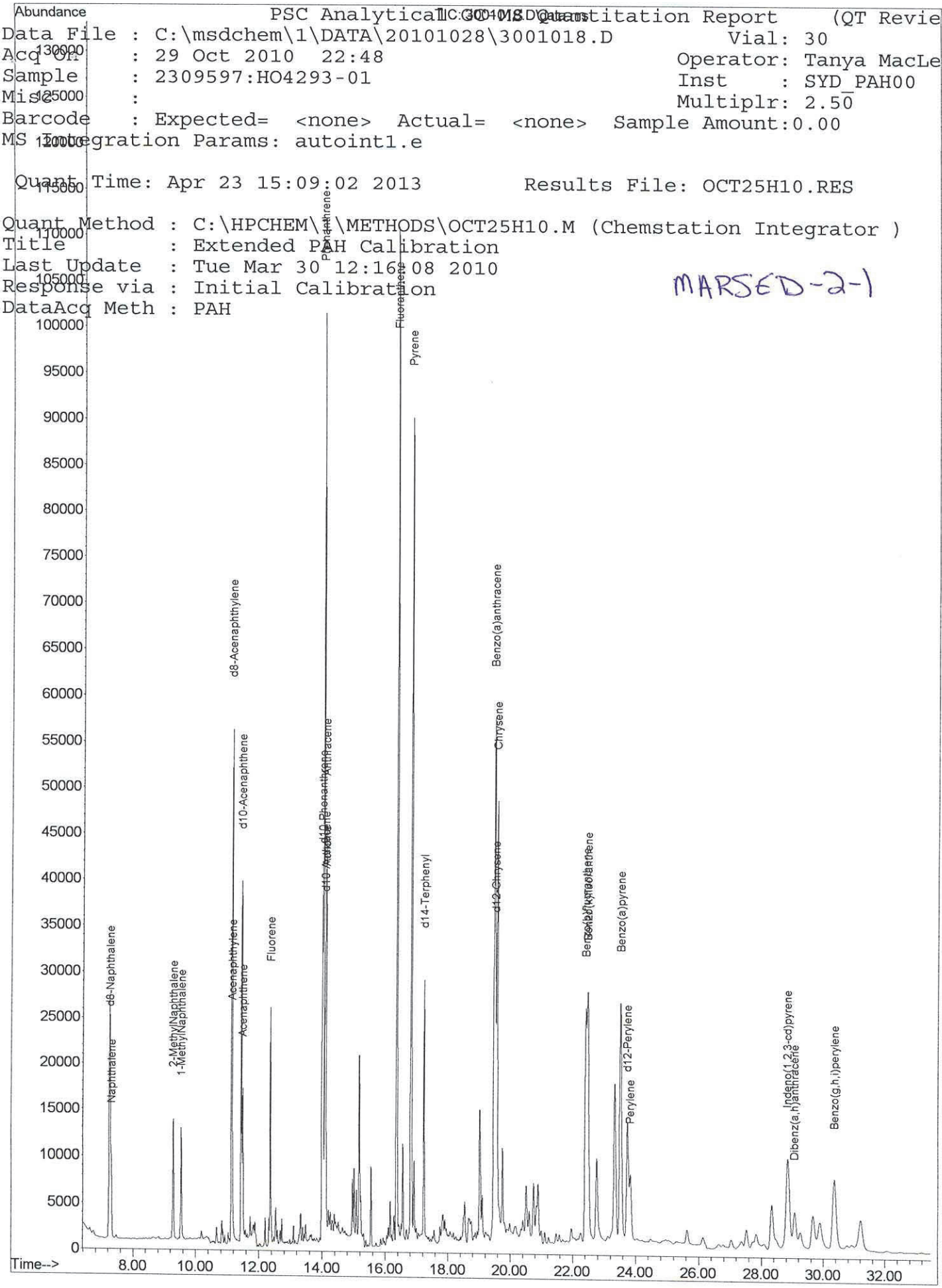
PSC Analytical GC-MS Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20101028\3001018.D Vial: 30
Acq On : 29 Oct 2010 22:48 Operator: Tanya MacLennan
Sample : 2309597:HO4293-01 Inst : SYD_PAH00
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: autoint1.e

Quant Time: Apr 23 15:09:02 2013 Results File: OCT25H10.RES

Quant Method : C:\HPCHEM\\METHODS\OCT25H10.M (Chemstation Integrator)
Title : Extended PAH Calibration
Last Update : Tue Mar 30 12:16:08 2010
Response via : Initial Calibration
DataAcq Meth : PAH

MARSED-2-1



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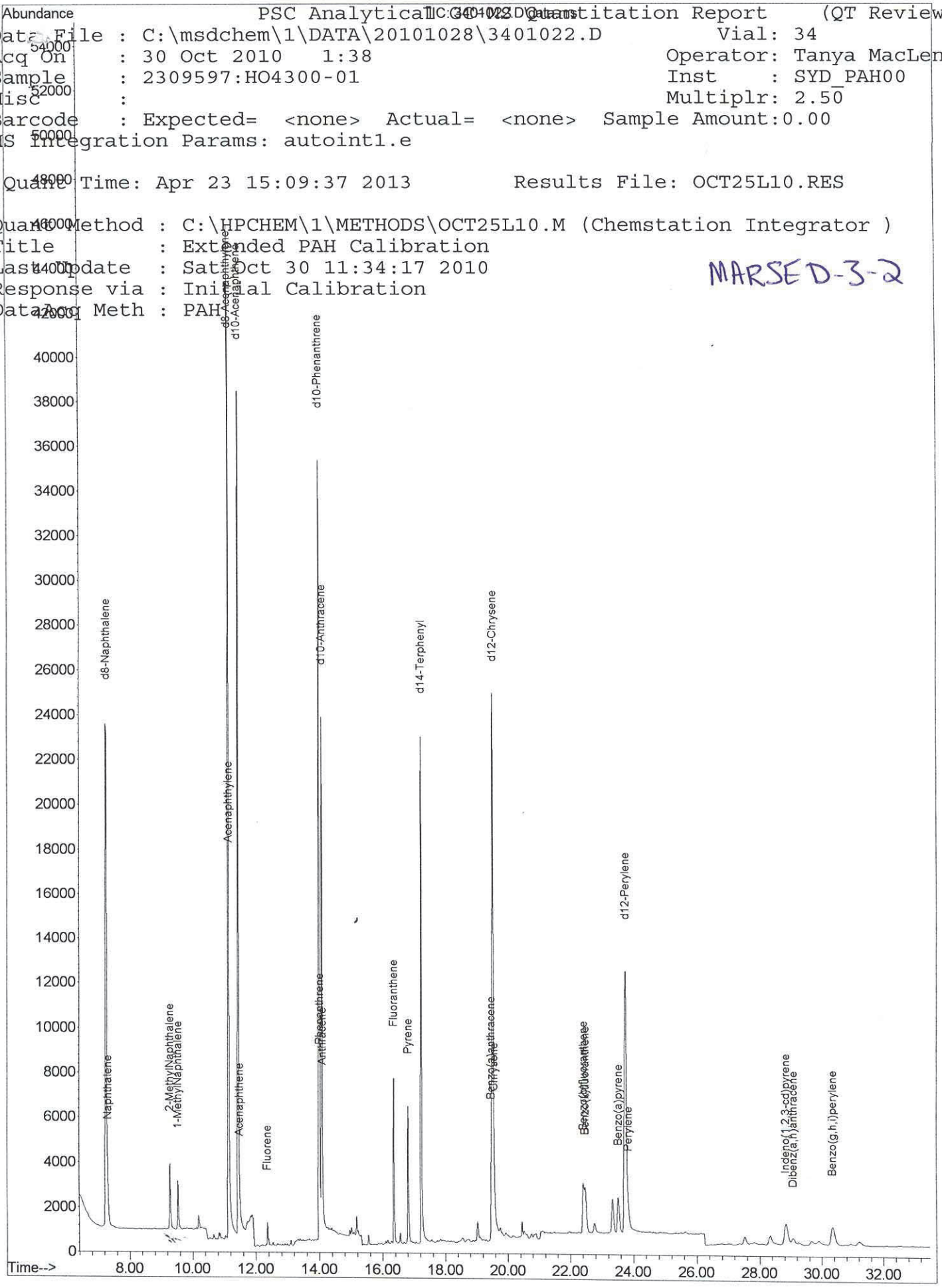
PSC Analytical TIC: 3401022.D Quantitation Report (QT Reviewed)

Data File : C:\msdchem\1\DATA\20101028\3401022.D Vial: 34
Acq On : 30 Oct 2010 1:38 Operator: Tanya MacLennan
Sample : 2309597:HO4300-01 Inst : SYD_PAH00
Misc : Multiplr: 2.50
Barcode : Expected= <none> Actual= <none> Sample Amount:0.00
MS Integration Params: autoint1.e

Quant Time: Apr 23 15:09:37 2013 Results File: OCT25L10.RES

Quant Method : C:\HPCHEM\1\METHODS\OCT25L10.M (Chemstation Integrator)
Title : Extended PAH Calibration
Last Update : Sat Oct 30 11:34:17 2010
Response via : Initial Calibration
Data Acq Meth : PAH.M

MARSED-3-2



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Appendix 5 – Correlation Analysis Results Spreadsheet

APPENDIX 4 - PEARSON CORRELATION COEFFICIENTS

	ASTM Ref. Mat.	Wash Brook Arm	South Pond Phase	South Pond Phase	South Pond Phase	North Pond Phase	North Pond Phase	North Pond Phase	North Pond Phase	North Pond Phase	Urban Soil 1	Urban Soil 2	Urban Soil 3	Urban Soil 4	Urban Soil 5	Urban Soil 6	Urban Soil 7	Urban Soil 8	Urban Soil 9	Urban Soil 10	Urban Soil 11	Urban Soil 12	Urban Soil 13
Wash Brook Arm	0.55																						
	0.01																						
South Pond Phase	0.96	0.38																					
	0.00	0.11																					
South Pond Phase	0.81	0.93	0.69																				
	0.00	0.00	0.00																				
South Pond Phase	0.97	0.54	0.98	0.81																			
	0.00	0.02	0.00	0.00																			
North Pond Phase	0.96	0.68	0.93	0.90	0.99																		
	0.00	0.00	0.00	0.00	0.00																		
North Pond Phase	0.96	0.64	0.95	0.87	0.99	1.00																	
	0.00	0.00	0.00	0.00	0.00	0.00																	
North Pond Phase	0.51	1.00	0.33	0.91	0.50	0.64	0.59																
	0.03	0.00	0.17	0.00	0.03	0.00	0.01																
North Pond Phase	0.94	0.75	0.89	0.94	0.96	0.99	0.99	0.71															
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00															
North Pond Phase	0.90	0.82	0.83	0.97	0.92	0.97	0.96	0.79	0.99														
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00														
North Pond Phase	0.90	0.84	0.81	0.98	0.91	0.97	0.95	0.81	0.99	1.00													
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00													
Urban Soil 1	0.15	0.69	-0.06	0.48	0.06	0.19	0.16	0.70	0.28	0.36	0.39												
	0.55	0.00	0.81	0.04	0.80	0.44	0.53	0.00	0.26	0.13	0.10												
Urban Soil 2	-0.02	0.31	-0.17	0.13	-0.13	-0.06	-0.06	0.32	0.02	0.07	0.08	0.84											
	0.94	0.20	0.50	0.60	0.61	0.81	0.81	0.19	0.95	0.78	0.75	0.00											
Urban Soil 3	0.02	0.31	-0.13	0.14	-0.09	-0.03	-0.03	0.31	0.04	0.09	0.10	0.82	0.99										
	0.93	0.20	0.60	0.57	0.72	0.91	0.92	0.20	0.86	0.71	0.68	0.00	0.00										
Urban Soil 4	0.05	0.30	-0.10	0.14	-0.07	-0.01	-0.01	0.30	0.06	0.10	0.11	0.82	0.96	0.96									
	0.84	0.22	0.68	0.56	0.78	0.97	0.97	0.21	0.82	0.67	0.64	0.00	0.00	0.00									
Urban Soil 5	0.15	0.43	-0.01	0.29	0.05	0.12	0.12	0.43	0.19	0.24	0.25	0.84	0.95	0.95	0.97								
	0.54	0.07	0.98	0.23	0.85	0.63	0.63	0.07	0.44	0.32	0.30	0.00	0.00	0.00	0.00								
Urban Soil 6	0.10	0.54	-0.10	0.34	-0.02	0.09	0.06	0.55	0.17	0.24	0.27	0.96	0.89	0.88	0.92	0.91							
	0.70	0.02	0.67	0.16	0.95	0.72	0.79	0.02	0.50	0.32	0.27	0.00	0.00	0.00	0.00	0.00							
Urban Soil 7	0.11	0.66	-0.10	0.44	0.02	0.14	0.11	0.66	0.23	0.32	0.34	0.99	0.83	0.81	0.84	0.85	0.98						
	0.64	0.00	0.69	0.06	0.93	0.56	0.66	0.00	0.35	0.19	0.15	0.00	0.00	0.00	0.00	0.00	0.00						
Urban Soil 8	0.13	0.42	-0.05	0.26	0.01	0.08	0.07	0.42	0.15	0.21	0.22	0.89	0.94	0.95	0.98	0.97	0.97	0.91					
	0.60	0.08	0.85	0.28	0.98	0.74	0.77	0.08	0.54	0.40	0.36	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
Urban Soil 9	0.25	0.21	0.15	0.19	0.16	0.17	0.19	0.20	0.21	0.22	0.22	0.54	0.70	0.77	0.70	0.70	0.58	0.51	0.70				
	0.31	0.39	0.55	0.44	0.52	0.48	0.43	0.41	0.39	0.37	0.36	0.02	0.00	0.00	0.00	0.00	0.01	0.03	0.00				
Urban Soil 10	-0.01	0.35	-0.16	0.16	-0.11	-0.04	-0.04	0.36	0.04	0.09	0.10	0.85	1.00	0.99	0.95	0.95	0.88	0.83	0.93	0.69			
	0.98	0.15	0.51	0.51	0.64	0.87	0.86	0.14	0.88	0.70	0.68	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
Urban Soil 11	0.05	0.47	-0.12	0.27	-0.05	0.05	0.03	0.48	0.13	0.20	0.21	0.94	0.97	0.96	0.96	0.95	0.97	0.93	0.97	0.69	0.96		
	0.83	0.04	0.62	0.26	0.85	0.85	0.89	0.04	0.61	0.42	0.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Urban Soil 12	0.07	0.38	-0.08	0.22	-0.03	0.04	0.04	0.38	0.11	0.17	0.18	0.87	0.95	0.95	0.99	0.97	0.95	0.89	0.99	0.71	0.93	0.97	
	0.77	0.11	0.73	0.37	0.90	0.87	0.88	0.11	0.65	0.49	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Urban Soil 13	0.05	0.45	-0.13	0.25	-0.06	0.03	0.02	0.45	0.11	0.18	0.19	0.91	0.98	0.98	0.95	0.95	0.93	0.89	0.96	0.73	0.98	0.99	0.95
	0.85	0.06	0.61	0.29	0.82	0.89	0.92	0.05	0.64	0.47	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-1 TRAP	0.15	0.45	-0.01	0.31	0.05	0.13	0.13	0.46	0.20	0.26	0.27	0.82	0.87	0.87	0.90	0.95	0.87	0.82	0.91	0.64	0.87	0.90	0.91	0.89
	0.55	0.05	0.98	0.20	0.84	0.60	0.61	0.05	0.40	0.28	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-2 TRAP	0.33	0.41	0.25	0.37	0.27	0.32	0.33	0.39	0.37	0.39	0.39	0.70	0.81	0.83	0.84	0.90	0.74	0.67	0.83	0.72	0.81	0.81	0.84	0.82
	0.17	0.09	0.31	0.12	0.26	0.19	0.17	0.10	0.12	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-3 TRAP	0.24	0.41	0.13	0.33	0.17	0.22	0.23	0.40	0.29	0.32	0.32	0.77	0.88	0.90	0.90	0.95	0.82	0.74	0.90	0.75	0.88	0.89	0.91	0.90
	0.31	0.08	0.59	0.17	0.49	0.36	0.34	0.09	0.24	0.18	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-4 TRAP	0.20	0.40	0.06	0.29	0.10	0.15	0.16	0.40	0.22	0.27	0.27	0.79	0.87	0.87	0.92	0.95	0.86	0.79	0.92	0.65	0.86	0.89	0.92	0.88
	0.43	0.09	0.81	0.23	0.70	0.53	0.52	0.09	0.36	0.27	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-2-4 TRAP	0.20	0.50	0.03	0.36	0.09	0.17	0.17	0.50	0.25	0.31	0.32	0.83	0.82	0.83	0.88	0.92	0.89	0.84	0.91	0.66	0.81	0.89	0.91	0.87
	0.41	0.03	0.91	0.13	0.72	0.48	0.50	0.03	0.31	0.20	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-3-1 TRAP	0.20	0.41	0.06	0.31	0.11	0.17	0.18	0.41	0.24	0.28	0.29	0.75	0.82	0.85	0.87	0.91	0.81	0.75	0.88	0.83	0.81	0.85	0.90	0.86
	0.41	0.08	0.81	0.20	0.65	0.48	0.47	0.08	0.32	0.24	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-4-1 TRAP	0.34	0.53	0.21	0.45	0.27	0.34	0.33	0.52	0.40	0.44	0.45	0.81	0.81	0.83	0.84	0.90	0.83	0.79	0.88	0.76	0.81	0.87	0.88	0.86
	0.16	0.02	0.39	0.05	0.27	0.16	0.17	0.02	0.09	0.06	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-1 (2010)	0.30	0.37	0.22	0.34	0.24	0.28	0.30	0.36	0.34	0.35	0.35	0.67	0.81	0.83	0.83	0.89	0.71	0.64	0.82	0.75	0.81	0.80	0.83	0.82
	0.22	0.12	0.37	0.16	0.32	0.24	0.22	0.13	0.16	0.14	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-1 (2012)	0.08	0.28	-0.02	0.16	-0.01	0.04	0.05	0.28	0.10	0.14	0.14	0.71	0.89	0.89	0.87	0.90	0.76	0.68	0.85	0.65	0.90	0.86	0.84	0.88
	0.74	0.25	0.92	0.52	0.97	0.88	0.84	0.25	0.68	0.57	0.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED 1-4 (2010)	0.33	0.39	0.23	0.34	0.25	0.29	0.30	0.37	0.34	0.36	0.36	0.74	0.83	0.84	0.88	0.91	0.80	0.73	0.88	0.69	0.82	0.84	0.88	0.84
	0.17	0.10	0.35	0.15	0.30	0.23	0.21	0.12	0.16	0.13	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-4 (2012)	0.15	0.32	0.04	0.22	0.05	0.10	0.11	0.32	0.17	0.20	0.20	0.75	0.91	0.91	0.90	0.93	0.80	0.72	0.88	0.66	0.91	0.88	0.88	0.90
	0.55	0.18	0.89	0.37	0.83	0.68	0.65	0.18	0.50	0.41	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED 2-4 (2010)	0.30	0.44	0.17	0.37	0.21	0.27	0.27	0.43	0.33	0.36	0.37	0.75	0.80	0.83	0.86	0.91	0.81	0.74	0.88	0.78	0.80	0.84	0.89	0.84
	0.21	0.06	0.48	0.12	0.38	0.26	0.26	0.07	0.17	0.13	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-2-4 (2012)	0.14	0.51	-0.03	0.34	0.03	0.12	0.11	0.52	0.20	0.27	0.28	0.87	0.87	0.87	0.87	0.91	0.89	0.85	0.90	0.61	0.88	0.91	0.89	0.91
	0.56	0.03	0.91	0.15	0.90	0.61	0.64	0.02	0.40	0.26	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
MARSED-3-2 (2010)	0.26	0.36	0.12	0.29	0.16	0.21	0.21	0.36	0.26	0.29	0.30	0.69	0.74	0.79	0.81	0.83	0.75	0.69	0.82	0.87	0.73	0.79	0.84	0.79
	0.28	0.13	0.61	0.22	0.52	0.40	0.39	0.14	0.28	0.23	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-3-2 (2012)	0.20	0.45	0.04	0.33	0.09	0.17	0.16	0.46	0.23	0.29	0.30	0.80	0.81	0.83	0.86	0.88	0.86	0.81	0.89	0.70	0.80	0.86	0.88	0.86
	0.41	0.05	0.88	0.17	0.71	0.50	0.51	0.05	0.34	0.23	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-4-1 (2010)	0.29	0.40	0.19	0.34	0.22	0.26	0.27	0.39	0.32	0.35	0.35	0.74	0.84	0.87	0.88	0.93	0.79	0.72	0.88	0.76	0.84	0.85	0.89	0.86
	0.22	0.09	0.45	0.15	0.38	0.28	0.26	0.10	0.18	0.14	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-4-1 (2012)	0.16	0.36	0.03	0.25	0.06	0.11	0.12	0.36	0.18	0.22	0.23	0.78	0.89	0.90	0.90	0.93	0.83	0.76	0.90	0.67	0.89	0.89	0.89	0.90
	0.51	0.13	0.90	0.31	0.82	0.64	0.63	0.13	0.46	0.36	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
COAL-1	0.32	0.36	0.23	0.33	0.24	0.27	0.29	0.36	0.32	0.35	0.34	0.69	0.82	0.83	0.84	0.89	0.75	0.66	0.84	0.69	0.82	0.82	0.83	0.82
	0.19	0.13	0.35	0.17	0.33	0.26	0.23	0.14	0.18	0.15	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
COAL-2	0.04	0.21	-0.05	0.10	-0.04	0.00	0.01	0.22	0.06	0.09	0.09	0.65	0.84	0.83	0.84	0.87	0.75	0.65	0.82	0.61	0.83	0.81	0.81	0.82
	0.86	0.39	0.85	0.69	0.87	0.99	0.96	0.37	0.82	0.72	0.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
MARSED-4-1 SC	0.34	0.53	0.21	0.45	0.27	0.34	0.33	0.52	0.40	0.44	0.45	0.81	0.81	0.83	0.84	0.90	0.83	0.79	0.88	0.76	0.81	0.87	0.88	0.86
	0.16	0.02	0.39	0.05	0.27	0.16	0.17	0.02	0.09	0.06	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-3 SC	0.24	0.41	0.13	0.33	0.17	0.22	0.23	0.40	0.29	0.32	0.32	0.77	0.88	0.90	0.90	0.95	0.82	0.74	0.90	0.75	0.88	0.89	0.91	0.90
	0.31	0.08	0.59	0.17	0.49	0.36	0.34	0.09	0.24	0.18	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MARSED-1-2 SC	0.33	0.41	0.25	0.37	0.27	0.32	0.33	0.39	0.37	0.39	0.39	0.70	0.81	0.83	0.84	0.90	0.74	0.67	0.83	0.72	0.81	0.81	0.84	0.82
	0.17	0.09	0.31	0.12	0.26	0.19	0.17	0.10	0.12	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WB-1-SED (2010)	0.15	0.47	-0.05	0.31	0.02	0.11	0.09	0.48	0.18	0.24	0.27	0.88	0.87	0.89	0.91	0.91	0.93	0.88	0.95	0.74	0.86	0.93	0.94	0.92
	0.55	0.04	0.85	0.20	0.94	0.67	0.70	0.04	0.46	0.32	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WB-1-SED (2011)	0.13	0.38	-0.03	0.24	0.01	0.08	0.08	0.38	0.15	0.20	0.21	0.83	0.92	0.93	0.96	0.97	0.91	0.84	0.96	0.72	0.91	0.94	0.97	0.93
	0.61	0.11	0.91	0.32	0.96	0.75	0.75	0.11	0.54	0.41	0.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WB-1-SED (2012)	0.11	0.62	-0.09	0.41	0.01	0.13	0.10	0.63	0.21	0.30	0.32	0.96	0.85	0.83	0.86	0.88	0.96	0.96	0.92	0.52	0.85	0.93	0.90	0.91
	0.65	0.01	0.70	0.08	0.98	0.61	0.69	0.00	0.38	0.22	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
CB-SED (2010)	0.03	0.38	-0.13	0.20	-0.08	0.00	0.00	0.38	0.08	0.13	0.15	0.85	0.94	0.95	0.94	0.95	0.91	0.84	0.95	0.66	0.94	0.95	0.94	0.96
	0.90	0.11	0.60	0.42	0.75	1.00	0.99	0.11	0.76	0.59	0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CB-SED (2011)	0.06	0.37	-0.10	0.20	-0.06	0.02	0.01	0.38	0.09	0.15	0.16	0.85	0.92	0.94	0.95	0.96	0.93	0.86	0.97	0.68	0.92	0.95	0.96	0.95
	0.80	0.12	0.68	0.40	0.82	0.94	0.96	0.11	0.72	0.55	0.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CB-SED (2012)	0.41	0.47	0.27	0.44	0.32	0.37	0.37	0.46	0.42	0.44	0.46	0.68	0.71	0.77	0.77	0.82	0.72	0.67	0.81	0.85	0.72	0.76	0.80	0.78
	0.08	0.04	0.26	0.06	0.19	0.12	0.12	0.05	0.07	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

NOTES:

Cells: Pearson Correlation Coefficient

p-Value

- Correlation Coefficient is greater than 0.8

- Correlations between intramedia samples (e.g., all Tar Ponds Sediments)

APPENDIX 4 - PE/

	MARSED-1-1 TRAP	MARSED-1-2 TRAP	MARSED-1-3 TRAP	MARSED-1-4 TRAP	MARSED-2-4 TRAP	MARSED-3-1 TRAP	MARSED-4-1 TRAP	MARSED-1-1 (2010	MARSED-1-1 (2012	MARSED 1-4 (2010	MARSED-1-4 (2012	MARSED 2-4 (2010	MARSED-2-4 (2012	MARSED-3-2 (2010	MARSED-3-2 (2012	MARSED-4-1 (2010	MARSED-4-1 (2012	COAL-1	COAL-2	MARSED-4-1 SC	MARSED-1-3 SC	MARSED-1-2 SC	WB-1-SED (2010)	WB-1-SED (2011)	WB-1-SED (2012)	CB-SED (2010)	CB-SED (2011)
Wash Brook Arm																											
South Pond Phase																											
South Pond Phase																											
South Pond Phase																											
North Pond Phase																											
North Pond Phase																											
North Pond Phase																											
North Pond Phase																											
North Pond Phase																											
North Pond Phase																											
Urban Soil 1																											
Urban Soil 2																											
Urban Soil 3																											
Urban Soil 4																											
Urban Soil 5																											
Urban Soil 6																											
Urban Soil 7																											
Urban Soil 8																											
Urban Soil 9																											
Urban Soil 10																											
Urban Soil 11																											
Urban Soil 12																											
Urban Soil 13																											
MARSED-1-1 TRAP																											
MARSED-1-2 TRAP	0.91																										
	0.00																										
MARSED-1-3 TRAP	0.95	0.98																									
	0.00	0.00																									
MARSED-1-4 TRAP	0.99	0.93	0.96																								
	0.00	0.00	0.00																								
MARSED-2-4 TRAP	0.97	0.87	0.92	0.97																							
	0.00	0.00	0.00	0.00																							
MARSED-3-1 TRAP	0.91	0.91	0.94	0.90	0.93																						
	0.00	0.00	0.00	0.00	0.00																						
MARSED-4-1 TRAP	0.92	0.95	0.96	0.93	0.93	0.95																					
	0.00	0.00	0.00	0.00	0.00	0.00																					
MARSED-1-1 (2010)	0.90	0.99	0.98	0.92	0.86	0.91	0.95																				
	0.00	0.00	0.00	0.00	0.00	0.00	0.00																				
MARSED-1-1 (2012)	0.93	0.91	0.94	0.94	0.86	0.84	0.86	0.92																			
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00																			
MARSED 1-4 (2010)	0.92	0.97	0.97	0.95	0.89	0.89	0.94	0.96	0.91																		
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00																		
MARSED-1-4 (2012)	0.94	0.93	0.96	0.96	0.89	0.86	0.89	0.94	0.99	0.94																	
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00																	
MARSED 2-4 (2010)	0.93	0.96	0.97	0.94	0.95	0.97	0.98	0.95	0.87	0.95	0.90																
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00																
MARSED-2-4 (2012)	0.96	0.86	0.92	0.95	0.96	0.87	0.90	0.85	0.93	0.88	0.94	0.90															
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00															
MARSED-3-2 (2010)	0.83	0.86	0.89	0.84	0.88	0.98	0.91	0.86	0.77	0.86	0.79	0.95	0.81														
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00														
MARSED-3-2 (2012)	0.91	0.82	0.88	0.91	0.95	0.91	0.87	0.81	0.85	0.85	0.86	0.90	0.94	0.88													
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00													
MARSED-4-1 (2010)	0.93	0.99	0.99	0.95	0.91	0.95	0.96	0.98	0.91	0.98	0.94	0.98	0.89	0.91	0.87												
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00												
MARSED-4-1 (2012)	0.96	0.92	0.96	0.97	0.93	0.88	0.90	0.91	0.98	0.93	0.98	0.92	0.97	0.83	0.92	0.94											
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00											
COAL-1	0.92	0.94	0.94	0.94	0.88	0.85	0.93	0.95	0.93	0.93	0.95	0.91	0.87	0.79	0.81	0.93	0.92										
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00										
COAL-2	0.89	0.83	0.86	0.90	0.83	0.78	0.82	0.84	0.90	0.81	0.90	0.81	0.83	0.69	0.77	0.82	0.88	0.94									
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00									
MARSED-4-1 SC	0.92	0.95	0.96	0.93	0.93	0.95	1.00	0.95	0.86	0.94	0.89	0.98	0.90	0.91	0.87	0.96	0.90	0.93	0.82								
	0.00	0.00	0.00	0.00	0.00	0.00 *		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00								
MARSED-1-3 SC	0.95	0.98	1.00	0.96	0.92	0.94	0.96	0.98	0.94	0.97	0.96	0.97	0.92	0.89	0.88	0.99	0.96	0.94	0.86	0.96							
	0.00	0.00 *		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
MARSED-1-2 SC	0.91	1.00	0.98	0.93	0.87	0.91	0.95	0.99	0.91	0.97	0.93	0.96	0.86	0.86	0.82	0.99	0.92	0.94	0.83	0.95	0.98						
	0.00 *		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00						
WB-1-SED (2010)	0.91	0.80	0.88	0.90	0.95	0.91	0.87	0.78	0.82	0.84	0.84	0.90	0.93	0.89	0.96	0.87	0.90	0.79	0.75	0.87	0.88	0.80					
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
WB-1-SED (2011)	0.95	0.88	0.94	0.96	0.96	0.92	0.89	0.86	0.90	0.91	0.92	0.93	0.94	0.87	0.94	0.93	0.95	0.88	0.85	0.89	0.94	0.88	0.97				
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
WB-1-SED (2012)	0.89	0.76	0.83	0.87	0.91	0.82	0.85	0.73	0.79	0.81	0.82	0.83	0.94	0.76	0.87	0.81	0.86	0.74	0.70	0.85	0.83	0.76	0.92	0.89			
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
CB-SED (2010)	0.93	0.86	0.93	0.93	0.92	0.88	0.86	0.85	0.92	0.88	0.94	0.88	0.96	0.81	0.91	0.90	0.96	0.84	0.83	0.86	0.93	0.86	0.95	0.98	0.91		
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
CB-SED (2011)	0.94	0.84	0.92	0.94	0.94	0.89	0.87	0.83	0.89	0.88	0.91	0.90	0.94	0.83	0.92	0.89	0.94	0.84	0.83	0.87	0.92	0.84	0.97	0.99	0.91	0.99	
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
CB-SED (2012)	0.81	0.87	0.88	0.82	0.85	0.95	0.91	0.87	0.76	0.85	0.79	0.93	0.80	0.95	0.87	0.90	0.81	0.82	0.70	0.91	0.88	0.87	0.86	0.84	0.74	0.79	0.81
	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

NOTES:

Cells: Pearson Correlation Coefficient

p-Value

- Correlation Coefficient is greater than 0.8

- Correlations between intramedia samples (e.g., all Tar Ponds Sediments)

Appendix 6 – Mann Whitney Non-Parametric Test Results

TAR PONDS VS TAR PONDS

	N	Median
South Pond Phase I	19	0.0162
South Pond Phase I_2	19	0.0112

Point estimate for ETA1-ETA2 is 0.0032

95.3 Percent CI for ETA1-ETA2 is (-0.0045,0.0283)

W = 397.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.4391

The test is significant at 0.4370 (adjusted for ties)

In this test, p>alpha (0.05), so we do not reject Ho (that the populations medians are equal). These samples are both from South Pond Sediment, so similar PAH Fingerprints are expected for these samples.

TAR PONDS VS ASTM COAL TAR REFERENCE MATERIAL

	N	Median
SRM 1597a	19	0.0291
South Pond Phase I	19	0.0162

Point estimate for ETA1-ETA2 is 0.0125

95.3 Percent CI for ETA1-ETA2 is (-0.0104,0.0291)

W = 415.0

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.1989

The test is significant at 0.1987 (adjusted for ties)

In this test, p>alpha (0.05), so we do not reject Ho (that the population medians are equal). This is the coal tar reference material and the South Pond Sediment. Once again, it is expected to see similar PAH Fingerprints in the Coal Tar Reference Material and the Sydney Tar Ponds.

HARBOUR SEDIMENT VS HARBOUR SEDIMENT

	N	Median
MARSED-4-1	19	0.05263
MARSED-3-2	19	0.05000

Point estimate for ETA1-ETA2 is 0.00114

95.3 Percent CI for ETA1-ETA2 is (-0.02589,0.02807)

W = 373.0

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.9534

The test is significant at 0.9534 (adjusted for ties)

These two Harbour Sediment sites are the furthest apart geographically. And yet p>>alpha (0.05), that we must not reject Ho and accept that the population medians for PAH distributions in Harbour Sediments from one end of the Sydney Harbour to the other are significantly equal.

UPSTREAM SEDIMENTS VS TAR PONDS SEDIMENT

1.	N	Median
North Pond Phase II	19	0.0101
Wash Brook	19	0.0314

Point estimate for ETA1-ETA2 is -0.0189

95.3 Percent CI for ETA1-ETA2 is (-0.0396,-0.0025)

W = 285.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0136

The test is significant at 0.0136 (adjusted for ties)

In this test, p<alpha(0.05). So there is sufficient evidence to reject Ho and consider the population medians as significantly different. This result suggests that the PAH distribution in samples from Wash Brook is not the same as that in the North Pond.

2. N Median

South Pond Phase I_2 19 0.0112

Cagney Brook 19 0.0428

Point estimate for ETA1-ETA2 is -0.0210

95.3 Percent CI for ETA1-ETA2 is (-0.0582,-0.0018)

W = 292.0

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0228

The test is significant at 0.0227 (adjusted for ties)

In this test, p<alpha(0.05). So there is sufficient evidence to reject Ho and consider the population medians as significantly different. This is an important result, it suggests that the PAH distribution in Cagney Brook is not the same as that in the South Pond.

UPSTREAM SEDIMENT VS HARBOUR SEDIMENT

1. N Median

Wash Brook 19 0.03933

MARSED-1-1 19 0.05784

Point estimate for ETA1-ETA2 is -0.00592

95.3 Percent CI for ETA1-ETA2 is (-0.03375,0.01941)

W = 351.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.5891

The test is significant at 0.5890 (adjusted for ties)

In this test, p>>alpha(0.05). So there is NOT sufficient evidence to reject Ho. It would seem that PAH distribution in the Wash Brook is similar to that at Harbour Sediment 1-1. This might suggest a PAH source in Sydney Harbour that is similar to a PAH source in Wash Brook. These anthropogenic sources differ from those observed in the Tar Ponds sediments (as shown in the previous test).

UPSTREAM SEDIMENT VS COAL SEDIMENT

	N	Median
Cagney Brook	19	0.05670
COAL-2	19	0.04413

Point estimate for ETA1-ETA2 is 0.00026

95.3 Percent CI for ETA1-ETA2 is (-0.02262,0.02812)

W = 373.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.9418

The test is significant at 0.9418 (adjusted for ties)

In this test, p>>alpha(0.05). So there is NOT sufficient evidence to reject Ho. It would seem that PAH distribution in the Cagney Brook is similar to that in the Coal Sediments. This may suggest a source of PAH impacts in Cagney Brook, which may be associated with former coal storage operations at the site or upstream residential/commercial operations. This test supports the hypothesis that the PAH impacts observed upstream as well as in the Sydney Harbour do not share the same PAH distribution as the Sydney Tar Ponds Sediments.

TAR PONDS VS HARBOUR SEDIMENTS

1.	N	Median
South Pond Phase I	19	0.0162
MARSED-1-4 TRAP	19	0.0411

Point estimate for ETA1-ETA2 is -0.0178

95.3 Percent CI for ETA1-ETA2 is (-0.0456,-0.0018)

W = 293.0

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0246

The test is significant at 0.0244 (adjusted for ties)

2. N Median

South Pond Phase I 19 0.0162

MARSED-4-1_1 19 0.0526

Point estimate for ETA1-ETA2 is 0.0213

95.3 Percent CI for ETA1-ETA2 is (0.0040,0.0515)

W = 451.0

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0195

The test is significant at 0.0194 (adjusted for ties)

3. N Median

North Pond Phase II_1 19 0.0141

MARSED 2-4 19 0.0520

Point estimate for ETA1-ETA2 is -0.0299

95.3 Percent CI for ETA1-ETA2 is (-0.0520,-0.0075)

W = 276.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0063

The test is significant at 0.0063 (adjusted for ties)

4. N Median

North Pond Phase III_1 19 0.0110

MARSED-3-2_1 19 0.0500

Point estimate for ETA1-ETA2 is -0.0239

95.3 Percent CI for ETA1-ETA2 is (-0.0451,-0.0023)

W = 290.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0203

The test is significant at 0.0202 (adjusted for ties)

In these four iterations using four different samples of Tar Ponds Sediments and tested with four different samples of Harbour Sediments, including the southernmost, northernmost and closest sampling locations, as well as a sediment trap designed to capture new sediment depositions, results indicated p-values for the tests that are less than 0.0246 (maximum) which are lower than the selected alpha value of 0.05. This means the null hypothesis can be rejected and consider the population medians for the Tar Ponds Sediments significantly different from the population medians for Harbour Sediments. Therefore, the PAH distributions for the Sydney Tar Ponds are also considered to be significantly different from the PAH distributions of the Harbour Sediments.

TAR PONDS VS COAL SEDIMENTS

1.	N	Median
South Pond	19	0.0162
COAL-1	19	0.0543

Point estimate for ETA1-ETA2 is -0.0201
95.3 Percent CI for ETA1-ETA2 is (-0.0532,-0.0076)
W = 279.0
Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0079
The test is significant at 0.0078 (adjusted for ties)

2.	N	Median
South Pond	19	0.0112
COAL-2	19	0.0441

Point estimate for ETA1-ETA2 is -0.0259
95.3 Percent CI for ETA1-ETA2 is (-0.0578,-0.0091)
W = 268.0
Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0029
The test is significant at 0.0029 (adjusted for ties)

3. N Median

North Pond 19 0.0141

COAL-2 19 0.0441

Point estimate for ETA1-ETA2 is -0.0214

95.3 Percent CI for ETA1-ETA2 is (-0.0518,-0.0039)

W = 288.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0173

The test is significant at 0.0173 (adjusted for ties)

4. N Median

North Pond 19 0.0028

COAL-1 19 0.0543

Point estimate for ETA1-ETA2 is -0.0233

95.3 Percent CI for ETA1-ETA2 is (-0.0598,-0.0100)

W = 265.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.0023

The test is significant at 0.0022 (adjusted for ties)

In these 4 tests, p<alpha(0.05). So there is sufficient evidence to reject Ho and consider the population medians as significantly different. These are important results. It presents dissimilarity between the distribution of PAHs in the Tar Pond Sediment and the Coal Sediments at the coal piers in the Sydney Harbour.

HARBOUR SEDIMENT VS COAL SEDIMENT

1. N Median

MARSED-4-1 19 0.05263

COAL-1 19 0.05432

Point estimate for ETA1-ETA2 is -0.00062

95.3 Percent CI for ETA1-ETA2 is (-0.02960,0.02321)

W = 368.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.9651

The test is significant at 0.9651 (adjusted for ties)

In this test, p>>alpha(0.05). So we do not reject Ho and we consider the population medians significantly similar. The p value is so high, that it is interesting to note that this is 4-1 Harbour Sediment, which is located in the inner harbour, less susceptible to storm effects but more susceptible to an accumulation of anthropogenic inputs.

2.	N	Median
MARSED-1-1	19	0.05098
COAL-1	19	0.05432

Point estimate for ETA1-ETA2 is -0.00040

95.3 Percent CI for ETA1-ETA2 is (-0.02628,0.02696)

W = 364.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.8724

The test is significant at 0.8724 (adjusted for ties)

3.	N	Median
MARSED-2-4 TRAP	19	0.04797
COAL-1	19	0.05432

Point estimate for ETA1-ETA2 is -0.00081

95.3 Percent CI for ETA1-ETA2 is (-0.02814,0.02078)

W = 369.0

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.9767

The test is significant at 0.9767 (adjusted for ties)

4.	N	Median
MARSED-3-2	19	0.05000
COAL-1	19	0.05432

Point estimate for ETA1-ETA2 is -0.00305

95.3 Percent CI for ETA1-ETA2 is (-0.02722,0.02257)

W = 365.5

Test of ETA1 = ETA2 vs. ETA1 not = ETA2 is significant at 0.8955

The test is significant at 0.8954 (adjusted for ties)

In these tests, p>>alpha (0.05). So we do not reject Ho and we consider the population medians for these samples to be significantly equal. This means that the PAH distributions of the various Harbour Sediments are significantly equal to the PAH distributions in the Coal Sediments located beneath the coal piers. The p value is so high, that it is interesting to note that these Harbour Sediment Locations are 1) the southernmost sample point in Sydney Harbour, 2) one of the closest sample points to the Tar Ponds as well as the coal piers, 3) a sediment trap accumulating "new" sediment during the project, located on the NE shoreline, and 4) the far-field reference site located at the northernmost sample point.