

Linda Hanefeld
Remediation and Redevelopment Team Supervisor
Wisconsin Department of Natural Resources
South Central Region
3911 Fish Hatchery Rd
Fitchburg WI 53711

Subject:

Polynuclear Aromatic Hydrocarbons (PAHs) Evaluation, Madison-Kipp Corporation (MKC) Site, 201 Waubesa Street, Madison, Wisconsin.

Dear Ms. Hanefeld:

On December 7, 2012, the Wisconsin Department of Natural Resources (WDNR) issued a letter to Madison-Kipp Corporation (MKC) directing MKC to submit a work plan “either...for determining whether any of the health-based direct contact exceedances can be attributed to background concentrations or...a remedial action plan to be employed by MKC...”. In response to the WDNR request, ARCADIS, on behalf of MKC, submitted the *Polynuclear Aromatic Hydrocarbons (PAH) Work Plan, Determination of Whether Health-Based Direct Contact Exceedances Can Be Attributed to Background Concentrations* (Work Plan) on December 14, 2012.

The Work Plan presented an evaluation methodology designed to determine whether any of the health-based direct contact exceedances can be attributed to background concentrations. The attached *Polynuclear Aromatic Hydrocarbons Evaluation* report has been prepared to document the evaluation presented in the Work Plan. We look forward to discussing this report with you.

ARCADIS U.S., Inc.
126 North Jefferson Street
Suite 400
Milwaukee
Wisconsin 53202
Tel 414 276 7742
Fax 414 276 7603
www.arcadis-us.com

ENVIRONMENT

Date:
January 21, 2013

Contact:
Jennine Trask

Phone:
414.277.6203

Email:
Jennine.Trask@arcadis-us.com

Our ref:
WI001283.0006

ARCADIS

If you have any questions or require any additional information, please contact us at 414.276.7742.

Sincerely,

ARCADIS U.S., Inc.



Jennine L. Trask, PE
Project Manager

Copies:

David Crass – Michael Best
Mark Meunier – Madison Kipp
Bob Nauta – RJN Environmental Services (electronic)
Steve Tinker – Wisconsin Department of Justice (electronic)
Mike Schmoller – WDNR (electronic)



Madison Kipp Corporation

**Polynuclear Aromatic
Hydrocarbons Evaluation**

January 2013



A handwritten signature in black ink that reads "Brian Magee".

Brian Magee, Ph.D.
Vice President, Principal Toxicologist

A handwritten signature in blue ink that reads "Evan Nyer".

Evan Nyer
Senior Vice President

Polynuclear Aromatic Hydrocarbons Evaluation

Prepared for:
Madison Kipp Corporation

Prepared by:
ARCADIS U.S., Inc.
126 North Jefferson Street
Suite 400
Milwaukee
Wisconsin 53202
Tel 414 276 7742
Fax 414 276 7603

Our Ref.:
WI001283

Date:
January 21, 2013

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Acronyms and Abbreviations

ACE	acenaphthene
ANY	acenaphthylene
BaA	benzo(a)anthracene
BaP	benzo(a)pyrene
BbF	benzo(b)fluoranthene
BMP	Best Management Practices
CHR	chrysene
cm	centimeters
DBA	dibenzo(a,h)anthracene
Ft bgs	feet below ground surface
FLU	fluorene
IP	indeno(1,2,3-c,d)pyrene
m/s	meters per second
$\mu\text{g}/\text{m}^2/\text{s}$	micrograms per square meter per second
$\mu\text{g}/\text{m}^3$	micrograms per cubic meter
MCA	multivariate cluster analysis
mg/kg	milligrams per kilograms
MKC	Madison-Kipp Corporation
NAP	naphthalene
NATA	National-Scale Air Toxics Assessment
NIST	National Institute of Standards and Technology
PAH	polynuclear aromatic hydrocarbons
PC	principal components
PCA	principal component analysis
PCB	polychlorinated biphenyls

PHE	phenanthrene
ppm	parts per million
PYR	pyrene
r	correlation coefficient
R²	coefficient of determination
RCL	Residual Contaminant Levels
U.S. EPA	United States Environmental Protection Agency
VOCs	volatile organic compounds
WDNR	Wisconsin Department of Natural Resources

Expert Report

It is our opinion that the polynuclear aromatic hydrocarbons (PAHs) found in the yards surrounding the Madison-Kipp Corporation (MKC) facility (Site) are part of the normal background concentrations of PAHs found in Madison, Wisconsin and other urban areas in the United States. It is also our opinion that the source of PAHs found in the yards surrounding the Site are not from MKC.

These opinions, as well as all of the opinions and conclusions stated herein, are to a reasonable degree of scientific certainty, based on our knowledge, background, experience and site-specific research including the following:

- Total PAHs at the Site
- Specific PAH compounds identified in each sample
- Mixtures of PAH compounds found in each sample
- Potential sources of PAHs from the MKC manufacturing facility
- Transport mechanisms for PAHs including deposition of particulate matter from air or possible overland flow associated with water runoff
- Potential sources of PAHs from areas other than the Site

In rendering these opinions, we surveyed research regarding 'background' PAH concentrations.¹ The Wisconsin Department of Natural Resources' published policy documents on background PAHs were reviewed by ARCADIS. The published materials clearly show that it is widely known that, in Wisconsin, there are statewide sources of PAHs from coal-fired powered plants and other heating systems, dust from asphalt, and many other sources that combine to form a small mass of airborne PAHs that settle on all surfaces including non-covered soils in residential areas. The same type of policy documentation has been prepared in several other states across the country and all of these documents were confirmed by several policies on background

¹ The information and opinions presented in this report may be modified as additional information is reviewed or becomes available.

PAHs written by the United States Environmental Protection Agency (U.S. EPA). Background PAHs are found throughout the country and are expected in any urban, non-covered soil.

Furthermore, we completed a statistical analysis of the 341 PAH samples collected as part of the site investigation activities conducted on and around the Site. Based upon this analysis, the PAHs found in the backyards (off Site) were comprised of background mixtures of PAHs, not PAHs attributable to sources at MKC. During this study a statistical evaluation was completed to separate the PAH data into 6 groups. The individual groups were designated based upon the relative proportions of various PAHs and the ratios of the types of PAHs found in the samples. All samples from residential locations were associated with PAH profiles that are indicative of combustion sources including coal and cinders, urban dust or asphalt, as defined by two PAH profile groups identified during the statistical evaluation. Samples from the Site were represented by all six PAH profile groups, which were dominated by combustion related PAHs or had varying contributions from potential petroleum related PAH sources.

All of the samples that were collected from the Site itself (on Site) were represented by all six of the PAH profile groups. Many of the samples had a similar pattern to the combustion related PAHs identified in the residential yards. However, the other PAH groups that were found exclusively on the Site consisted of a lighter (lower molecular weight) PAH mixture with a higher naphthalene content that likely represents PAHs from potential petroleum related PAH sources. These PAHs are associated with petroleum hydrocarbons that could be the result of normal truck and car traffic at the facility, and the types of petroleum products that were likely used at the Site.

This clear distinction between the on-Site and off-Site samples was then further analyzed. The data demonstrates that the PAHs found on Site did not travel to the surrounding properties. The transport potential of PAHs off Site by water and airborne deposition was studied. The storm water permit for the Site was used as a basis for determining the exit point for water from the site. This clearly showed that most of the water runoff from the Site would end up at the north end of the property. While single events like floods may have a different pattern than normal storm runoff, the preponderance of runoff material over the years would be with the normal storm water flows. Despite this, it was very clear that the off-Site samples in the north consisted of the same background concentrations and mixtures found on the rest of the off-Site properties. There was no evidence that the lower molecular weight PAHs found on the Site were found in the northern off-Site properties.

Local wind data was used to determine the preferential wind flow pattern at the Site. This data set was used to evaluate general air discharges and point source (exhaust fans) air discharges from the property. The preferential air flow pattern is to the north. The offsite samples in the north were compared to the PAHs samples found on Site. Once again, all of the northern off-Site samples were comprised of background PAHs. There was no evidence that the lower molecular weight PAHs found on Site or the lower molecular weight PAHs found in the petroleum products used at the Site traveled to the northern off-Site properties. Further, there is no evidence of a correlation between PAHs detected off-Site and the locations of the exhaust fan air discharges.

The known potential sources of PAHs that were historically used at the Site were petroleum-based products. The only PAHs associated with these products were the lower molecular weight PAHs. While evidence of lower molecular weight PAHs was indicated in the on-Site samples, there was no evidence of these compounds in the off-Site samples. The PAHs from the facility were not the source of PAHs found in the neighbors' backyards, but rather the off-Site samples are consistent with general PAH mixtures found in urban areas (a.k.a. "background").

The Madison-Kipp facility did use coal fired boilers over many decades. However, this potential source is not responsible for PAHs identified in the neighbors' backyards for the following reasons:

- The coal used at the Madison-Kipp facility was a minor proportion of the total coal used in the area for homeowners and businesses. Coal was the predominant historic fuel source for homeowners and businesses throughout East Madison.
- The airborne discharge of PAHs from coal combustion historically at the Madison-Kipp facility would have been from stacks at the Site. While this discharge may have become a small part of the overall background PAHs in Madison, the stacks were specifically designed to move and disperse atmospheric emissions.

Based on this information, an evaluation was completed for potential sources of the PAHs found in the backyards. The U.S. EPA has completed very specific studies on PAHs in the air of various urban areas. These studies included the airborne PAH concentrations for Dane county for several years. The U.S. EPA also provided a method to calculate the amount of PAHs expected to settle onto the soil based upon

the concentrations found in the air. Based upon these calculations, the PAHs found in the backyards are within the expected concentrations for urban areas.

The evaluation methods used in this assessment are consistent with the state of the science as practiced in source identification studies. All methods used, including multivariate cluster analysis, principal component analysis, diagnostic ratio analysis and source correlation, indicate that the PAHs found in the backyards are consistent with background sources².

It is our opinion that, to a reasonable degree of scientific certainty, the following conclusions can be drawn from the forensic PAH evaluation presented herein:

- 1) Statistical analysis of PAH distributions within individual samples clearly indicates that several PAH profiles are present in the data set.
- 2) The majority of samples meeting the inclusion criterion for the forensic evaluation cluster are in a single group (Group 1) and represent 86.8% of the data set, with the remaining samples being separated into five additional groups.
- 3) The remaining five groups are differentiated from the main Group 1 profile based on the relative proportion of light 2-ring PAHs or heavier 6-ring PAHs.
- 4) Residential samples tend to be associated with the primary Group 1 type of PAH profile, with 63 of 65 residential samples being in this group. The remaining two samples were associated with the group having a slightly heavier PAH assemblage, but in any case unassociated with the lighter ring PAHs identified on the MKC facility.
- 5) When compared to representative PAH source materials, the PAH profiles for Group 1 samples are consistent with PAH assemblages derived from combustion related sources such as coal fines, cinders, urban dust or asphalt. The PAH profile for this group is not consistent with PAH sources from cutting oil, waste oil, diesel contaminated soils, coal tar or coal tar pitch.

² MCA Murakimi et al., 2005; PCA Stout et al., 2003; Diagnostic Ratios Yunkers, 2002; source correlation Burns et al., 2006

- 6) The spatial distribution of Group 1 shows that these samples are evenly distributed among all locations without a strong preference for clustering in a given area.
- 7) Group 2 samples are similar to Group 1 with the exception of having a high relative proportion of 6-ring PAHs. The PAH profile for this group is also consistent with combustion related sources including asphalt, urban dust and coal tar pitch.
- 8) Groups 3, 4, 5 and 6 have greater relative proportions of light 2- and 3-ring PAHs. Based on comparisons with PAH reference material profiles from known sources, these groups most likely are influenced by PAH sources with higher naphthalene proportions including diesel contaminated soils or waste oils superimposed on combustion related PAH sources and are more indicative of the types of PAH source materials utilized at the MKC facility.

1. Introduction

ARCADIS has been retained to assist the Madison-Kipp Corporation (MKC) with environmental investigation and remediation activities at the facility located at 201 Waubesa Street in Madison, Wisconsin (Site). As part of the investigation activities, Site and off-Site residential backyard soil samples were collected for analysis of polynuclear aromatic hydrocarbons (PAHs). The Site data set consists of 341 soil samples analyzed for PAHs from both on- and off-Site locations.

Based on the results of the investigation activities completed, the *Off-Site Residential Polycyclic Aromatic Hydrocarbon (PAH) Results Summary* letter, dated September 11, 2012 was submitted to the Wisconsin Department of Natural Resources (WDNR) to present the PAH results and recommendations. The PAHs detected in soil were compared to the WDNR Non-Industrial Direct Contact Residual Contaminant Levels (RCLs) as calculated using the U.S. EPA's Regional Screening Level web calculator. As previously communicated to WDNR, at most of the sample locations, one or more PAHs from 0 to 2 ft below ground surface (ft bgs) exceeded WDNR's RCL at a cancer risk level of 1×10^{-6} or a non-cancer hazard index of 1. At only a few sample locations, PAH results from 2 to 4 ft bgs also exceeded the RCLs. U.S. EPA has determined the acceptable range for RCLs for PAHs to be between 1×10^{-6} and 1×10^{-4} [40 CFR § 300.430 (e)(2)(i)(A)(2)] and WDNR's Soil Cleanup Standards in Wis. Admin. Code Ch. NR 720 applies 10^{-5} as the cumulative acceptable risk for all sites throughout the state. U.S. EPA has established preliminary remediation goals at various sites in Wisconsin utilizing 1×10^{-5} to 1×10^{-4} risk.

The September 11, 2012 letter included the following summary regarding the PAHs on the Site:

PAHs are common industrial compounds, as indicated by their presence on properties such as Madison Kipp and the nearby Goodman Center. However, PAHs are also associated with a broad range of sources unrelated to industrial activity. Based on this information, there is insufficient evidence to establish that PAHs in residential soil are associated with the Madison Kipp property and are anything other than typical background PAHs present in an urban setting. In addition, the concentrations of PAHs present off-site are less than the risk-based levels developed for similar sites in Wisconsin. Therefore, there is no need to implement remedial measures for these constituents at off-site locations. PAHs are ubiquitous in an urban environment from many different activities, the majority of

which have no relation to activities at Madison Kipp. As a result, PAHs should not be a driver for off-site remediation in relation to the Madison Kipp site.

The WDNR issued a letter dated December 7, 2012 directing MKC to submit a work plan "either...for determining whether any of the health-based direct contact exceedances can be attributed to background concentrations or...a remedial action plan to be employed by MKC...". On December 14, 2012, ARCADIS, on behalf of MKC, submitted the *Polynuclear Aromatic Hydrocarbons (PAH) Work Plan, Determination of Whether Health-Based Direct Contact Exceedances Can Be Attributed to Background Concentrations* (Work Plan). The Work Plan presented an evaluation methodology designed to determine whether any of the health-based direct contact exceedances can be attributed to background concentrations. This methodology was aimed at data analyses, the objective of which is to better understand the source, fate and transport concerning the PAHs present at the Site and on adjoining residential properties.

1.1 Site Description

The Site is approximately 7.5 acres in size. A 130,000-square foot building occupies much of the Site. Asphalt parking lots are located in the northeastern, southwestern and southeastern portions of the Site. The building has a 25,000-square foot second floor and a 25,000-square foot basement. Figure 1-1 depicts the layout of the Site. The Site is zoned M-1 (industrial/manufacturing). The Site is currently used as a metals casting facility.

The Site is located in the eastern portion of Madison, in a mixed use area of commercial, industrial and residential land use. The Site is bounded by a bicycle trail (Capital City Trail) constructed on a former railroad line to the north, Atwood Avenue to the south, and Waubesa Street to the west. Residences are located adjacent to the east and west sides of the Site, and further west (across Waubesa Street) and east (across Marquette Street). Commercial properties are located to the south (across Atwood Street) and further east. The Goodman Community Center is located to the north (across the Capital City Trail) and was the site of former industrial activities.

The Site is also located at the northeast end of the Madison isthmus, approximately 1,500 feet north of Lake Monona and approximately 6,800 feet east of Lake Mendota. The topography of the Site is relatively flat, with an elevation ranging from approximately 870 to 880 feet above mean sea level. The Site and surrounding area is serviced by municipal water supply and sewerage systems.

1.2 Site History

In the late 1800s, the United States Navy constructed a foundry at the Site for the purpose of casting cannon barrels. Although no barrels were ultimately cast at the Site, the facility has been used for casting metals since that time. Originally two separate buildings (one on Atwood Avenue and one to the north on Waubesa Street) were located on the Site. Various construction activities over the years joined the buildings, resulting in the current facility configuration (Figure 1-1).

Multiple industrial products have been used during the history of the facility, including cutting oils, lubrication oils, degreasing chemicals and miscellaneous other products. These products contained various petroleum compounds, chlorinated volatile organic compounds (VOCs), and polychlorinated biphenyls (PCBs).

2. General Discussion Of PAH Background Sources In Urban Areas

PAHs in urban soils have many natural and anthropogenic sources. Natural sources include PAHs resulting from forest fires, volcanic eruptions, and petroleum and tar seeps. Anthropogenic sources include fireplaces, wood burning stoves, home heating boilers, cars, trucks, busses, trains, backyard garbage and brush burning, accidental building fires, wood and coal ash, electric power generation plants, industrial boilers, coke ovens, petroleum refineries, road and roofing tar, driveway sealers, petroleum fuels and lubricating oils, oil spills, and many others, including individual industrial plants and waste disposal or spill sites (ATSDR, 1995).

Today many anthropogenic PAH sources are controlled as point sources under various regulatory programs. For instance, a coke oven or a petroleum refinery has emission limitations it must adhere to in accordance with a government issued permit. Historically, such sources were not controlled, however, and emissions that occurred decades ago from such point sources are important sources of current anthropogenic background levels of PAHs.

Background PAH sources consist of both of these groups of natural and anthropogenic sources. PAHs that cannot be traced to a specific source are defined as background PAHs from one or many sources. It is generally recognized that in areas that have been heavily urbanized for decades or even hundreds of years, there are many anthropogenic background sources of PAHs.

2.1 Discussion of Wisconsin Regulations and Guidance Regarding Background Sources

Wisconsin regulations for Soil Cleanup Standards (Wis. Admin. Code Ch. NR 720) specifically address the issue of background levels of constituents, such as PAHs in soils in urban areas. Specifically, NR 720.11(5)(b) states:

“(b) If the background concentration for a substance in soil at a site or facility is higher than the residual contaminant level for that substance listed in Table 2 or determined using the procedure in s. NR 720.19 (3), the background concentration in soil may be used as the residual contaminant level for that substance. The background concentration for a substance in soil shall be determined using a department-approved and appropriate method.”

WDNR (2005) also published a guidance document entitled *Guidance for Determining Soil Contaminant Background Levels at Remediation Sites*. It specifically cites PAHs

as “ubiquitous organics...from widespread atmospheric deposition” that are candidates for background soil determinations because they cannot be traced to a specific source. In fact, the definition of “background soil quality” refers to “lead, polynuclear aromatic hydrocarbons or polychlorinated biphenyls attributable to atmospheric deposition” according to NR 700.03(2).

In addition, WDNR (2011) in its *Soil Residual Contaminant Level Determinations Using the U.S. EPA Regional Screening Level Web Calculator*, specifically states that the Regional Screening Level web calculator does not address soil background levels, and that the soil background levels must be addressed separately when deriving Residual Contaminant Levels.

2.2 Discussion of Other State Regulations and Guidance Regarding Background Sources

WDNR is not alone in considering the widespread atmospheric deposition of PAHs to constitute background. For instance, Massachusetts (1995) defines “background” in the following manner:

“Background means those levels of oil and hazardous material that would exist in the absence of the disposal site of concern which are:

- a) Ubiquitous and consistently present in the environment at and in the vicinity of the disposal site of concern; and
- b) Attributable to geologic or ecologic conditions, atmospheric deposition of industrial processes or engine emissions, fill materials containing wood or coal ash, releases to groundwater from a public water supply system, and/or petroleum residues that are incidental to the normal operation of motor vehicles.”

Massachusetts specifically names engine emissions, wood ash, coal ash and petroleum residues associated with motor vehicle operation as anthropogenic sources of PAHs to the environment.

Further, Massachusetts recently released a document entitled *Best Management Practices For Controlling Exposure To Soil During The Development Of Rail Trails* that explicitly recognizes that historical contamination has occurred along railways, but because historical contamination is considered background, it is excluded from the

Massachusetts Contingency Plan, which governs site release investigations and clean ups.

Specifically, the document defines Best Management Practices (BMPs) that were “developed to eliminate or minimize potential exposures to residual oil or hazardous materials commonly found along railroad rights-of-way being converted to rail trails.” These BMPs do not require constituent characterization and remediation as noted below:

“Some historic railroad operations involved the use of chemicals that may have resulted in presence today of contamination.... Lubricating oil and diesel that dripped from the trains are likely sources of the petroleum product found along the lines. Other sources of contaminants associated with historic railroad operation may include coal ash from engines, creosote from ties, and polynuclear aromatic hydrocarbons (“PAHs”) from the diesel exhaust. The BMPs outlined in this document are specifically designed to be protective of public health and provide a practical alternative to extensively testing for and possibly removing these “typical” residues expected from the historic operation of a rail line.”

In the Illinois Tiered Approach to Corrective Action program, "Area Background" is defined to incorporate anthropogenic sources of constituents:

““Area Background” means concentrations of regulated substances that are consistently present in the environment in the vicinity of a site that are the result of natural conditions or human activities, and not the result solely of releases at the site.”

California (2009) incorporates anthropogenic sources in their definition of “ambient conditions” for organics, such as PAHs, as noted below:

“Polynuclear aromatic hydrocarbons (PAHs) are associated with the combustion of fossil fuels, industrial and commercial activities, and natural sources such as wildfires and volcanic activity. PAHs are found in soils within both rural and urban areas, reflecting the many natural and anthropogenic sources of PAHs in the environment. PAHs that are not attributable to a specific point source are referred to as “ambient”. PAHs are typically found at higher ambient concentrations in urban areas, near more heavily traveled roadways, in areas that have had longer human occupation, in areas receiving runoff from surface soils containing PAHs, and areas downwind of urbanized areas (Wang et al., 2008; Nam et al. 2008).

Some studies have found that higher ambient concentrations can also be associated with soils having higher organic matter and/or clay content.”

“For sites where PAH-impacted soils have been identified and require cleanup, it may be necessary to evaluate ambient concentrations of PAHs in soil. This assessment may be needed because the calculated health-based or ecologically-based cleanup goal for PAHs can be one to two orders of magnitude below ambient PAH concentrations in developed areas. In general, DTSC does not require cleanup of sites to concentrations that are less than ambient. In these instances, the cleanup approach can be developed based on ambient PAH concentrations. This approach ensures that the health risks associated with exposure to the PAHs do not pose a health risk greater than that posed by ambient concentrations of PAHs. (California DTSC, 2009)”.

Kentucky (2004) also defines background to include anthropogenic sources:

“Background, as defined in 401 KAR 42:005 (definitions codified to support the Underground Storage Tank regulations), means the concentration of substances consistently present in the environment at, or regionally proximate to, a release but outside the influence of the release. There are two types of background:

- a) Natural background is the amount of naturally occurring substances in the environment, exclusive of that from anthropogenic sources.
- b) Ambient background means the concentrations of naturally occurring inorganic substances and ubiquitous anthropogenic inorganic substances in the environment that are representative of the region surrounding the site and not attributable to an identifiable release.”

Another state that includes anthropogenic sources in its definition of background is West Virginia, as noted below:

“The Rule specifies that where the De Minimis Standard is below natural background and where the Uniform and Site-Specific Risk-Based Standards are below anthropogenic background, that natural background may be used in place of the De Minimis Standard, and natural or anthropogenic background may be used in place of the Uniform and Site-Specific Risk-Based Standards.”

“Anthropogenic background refers to concentrations of elements that occur over a widespread area as a result of human activities.”

2.3 Discussion of Federal Regulations and Guidance Regarding Background Sources

Like many states, the Federal government has a detailed policy on background levels of chemicals in urban soils that recognizes the important role of widespread aerial deposition of chemicals like PAHs in determining the background levels of chemicals in soils. EPA's *Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites* (EPA, 2002) defines background to include both naturally occurring and anthropogenic substances in site media, such as soil. Specifically, EPA states:

“For the purposes of this policy, the following definitions are used.

Background refers to constituents or locations that are not influenced by the releases from a site, and is usually described as naturally occurring or anthropogenic (EPA, 1989; EPA, 1995a):

- 1) Anthropogenic - natural and human-made substances present in the environment as a result of human activities (not specifically related to the CERCLA release in question); and,
- 2) Naturally occurring - substances present in the environment in forms that have not been influenced by human activity.”

According to EPA, both types of background substances can be treated the same way in a background investigation: “Generally, the type of background substance (natural or anthropogenic) does not influence the statistical or technical method used to characterize background concentrations.” EPA is clear that site clean-up decisions should focus on substances released by the site or facility and not on substances present at levels that constitute natural or human-induced historic background. Specifically, EPA (2002) states:

“Background information is important to risk managers because the CERCLA program, generally, does not clean up to concentrations below natural or anthropogenic background levels. (Page B-3)

Generally, under CERCLA, cleanup levels are not set at concentrations below natural background levels. Similarly, for anthropogenic contaminant concentrations, the CERCLA program normally does not set cleanup levels below anthropogenic background concentrations (EPA, 1996; EPA, 1997b; EPA, 2000). The reasons for this approach include cost-effectiveness, technical practicability, and the potential for recontamination of remediated areas by surrounding areas with elevated background concentrations. In cases where area-wide contamination may pose risks, but is beyond the authority provided under CERCLA, EPA may be able to help identify other programs or regulatory authorities that are able to address the sources of area-wide contamination, particularly anthropogenic (EPA, 1996; EPA, 1997b; EPA, 2000). (Page B-6)".

EPA's *Risk Assessment Guidance for Superfund* (EPA, 1989) gives an almost identical definition of background as noted below:

"There are two different types of background levels of chemicals:

- 1) Naturally occurring levels, which are ambient concentrations of chemicals present in the environment that have not been influenced by humans (e.g., aluminum, manganese); and
- 2) Anthropogenic levels, which are concentrations of chemicals that are present in the environment due to human-made, non-site sources (e.g., industry, automobiles)"

EPA's definition of background levels of PAHs in soils specifically includes all "area-wide contamination" including that from industrial emissions and automobiles.

2.4 Summary

It is our opinion to a reasonable degree of scientific certainty that the Site and surrounding area would be expected to be impacted by naturally occurring and anthropogenic levels of PAHs. As such, the next step in our analysis was to evaluate the specific PAHs found in the soil samples collected from on-Site and residential areas and determine if the PAHs detected in these samples are from the background PAHs or activities at the Site.

3. Forensic Evaluation of PAH Distribution in On-Site and Residential Samples

An essential element of our analysis was identifying potential sources for the PAHs identified both on-Site and in residential samples. Because PAHs are derived from a variety of natural, industrial and general anthropogenic sources, it is possible to evaluate the relative proportions of PAHs in a sample to gain information related to these various sources (Costa and Sauer, 2005; Jansen et al., 2007; Kaplan et al., 1997; Kaplan et al., 2001; Lima et al., 2005; Mitra et al., 1999; Manoli et al., 2004; Nam et al., 2008; Teaf, 2008; EPA, 2007; Uhler and Emsbo-Mattingly, 2006; Zemo, 2009). PAH forensic evaluation methods are well established in the peer-reviewed literature (Burns et al., 1997; Iqbal et al., 2008; Kimbrough and Dickhut, 2006; Kose et al., 2008; Lee, 1999; Liu et al., 2010; Larsen and Baker, 2003; McGregor et al., 2012; Stout et al., 2001a; Stout et al., 2001b; Yunkers et al., 2002). Several of these methods have been employed to evaluate both the nature of the PAHs present both on-site and on residential properties, and to identify how the project-specific distribution of PAHs compares to distributions from known PAH source reference materials.

3.1 Analytical and Statistical Methods for PAH Evaluation

PAHs are ubiquitous in the terrestrial environment (Stout et al., 2001a; Yunkers, et al., 2002; Neff et al., 2005; Lima, et al., 2005). PAHs occur as complex mixtures in sediments and soils that are derived from multiple natural and anthropogenic sources, which may subsequently be subject to a variety of physical, biological and chemical processes that further modify the relative proportion of specific PAH compounds within a given location. An extensive body of work is available in the peer-reviewed literature that describes various PAH sources and transformational processes, as well as presents analytical and statistical methods that have been applied to identify the dominant initial PAH sources within various settings (Douglas et al., 1996; Christensen et al., 2005; Diblasi et al., 2009; Kose et al., 2008; Lima et al., 2005; Mitra et al., 1999; Pies et al., 2008; Stout et al., 2003; Walker et al., 2005; Wang et al., 2009). The fundamental purpose of a forensic PAH evaluation is to apply these methods to gain an understanding of these sources based on the sample-specific distributions of PAHs from a given study area, as compared to empirical and experimental data sets for known source materials as described in the literature, from references cited above.

Forensic PAH evaluations rely on the relative distribution or assemblages of multiple PAHs within a sample, rather than the absolute concentration of these compounds (Bzdusek et al., 2004; Stout et al., 2003). Early research on the source of PAHs in the environment identified three principal classifications of sources based on the

distribution patterns recognized in various environments. These include diagenetic (or biogenic), petrogenic and pyrogenic (Boehm and Farrington, 1984; Yunkers et al., 2003). Diagenetic assemblages arise from the biological transformation of natural organic matter within sediments. Petrogenic assemblages are generated through geological processes of elevated pressure and temperature that transform organic matter in sediments into a variety of PAH compounds that give rise to crude petroleum as well as various ranks of coal. Pyrogenic assemblages are created during the combustion or pyrolysis of organic matter that can include wood, coal, petroleum or other forms of biomass (Stout et al., 2001b).

A basic knowledge of PAH chemistry is important for the understanding of forensic evaluations (Lima et al., 2005). PAHs considered in most forensic evaluations consist of 2- to 6-fused aromatic rings, along with their alkylated homologues, that contain only carbon and hydrogen. These structures are illustrated on Figure 3-1. Parent PAHs include compounds that consist of only the fused aromatic rings, whereas their alkylated homologues have between one and four alkyl groups substituting for hydrogen along the boundary of the molecule. Naphthalene (NAP) and 2-methylnaphthalene (2mNAP) are examples of a parent and alkylated 2-ring PAH. (Note that in the current evaluation, the only alkylated PAHs measured were 1mNAP and 2-methylnaphthalene (2mNAP), although additional alkylated PAHs can be analyzed in other forensic applications.) Alkylated homologues are typically identified by their parent PAH name and the number of additional methyl groups on the structure. Thus, C3-phenanthrene has the basic structure of phenanthrene (PHE) with three methyl groups (or one methyl and one ethyl groups). For PAHs having three or more rings, PAH isomers are compounds that have the same chemical formula, yet have different structures. Fluorene (FLU) and pyrene (PYR) are examples of 4-ring PAH isomers. Table 3-1 provides a summary of chemical names and acronyms used throughout this report.

Over the past 20 years, significant advances have been made in improving analytical detection limits and the differentiation of various PAH compounds that can be analyzed (Wait, 2000; Douglas et al., 2004; Planas et al., 2006). Concurrently with advancement in laboratory analytical methods, several qualitative, quantitative and statistical methods have been developed to evaluate PAH distributions in a variety of sample types. PAH profiles are qualitative illustrations of the distribution of PAHs within a sample or group. PAH profiles illustrate either absolute concentrations within a sample or PAH proportions normalized to the total PAH concentration. Mean PAH profiles for a group are calculated as the average proportion of specific PAHs for samples within

that group. A profile is ordered with low molecular weight 2-ring PAHs to the left and high molecular weight 6-ring PAHs to the right.

Several multivariate statistical methods are typically employed to evaluate the complex relationships in PAH data sets. Principal component analysis (PCA) is the most common multivariate approach used in forensic evaluations (Burns et al., 1997; Stout et al., 2001b; Kimbrough and Dickhut, 2006). Given that multiple PAHs are available for interpretation, PCA is a statistical technique that explains the dispersion or variance in the data by calculating linear combinations of parameters (PAHs) as “principal components” (PC). The first PC (PC1) explains the greatest amount of variance in the data, with the second, third, fourth, etc. explaining sequentially lesser amounts of the variance. PCA results are illustrated on scatter plots that provide the distribution of PCA scores for samples against two different principal components (e.g. PC1 vs. PC2).

Where PCA is a statistical method for illustrating the variability in the PAH data, multivariate cluster analysis (MCA) is a statistical method used to classify samples based on their similarity to create groups of samples that have similar PAH distributions. MCA has been applied to PAHs and combustion materials in a variety of environments (Arditsoglou et al., 2004; Dreyer et al., 2005; Murakami et al., 2005; Morgan and Bull, 2006; Ribeiro et al., 2010). MCA results are presented on dendograms or branching diagrams that group samples together based on their similarities. By analogy, MCA techniques are used to identify “genetic families” of samples that have similar characteristic patterns of PAHs based on the relative distribution of PAHs within individual samples. MCA techniques are used in a variety of genetic, biological, medical research applications, and also have direct application to environmental chemistry and forensics. A full discussion of PCA and MCA techniques is beyond the scope of this report, however, Davis (2002) or Romesburg (2004) and the references cited above provide for a more complete treatment of these techniques.

Quantitative evaluation methods include evaluation of diagnostic ratios of specific PAHs (Douglas et al., 1996; Mitra et al., 1999; Yunkers et al., 2002; Yunkers and Macdonald, 2003; Countway et al., 2003; Costa et al., 2004; Costa and Sauer, 2005, Fernandes and Brooks, 2003; Stout et al., 2004; Stout and Emsbo-Mattingly, 2008). These diagnostic ratios have been empirically linked with either general source classifications (e.g. petrogenic or pyrogenic) or specific PAH sources (e.g. vehicle emissions, petroleum combustion, wood/coal combustion, creosote, coal tars, etc.). Diagnostic ratios are typically presented as cross-plots showing the variability of samples for two separate ratio pairs. Diagnostic ratio plots provide a perspective on

the relative consistency or variability of sample results within or between groups identified using PCA and MCA techniques.

Least-squares regression methods have been used to evaluate the PAH distributions between individual samples, samples and potential source materials, and mean group PAH distributions and source materials (Burns et al, 1997; Burns et al., 2006, Lee, 1999). Applications range from simple comparisons between two samples, to more complex mixing models where the relative contribution from multiple potential PAH sources is estimated to predict contributions in source apportionment studies. Least-squares regression involves comparing two data sets, where the pair-wise proportions of various PAHs represent the X and Y coordinates of the regression with X representing one sample for a given PAH and Y representing the second sample for the sample PAH. Hence, on the scatter plot, the various data points may represent the relative proportions of naphthalene for the two samples, or benzo(a)pyrene, and so on. Two parameters are considered in this type of regression analysis. The primary parameter is the Pearson product-moment correlation coefficient, r , which is a measure of the strength of the direct linear relationship between the two samples. The second parameter is the Coefficient of Determination, R^2 , which is a statistical estimate of the relative amount of variation in one sample that can be explained by the variation in the second sample. The Coefficient of Determination is calculated as the square of the correlation coefficient. The closer that r or R^2 is to 1, the stronger the correlation between the two samples. The statistical significance of either r or R^2 is determined from the p-value of the coefficient and the number of data points used in the regression.

3.2 Data Evaluation

A forensic evaluation following the methodologies detailed above has been conducted on soil samples from the Site and in the nearby area to characterize the distribution of PAHs and to identify patterns that may indicate potential sources of PAHs. The objective of this evaluation was to identify the similarities and differences between individual samples utilizing forensic methodologies from the published literature described above, and subsequently to identify the most likely types of PAH source materials that have similar characteristics to these samples.

It is our opinion that, to a reasonable degree of scientific certainty, the following conclusions can be drawn from the forensic PAH evaluation presented herein:

- 1) A large data set consisting of 341 samples was available for forensic evaluation, with 152 samples having a sufficient number of PAH compounds (10 or more) per sample to meet inclusion criteria for statistical analysis (See Section 3.3 for a summary of the inclusion criteria). Of these samples, 87 samples (57.2%) were from on the facility and 65 (42.8%) were from adjacent residential properties.
- 2) The methods used in the forensic evaluation were consistent with methods employed by multiple researchers as published in the peer-reviewed scientific literature, as previously cited. Methods included correlation analysis (least-squares), MCA, PCA, and diagnostic ratio analysis. Least-squares correlation analysis was also employed to compare results of the forensic evaluation against PAH profiles for known PAH source materials. Analysis was completed without regard to the source of the sample (i.e. on-Site or off-Site).
- 3) Six representative PAH profiles were identified using the MCA method. Group 1 includes 132 samples representing 86.8% of the data set. This group includes 63 of the 65 samples (96.9%) collected from the residential properties. Group 2 was broadly similar to Group 1, with a greater relative proportion of 6-ring PAHs. Group 3 was the most unique in comparison with the main body of data and included only two samples (1.3%). Both of these samples were collected on-Site, from depth, and were characterized by higher relative naphthalene proportions. The remaining three groups had PAH profiles that were intermediate between the dominant Group 1 PAH profile and the more naphthalene-rich Group 3 profile.
- 4) Diagnostic ratios were used to differentiate between PAH contributions from combustion related and petroleum related sources. This evaluation indicated that the vast majority of samples were derived from mixed combustion sources or wood/coal combustion sources. Where lighter PAHs are included in the ratio being evaluated, a small number of samples are shown to plot in areas designated as petroleum or petroleum combustion superimposed on the mixed or wood/coal combustion signal.
- 5) Based on least-squares regression analysis against PAH distributions from known sources, the majority of samples (Groups 1 and 2) were derived from materials similar to coal fines, cinders, urban dust or asphalt. Group 3 samples were similar to PAH profiles derived from diesel contaminated soils or low-naphthalene coal tars. Groups 4, 5 and 6 had PAH profiles that were consistent with mixtures of combustion-derived PAHs similar to Group 1 and PAH source

materials having a greater proportion of naphthalene such as waste oil or low-naphthalene coal tars.

- 6) The spatial distribution of samples (Figure 3-2) from the different PAH groups does show some degree of clustering where more than two samples are in a group. All samples from groups 3, 4, 5 and 6 are located on the industrial site. Group 1 is widely dispersed across the project area with samples occurring both on the industrial site and on residential properties. Group 2 is clustered with 3 of 4 samples located in fairly close proximity in the east central portion of the project area. Group 5 is primarily clustered in the east central portion of the industrial, whereas all of the Group 6 samples are situated along the northern margin of the industrial property near the former railroad tracks.
- 7) Based on the forensic evaluation conducted on this data set, we concluded that the majority of the samples for both the industrial site and residential properties are associated with combustion related PAH sources including coal, cinders and urban dust (i.e. background). Samples that may have some petroleum-derived constituents (e.g. greater naphthalene proportions) are all located on the industrial site and therefore, are determined to be source-related; these petroleum-derived constituents were not identified on any of the residential properties. Therefore, we concluded that PAH sources that are unique to the Site did not contribute to the PAH profiles at the off-Site residential properties in any detectable concentration. Although both the MKC facility and the off-Site residential soils contain PAHs attributable to urban background, the source-derived PAHs from petroleum constituents present on the MKC site are wholly absent from the off-Site residential samples.

3.3 Data Sources, Inclusion Criteria and Forensic Approach

The initial data set included 341 soil analyses of U.S. EPA Priority Pollutant PAH compounds (16 PAHs plus 1- and 2-methylnaphthalene) in total collected from both on- and off-Site. This sample set was differentiated into two groups, including surface samples (mean sample depth less than 1 foot below grade) and subsurface samples (mean sample depth greater than 1 foot). A total of 141 (41.3%) samples were from surface locations and 200 (58.7%) samples were from depth. A total of 213 of the 341 samples (62.5% of all samples) had one or more PAH detected.

Based on our experience and standard practice, an inclusion criterion was established for the forensic evaluation to ensure sufficient information content in the sample results

for statistical assessment. In order for samples to be included in the statistical assessment, a minimum of 10 of the 18 PAHs were required to have positive detections (i.e. results greater than the method detection limit, including J-flag estimated concentrations). A total of 152 samples (44.6% of all samples) met this inclusion criterion. Of these samples, 87 samples were collected from on-site locations (57.2%) and 65 samples were collected from adjacent residential properties (42.8%). Of the 152 samples meeting the inclusion criterion, 122 (80.3%) were surface samples and 30 (19.7%) were subsurface samples. The majority of the samples that did not have any PAHs detected (126 of 128 samples) were from subsurface locations. The relative distribution of samples meeting the inclusion criterion vs. having insufficient detections or no detections of PAHs is shown on Figure 3-3.

121 samples were collected off Site. Of these, 65 (53.7%) of the samples met the minimum number of 10 PAHs present. 35 (28.9%) of the off-Site samples had no PAHs present. Only 21 off-Site samples had some but less than 10 PAHs present. The samples that did not meet the inclusion criteria were further evaluated. None of these off-Site samples had increased levels of low molecular weight PAHs indicative of on-Site samples. Furthermore, samples with fewer than 10 PAHs detected tended to have significantly lower concentrations than those samples meeting the inclusion criteria, with consequently lower concentrations of benzo(a)pyrene(BaP) and other risk drivers. In total 98.3% of the samples from the residential properties either showed PAH assemblages that are characteristic general anthropogenic PAH sources (Group 1), had no PAHs detected, or when fewer than 10 PAHs were detected, had characteristics similar to the other residential samples.

The forensic evaluation followed a step-wise approach consistent with the scientifically accepted methodologies cited above. PAH profiles were calculated for each sample meeting the inclusion criterion, which served as the primary database. Correlation analysis was conducted by least-squares to evaluate the internal consistency of the data set. Statistical analyses were subsequently completed using MCA and PCA. MCA was utilized to identify PAH groups having similar distributions, and PCA was utilized for illustration purposes to show the relationships between these groups on a sample-specific basis. Diagnostic ratios were calculated to evaluate the general source characteristics in terms of combustion (pyrogenic) or petroleum-based (petrogenic) source associations. Finally, least-squares regression analysis was conducted to compare the MCA groups against several characteristic PAH source materials (Burns et al., 1997; Burns et al., 2006).

As an *a priori* element of the MCA statistical evaluation, it was decided to differentiate sample results into six MCA groups in order to identify the major types of PAH distributions. This approach is capable of identifying either individual samples that may be outliers or to identify unique groups within the data sets (Romesburg, 2004). As a cross-check, MCA was performed with more and fewer groups to determine whether or not different number of groups would provide improved resolution of the relevant PAH profiles in the data set. However, it was determined that six groups provided sufficient differentiation of the various PAH profiles. The initial statistical evaluation was conducted using a “single blind” approach, where the investigator did not have knowledge of the specific sample geographic locations. This approach minimizes potential bias in the statistical evaluation.

The six final MCA groups were subsequently compared to ten different PAH source materials that were obtained from the peer-reviewed literature or were developed from empirical measurements from known source materials (Bzdusek et al., 2004; Stout et al., 2003; Yunkers and Macdonald, 2003). Source materials included cutting oil, diesel fuel contaminated soils, National Institute of Standards and Technology (NIST) coal tar standard, coal tar, cinder fill, NIST urban dust, coal, waste oil, asphalt and coal tar pitch (Arditsoglou et al., 2004; Brown et al., 2006; Domeño and Nerin, 2003; Dominguez et al., 1996; Iwrin et al., 1997; Khalili et al., 1995; Li and Kaplan, 2008; Lima et al., 2005; Manoli et al., 2004; NIST, 1992; NIST, 2000; NIST, 2001; Riberio et al., 2010; Stout et al., 2003; Stout and Emsbo-Mattingly, 2008).

3.4 Fate and Transport

Potential fate and transport mechanisms have been evaluated for the PAH content of samples from the off-Site residential areas. Air deposition and overland flow with runoff are identified as the two possible mechanisms for transport of PAHs from the MKC facility to residential locations. Air deposition (from exhaust fans and any other air discharges) from the facility would be affected by the prevailing wind direction, if it is assumed that the site would be a source. Prevailing wind direction obtained from the Wisconsin State Climatology Office for the period 1948 to 2009 (<http://www.aos.wisc.edu/~sco/clim-history/stations/msn/madwind.html>) indicated that the dominant annual prevailing wind direction is from the south to the north at 12.4 miles per hour (mph), with winds during the December to March period having a prevailing component from the west-northwest (Figure 3-4). Based upon the 1994 topographic map, an evaluation of topography and possible overland surface runoff flow was performed (Figure 3-4). Based upon that evaluation, surface water movement would also be toward the north. Daily air and water flow could be in alternate

directions, but the evaluation clearly showed that the dominant anticipated affect from the Site, were it to be a source of PAHs to off-Site areas, would have been to the north and northeast.

It is our opinion that if the releases from the Site have impacted residential properties, then it would be reasonable to expect that samples collected from the residential properties on the northern portion of the sampling area would have PAH profiles that are similar to the more unique PAH profiles originating from the Site. It would also be expected that total PAH concentrations would be greater to the north as compared with other residential samples. A total of 21 samples having 10 or more PAHs were analyzed from this area. These samples include 102-1, 102-1-34, 102-2, 106-1, 106-2, 110-1, 110-1-34, 110-2, 110-2-34, 114-1, 118-1, 118-2, 126-1, 126-2, 128-1, 128-2, 130-1, 134-1, 134-2, 138-1, and 138-2. It is noted that all of these samples are associated with Group 1 PAH profiles, and none of the samples exhibit the characteristics of PAH profiles from the MKC facility containing the higher proportions of low molecular weight PAHs. In terms of the concentration of total PAHs in these samples, the geometric mean concentrations for this group of 21 samples is 1.23 milligrams per kilograms (mg/kg), which is slightly lower than the geometric mean concentration of 1.54 mg/kg for other Group 1 residential samples from south and west of this area. Furthermore, the geometric mean concentrations for samples from this area is lower than other Group 1 samples from the facility (3.83 mg/kg) and other non-Group 1 samples from the facility (4.86 mg/kg). Given that this area is both down wind and down flow from the facility, and that the PAH signatures for samples from these residential properties is not similar to the samples having profiles exclusive to the facility, we concluded that the residential properties have not been impacted by PAH releases that could be source-derived from the MKC facility.

In addition, the PAH particles present in any air emissions from any coal combustion processes at the MKC facility would have been emitted from stacks. In 1991, the heights of these stacks ranged from 68 to 78 feet above ground level (Kipp-Neighborhood Group Report, 1991). Based on experience and general knowledge of air dispersion principles and processes, the PAHs present in the hot exhaust gases (199 to 358 degrees Fahrenheit) (Kipp-Neighborhood Group Report, 1991) would rise vertically to a significant height from the stacks before dispersing with the winds (EPA, 2004). The particles from these stacks would travel a considerable horizontal distance before falling to the ground by dry and wet deposition processes (EPA, 2004). They would not deposit in the residential yards immediately adjacent to the facility. Instead, they would become part of the overall background levels such as those reported by the EPA National-Scale Air Toxics Assessment (EPA, 2012c).

3.5 Findings

Summary statistics for the number of detections and the relative detection frequency are provided in Table 3-2. This table differentiates between all samples available for analysis, and the samples included in the forensic evaluation. Four PAHs were detected in all samples used in the forensic evaluation, including fluoranthene (FLA), PYR, chrysene (CHR), and (BaP). PAHs having detection frequencies of approximately 80% or greater include benzo(b)fluoranthene (BbF 99.3%), benzo(a)anthracene (BaA 98.7%) phenanthrene (PHE, 98.7%), benzo(g,h,i)perylene (BPE 96.7%), indeno(1,2,3-c,d)pyrene (IP 95.4%) and dibenzo(a,h)anthracene (DBA 79.6%). PAHs that had the lowest detection frequencies included fluorene (FLU 59.9%), naphthalene (NAP 55.9%), acenaphthene (ACE 44.7%), acenaphthylene (ANY 32.9%), 1-methylnaphthalene (1mNAP 33.6%) and 2-methylnaphthalene (2mNAP 17.8%). It is noted that the forensic evaluation is based on the relationship between various PAHs within a given sample, and is not dependent on the total concentration of individual PAHs. Therefore, this discussion focuses on the relevant patterns of PAHs within individual samples and in PAH groups identified using statistical methods.

The MCA approach was able to successfully differentiate between multiple groups within the data set. PAH profile plots were constructed for each group identified by MCA representing the mean PAH proportion for each group. PCA plots were evaluated to visually inspect the distribution of individual samples within each MCA group as compared to the overall distribution of data points. The MCA dendrogram for the PAH data set is provided on Figure 3-5, and the corresponding PAH profiles for each group are shown on Figure 3-6. PCA plot for PC1 vs. PC2 and PC1 vs. PC3 are shown on Figure 3-7. Figure 3-8 illustrates the relative loading of different PAHs on the PC1 vs. PC2 plots, which facilitates the interpretation of the relative sample-specific locations in the multiple PAH evaluation.

The following provides a descriptive summary of the six groups derived from the MCA modeling of the data set. PAH profiles are color coded to indicate the number of aromatic rings in the structures as follows: a) orange/yellow, 2-ring PAHs; b) green, 3-ring PAHs, c) blue, 4-ring PAHs; d) purple, 5-ring PAHs; and e) dark red, 6-ring PAHs.

Nearly all MCA cluster group profiles indicated that combustion related sources are the primary contributors to the PAHs in the samples. Diagnostic ratios indicate that the relative contribution from petrogenic (petroleum or coal) and pyrogenic (petroleum combustion, wood/coal combustion, creosote/coal tar) sources varies between the

different MCA groups, as shown on Figure 3-9. The MCA Groups presented below are ordered following in accordance with the specific group number derived from the Minitab analysis (MiniTab is one of several commercially available statistical software package that is commonly used for advanced statistical analysis, Minitab, 2010). The six forensic PAH profiles are described as follows:

Group 1 (n=132, 86.8% of samples); Predominantly composed of 4- and 5-ring PAHs that are consistent with combustion sources such as wood/coal combustion source contribution. This group includes all except for two of the residential samples. Samples cluster in a fairly confined region in the PCA diagrams. Of the Group 1 samples, 111 samples (84.1%) were from surface locations, 18 samples (13.6%) were from the 1 to 6 foot interval, and 3 samples (2.3%) were from 10 feet or more below grade.

Group 2 (n=4, 2.6% of samples); Predominantly composed of 5- and 6-ring PAHs with lower proportions of 4-ring PAHs than Group 1. This group also contains a low relative proportion of 2- and 3-ring PAHs that is slightly greater than Group 1. The PAH profile is consistent with combustion sources such as wood/coal combustion source contribution. This group includes the only two residential samples that are not in Group 1. Group 2 samples cluster in near Group 1 on the PCA diagrams, yet are pulled in the direction of 6-ring PAHs relative to Group 1. Two of the Group 2 samples were from surface locations and two were from the 2 to 4 feet below grade.

Group 3 (n=2, 1.3% of samples); Predominantly composed of 2-ring PAHs that are consistent with a petroleum source such as diesel, with less abundant 3- and 4-ring PAHs, and negligible 5- and 6-ring PAHs. This group is the most unique as compared to the main body of samples represented by Group 1, and is pulled in the direction of 2-ring PAHs relative to Group 1 on the PCA diagrams. Both samples in Group 3 were collected from on-Site sub-surface zones between 7 to 9.4 feet below grade.

Group 4 (n=2, 1.3% of samples); Predominantly 3- and 4-ring PAHs with modest contribution from 2-ring PAHs. The PAH distribution includes fairly low proportions of 5- and 6-ring PAHs. The PAH profile is consistent with a weathered petroleum source that includes a component of petroleum or wood/coal combustion. This group is also unique as compared to the main body of samples represented by Group 1, and is pulled in the direction of 2- and 3-ring PAHs relative to Group 1 on

the PCA diagrams. Both samples in Group 4 were collected from on-Site subsurface zones between 1 to 15 feet below grade.

Group 5 (n=8, 5.3% of samples); Predominantly 3- and 4-ring PAHs with modest contribution from 5-, 6-, and 2-ring PAHs. The PAH profile is consistent with a combustion related PAH source that may include a minor petroleum component. This group is situated between the main Group 1 samples and the Group 4 samples on the PCA diagrams. Six of the Group 5 samples were from on-Site surface locations with the two remaining samples being from 2 to 11 feet below grade.

Group 6 (n=4, 2.6% of samples); Predominantly 2-, 3- and 4-ring PAHs with modest contribution from 5- and 6-ring PAHs. The PAH profile is consistent with mixture of petroleum and combustion related PAH source. This group is situated between the main Group 1 samples and the Group 2 samples on the PCA diagrams. Three of the Group 6 samples were from on-Site surface locations and one sample was from the 2 to 4 feet below grade.

Diagnostic ratios were evaluated for all samples where both PAHs in a given ratio were detected in a sample. Five different ratios were evaluated including light PAH to heavy PAH ratio (LPAH:HPAH ratio of 2- and 3-ring PAHs to 4-, 5- and 6-ring PAHs), ANT:[ANT+PHE] (mass 178) ratio, FLA:[FLA+PYR] (mass 202) ratio, BaA:[BaA+CHR] (mass 228) ratio, and IP:[IP+BPE] (mass 278) ratio. Each of these ratios focuses on a different mass range for the PAHs depending on the ring structures. The LPAH:HPAH ratio provides an indication of the relative contribution of light PAHs that are indicative of petroleum or coal tar sources to heavy PAHs that are more indicative of combustion sources. The remaining diagnostic ratios are the relative proportion of one PAH to the sum of two PAHs of a given mass. These ratios are then compared to “cut points” that can be used to differentiate between PAH sources such as petroleum, petroleum combustion, mixed combustion sources and predominantly coal/wood combustion (Yunkers et al., 2002). The cut points have been presented in the peer-reviewed literature, and have been established on the basis of empirical observations from known sources and thermodynamic principles related to the stability of different PAHs at various formation temperatures. Diagnostic ratios are plotted either on single axis plots, or on cross-plots where two ratios are shown on a scatter diagram.

The LPHA:HPAH ratio plot clearly shows the differentiation between MCA Groups 1 and 2 from Groups 3, 4, 5 and 6. The former groups clearly overlap with fairly low ratios that are indicative of heavy PAHs being dominant in the PAH assemblage.

Group 3 has the highest ratios, which can be indicative of a naphthalene-based PAH source such as diesel or a high naphthalene coal tar. Groups 4, 5 and 6 have ratios that fall between those of Group 1 (combustion dominated) and Group 3 (naphthalene dominated), suggesting the influence of both PAH source types. Cross-plots for PAH proportions indicate that most samples fall in regions dominated by mixed combustion sources or wood/coal combustion sources. In general, there is a broad overlap of the different MCA groups, with Groups 1, 2, 4 and 5 consistently plotting in the same regions. Where lighter PAHs are included in the ratios, a small number of samples are shown to plot in areas designated as petroleum or petroleum combustion.

Regression analysis was conducted to identify potential correlations between the different MCA groups and between MCA Group 1 and Group 3 against selected PAH source materials. Input data for each MCA group was the mean proportion for each of the 18 PAHs for that group. When comparing the MCA groups to the PAH source materials, the two methylnaphthalene compounds were dropped because these compounds were not reported for the reference source materials and the PAH profile was re-normalized to the remaining 16 PAHs which were also available for the reference materials. Selected source materials used for comparison included cutting oil, waste oil, diesel contaminated soils, high-naphthalene coal tar (NIST reference material), low-naphthalene coal tar, coal tar pitch, asphalt, coal fines, cinder fill material and urban dust (NIST reference material), as cited previously. Least-squares regression was used to calculate the correlation coefficient, r , Coefficient of Determination, R^2 , and slope of the regression line. It is noted that it is important to consider both the correlation coefficient and the slope of the regression line when evaluating the linear relationship between two data sets. The correlation coefficient reflects the relative amount of scatter around the regression, whereas a slope of approximately 1 indicates similar overall trends in relative composition between the two profiles being compared (Davis, 2004).

In general, the different MCA groups showed some degree of correlation with each other, with the exception of Group 3, which was dominated by high naphthalene content. This suggests that there is an underlying common source for most PAH distributions except for Group 3. When comparing the R^2 values for Group 1 vs. the remaining groups, it is determined that 38% to 68% of the variability in Groups 2, 5 and 6 can be explained by the PAH distribution in Group 1, whereas only 4% to 11% of the variability in Groups 3 and 4 can be explained by the PAH distribution in Group 1. In comparison, the R^2 value for Group 3 comparisons indicates that very little of the variation in Groups 1 and 2 can be explained by (1% and 5%, respectively) the

variability in Group 3. However, the distribution of PAHs in Group 3 can explain 25% to 52% of the variability in Groups 4, 5 and 6.

In summary, Group 1 is the dominant type PAH mixture in the data set, representing 86.8% of the samples. Group 3 is the most unique group in comparison to Group 1, representing 1.3% of the samples. There are distinct similarities between Groups 1 and 2, which are not consistent with the other MCA groups. The remaining two groups show characteristics that may be a mixture of Group 1 and Group 3 type signatures.

Each MCA group was compared to the ten PAH source material profiles by least-squares regression. PAH profiles for reference source materials are shown on Figure 3-10. The regression plots are shown for Groups 1 and 3 as compared to selected PAH source materials on Figure 3-11. We conclude to a reasonable degree of scientific certainty that the regression evaluation for the various MCA groups shows the following:

- 1) Group 1 showed the strongest correlation with coal fines and cinder materials based on both R^2 and slope values, with urban dust and asphalt also showing strong correlations. Group 1 did not show any correlation with cutting oil, waste oil, diesel contaminated soil, coal tar or coal tar pitch.
- 2) Group 2 showed the strongest correlation with asphalt, urban dust and coal tar pitch (a common precursor for asphalt used as a binder). This group did not show a significant relationship with any of the remaining PAH source materials.
- 3) Group 3 showed the strongest correlation with diesel contaminated soils and high-naphthalene coal tar, and also a strong correlation with waste oil and low-naphthalene coal tar. This group was not correlated with cutting oil, coal tar pitch, asphalt, coal, cinders or urban dust.
- 4) Group 4 showed the strongest correlation with low-naphthalene coal tar and had a strong correlation with waste oil. This group is not correlated with cutting oil, high naphthalene coal tar, diesel contaminated soil, coal tar pitch, coal, cinders, asphalt or urban dust.
- 5) Group 5 shows the strongest correlation with coal fines, low-naphthalene coal tar and cinders, with urban dust and asphalt also showing a fairly strong correlation. This group is not correlated with cutting oil, diesel contaminated soil, high naphthalene coal tar or coal tar pitch.

- 6) Group 6 shows the strongest correlation with coal fines and cinders, with urban dust and low-naphthalene coal tar also showing relatively strong correlation. This group is not correlated with cutting oil, waste oil, diesel contaminated soil, high-naphthalene coal tar or asphalt.

A final PCA run was conducted that included all samples and the ten PAH source materials. Figure 3-12 shows the relationships between sample values and these PAH source materials as plotted on PC1 and PC2. This figure clearly shows the similarity between the coal and cinder materials and the main body of Group 1 samples. Group 2 samples are pulled in the direction of urban dust and coal tar pitch, whereas Group 3 is pulled in the direction of diesel contaminated soils or high-naphthalene coal tar. Groups 4, 5 and 6 are generally pulled in the direction of waste oil.

It is noted that the least-squares regression and final PCA plot are intended to show the relative location of the various samples and PAH source materials in the context of complex chemical mixtures. It is clearly evident that the majority of the samples in the data set correspond with the PAH signature of coal, cinders, asphalt and urban dust. There are a few samples that are pulled in the direction of PAH source materials with higher naphthalene content, such as diesel fuel. The PAH source material that is least similar to any of the samples is cutting oil.

3.6 Conclusions

The following conclusions can be drawn from the forensic PAH evaluation presented above:

- 1) Statistical analysis of PAH distributions within individual samples clearly indicates that several PAH profiles are present in the data set.
- 2) The majority of samples meeting the inclusion criterion for the forensic evaluation cluster are in a single group (Group 1) and represent 86.8% of the data set, with the remaining samples being separated into five additional groups.
- 3) The remaining five groups are differentiated from the main Group 1 profile based on the relative proportion of light 2-ring PAHs or heavier 6-ring PAHs.
- 4) Nearly all residential samples are associated with the primary Group 1 type of PAH profile, with 63 of 65 residential samples being in this group. The remaining

two samples were associated with the group having a slightly heavier PAH assemblage.

- 5) When compared to representative PAH source materials, the PAH profiles for Group 1 samples are consistent with PAH assemblages derived from combustion related sources such as coal fines, cinders, urban dust and/or asphalt. The PAH profile for this group is not consistent with PAH sources from cutting oil, waste oil, diesel contaminated soils, coal tar or coal tar pitch.
- 6) The spatial distribution of Group 1 shows that these samples are evenly distributed among all locations without a strong preference for clustering in a given area.
- 7) Group 2 samples are similar to Group 1 with the exception of having a high relative proportion of 6-ring PAHs. The PAH profile for this group is also consistent with combustion related sources including asphalt, urban dust and coal tar pitch.
- 8) Groups 3, 4, 5 and 6, which contain samples collected exclusively from on-Site, have greater relative proportions of light 2- and 3 ring PAHs. Based on comparisons with PAH reference material profiles from known sources, these groups most likely are influenced by on-Site derived PAH sources with higher naphthalene proportions including diesel contaminated soils or waste oils superimposed on combustion related PAH sources.

4. Discussion of PAH Background Sources Related to the Site

Based on the results of the forensic analysis, we conclude that the sources of PAHs in the residential backyards are background sources. More specifically, we conclude that the PAH mixtures in the soils chemically match combustion sources. This section summarizes the investigation into specific PAH sources in Madison that are the likely sources of the PAHs in these residential soils.

4.1 Discussion of PAH Background Sources in East Madison, Wisconsin

A review of historical sources of PAH emissions into the air was undertaken to determine if there were a significant number of sources that might explain the presence of background PAHs measured in residential soils in the neighborhood surrounding the Site. The area around the Site has been heavily urbanized for decades and there are multiple background sources.

In fact, most of East Madison in the area of the Site is an area that was industrialized for the better part of a century. A 1931 map (University of Chicago, 2012) shows industrial zoning along both sides of Waubesa Street from Atwood Street up to La Follette Avenue, both sides of Corey Street and Ohio Street, from Atwood Street up to the railroad tracks, all along both sides of Atwood Street throughout East Madison, along both sides of Winnebago Street from First Street to Milwaukee Street, and throughout other areas of Madison. About one-half of the land area in East Madison was zoned for commercial or industrial use in 1931 (University of Chicago, 2012).

Madison had many coal fired power plants over the decades that emitted PAHs into the atmosphere. For instance, the Capitol Heat and Power Plant operated for over a century in downtown Madison (Wisconsin State Journal, 2010a). It ceased burning coal in 2010. The University of Wisconsin at Madison also operated a coal fired power plant since the mid 1950's in downtown Madison (Wisconsin State Journal, 2010b). This plant used coal and used tires as fuel. Both fuels cause the emission of PAHs from stacks. A large coal fired power plant also has operated since 1975 in nearby Dekorra, Wisconsin, supplying power to Madison (Madison Gas and Electric, 2012a). Also, Madison is the home to the Blount Generating Station, which burned coal from 1902 to 2011 (Madison Gas and Electric, 2012b). From 1979 to 1993, this Madison Power Plant also burned refuse-derived fuel. The Blount Generating Station is two miles southeast of the Site. Although the current and historic power plants were several miles from the Site location, they have been a significant source of PAH deposition onto nearby residential soils because emissions from power plant smoke stacks can

travel several miles before they deposit by dry and wet deposition processes (EPA, 2004).

According to EPA (1985), the Madison Gas Light and Coke Company operated manufactured gas plant sites in Madison from 1898 to 1950 producing $1,012 \times 10^{12}$ cubic feet of gas per year at its peak in 1950. Manufactured gas plant sites made gas from coal in a manner similar to a coke oven, emitting PAHs in the process. These PAHs were emitted from stacks that were elevated, and the emissions dispersed widely in the local environment before depositing onto soils (EPA, 2004).

There were also several industrial facilities in East Madison very near the Site (EDR, 2012). The Theo Kupfer Iron Works, 149 Waubesa Street, 350 feet from the Site, operated an iron foundry from 1940 to 1985 (Goodman Community Center, undated). Prior to the iron works, the American Shredder Company operated from 1903 to 1906 (Goodman Community Center, undated). In 1906, the Steinle Turret Lathe Machine Company occupied the building until 1934. In 1990, the Durline Scale Company occupied the building until 2001 (Goodman Community Center, undated). Madison Brass Works at 214 Waubesa Street (100 feet from the Site) was a foundry that produced brass, bronze, aluminum, nickel and white metal castings (EDR, 2012). Berntsen Brass and Aluminum Foundry at 2334 Pennsylvania Avenue was established in 1946 and is 1 mile to the east of Site (EDR, 2012). Theo Kupfer Iron Works, Madison Brass Works, and Berntsen Brass and Aluminum Foundry all had smoke stacks that emitted PAHs into the atmosphere for many decades while in operation.

Consolidated Paving, Inc. operated at 2318 Atwood Avenue, 0.4 miles from the Site making asphalt paving mixtures and blocks (EDR, 2012). Four Lakes Paving was located at 3030 Gateway Place, 0.6 miles from the Site (EDR, 2012). Clark Refining and Marketing was located at 2801 Atwood Street, also less than a mile from the Site (EDR, 2012). Rayovac Corporation at 2317 Winnebago Street manufactured batteries about 0.5 miles from the Site (EDR, 2012). Asphalt paving manufacturers and oil terminals all emitted PAHs over the years within a mile of the MKC facility (ATSDR, 1995).

Releases of PAHs into the air near the Site have been reported by EPA. EPA's Toxic Release Inventory (EPA, 2012) reports that 9,605 pounds of PAHs were released to the environment from 2000 to 2011. Of this, 400 pounds were released to the air. The major PAH emitters in Dane County were the ExxonMobil Terminal about 6 miles to the south of the Site (EPA, 2012b). Madison Gas & Electric's Blount Generating Station was another major emitter, located 2 miles to the southwest of the Site (EPA, 2012b).

Also emitting PAHs were Safety-Kleen Systems 4 miles to the southeast and Flint Hills Resources Pine Bend terminal 6 miles to the south east (EPA, 2012b). MKC is not listed on EPA's Toxic Release Inventory as an emitter of PAHs (EPA, 2012b).

PAHs have also been released to the air for decades from residential properties all over Madison, Wisconsin, including the residences abutting MKC. According to the U.S. Census (2012), 63% of homes in Wisconsin in 1940 were heated by coal or coke and 27% were heated by wood. In 1950, 49% were heated by coal or coke and 12% were heated by wood. Statistics for the years prior to 1940 were not listed in the U.S. Census report, but it is common knowledge that wood and coal were the main fuels used for home heating prior to 1940 throughout the United States.

Bottom ash from coal and coke burning is not classified as a hazardous waste at the present time, and it was certainly not handled or disposed in any special way in the early half of the twentieth century. Much of the bottom ash from home heating was disposed on the residential property itself. In many northern locations, coal and coke ash was routinely used for ice and snow control on roadways (EPRI, 1998). EPA (2012a) states that 30% of coal bottom ash is used for snow and ice control and other miscellaneous applications even today. Thus, it is likely that bottom ash from home heating systems were one source of PAHs in soils in the residential lots.

Other sources of PAHs in soils in East Madison are combustion emissions from the transportation sector. The Chicago, Milwaukee, St. Paul and Pacific Railroad and the Chicago and North Western Railroad lines both run very close to the MKC facility. The former started operation in 1847 and the latter in 1859 (American-Rails, 2012). Railroad spurs entered the MKC property itself. In addition, the 1931 map (University of Wisconsin, 2012) shows that major roadways present in East Madison today were present as early as 1931, if not earlier. Major roadways near the Site that have been present for decades include Washington Street, Atwood Avenue, Milwaukee Street, Winnebago Street, and others. It is our opinion that vehicle emissions from millions of cars and trucks that have traveled the East Madison roadways for a century contribute to the PAH levels in residential soils throughout East Madison.

Backyard trash burning is also a source of PAHs in East Madison soils. According to the Wisconsin Division of Public Health (2001), backyard trash burning was historically quite common: "Before scientists learned about the dangers of burning trash, it was commonly burned at homes and landfills." According to WDNR (2003), "open burning and backyard dumping is a significant problem in Wisconsin and is difficult to enforce." Also, "Open Burning is the number one source of citizen complaints to the DNR Bureau

of Air Management.” PAHs are emitted from the open burning of trash (Great Lakes Binational Toxics Strategy, 2004).

In conclusion, soils throughout Madison, Wisconsin and the residential neighborhood around the Site contain urban background levels of PAHs from many sources, as they do in all cities in America. For East Madison soils, the sources of PAHs include over a hundred years of deposition from coal fired power plants, home and commercial heating systems, railroads, motor vehicles, iron and brass foundries, asphalt production plants, backyard burning, and miscellaneous industries with industrial boilers. These numerous sources of PAH emissions into ambient air explain the low levels of PAHs in the residential soils, as discussed in the next section.

4.2 Comparison of PAH Background Levels In Different Urban Settings

The levels of PAHs in the residential soils at properties abutting the Site are very low and, in fact, are lower than the typical levels seen in other urban settings (see Table 4.1). Thus, the PAHs at the residential properties are entirely consistent with background levels and background sources. Specifically, the 95th Upper Confidence Limit on the mean of total PAH levels and benzo(a)pyrene-toxic equivalent levels [B(a)P-TE] whether calculated using all surface data or by using data that was averaged by property and then averaged over all properties, are all about ten times *less* than the typical urban background levels reported in several comprehensive PAH background sampling efforts (see Table 4.1). In addition, the highest property average was also about ten times *less* than typical urban background levels (see Table 4.1).

Urban background studies in other areas of the United States have focused on urban areas with long histories of industry, power generation and vehicle traffic. The fact that the residential samples near the MKC Site are so much lower than the urban background samples collected elsewhere unquestionably demonstrates that the PAHs in the residential soils have ubiquitous urban background sources from widespread atmospheric deposition rather than a specific, nearby source-derived contributor.

Table 4.1. Comparison of Residential PAH Levels and Typical Urban Background Levels

Citation	95th UCL Total PAH (ppm)¹	95th UCL B(a)P-TE ² (ppm)
Madison, Wisconsin		
Residential Properties, 63 samples	2.2	0.3

Table 4.1. Comparison of Residential PAH Levels and Typical Urban Background Levels

Citation	95 th UCL Total PAH (ppm) ¹	95 th UCL B(a)P-TE ² (ppm)
Residential Properties, 32 yards	1.4	0.2
Worst Case Residential Property	3.6	0.4
Published Urban Background Studies		
Magee, et al. (1994) New England	24.8	3.3
MADEP (2002) Massachusetts	24.5	3.0
IEPA (2007) Chicago	14.2	1.9
IEPA (2007) Metro Areas	24.8	3.1
USGS (2003) Chicago	133.2	19.1
EPRI (2003) Western New York	30.5	4.3
EPRI (2008) Urban Soil	23.2	3.4

¹ppm = parts per million (mg/kg)

² B(a)P-TE, benzo(a)pyrene toxic equivalents (EPA, 1993)

4.3 Quantitative Estimation of Residential PAH Background Concentrations in Dane County, Wisconsin

There is additional strong evidence to support our conclusion that the PAHs in the residential soils at the properties abutting the Site are present due to the deposition of PAHs from the air from background sources near and far. EPA performed its National-Scale Air Toxics Assessment (NATA) in 1996, 1999, 2002 and 2005 (EPA, 2012c). Total PAH average ambient air concentrations were estimated by EPA for Dane County, Wisconsin. As noted in Table 4.2, the estimated air concentrations vary from 0.016 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) in 2002 and 2005 in Dane County to 0.049 $\mu\text{g}/\text{m}^3$ in Dane County in 1996.

**Table 4.2. Estimated Total PAH
Background Ambient Air Concentrations
($\mu\text{g}/\text{m}^3$) that Deposit onto Dane County
Soils**

Year	Dane County
1996	0.049
1999	0.024
2002	0.016
2005	0.016

PAHs are present in air as fine particulate material which settles to the ground by gravity (dry deposition) and by rainfall (wet deposition.) Dry deposition can be estimated using a standard EPA equation:

$$\text{Dry deposition flux } (\mu\text{g}/\text{m}^2/\text{s}) = \text{Concentration } (\mu\text{g}/\text{m}^3) \times \text{Deposition velocity } (\text{m}/\text{s})$$

$$(\mu\text{g}/\text{m}^2/\text{s}) = \text{micrograms per square meter per second}$$

$$(\mu\text{g}/\text{m}^3) = \text{micrograms per cubic meter}$$

$$(\text{m}/\text{s}) = \text{meters per second}$$

A regulatory default deposition velocity (SCAQMD, 2011) is 0.02 m/s. Estimated background soil deposition rates can be calculated from the background air concentrations and the default deposition velocity. This will underestimate total background deposition, because it estimates dry deposition only and ignores wet deposition. Soil concentrations can then be estimated using the EPA guidance document for estimating soil concentrations from emissions of particulate matter from combustors. According to EPA (2005), particulate matter that is deposited onto soil will become incorporated into the top 2 centimeters (cm) of the soil. The estimated background soil concentrations after 30 and 100 years of deposition are shown in Tables 4.3 and 4.4.

Table 4.3. Estimated Total PAH Ambient Background Soil Concentration Assuming 30 Years of Deposition ($\mu\text{g/g}$, ppm)

Year	Dane County
1996	31
1999	15
2002	10
2005	10

Table 4.4. Estimated Total PAH Ambient Background Soil Concentration Assuming 100 Years of Deposition ($\mu\text{g/g}$, ppm)

Year	Dane County
1996	103
1999	50
2002	34
2005	34

As demonstrated by the tables above, it is our opinion to a reasonable degree of scientific certainty that background levels of PAHs in the ambient air throughout Madison, Wisconsin, can entirely explain the surface soil PAH levels observed in the residential yards near the Site, which are summarized in Table 4.1. The 95th Upper Confidence Limit on the mean total PAH concentration in the surface soil of residential yards is 2.2 ppm, and the worst case residential property had a total PAH concentration of 3.6 ppm (see Table 4.1). Estimated soil concentrations based on background ambient air concentrations of total PAHs range from 10 to 103 ppm depending on the data set year used and the number of years of deposition assumed (see Tables 4.3 and 4.4).

It is likely that these soil concentrations are underestimates, because emissions of particulate matter have declined significantly over the twentieth century. In earlier decades, there were more coal fired power plants, more homes heated with coal, coke, and wood, more vehicle emissions, and more industrial emissions of all sorts. Accordingly, the total PAH levels in the air were undoubtedly much higher from 1900 to 1996 than they were in and after 1996 when EPA initiated the NATA program.

The PAHs that deposited onto residential soil on these properties abutting the Site from 1908 onward in time would have become incorporated into the surface soil as modeled using the EPA (2005) method. According to the Sanborn Map from 1908 (EDR, 2012), most of these properties were vacant lots in 1908, with several homes present. By 1942 almost all of the lots had houses on them. Thus, none of these lots were covered by paving or large buildings. They were all open lots. Thus, the EPA (2005) approach to estimating deposition in soils is scientifically reasonable.

Over the course of the 30 to 100 years, some of the deposited PAHs could have been incorporated by physical mixing into the soil column to a depth deeper than EPA's default assumption of 2 cm. If so, then the estimated soil concentrations from background PAHs in the air could have been diluted by 5 to 10 fold compared to the estimates shown in Tables 4.3 and 4.4. Even so, the estimated soil concentrations are still equal to or higher than the measured surface soil concentrations in these residential yards.

The estimated total PAH concentrations are not for any specific location in Dane County, Wisconsin. Instead, the estimates are based on EPA's average total PAH concentrations in the air throughout all of Dane County. Thus, it is expected from EPA's NATA dataset that the total PAH concentration in residential soil at any location in Dane County would be at least 10 ppm and could be higher. This is not surprising because the typical measured urban background PAH concentrations published in several comprehensive studies varies from 14 ppm to 133 ppm as shown in Table 4.1.

4.4 Summary of Historical Sources of PAH Emissions in the Area of the MKC Facility

Several lines of investigation have been presented to determine if the concentrations of PAHs in residential soils near the Site are unusually high compared to the expected levels in any urban area with a history of multiple sources of PAH emissions into the ambient air or whether they are typical of urban background sources. All lines of inquiry conclude that the PAH concentrations are neither elevated nor unexpected. The measured concentrations are entirely consistent and are, in fact, *lower* than expected for urbanized areas with a history of commercial and industrial development based on the sources cited above. The results are also consistent with the soil concentrations that would be predicted from the aerial deposition from the average PAH concentrations in air reported by EPA in its NATA Assessments for Dane County, Wisconsin. Further historical research identified many sources of PAH emissions to ambient air that, collectively, explain the presence of PAHs in soils at residential

properties adjacent to the MKC facility. Similar levels are predicted for all of East Madison and Dane County. PAH emission sources include, but are not limited to:

- Capitol Heat and Power Plant
- University of Wisconsin at Madison Power Plant
- Blount Generating Station
- Madison Gas Light and Coke Company Manufactured Gas Plants
- Theo Kupfer Iron Works
- Madison Brass Works
- Berntsen Brass and Aluminum Foundry
- Consolidated Paving, Inc.
- Four Lakes Paving
- Clark Refining and Marketing
- Rayovac Corporation
- ExxonMobil Terminal
- Safety-Kleen Systems
- Flint Hills Resources Pine Bend terminal
- Residential wood, coal and coke burning for heating and cooking
- Wood, coal and coke bottom ash disposal
- Chicago, Milwaukee, St. Paul and Pacific Railroad
- Chicago and North Western Railroad

- Motor vehicle emissions
- Backyard burning.

5. Review of Expert Report of Dr. Lorne Everett

The expert report of Dr. Lorne Everett has been reviewed for insights into the alleged sources, fate and transport of the PAHs at the Site. The review comments are provided below and listed in the order found in the expert report, starting with the page number where they can be located:

Page 12 - Contamination also spreads into surficial soil by windblown dust, exhaust fallout and by sediment transport during rain and flooding events. The PAH, PCB and metal contamination spreads away from the Madison-Kipp property primarily by these methods. The PAHs, PCBs and metals now being found in neighbors' soil has migrated from the highly contaminated soil on Madison-Kipp property and/or has been discharged directly from Madison-Kipp's vents and stacks and contaminated particulate matter subsequently settled out of the air onto the neighbors' yards.

There are no facts or figures referenced in this statement and no data analysis was performed.

Page 20 - Mr. Schmoller succinctly summarized this interpretation: "If you just look at the distribution of PCE all around the site, it makes sense that -- and you look at it in conjunction with the PCB data and the on-site PAH data, I think the three of those together give a pretty clear picture that whatever fluids were spread for dust suppressant in the northeast or southwest, had those components" (Schmoller Deposition, 2012, p. 283).

This quote is Mr. Schmoller's opinion. We are aware of no independent analysis of the PAH data performed by the WDNR.

*Page 21 - **Madison-Kipp is a source of PAH's on Madison-Kipp and surrounding Class Area Properties** PAHs are present in fuel oil and petroleum combustion products. The location of the former above ground fuel oil storage tank (AST) was identified in the northern most part of the building and noted in Exhibit 2. Madison-Kipp used fuel oil for heating and released PAH's through its smoke stacks and vents. WDNR agrees with my interpretation that Madison-Kipp is the source of PAH's found in the environment on and around the facility: PAHs have been identified in many soil samples (both onsite and offsite) often at levels that exceed the Wisconsin PAH cleanup criteria. Mr. Schmoller indicates that in his opinion both the VOC's and the PAHs are coming from Madison-Kipp (Schmoller Deposition, 2012, p.100).*

MKC did use fuel oil and other petroleum based products at their facility Section 3.5, (Figure 3-11). Section 3.5 reviews the types of PAHs that would be associated with the products used at the facility. Our analysis of the off-site data (Section 3.5) shows that the PAHs found off-Site are not related to petroleum products used at the MKC facility.

Page 43 - There can be no dispute that the industrial chemicals used and released at Madison-Kipp such as PCE, PCBs, and PAHs are hazardous wastes, within the meaning of RCRA. Madison-Kipp engaged in the handling, storage, transportation and disposal of this hazardous waste. 9 U.S. EPA, October 20, 1997, Memorandum, Subject: Transmittal of Guidance on the Use of Section 7003 of RCRA. The contaminants PCE, PCBs and PAHs - - emanating from Madison-Kipp's property - - have been found throughout the Class Area (and beyond) in soil, soil gas, subslab vapor and, for some homes, in the indoor air. PCE from Madison-Kipp likewise contaminates the shallow groundwater just 20 or so feet below these homes, and the deeper groundwater aquifer below that. In short, toxic chemicals from Madison-Kipp contaminate, or threaten to contaminate, virtually every dimension of the surrounding neighborhood, including the Class Area.

There is no evidence that the PAHs were a hazardous waste generated or stored on the site. PAHs were a minor portion of petroleum products used at the Site. The data analysis in this report shows that the PAHs that were part of these petroleum products were not the source of PAHs at the adjoining residential properties. (Section 3.5)

Page 53 - The on-site soil investigation for PAHs needs to be expanded in the southern parking lots (impacts resulting from oil spreading for dust suppression and also from PAHs likely emitted from Madison-Kipp's exhaust fans and stacks). In my opinion, this phase of the on-site investigation will require approximately 50 sample locations with samples collected from at least two depths at each location: one surface sample in the upper 6 inches of soil and one sample at a depth of 1 to 2 feet.

The 50 sample locations suggested here seem to be based upon a random number. Dr. Everett does not explain how he arrived at this number, his rationale or his methodology. He presented no statistical analysis to predict how many samples would be needed for a statistically significant sample size. He did not present a surface analysis to determine the amount of open land available in the area that he wanted to sample. He did not present an analysis of the data from the 341 PAH samples that have already been collected as we have done here.

Page 55 - As of September 2012, PAHs have been found at every off-site property sampled (see Exhibit 7). Madison-Kipp almost certainly released PAHs to the environment. Petroleum-based lubricants used on die-cast molds are partly combusted each time molten metal is injected into a mold. PAHs are formed during this combustion process and would have been vented to the atmosphere. Madison-Kipp's current consultant, ARCADIS, has recommended that cleanup in the neighborhood not be driven by the widespread PAH contamination because the PAHs can originate from numerous sources (including backyard grilling), not just Madison-Kipp. If one wanted to identify the source of the PAHs, there are well known forensic techniques such as hydrocarbon fingerprinting which could have provided insight into the source of the PAHs. It has been known for at least 50 years that benzo(a)pyrene is a potent chemical carcinogen. This is one of the PAHs identified in the soil at neighboring properties. Since PAHs are a substantial human health risk, it is unacceptable that ARCADIS would find elevated PAHs everywhere it looked, yet try to trivialize the issue by suggesting the PAHs are the result of back yard grilling activity or otherwise blaming the neighbors. Clearly further forensic inquiry was required in this situation before ARCADIS could reach such a conclusion, especially in the light of compelling evidence showing that Madison-Kipp is the source of the PAHs. For example, ARCADIS could have looked at the Madison-Kipp oil and gas purchases on a year-round basis to determine if the PAHs released from the stacks and vents at Madison-Kipp were cyclic. The PAHs were identified nearly everywhere they were sampled and the distribution of PAHs can be attributed to emissions from Madison-Kipp's die cast operations and spreading of hydraulic fluids containing the PAHs, PCE and PCBs on the gravel topped parking lots towards the north central part of the facility and the (yet to be characterized) old parking lot in the southwest part of the facility (bearing in mind however that the southwest part of the facility parking lot has been partially covered over by a building). I personally walked along the very narrow walkway between the Madison-Kipp facility and homes at 269-233 East Waubesa Street. While standing behind the home at 233 E. Waubesa Street, I took photos of large exhaust fans at Madison-Kipp (see Photo 22) which clearly showed they were dripping with petroleum residues. I further looked at the concentrations of PAHs in the backyards of the homes immediately adjacent to these exhaust fans. The highest concentrations of PAHs are located in the yards directly adjacent to the exhaust fans, strongly suggesting that emissions from the fans were a source of the PAHs. ARCADIS, as an advocate for Madison-Kipp, is trying to avoid addressing the PAH problem, which would reduce the cost of further investigation and remediation. After completion of the off-site soil testing program referenced earlier in this report, all residential yards with PAH above WDNR's action level, should be excavated to remove the impacted soil and replaced with clean backfill.

Once again Dr. Everett mentions the use of forensic techniques to determine the origin of PAHs at the Site but fails to apply those techniques in this expert report as we have done here. Section 3.5 of this report applies those techniques to show that the PAHs found in the surrounding properties did not originate from MKC.

Dr. Everett states that benzo(a)pyrene is a major contributor to the human health risk and a significant reason for addressing the PAHs at this Site. Our analysis shows that benzo(a)pyrene was not part of the PAHs found in products used at the manufacturing facility (Section 3.5). Our analysis also showed that benzo(a)pyrene was more prevalent off-Site than it was on-Site (Section 3). Further, this compound was part of the background concentrations found at the Site and not related to the activities at the MKC facility (Sections 3 and 4)

Finally, Dr. Everett states that he witnessed the exhaust fans “*dripping with petroleum residues*”, however produced no data that showed what was in the condensate allegedly coming from the fans. Since he does not even state that he found a petroleum odor associated with these fans, we do not understand the basis of this opinion. He then goes on to say that the concentrations found in the yards closest to these fans had the highest concentrations of PAHs. This is not true. The highest concentrations at the site were found at samples B-56(0-2), B-54(0-2), B-21(0-2), B-55(0-2), B-22(0-2), and B-19(0-2), and these samples are on opposite sides of the building (three on the east side and three on the west side of the building). This clearly shows that there is no correlation between the location of exhaust fans and the highest concentrations of PAHs found in the adjacent residential properties.

Page 59 - Shallower on-site soils are more likely to be impacted with multiple contaminants. This is because both PCBs and PAHs have an affinity to strongly sorb to soil grains and organics in soil, thus are generally restricted to surficial soil and usually do not leach deeply into the soil profile. For this reason, I believe excavation and off-site disposal at a licensed treatment or disposal facility is the most appropriate approach for on-site shallow soil. For off-site shallow soil, excavation is the appropriate remediation technique because accomplishing cleanup rapidly should be a high priority for contaminated soil in residential yards where the risk of dermal contact and incidental ingestion are so great.

We agree with the statement that we would only expect to find PAHs in the shallow soil due to strong adsorption to the soil particles. This report shows that the PAHs in the backyard are associated with background sources of PAHs and that removing them by excavation is, therefore, not supportable and would be inconsistent with regulatory precedent.

6. Expert Summary of Findings

It is our opinion to a reasonable degree of scientific certainty that the PAHs found at the residential properties surrounding the MKC facility are part of the normal background concentrations of PAHs found in Madison, Wisconsin and other urban areas in the United States. It is also our opinion to a reasonable degree of scientific certainty that the sources of PAHs found at the residential properties surrounding the Site are not from MKC. We developed these opinions based upon a thorough review of the regulations, published papers and peer reviewed scientific literature, and the execution of a statistical evaluation of the data from the Site. We specifically found that:

- Several states, including Wisconsin, accept the reality of PAH background concentrations
- U.S. EPA accepts the reality of PAH background concentrations
- Forensic analysis showed that the off-Site PAHs were background – MKC was not the source of off-Site PAHs
- Forensic analysis showed that the PAHs on Site had a higher contribution from the lower molecular weight PAHs found in petroleum hydrocarbons. These mixtures were not found off Site showing that MKC was not the source of off-Site PAHs
- Group 1 showed the strongest correlation with coal fines and cinder materials based on both R^2 and slope values, with urban dust and asphalt also showing strong correlations. Group 1 did not show any correlation with cutting oil, waste oil, or diesel contaminated soil
- Fate and transport analysis showed that the PAHs from the Site would have been deposited North and Northeast of the Site. Data from that specific geographic sample set showed that the PAHs were at background concentrations and that MKC was not the source of off-Site PAHs.
- U.S. EPA and local data specified several sources of PAHs in the area around MKC – MKC was not listed as a PAH source by U.S. EPA

7. References

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Tables

Table 3-1 Chemical Names and Abbreviations

Abbreviation	Chemical Name	CAS No.	Rings
NAP	Naphthalene	91-20-3	2
1mNAP	1-Methylnaphthalene	90-12-0	2
2mNAP	2-Methylnaphthalene	91-57-6	2
ANY	Acenaphthylene	208-96-8	3
ACE	Acenaphthene	83-32-9	3
FLU	Fluorene	86-73-7	3
ANT	Anthracene	120-12-7	3
PHE	Phenanthrene	85-01-8	3
FLA	Fluoranthene	206-44-0	4
PYR	Pyrene	129-00-0	4
BaA	Benzo(a)anthracene	56-55-3	4
CHR	Chrysene	218-01-9	4
BbF	Benzo(b)fluoranthene	205-99-2	5
BkF	Benzo(k)fluoranthene	207-08-9	5
BaP	Benzo(a)pyrene	50-32-8	5
DBA	Dibenzo(a,h)anthracene	53-73-3	5
IP	Indeno(1,2,3-c,d)pyrene	53-70-3	6
BPE	Benzo(g,h,i)perylene	191-24-2	6

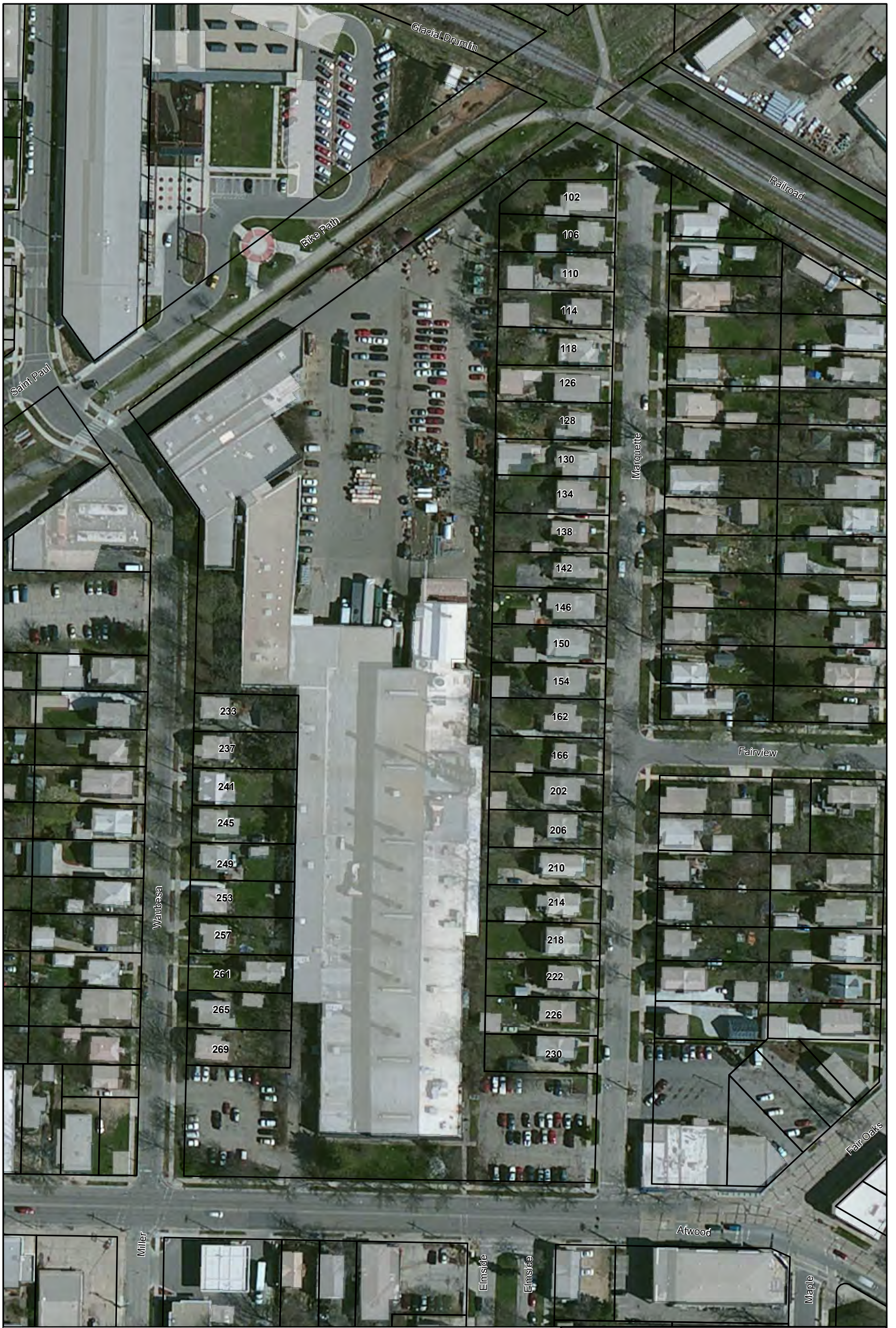
Table 3-2 PAH Detection Frequency

PAH Designation	Detections in Full Data Set (n=341)	Detection Frequency in Full Data Set (%)	Detections in Forensic Data Set (n=341)	Detection Frequency in Forensic Data Set (%)
NAP	96	28.2%	85	55.9%
1mNAP	58	17.0%	51	33.6%
2mNAP	28	8.2%	27	17.8%
ANY	52	15.2%	50	32.9%
ACE	68	19.9%	68	44.7%
FLU	94	27.6%	91	59.9%
ANT	128	37.5%	124	81.6%
PHE	166	48.7%	150	98.7%
FLA	183	53.7%	152	100.0%
PYR	180	52.8%	152	100.0%
BaA	178	52.2%	150	98.7%
CHR	179	52.5%	152	100.0%
BbF	186	54.5%	151	99.3%
BkF	157	46.0%	148	97.4%
BaP	190	55.7%	152	100.0%
DBA	122	35.8%	121	79.6%
IP	151	44.3%	145	95.4%
BPE	161	47.2%	147	96.7%



% Percent

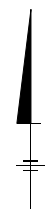
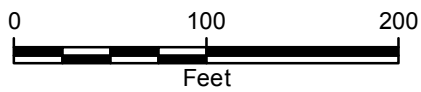
PAH abbreviations are provided in Table 3.1

Figures



LEGEND

-  PARCELS
-  BUILDING FOOTPRINTS



MADISON-KIPP
 201 WAUBESA STREET
 MADISON, WI

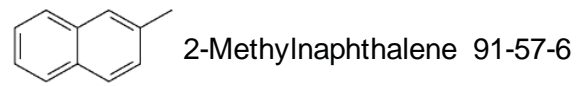
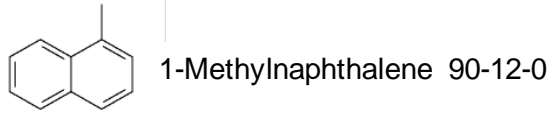
SITE LAYOUT



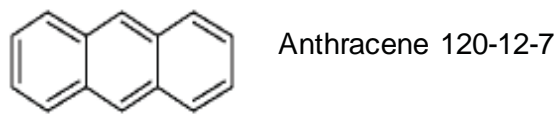
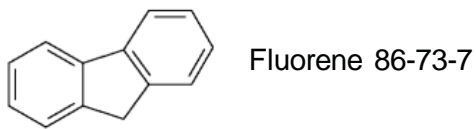
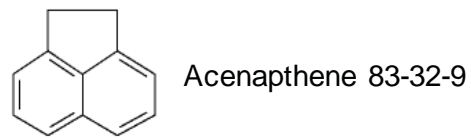
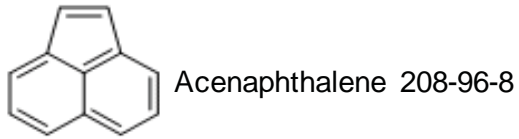
FIGURE
1-1

NOTES:
 1. AERIAL IMAGERY OBTAINED FROM BING IMAGERY
 SERVICE THROUGH ESRI ONLINE MAPPING, ACCESSED 1/11/13

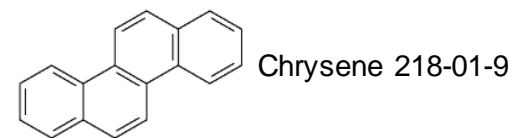
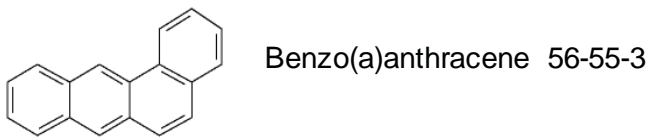
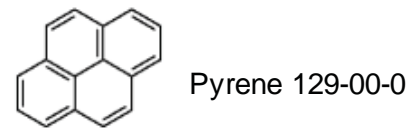
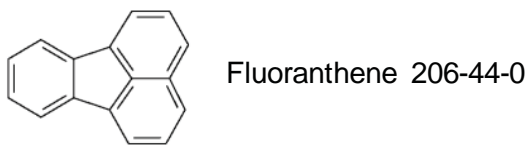
2-Ring PAHs



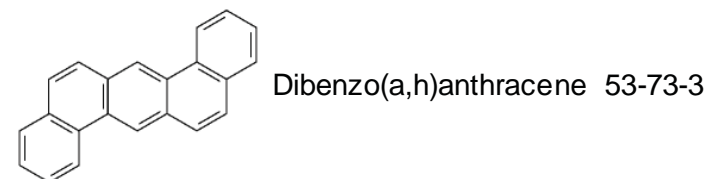
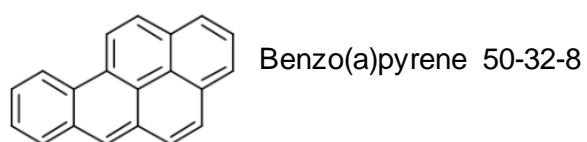
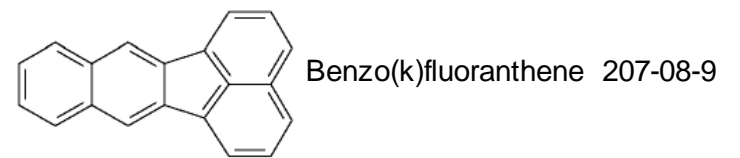
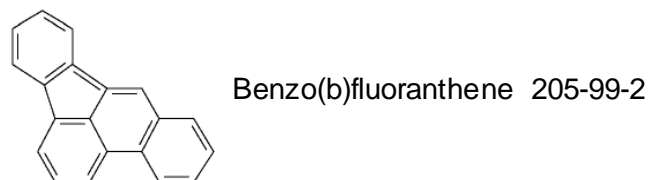
3-Ring PAHs



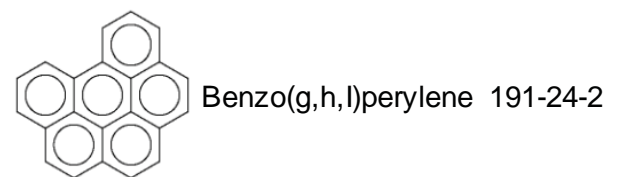
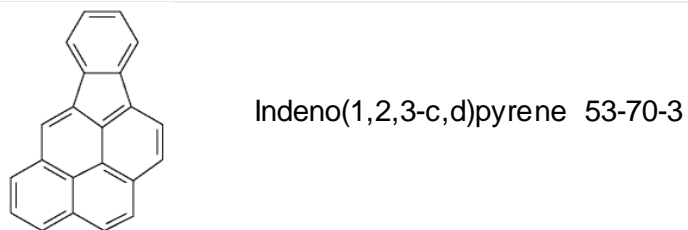
4-Ring PAHs



5-Ring PAHs



6-Ring PAHs



LEGEND

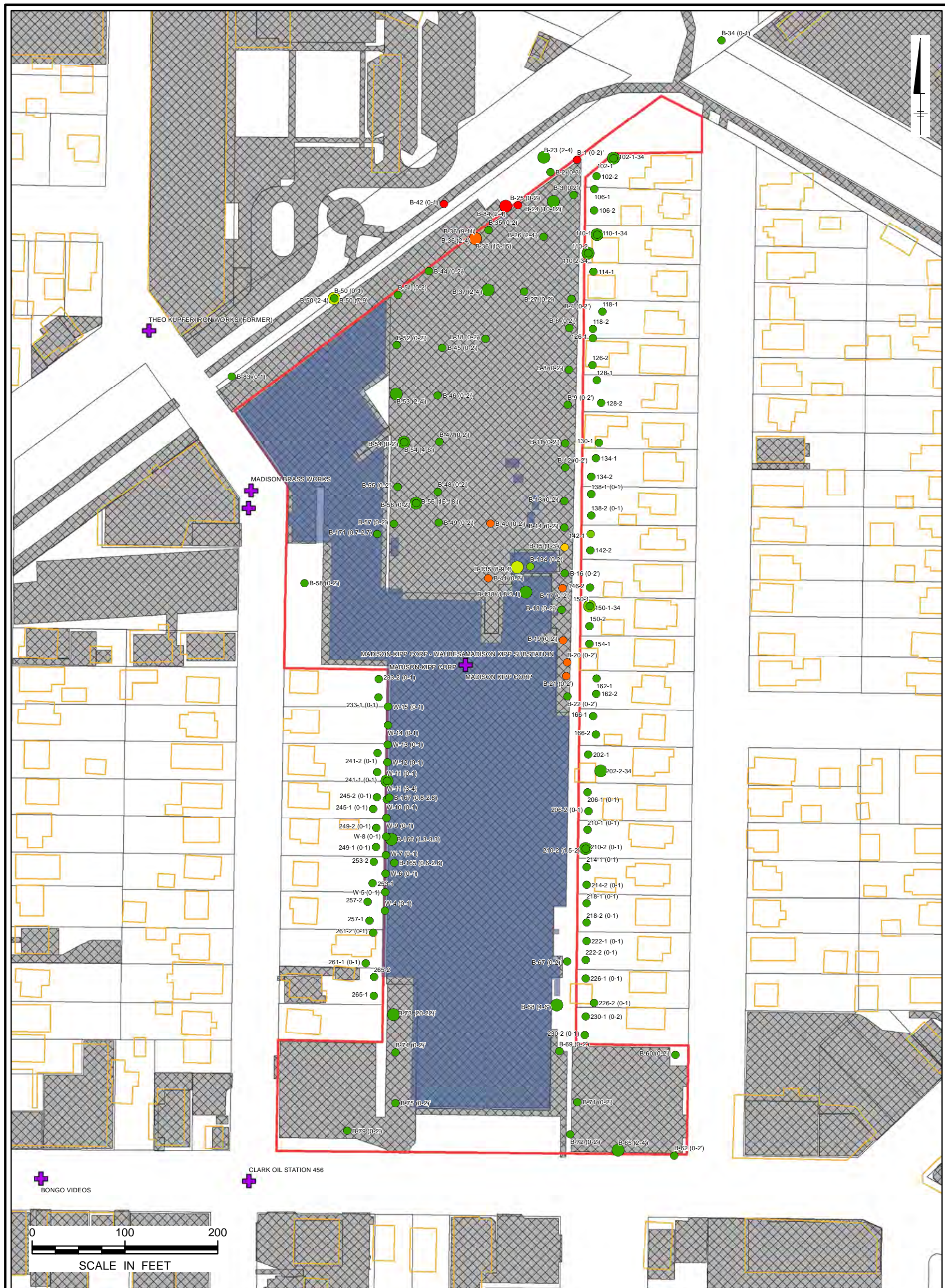
- PAHs Polynuclear Aromatic Hydrocarbons
53-70-3 Chemical Abstract Service (CAS) Number

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SUMMARY DIAGRAM OF PAH STRUCTURES



FIGURE
3-1



LEGEND

● GROUP 1	● GROUP 1	+ SITES OF INTEREST (EDR 1 MILE SEARCH)
● GROUP 2	● GROUP 2	 SITE STRUCTURES
● GROUP 3	● GROUP 3	 OFFSITE BUILDING FOOT PRINTS
● GROUP 4	● GROUP 4	 PROPERTY BOUNDARY
● GROUP 5	● GROUP 5	 PARCEL BOUNDARIES
● GROUP 6	● GROUP 6	 IMPERVIOUS FEATURES IN IMMEDIATE AREA (5.9 ACRES)
		 IMPERVIOUS AREAS

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SAMPLE GROUPS


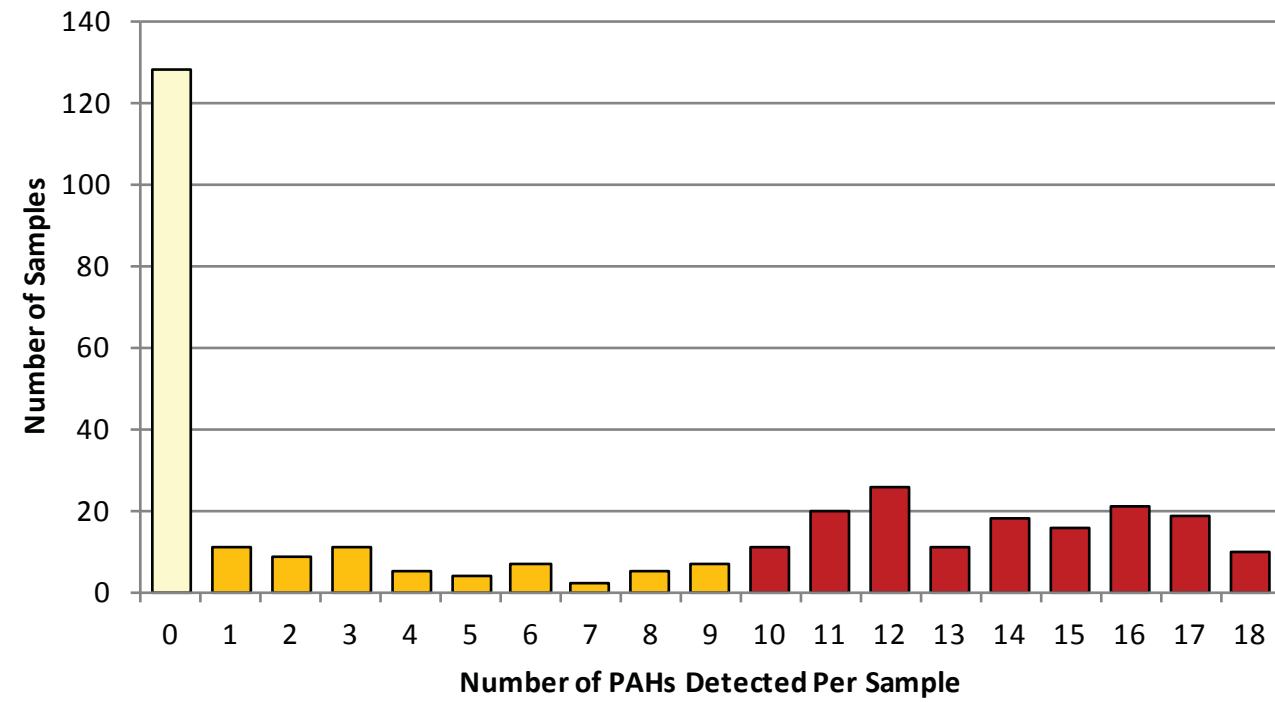


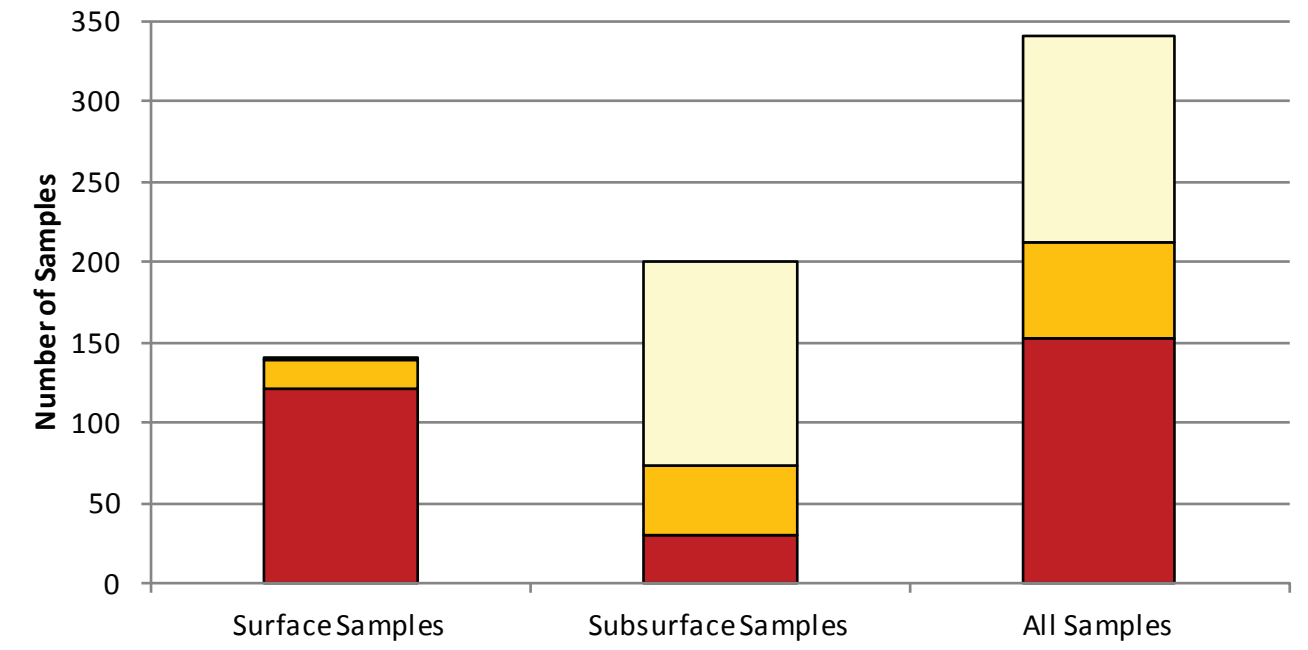
FIGURE
3-2

17 JAN 13 ENVIRONMENT\CKL\MB
MADISON\KPP\W007283\GRAPHICS\FIGURE 2 SUMMARY OR DATA SET.A1

Frequency of PAHs Detected Per Sample



Summary of Samples by Depth



■ 10 or more PAHs detected ■ 1 to 9 PAHs detected ■ PAHs not detected

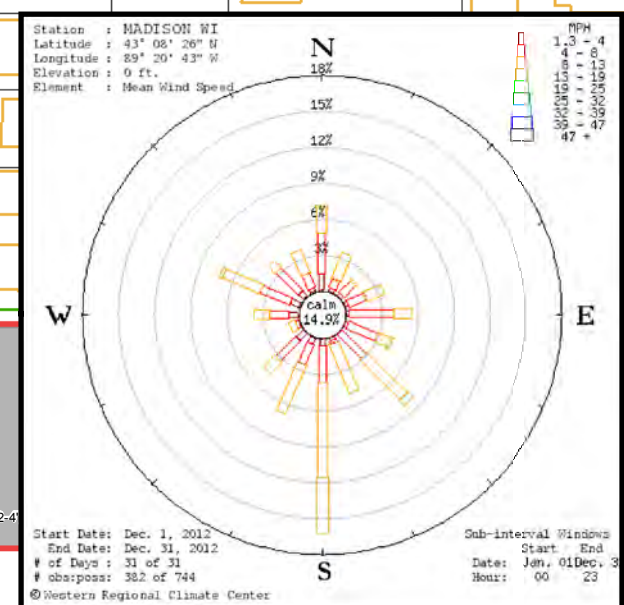
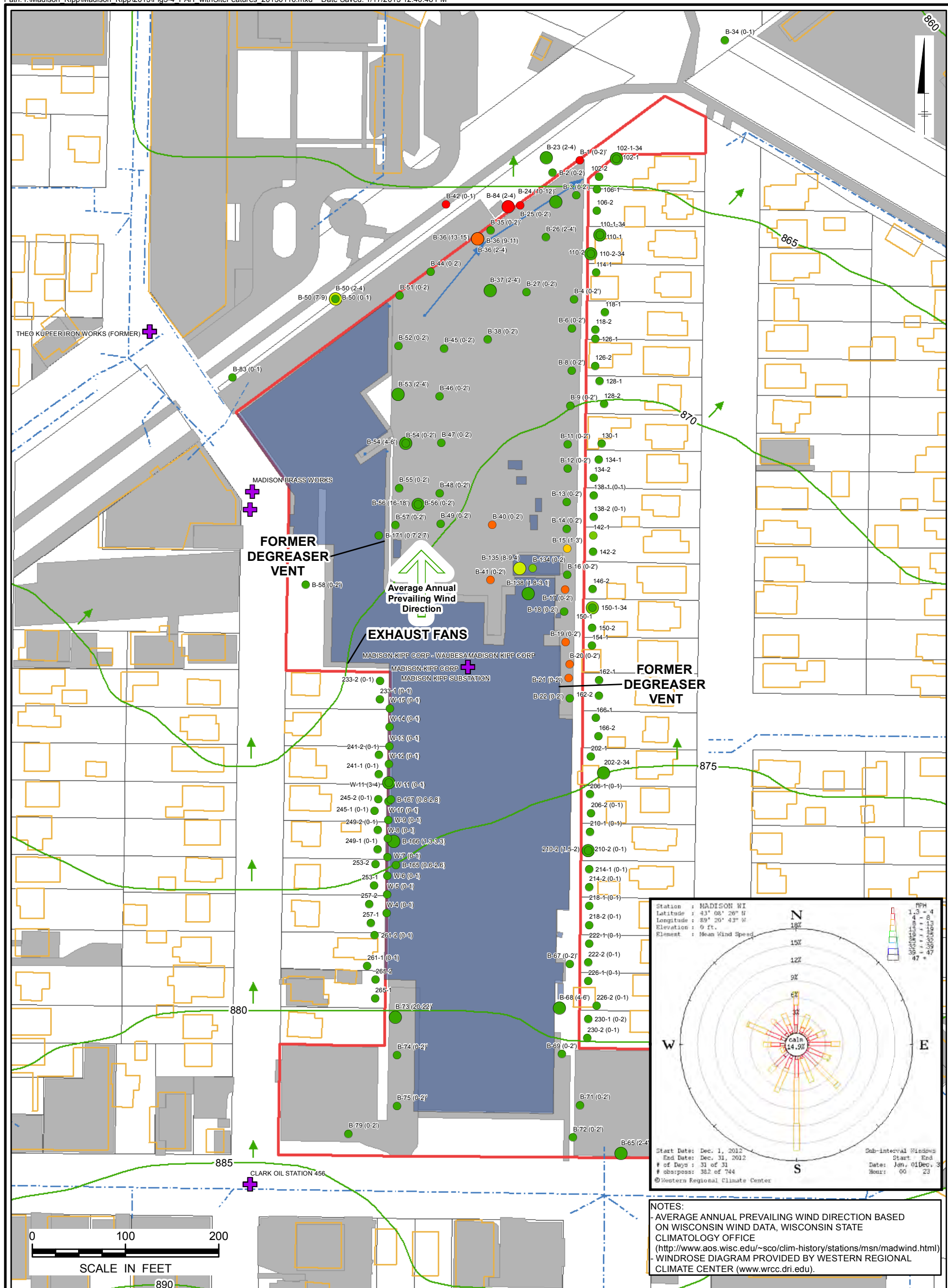
LEGEND

Surface Sample - mean sample depth less than 1 foot below grade.

Subsurface Sample - mean sample depth greater than 1 foot below grade.

PAHs - Polynuclear Aromatic Hydrocarbons.

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SUMMARY OF DATA SET BY INCLUSION CRITERIA AND DEPTH ZONE	
	FIGURE 3-3



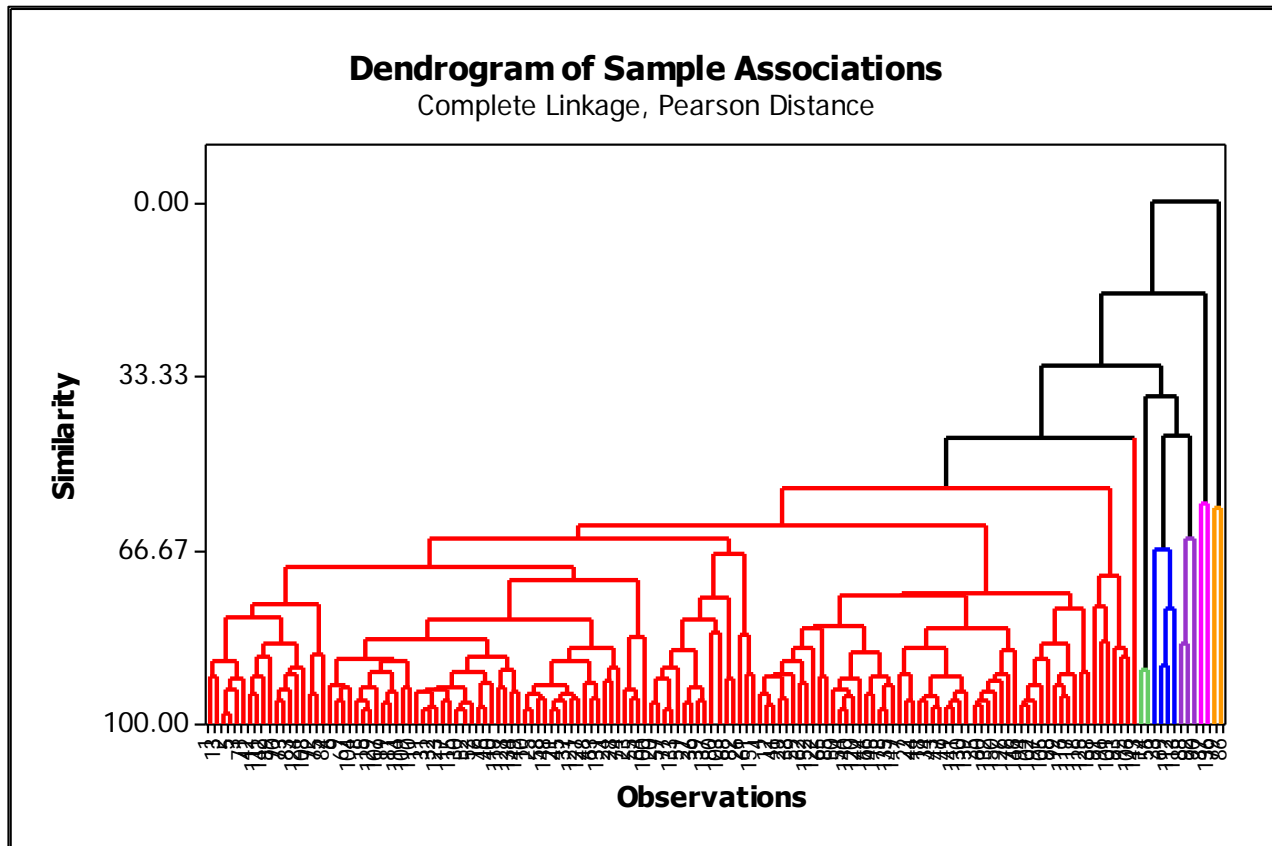
NOTES:
 - AVERAGE ANNUAL PREVAILING WIND DIRECTION BASED ON WISCONSIN WIND DATA, WISCONSIN STATE CLIMATOLOGY OFFICE (<http://www.aos.wisc.edu/~sco/clim-history/stations/msn/madwind.html>)
 - WINDROSE DIAGRAM PROVIDED BY WESTERN REGIONAL CLIMATE CENTER (www.wrcc.dri.edu).

- LEGEND**
- | | | |
|---------------------------------|------------------------------------|--|
| SURFACE SAMPLE LOCATIONS | SUBSURFACE SAMPLE LOCATIONS | + SITES OF INTEREST (EDR 1 MILE SEARCH) |
| ● GROUP 1 | ● GROUP 1 | ← PARTICLE TRACKING |
| ● GROUP 2 | ● GROUP 2 | — TOPOGRAPHIC CONTOURS (5FT INTERVAL) |
| ● GROUP 3 | ● GROUP 3 | - - - STORMWATER PIPES |
| ● GROUP 4 | ● GROUP 4 | — ONSITE STORM WATER DISCHARGE |
| ● GROUP 5 | ● GROUP 5 | ■ SITE STRUCTURES |
| ● GROUP 6 | ● GROUP 6 | □ OFFSITE BUILDING FOOT PRINTS |
| | | ■ IMPERVIOUS AREAS |
| | | ▣ IMPERVIOUS FEATURES IN IMMEDIATE AREA |
| | | □ PARCEL BOUNDARIES |

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SITE TRANSPORT

FIGURE
3-4



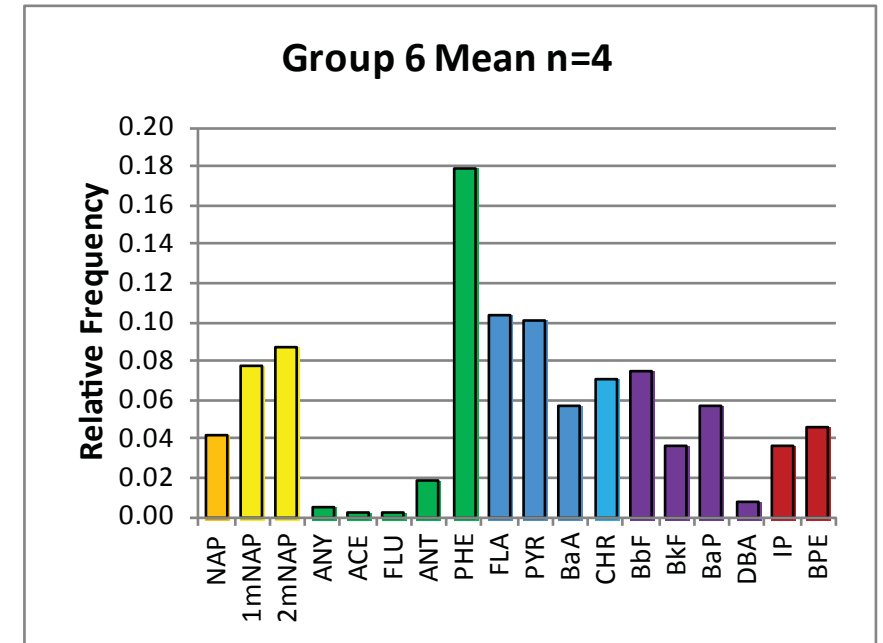
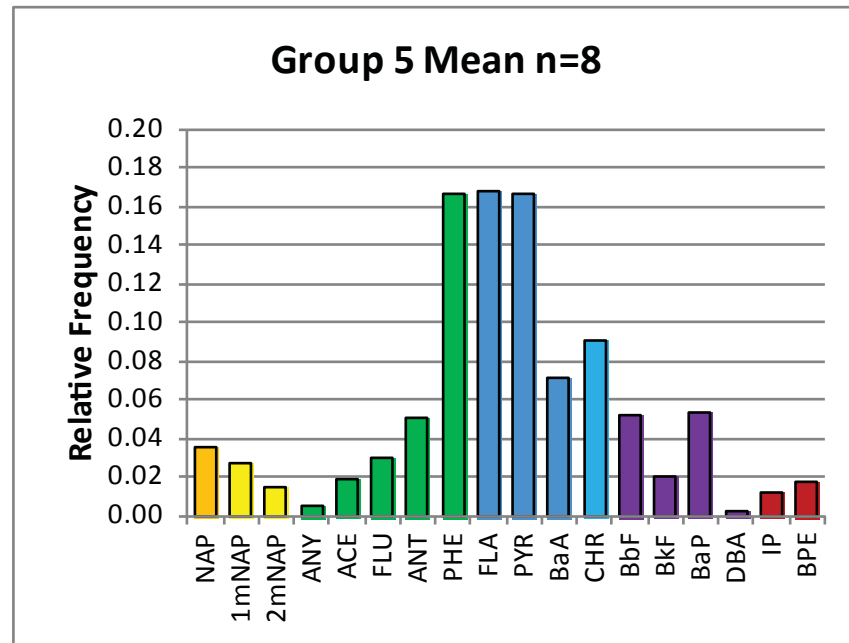
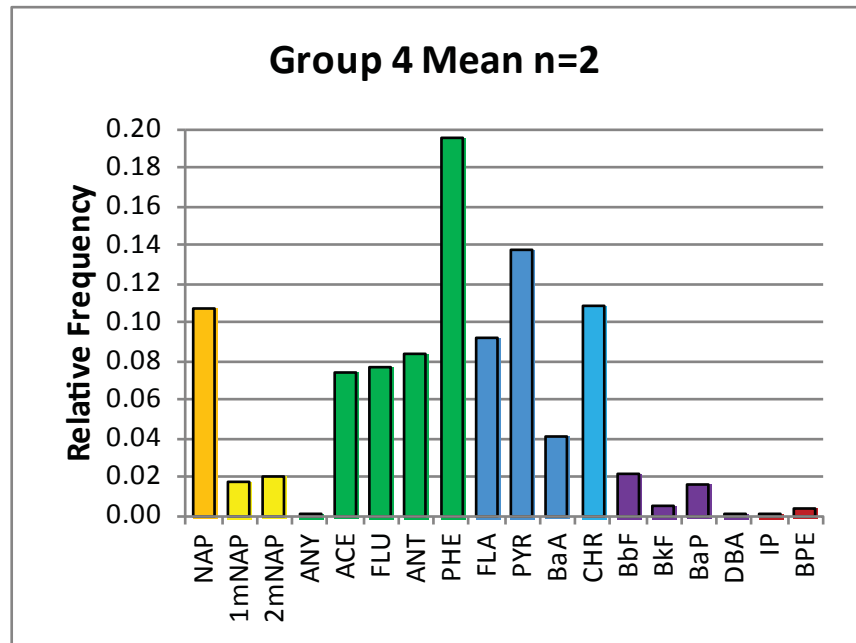
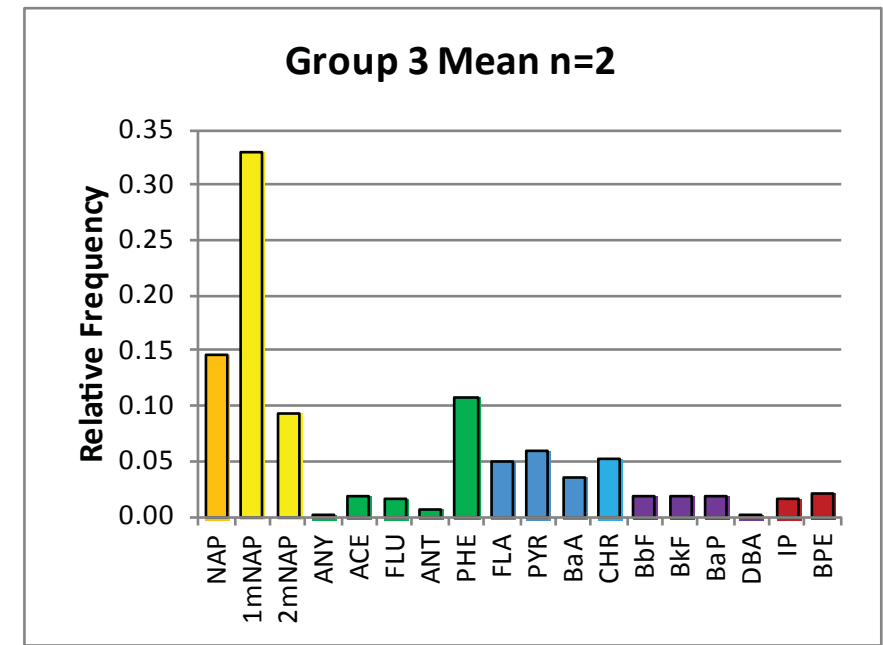
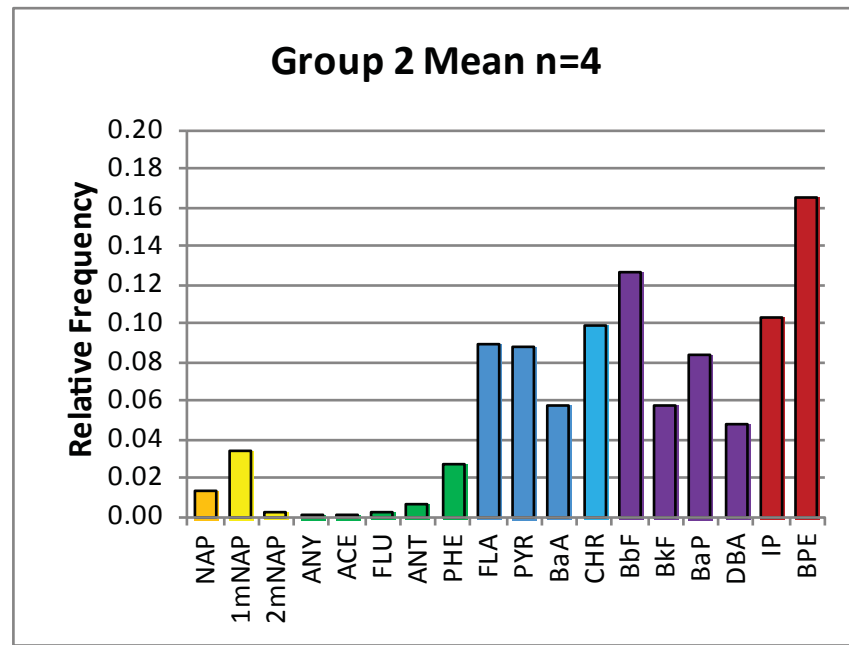
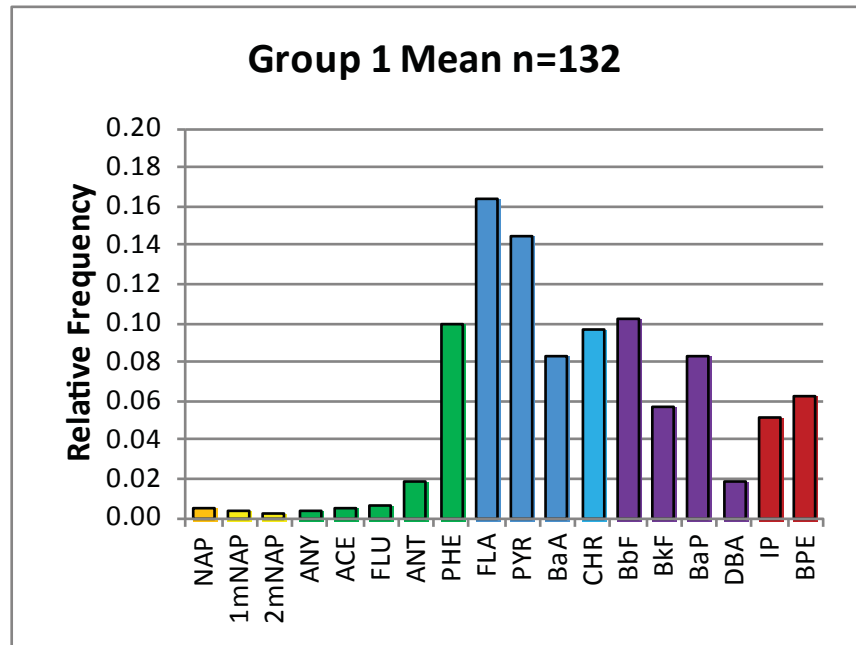
The various colors of the lines indicate the six different cluster groups identified by the analysis. Each vertical line represents an individual sample or subsequent group of related samples. The height of the horizontal connecting lines indicates the relative degree of similarity between groups of samples. Sample identification numbers are linked to statistical software used for the forensic evaluation.

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SUMMARY DENDROGRAM OF MULTIVARIATE CLUSTER ANALYSIS RESULTS



FIGURE
3-5



The vertical bars of each profile indicate the relative proportion of each individual PAH in the different group. Colors represent 2-ring (orange and yellow), 3-ring (green), 4-ring (blue), 5-ring (purple) and 6-ring (dark red) PAHs. Abbreviations for PAHs are described in the text. The number of samples in each cluster group is indicated.

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**PAH PROFILES FOR MEAN PAH PROPORTIONS
IN EACH MULTIVARIATE CLUSTER GROUP**


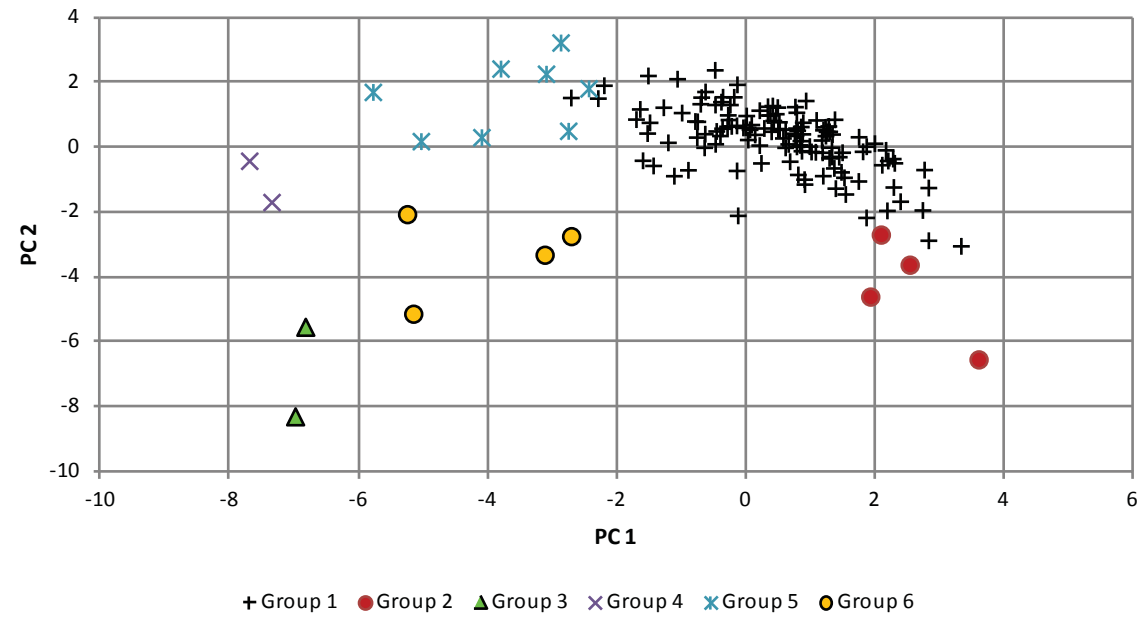
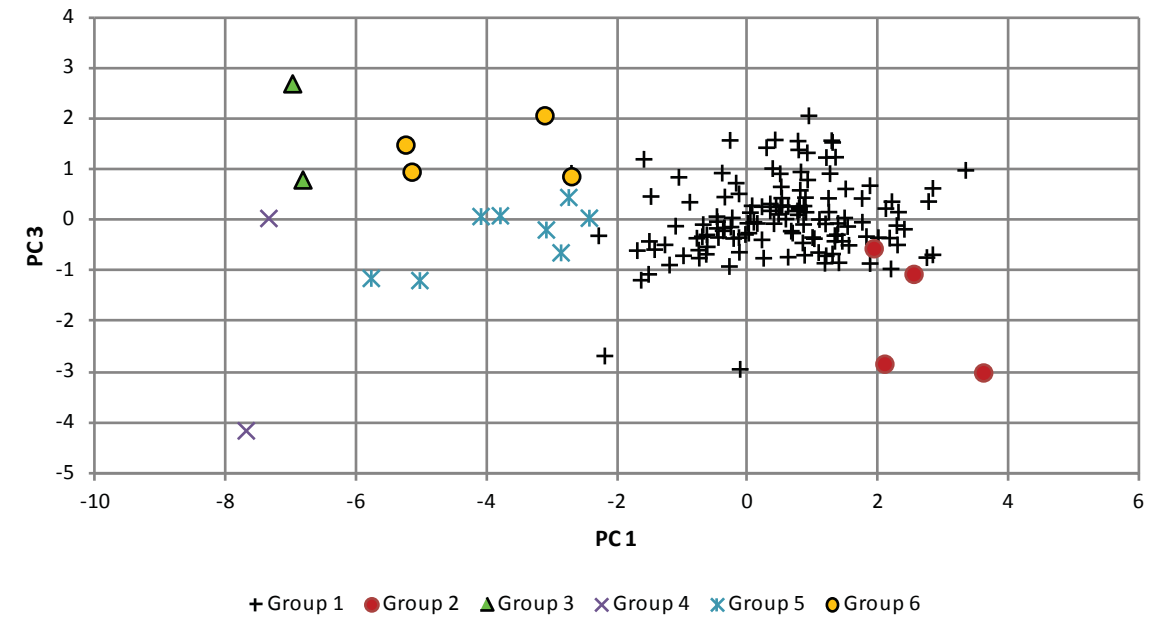


FIGURE
3-6

Principal Component Analysis - PC 1 vs. PC 2



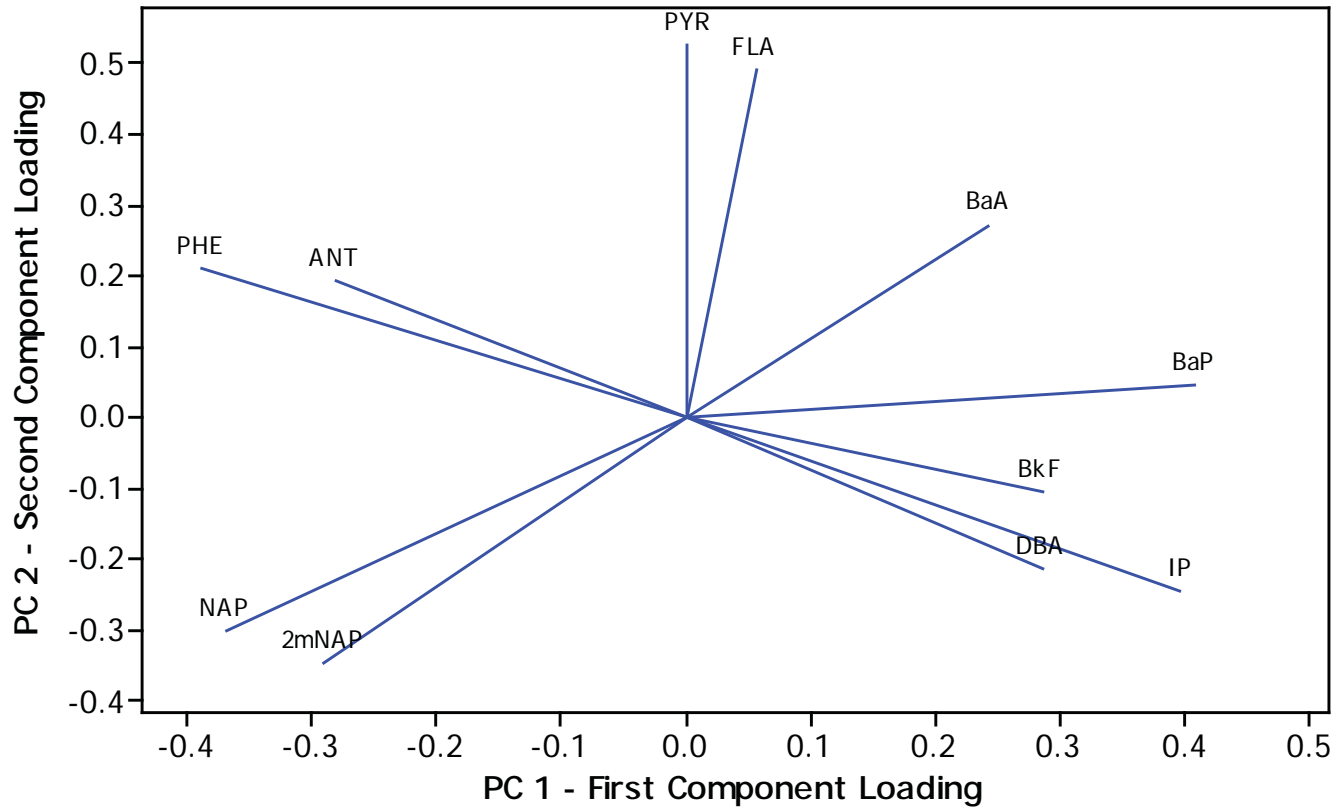
Principal Component Analysis - PC 1 vs. PC 3



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PRINCIPAL COMPONENT ANALYSIS





Abbreviations for PAHs are described in the text

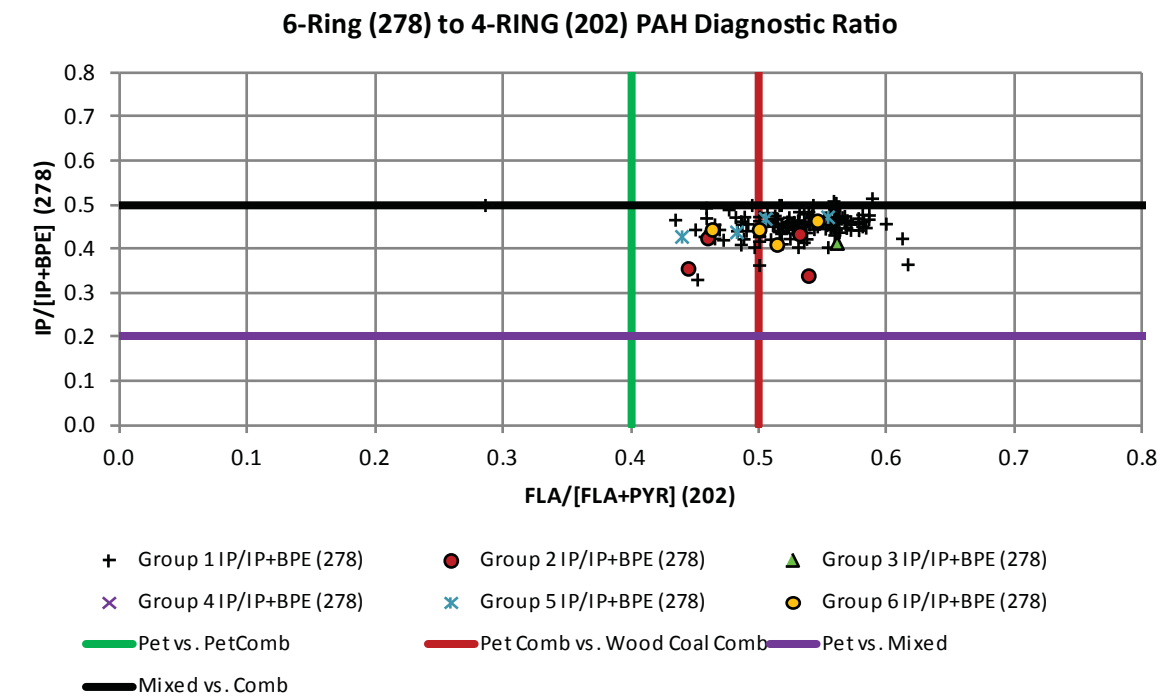
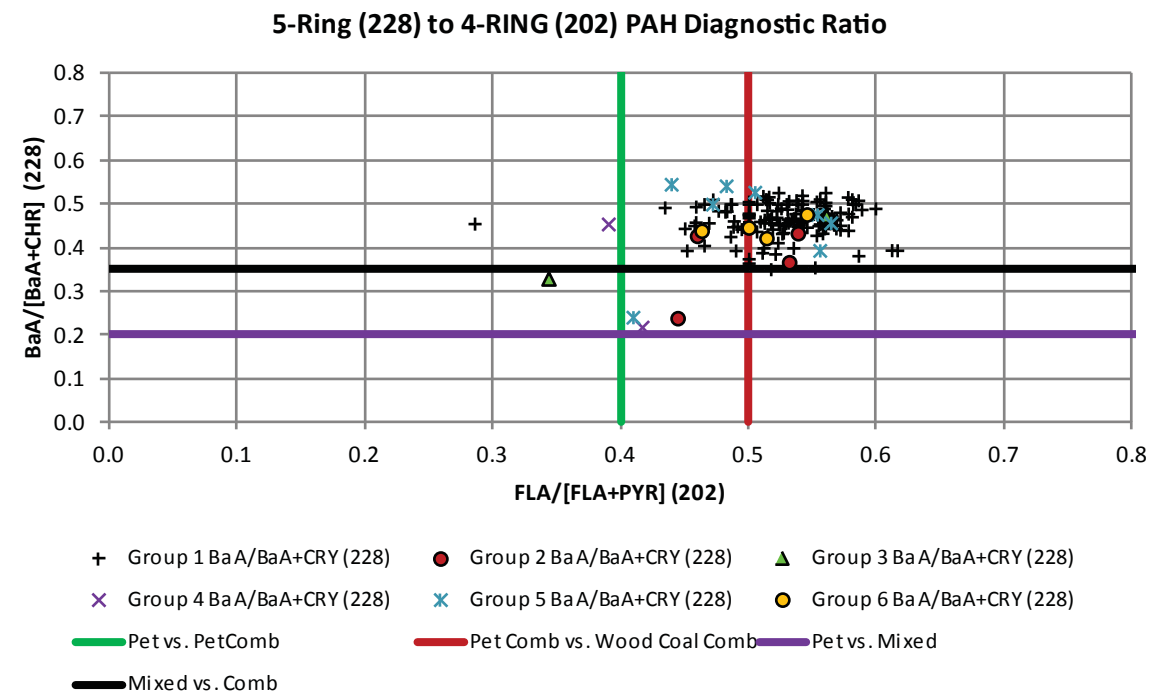
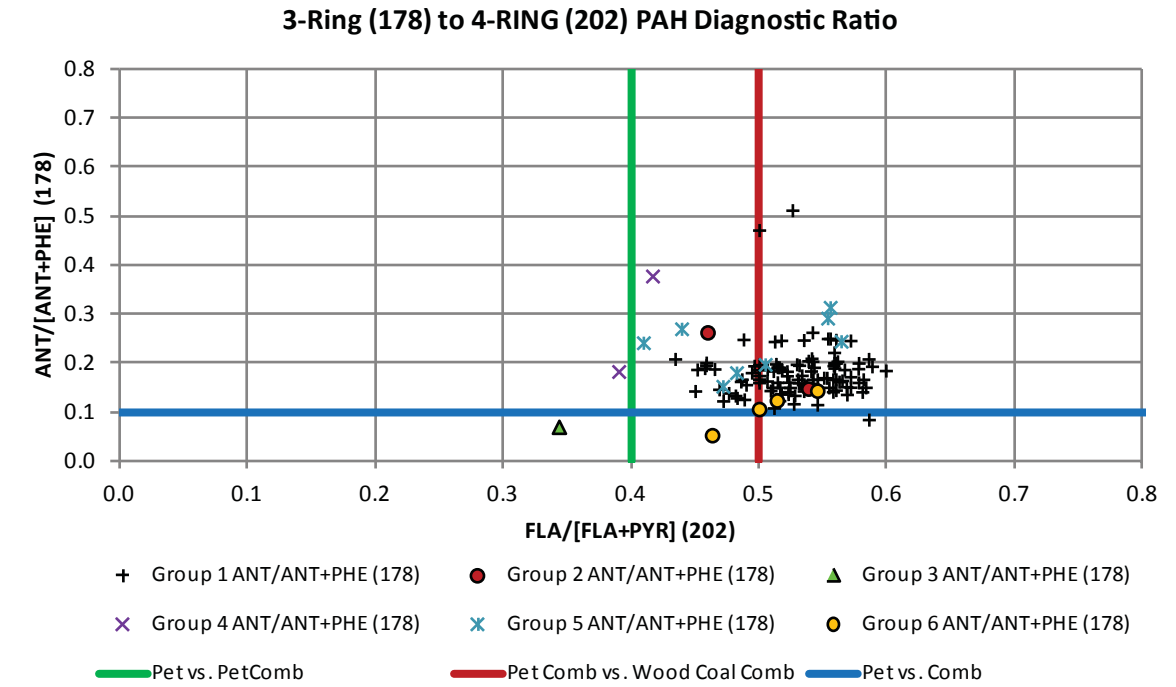
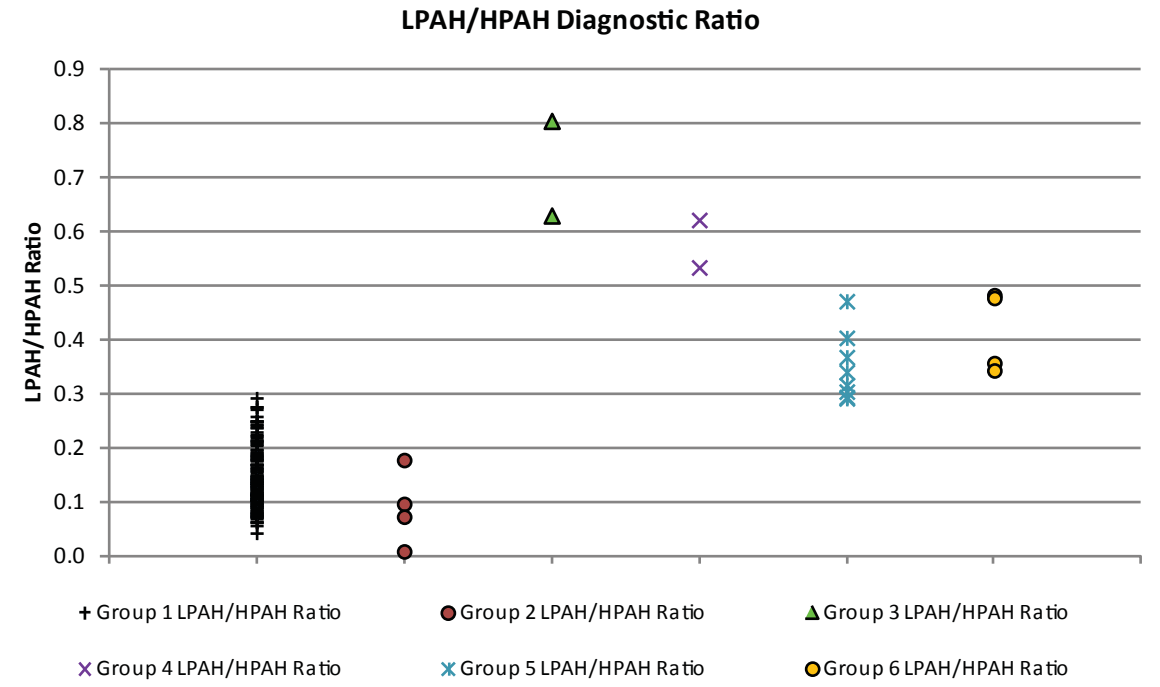
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**LOADING FACTORS FOR PRINCIPAL
COMPONENT ANALYSIS
PC1 VS PC2**



FIGURE
3-8

17JAN13\ENVIRONMENT\CKLMB\MADISON\KPP\W007283\GRAPHICS\FIGURE 7 DIAGNOSTIC RATIOS.A1



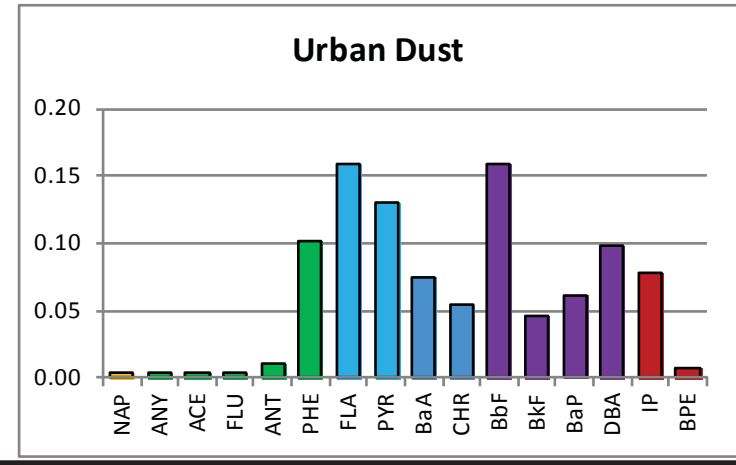
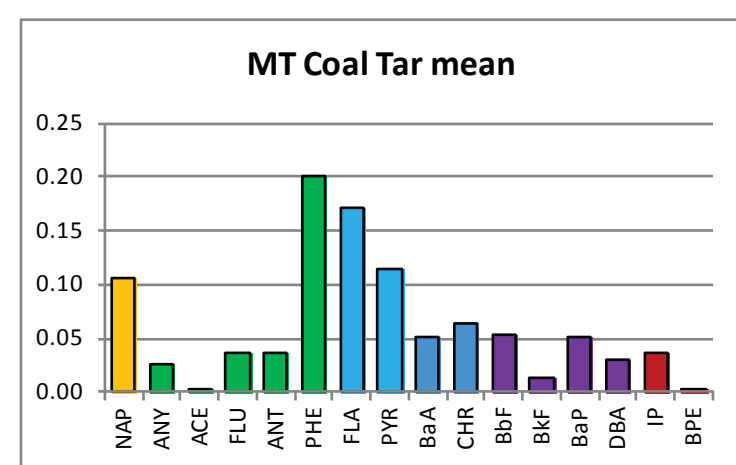
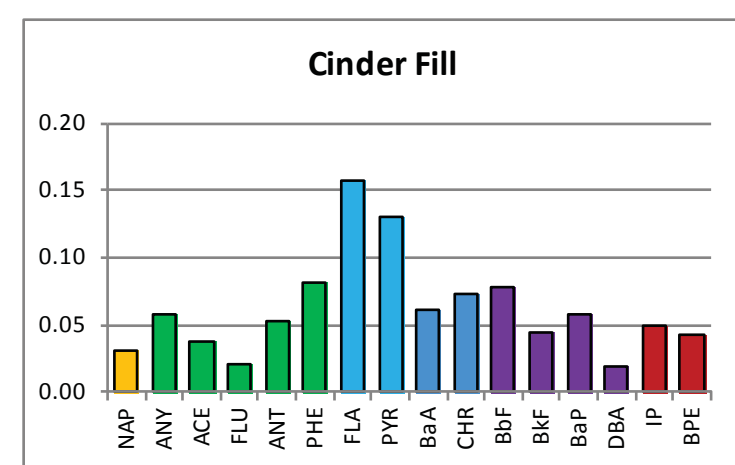
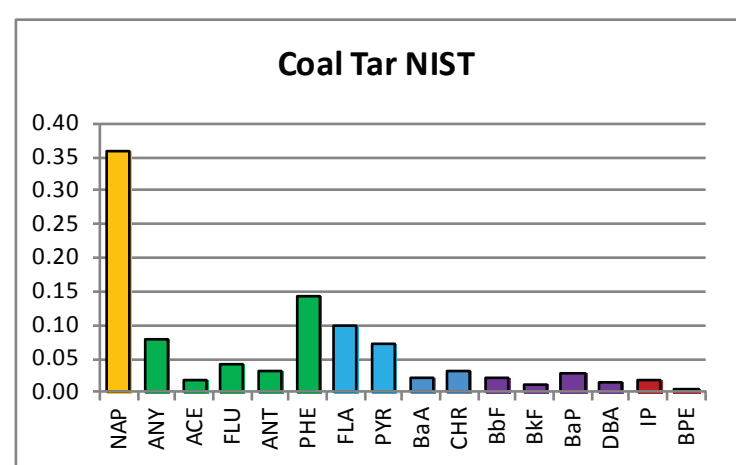
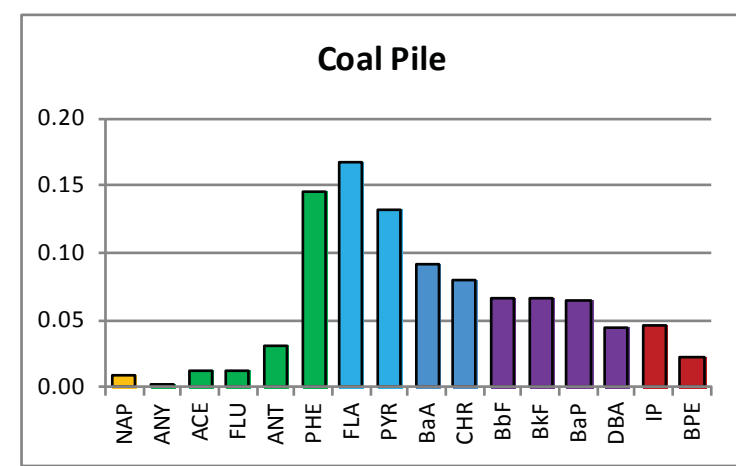
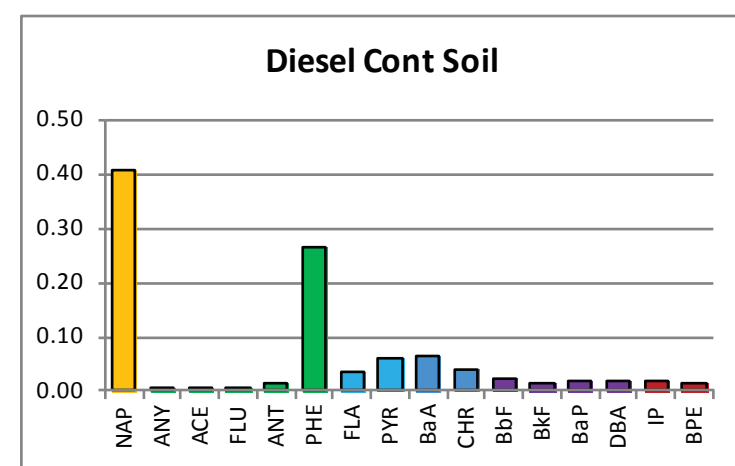
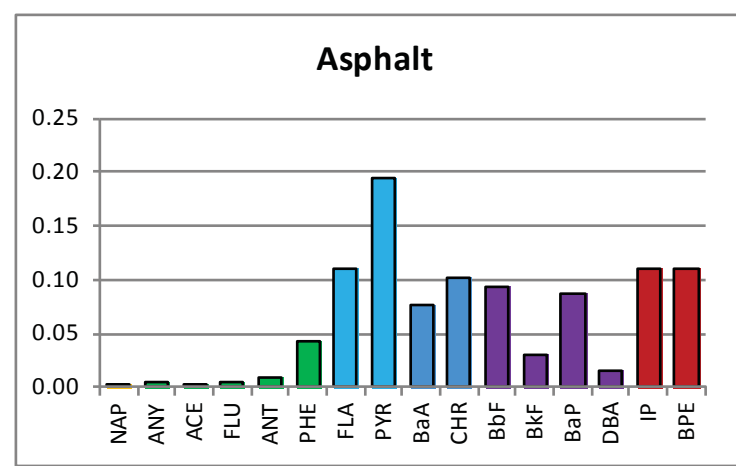
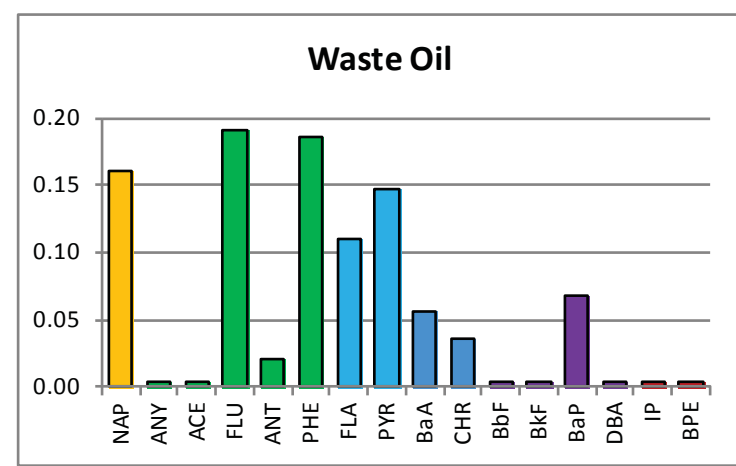
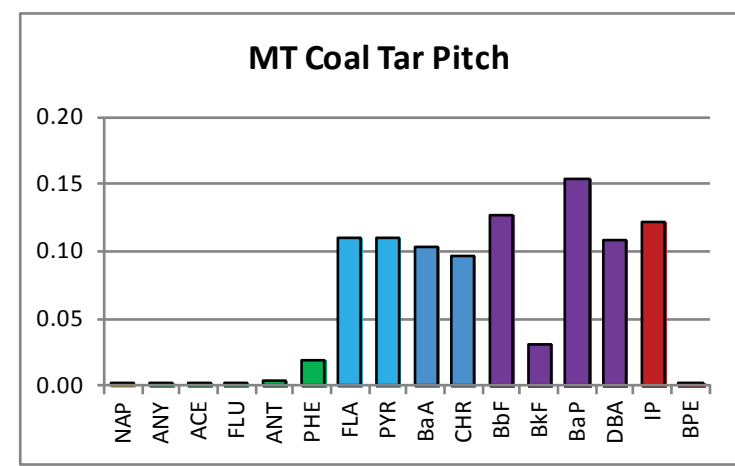
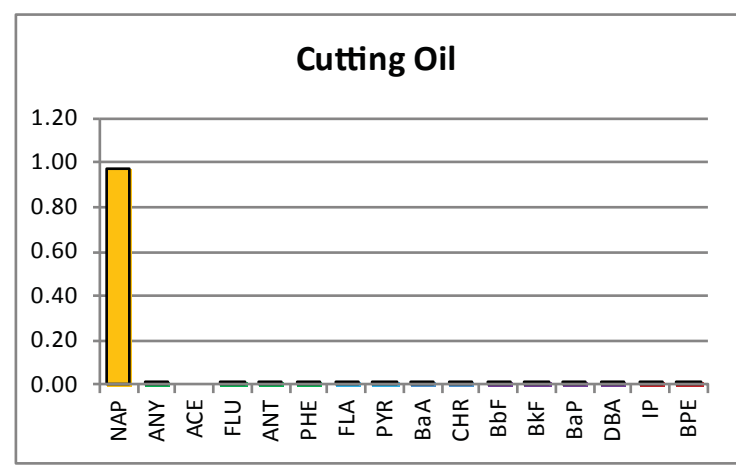
LEGEND

PAH	Polynuclear Aromatic Hydrocarbons
LPAH	Light PAH
HPAH	Heavy PAH
Pet	Petroleum
Pet Comb	Petroleum Combustion
Wood Coal Comb	Wood Coal Combustion
Mixed	Pet Comb and Wood Coal Comb

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DIAGNOSTIC RATIOS

FIGURE
3-9

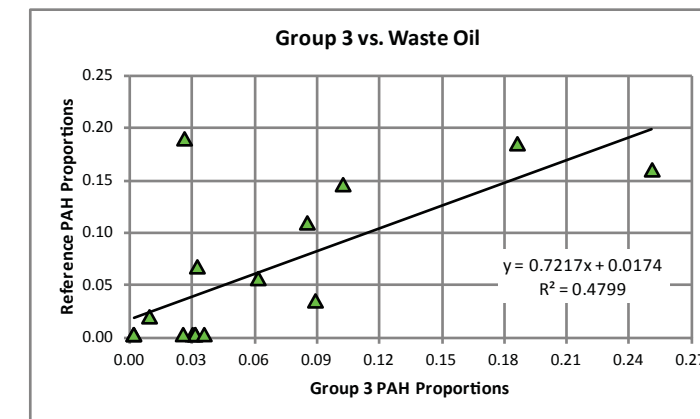
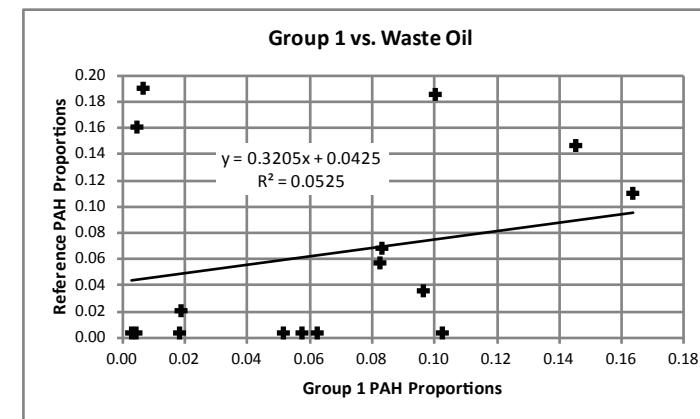
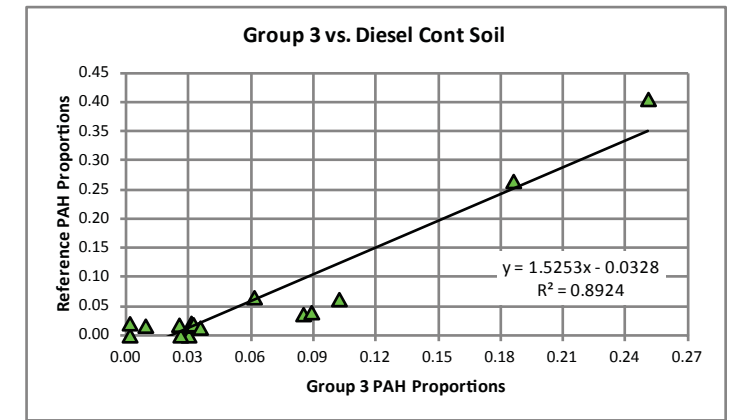
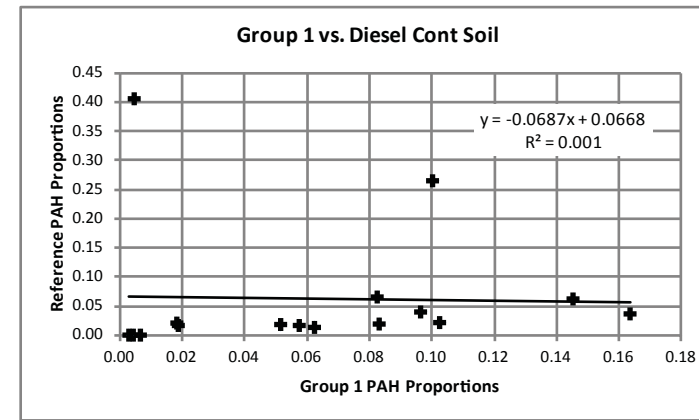
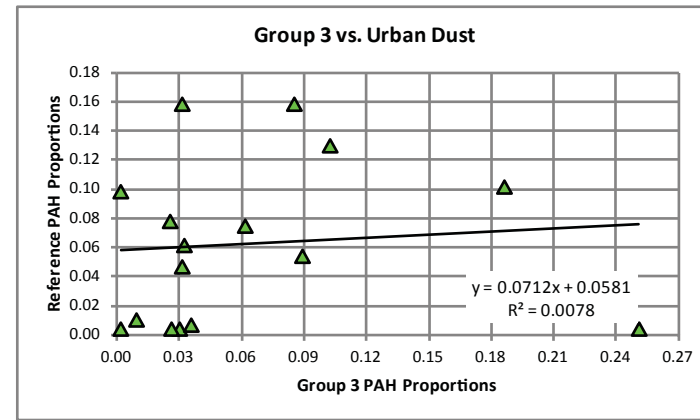
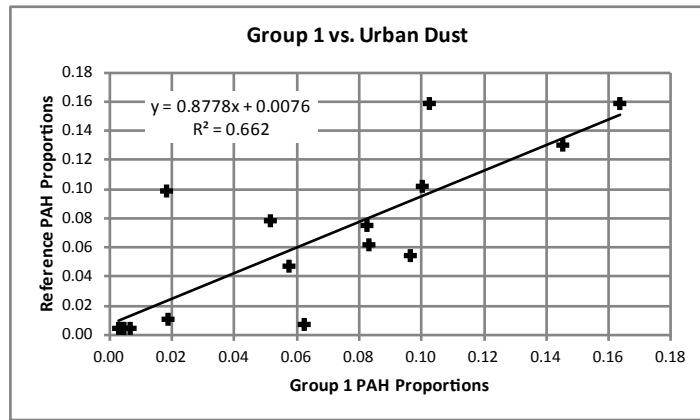
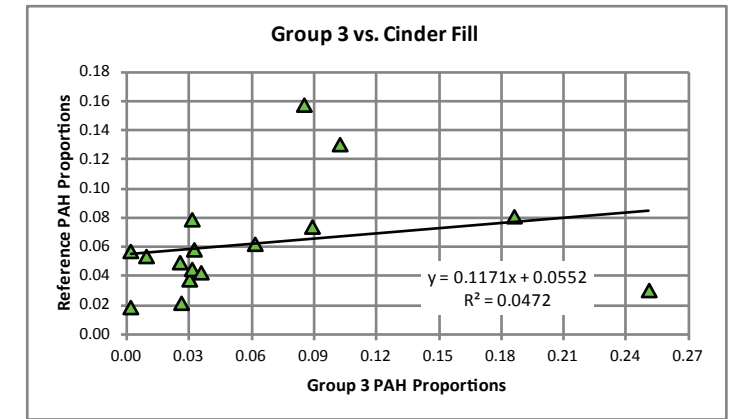
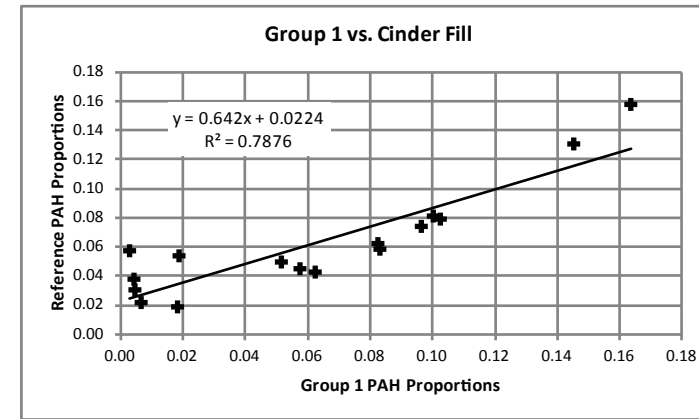
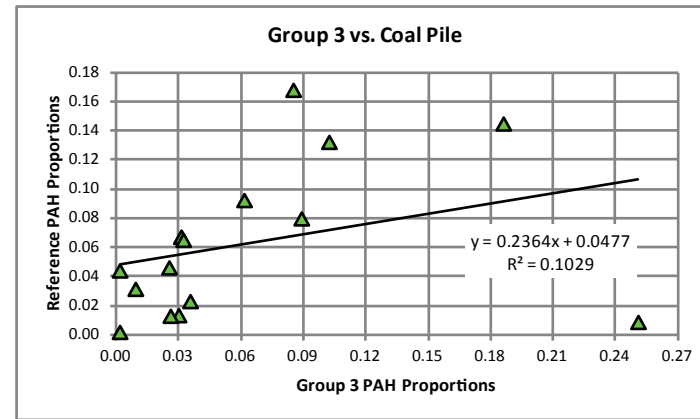
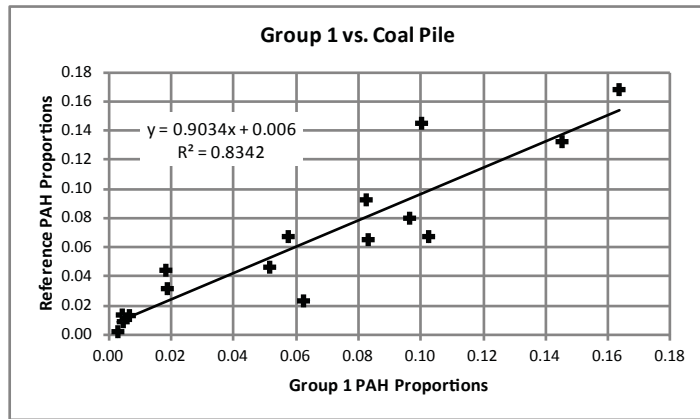


Abbreviations for PAHs are described in the text.

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**PAH PROFILES FOR REFERENCE
 SOURCE MATERIALS**

FIGURE
3-10



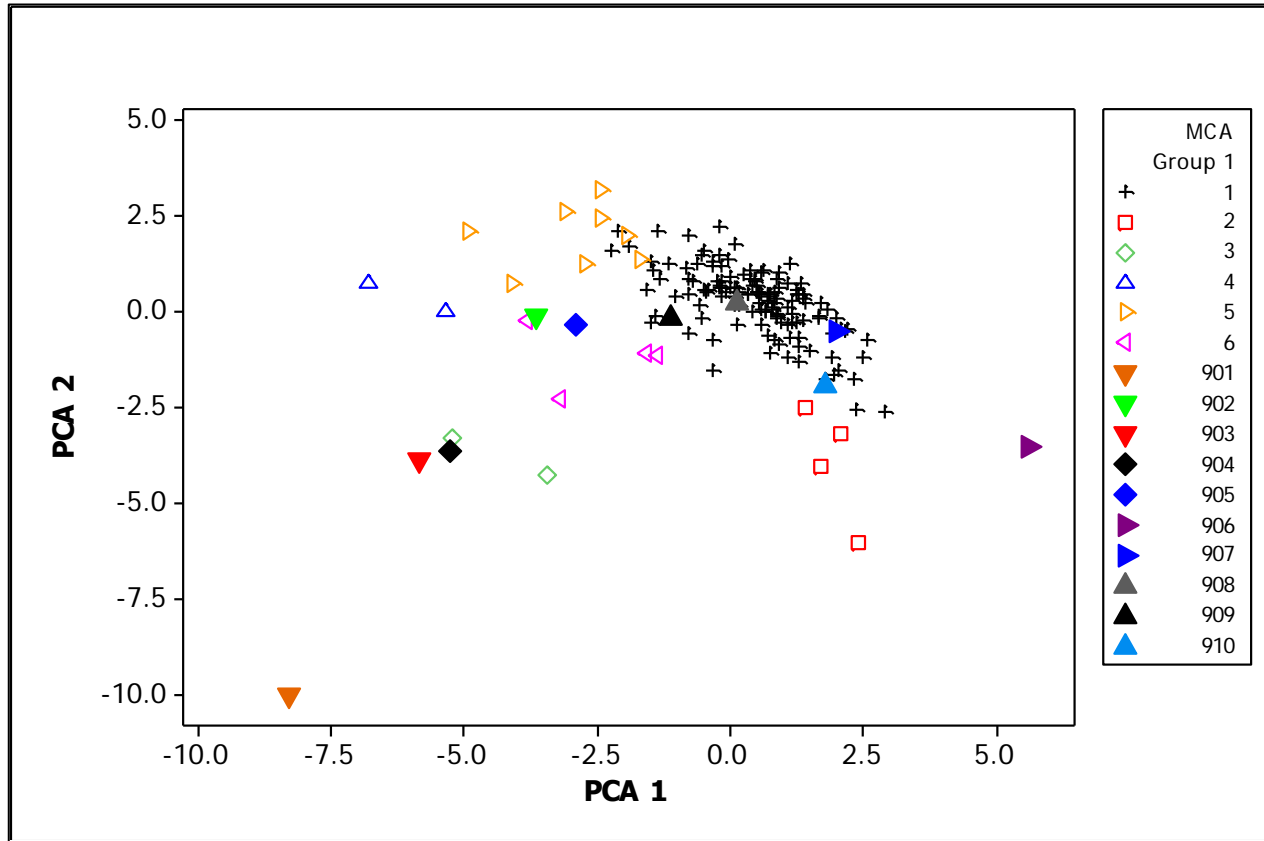
LEGEND

PAH Polynuclear Aromatic Hydrocarbons
Cont Contaminated

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REGRESSION RESULTS





- 901 - Cutting Oil
- 902 - Waste Oil
- 903 - Diesel Contaminated Soil
- 904 - Coal Tar (high-naphthalene)
- 905 - Coal Tar (low-naphthalene)
- 906 - Coal Tar Pitch
- 907 - Asphalt
- 908 - Coal Fines
- 909 - Cinder Fill
- 910 - Urban Dust

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**SCATTERPLOT OF PCA 2 VS PCA 1
WITH PAH SOURCE MATERIAL**

 **ARCADIS**