
***Evaluation of the extent and transport capabilities of
atmospheric polycyclic aromatic hydrocarbons in the Lake
Erie watershed***

Final Report

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ACRONYMS AND ABBREVIATIONS

ACNE	Acenaphthene
ACNY	Acenaphthalene
AN	Anthracene
AOC	Area of concern
BaA	Benz[a]anthracene
BaP	Benzo[a]pyrene
BbFLA	Benzo[b]fluoroanthene
BeP	Benzo[e]pyrene
BghiP	Benzo[g,h,i]perylene
BkFLA	Benzo[k]fluoroanthene
COR	Coronene
CY	Chrysene
DBahAN	Dibenz[a,h]anthracene
DEP	Department of Environmental Protection
DOE	Department of Energy
EPA	Environmental Protection Agency
FAA	Federal Aviation Agency
FL	Fluorene
FLA	Fluoranthene
GC	Gas chromatograph
GFF	Glass fiber filter
IADN	Integrated Air Deposition Network
IcdPYR	Indeno[1,2,3-cd]pyrene
MDL	Method detection limit
MIC	Meteorological Instruments Company
MS	Mass selective
ND	Non-detect
NOAA	National Oceanic and Atmospheric Administration
NWS	National Weather Service
PAH	Polycyclic aromatic hydrocarbon
PBT	Persistent bioaccumulative toxics
PE	Perylene
PEC	Probable effect concentration
PH	Phenanthrene
PIB	Presque Isle Bay
PUF	Polyurethane foam
PYR	Pyrene
RAIS	Risk Assessment Information System
RBC	Risk-based concentration
SIM	Selective ion monitoring
TEF	Toxic equivalency factor
TEQ	Toxic equivalency quantity
QAPP	Quality assurance program plan
SOP	Standard operating procedure
V_d	Deposition velocity

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EXECUTIVE SUMMARY

Research Summary:

The overall goal of this study was to quantify and characterize the transport of polycyclic aromatic hydrocarbons (PAHs) to Presque Isle Bay (PIB) and Lake Erie. A total of three sampling sites were set up to collect both air and precipitation samples from February 1, 2005 through January 19, 2006. One site was located in the City of Erie and the other two were sited in areas downwind and upwind of urban sources. In addition, dry deposition was quantified at the City of Erie site. This sampling scheme allowed for the comparison of ambient air concentrations between the sites and to characterize the transport of PAHs within the local area.

Major Findings:

A review and analysis of the monitoring data from the three sampling sites provided the following results:

1. The mean concentrations measured within the City of Erie for the majority of PAH species were higher than those measured at either the suburban or Presque Isle Bay sampling sites;
2. Phenanthrene was the predominant species accounting for approximately 40% of the Σ_{18} PAHs measured followed by fluoranthene, fluorene and pyrene, respectively;
3. Air concentrations at the Erie sampling site were comparable to those obtained from four other U.S. cities. For example, the geometric mean for phenanthrene at the City of Erie site was 11.0 ng/m³ (range: 0.97-59.8) compared to 70, 8.1 (0.92-25), 19 (5.4-97) and 26 (6.5-60) in the cities of Chicago, Los Angeles, Houston and Elizabeth, NJ, respectively. Strict comparisons between these studies are difficult due to differences in sampling and analytical procedures and other methodological differences.
4. The dry deposition velocities of PAHs estimated in this study were comparable to previous research studies in other locales. The mean annual loading of PAHs (evaluated in this study) to Presque Isle Bay was estimated at 52 kg/yr (range: 8 – 80 kg/year).
5. The results of the mass balance modelling were variable and highly dependent on which PAH species were included in the model as well as which source fingerprints were used. The results, therefore, should be interpreted with caution. The modelling results suggest that automobile and diesel exhaust, coke oven emissions, asphalt emissions and wood burning all contribute to the airborne PAH concentration. Due to the high variability, it is difficult to ascribe definitive percentages to each source contribution. To improve the modelling results, additional samples and other analytes, in addition to PAHs, should be incorporated into the model.

1 INTRODUCTION

1.1 Background:

Erie, the 4th largest city in Pennsylvania, is located in the state's northwestern corner along the shores of Lake Erie. The City has historically consisted of a heavy manufacturing base, combined with a mixture of commercial and residential areas. Presque Isle Bay (PIB), located adjacent to the City of Erie, is a harbor formed by a recurved sand spit named Presque Isle, which is now the location of a Pennsylvania State Park. The harbor is one of the oldest along the Great Lakes and measures approximately 4.5 miles long and a maximum of 1.5 miles wide.

Presque Isle Bay was designated as the 43rd Great Lakes Area of Concern (AOC) in 1991 due to two beneficial use impairments that included increased rates of fish tumors and other deformities and restrictions on dredging activities (PA DEP, 2002). Studies conducted by Battelle Ocean Sciences and Gannon University have found moderate to high levels of contaminants within the PIB sediments, with PAHs and trace metals being the predominant pollutants of concern (Battelle, 1997; Diz, 2002). Figure 1 shows the results of a 2000 study that examined the PAH concentrations within Presque Isle Bay sediments (Diz, 2002). A total of ten sampling sites were included in this study. Approximately 30 percent of the samples analyzed at 7 of the ten locations exceeded the probable effect concentration (PEC) of 22.8 mg/kg. Surface samples were more likely to exceed the PEC compared to samples from the bottom layer. This pattern is consistent with earlier studies (Battelle, 1997; PA DEP, 2002).

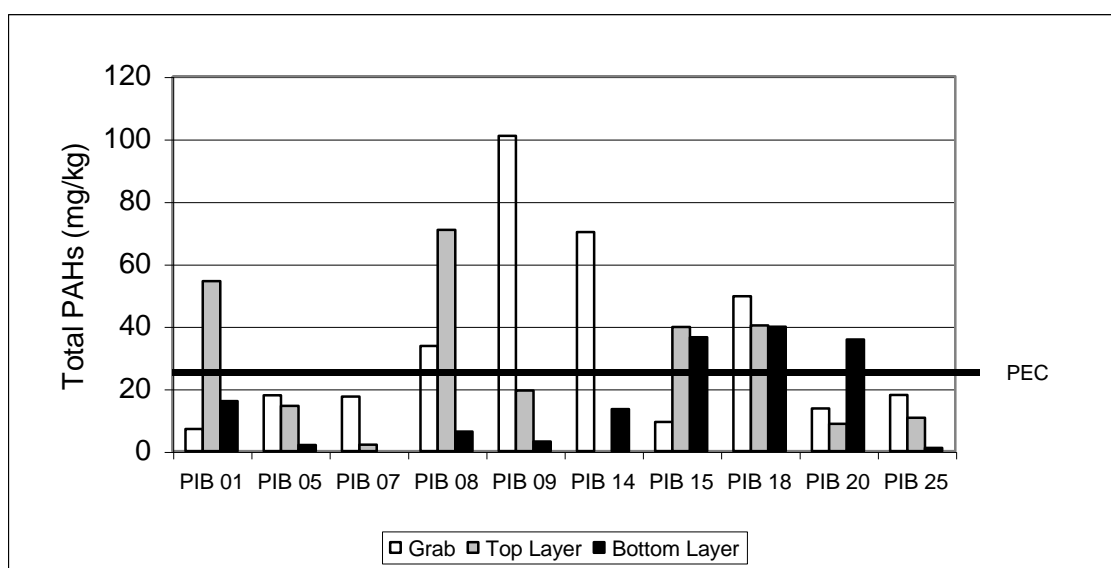


Figure 1: Distribution of PAHs in Presque Isle Bay sediments and comparison to the probable effect concentration (PEC) (Diz, 2002)

Due to continued improvements in the environmental health of the Bay over the past decade, the PA DEP has applied to the Environmental Protection Agency to change the status of PIB from an AOC in the “remediation stage” to one in the “recovery stage.” AOCs with the latter designation do not require further remediation efforts, but rather entail monitoring to ensure that conditions continue to improve (PA DEP, 2002). The air-monitoring project specified in this grant proposal will assist in this endeavor by providing data on the potential contribution of atmospheric deposition to the loading of PAHs to the Bay and greater Lake Erie waters. It also is not known whether sources may include local or distant sources. The aim of the present study, therefore, is to evaluate the potential contribution of atmospheric PAHs to the Presque Isle Bay watershed and, if found to be appreciable, to determine methods to reduce such loadings.

Air transport and deposition characteristics of PAHs are complex due to a number of factors that include: wind direction and speed, temperature, relative humidity, precipitation characteristics, particle size, and the particular phase of the pollutant. PAHs may exist in either the vapor or particulate phase. They can be deposited to land and water surfaces through both wet and dry deposition. They may specifically move from air to water, and vice versa, through air-water exchange (Delta Institute, 2000). In order to adequately assess all potential sources of PAHs, a total of three sampling sites were set up to evaluate both wet and dry PAH deposition, as well as gas exchange between air and water. One site was located within the City of Erie, and the two other sites were located in areas downwind and upwind of the Lake Erie watershed. This allowed for the comparison of PAH concentrations between the sites and the opportunity to characterize the transport of PAHs within the region.

In summary, PAHs were chosen for study based on the following rationale:

- PAHs as a class of chemicals are considered to be persistent bioaccumulative toxics (PBTs) and are listed as a contaminant of concern in numerous Great Lake programs and federal legislation;
- recent studies have found PAHs in moderate to high levels in Presque Isle Bay sediments (Battelle, 1997; Diz, 2002);
- PAHs in area waters have been implicated in causing adverse effects to wildlife (i.e., increased tumor incidence in brown bullheads);
- air monitoring for PAHs was not currently being performed within the Presque Isle Bay watershed;
- recent data from the Integrated Air Deposition Network suggest that benzo[a]pyrene loadings to the Great Lakes are not decreasing as with most other persistent bioaccumulative toxics (EPA, 2003);
- the air concentration of gaseous phase PAHs measured at sites in urban areas has been shown to be an order of magnitude higher than rural and over-lake monitoring sites, suggesting that local sources may be an important contributor (Delta Institute, 2000); and
- Gannon has the capabilities to analyze PAHs at the levels estimated to be found in air and precipitation samples.

1.2 Project Objectives

The primary objectives of this study were:

- to evaluate the concentration of airborne PAHs within the Erie area,
- to estimate the PAH fluxes to Presque Isle Bay by considering dry particle deposition and wet deposition via precipitation,
- to characterize the potential sources of PAHs within air and precipitation samples based on the relative proportions of various species,
- to estimate whether the potential sources of atmospheric PAHs are predominately from local or regional sources,
- to characterize the transport of PAHs within the local area by comparing data between sites upwind, downwind, and within the city of Erie, and
- to disseminate the data obtained from this study to appropriate agencies with the authority to influence the development of public policy.

2 METHODS

2.1 Sampling Sites

A total of three sampling sites were set up to collect both precipitation and air samples as shown in Figure 2. An analysis of wind direction data from three meteorological stations within the Erie area showed that winds are predominately out of the southwest, followed by the west and south, for the previous two years. Based on this information and the study objectives, one monitoring site was located within the City of Erie and the other sites were located in areas upwind (southwest) and downwind (northeast) of the City of Erie as noted in Table 1. This allowed for the comparison of PAH concentrations between the sites and the ability to characterize the transport of PAHs within the local area.



Figure 2: Project sampling sites: Site 1=City of Erie; Site 2 =Suburban (Harbor Creek); and Site 3 =Presque Isle Bay

One site was located on the roof of Gannon University library located within the City of Erie and approximately 1 kilometer (km) from Presque Isle Bay. This rooftop site provided a secure location with the electrical requirements necessary to operate the sampling equipment. Additional procedures were followed at this site in regard to separation distances of co-located monitors, inlet height and orientation, distance from walls, absence of furnace or incinerator flues, and other siting guidelines (EPA, 2000).

The two additional sites (Presque Isle and Harborcreek locations) were located as close to the lake as practical and, to the extent feasible, following the appropriate siting guidelines in regard to set-back requirements, inlet height and orientation, distance from interfering structures, etc. (Bigelow, 1984; EPA, 2000). Permissions and clearances to use the sites were obtained from the appropriate authorities. Site 2 was located within Harborcreek, Pennsylvania, an area approximately 11 kilometers east of the City of Erie site (site 1). The samplers were located within a vacant field away from trees and buildings. The samplers at the Presque Isle site (site 3) were co-located in an area on the east side of the peninsula (bay side) with other equipment operated by DEP and Pennsylvania State University.

An overview of the sampling methods and frequency is provided in Table 2 and is further detailed in section 2.2 of this report.

Table 1: Monitoring site description and measurements

	Description	Distance from Lake Erie	GPS Coordinates	Measurements
site 1	Rooftop of Gannon University library (3-story building located in the City of Erie)	1 km from Presque Isle Bay	N 42°07.676' W 080°05.294'	Air/particulate concentrations Wet deposition Dry deposition (indirect) Dry deposition (direct)
site 2	upwind of City of Erie within 1 km of lake (Harbor Creek, PA)	50 m	N 42°10.949' W 079°58.730'	Air/particulate concentrations Wet deposition
site 3	Co-located with other air sampling equipment on Presque Isle Bay peninsula	20 m	N 42°09.346' W 080°06.826'	Air/particulate concentrations Wet deposition

2.2 Sampling Procedures

Table 2 summarizes the sampling methods and data sources that were utilized in the study and their associated references. The sampling frequency and duration followed those indicated in the Integrated Air Deposition Network (IADN) or Lake Michigan Mass Balance study protocols.

Table 2: Summary of Sampling Methods, Frequency and References

Parameter	Sampling Method/Data Source	Method reference	Sampling frequency
Gas & particulate phase	HiVol sampler/PUF/GFF filters	EPA (1999)	24 hours/12 days
Wet Deposition	MIC Type B2 Precipitation Collector	Basu I and Lee AD. IADN version 1.2 (2003)	28 days
Dry Deposition	Deposition plate with stainless steel velcro	Holsen T & Paode, (1996) and Holsen T (2004)	Variable (24-36 hours)
Meteorological information	Erie County Airport FAA Meteorological Station		hourly average

2.2.1 Gas and Particulate Phase PAHs

Air samples were collected at each of the three monitoring sites using a Tisch high volume air sampler model TE-PNY1123 (Tisch Environmental, Cleves, OH). The sampling train included Whatman glass fiber filters to collect particulate-phase PAHs followed by two polyurethane foam (PUF) plugs to adsorb vapor-

phase PAHs. The samplers were calibrated to run at a flow rate of between 0.5 and 0.8 m³/min.

The sampling cycle consisted of one 24-hour sampling period every 12-day period. Sampling for gaseous phase and particulate PAHs began on February 1, 2005 and continued until January 17, 2006. A listing of the sampling dates is provided in Table A-1 of the appendix.

Several breakthrough studies were initially conducted in order to ensure that significant loss of small molecular weight PAHs was not occurring. Breakthrough was assessed by placing a known amount of deuterated PAH species on the first PUF plug and running the sampler for a 24-hour sampling period. The amount of the species on the first and second PUF plug were evaluated to ensure that breakthrough did not occur (defined as >10% of the amount on the first PUF).

Appropriate standard operating procedures were followed in order to ensure the integrity of the data (Basu and Lee, 2003). This included: weekly equipment inspections and cleanings, proper installation of sampling media, appropriate handling of samples, and inclusion of field and travel blanks. The volumetric flow rate of the sampler was checked once per month against a standard critical orifice calibrator. A water manometer calibrated to a primary standard was used to check flow rates before and after each sampling run. All inspection, calibration, and sampling data were logged into the appropriate field logs, laboratory logs, and chain of custody documents.

2.2.2 Wet Deposition

Wet deposition of PAHs were determined by collecting precipitation samples using a MIC Type B-2 precipitation collector (Meteorological Instruments Company, Canada). The collector has a shuttling roof and that opens only during precipitation events when detected by a conductivity sensor. The main components of the collector included a stainless steel funnel connected to a tube packed with approximately 15 grams of XAD-2 (styrene-divinylbenzene) resin (Supelco Supelpak-2 20-60 mesh) and a collection carboy. During colder weather, the interior of the collector was maintained at 15°C by a space heater in order to melt precipitation and prevent the XAD-2 resin from freezing. In warmer weather a detachable fan operated to prevent overheating of the unit.

Precipitation samples were collected simultaneously at each of the three monitoring sites using the MIC collectors. Samples were collected for a minimum of 1 year providing 6 sampling points per monitoring site. Total precipitation amounts were determined through the operation of a Belfort rain gauge.

Appropriate standard operating procedures were followed in order to ensure the integrity of the samples (Basu and Lee, 2003). This included: weekly equipment inspections and calibrations (rain sensor, heater, and fan), appropriate handling

of samples, proper installation of sampling media, and inclusion of field and travel blanks.

2.2.3 Dry Deposition (Direct)

A dry deposition sampler was constructed to collect particulate matter at site 1 (City of Erie site). The sampler was operated during dry weather (non-precipitation events). The sampler consisted of dry deposition plates with strips of Hi-Garde® brand stainless steel Velcro mounted to a wind vane which directed the plates into the wind (Holsen, 2004). The wind vane used was based on the design of the Eagle II described by Holsen and Paode (Holsen, 1996). The wind vane was made of steel pipe and EMT conduit and had the following dimensions: 159.4cm tall, the horizontal bar at the top that held the plates was 157.5cm long, and the tail made of a sheet of aluminum extended 34.3 cm from the axis and was 61cm x 61cm, angled so that the front of the sheet measured 10.2cm.

The deposition plates were constructed to include a sharp leading edge, less than 10 degrees, in order for laminar airflow over the plates. The plates were made from a sheet of 0.65cm thick PVC with dimensions of 7.6cm x 21.5cm. The plates were based upon design parameters outlined by Paode and Holsen (Holsen, 1996). The Velcro was cut into strips 2.54 cm x 7.6 cm and placed in a muffle furnace at 400°C for five hours to remove any residual organics.

Appropriate standard operating procedures were followed in order to ensure the integrity of the data. This included: weekly equipment inspections and calibrations, appropriate handling of samples, proper installation of sampling media, and inclusion of field and travel blanks. All inspection, calibration and sampling data were logged into the appropriate field logs, laboratory logs, and chain of custody documents.

2.2.4 Meteorological Data

Meteorological data (temperature and atmospheric pressure) used for calibrating the sampling equipment and determining final sample volumes were obtained from the National Weather Service meteorological station located at the Erie County Airport. These data were directly downloaded from the Pennsylvania State Climatologists website at <http://climate.met.psu.edu>. The values obtained were hourly averages and for each sampling period a minimum of 24 data points were obtained. A mean was calculated to provide an average temperature and pressure for each sampling period.

2.3 Laboratory Analysis and Quality Assurance

The "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Method TO-13A" 2nd edition was followed for the extraction, clean-up, and the concentration of PAHs from the samples (EPA, 1999). The samples were analyzed for 19 PAHs using a Hewlett Packard model 5890 series II gas chromatograph (GC) and a Hewlett Packard model 5972 mass selective detector

(MS). A fused silica DB-5MS column, 30m length, 0.25mm diameter, was used. The mass selective detector was run in selected ion monitoring (SIM) mode. The 19 target PAH species, their formulae and molecular weights are listed in Table 3. The analytical results for naphthalene were excluded due to quality control issues. The main concerns included blanks that contained naphthalene at levels exceeding the QA/QC guidelines and problems with the daily calibration related to this compound. Additionally, the relatively high vapor pressure of this compound makes naphthalene recovery difficult due to high evaporative losses.

All associated quality control and calibration procedures followed in this project are outlined in Table 4.

Table 3: Formulae and Molecular Weights of Target PAH Species

Compound	Formula	Molecular weight
naphthalene	C ₁₀ H ₈	128.2
acenaphthalene	C ₁₂ H ₈	152.2
acenaphthene	C ₁₂ H ₁₀	154.2
fluorene	C ₁₃ H ₁₀	166.2
anthracene	C ₁₄ H ₁₀	178.2
phenanthrene	C ₁₄ H ₁₀	178.2
fluoranthene	C ₁₆ H ₁₀	202.3
pyrene	C ₁₆ H ₁₀	202.3
benz[a]anthracene	C ₁₈ H ₁₂	228.3
chrysene	C ₁₈ H ₁₂	228.3
benzo[b]fluoroanthene	C ₂₀ H ₁₂	252.3
benzo[k]fluoroanthene	C ₂₀ H ₁₂	252.3
perylene	C ₂₀ H ₁₂	252.3
benzo[a]pyrene	C ₂₀ H ₁₂	252.3
benzo[e]pyrene	C ₂₀ H ₁₂	252.3
benzo[g,h,i]perylene	C ₂₂ H ₁₂	276.3
indeno[1,2,3-cd]pyrene	C ₂₂ H ₁₂	276.3
dibenz[a,h]anthracene	C ₂₂ H ₁₄	278.4
coronene	C ₂₄ H ₁₂	300.4

Table 4: Measurement Quality Objectives for the Laboratory Procedures

Parameter	Frequency	Acceptance Criteria
Reporting Units	All data	ng/m ³ .
Lower detection limit	Every time	To be determined
GC/MS calibration	Initially and after maintenance	To be determined
GC/MS continuing calibration	Every analytical day (12 hours)	Mid-range standard, +/- 30% of initial
GC/MS tuning	At the start of project and each day	Autotune with PFTBA
Field surrogates	All filters & PUFs	60-120% recovery
Lab surrogates	All filters & PUFs	1 µg of two deuterated PAHs, 60-120% recovery
Internal standards	All extracts	0.5 µg of five deuterated PAHs
Lab method blank	Every sample batch	-50% to +100% area response and ± 20 seconds retention time for internal stds; PAHs below MDL
Lab control spike	Every 20 samples	-50% to +100% area response and ± 20 seconds retention time for internal stds; 60-120% recovery of PAHs
Lab control spike duplicate	Every 20 samples	<30%
Field blank	Every 20 samples	-50% to +100% area response and ± 20 seconds retention time for internal stds; PAHs below MDL

A more detailed description of the quality assurance/quality control procedures are outlined in the QAPP for this study. For the purposes of this report, values are reported according to the Method Detection Limit (MDL). The MDL, as defined by EPA, is the value of the minimum concentration that is statistically different from zero. This is determined by making repeated measurements of 7 or more replicates of the target analyte (at a concentration just above the assumed MDL) measured against the instrument or reagent blank. The MDL is then defined as 3 times the standard deviation of the replicate data (represented by the 99% confidence level).

2.4 Source apportionment

The chemical mass balance (CMB) model was developed by EPA to assist in the source apportionment of various chemical species. The inputs required for the model include air monitoring data and source emission profiles. The model assumes that the profile of chemical species measured at the receptor site is a linear combination of the concentration of the species emitted from independent sources. Several assumptions are necessary in order to solve the model: (1) the composition of source emissions is consistent across the sampling period; (2) the chemical species do not react with each other; (3) all significant sources have been identified and have been characterized; (4)

the composition of different sources are linearly independent; and (5) measurement uncertainties are random, uncorrelated and normally distributed (EPA, 2004).

For this analysis version 8.2 of the CMB model was utilized (EPA, 2004). The data included in the model consisted of the air monitoring data as previously described. PAH species that had more than 10% of the sampling data as missing were not included in the model. These species included naphthalene, coronene, phenanthrene and indeno [1,2,3 cd] pyrene. Additional species were excluded due to a lack of specific emissions information. After excluding these species, missing values were replaced by a value that was $\frac{1}{2}$ the MDL for that particular species. The ambient monitoring data was initially run without any type of transformations to account for PAH degradation. For the purposes of this study it was assumed that sources were close to the receptor and therefore photodegradation would be minimal. This assumption is likely to be less valid for samples from the rural site (site 2). Since the number of ambient samples was low (N=75 for all sites combined), the model was run with data from all three sites.

PAH profiles (fingerprints) were collected for a variety of sources and included coke oven emissions, wood burning, gasoline vehicles, diesel vehicles, jet exhaust and asphalt roofing manufacturing. These sources were chosen based on potential local sources within the Erie area. The emission source data were collected from a variety of sources published in the literature as indicated in Table 5. The emissions data were transformed from units of mass or mass per unit volume to fraction of total by each PAH species as indicated in the CMB manual. The model was run using the elimination function which removes negative source contributions from the calculation one at a time (EPA, 2004).

Table 5: Fitting species and emission sources included in CMB model iterations

	1	2	3	4	5	6	7	8	9	10
SPECIES INCLUDED										
AcNE			X	X	X	X	X	X	X	X
ACNY			X	X	X	X	X	X	X	X
FL	X	X	X	X	X	X	X	X	X	X
BghiP	X	X	X	X	X	X	X	X	X	X
DBahAN			X	X	X	X	X	X	X	X
PE			X	X	X	X	X	X	X	X
AN			X	X	X	X	X	X	X	X
FLA			X	X	X	X	X	X	X	X
CY	X	X	X	X	X	X	X	X	X	X
PYR	X	X								
BaA	X	X								
BeP			X	X	X	X	X	X	X	X
BaP	X	X	X	X	X	X	X	X	X	X
BbFLA			X	X	X	X	X	X	X	X
SOURCES										
Auto exhaust 1C (Golumb, 2001)	X	X								
Diesel exhaust 1 (Golumb, 2001)	X	X								
Jet Exhaust (Golumb, 2001)	X	X								
Wood burning 1 (Golumb, 2001)	X									
No. 2 distillate fuel (Rogge, 1997a)			X	X		X	X	X		

Wood burning 2 (Rogge, 1998)						X			X	X
Wood burning 3 (Schauer, 2001)							X			
Wood burning 4 (Khalili, 1994)								X		
Wood burning mean (2,3 & 4)			X	X	X					
Diesel exhaust 2 (Rogge, 1993)						X				
Diesel exhaust 3 (Schauer, 1999)							X		X	
Diesel exhaust 4 (Khalili, 1995)								X		
Diesel exhaust 5 (Miguel, 1998)										X
Diesel exhaust mean (2-5)			X	X	X					
Auto exhaust 2C (Rogge, 1993)						X				
Auto exhaust 3C (Khalili, 1995)							X			
Auto exhaust 4C (Miguel, 1998)								X	X	X
Auto exhaust mean (2C-4C)			X	X	X					
Auto exhaust - NC (Rogge, 1993)				X		X		X		
Asphalt roofing tar (Rogge, 1997b)				X			X	X	X	
Asphalt Roofing Man (ARMA, 1998)			X			X				X
Coke oven (Khalili, 1995)			X	X		X	X	X	X	

3 RESULTS

3.1 Weather data

Figure 3 contains a wind rose summarizing the wind speed and direction during the sampling periods (24 hour period every 12 days). The predominant wind direction during the sampling period was south, southwest and west as indicated in the Table 6 and Figure 3. For a majority (69%) of the sampling period, the wind speed was 11 knots (approximately 9.6 miles per hour) or below. The wind was calm approximately 9 percent of time during the sampling period. A complete summary of the frequency distribution of wind direction data per sampling period is contained in Table A-1 of the appendix.

Table 6: Frequency distribution of wind speed and direction

Direction	Wind speed classes (knots)						ALL
	1 - 4	4 - 7	7 - 11	11 -17	17 - 21	> 21	
N	1.1	2.5	3.7	0.3	0	0	7.6
NE	0.7	1.1	5.1	2.8	0	0	9.7
E	0.8	1.3	1.8	0	0	0	3.9
SE	0.7	1.0	2.5	1.1	0	0	5.3
S	8.0	5.2	9.4	3.9	2.4	0.4	29.3
SW	1.1	2.0	4.4	0.7	0.1	0.3	8.6
W	0.3	1.7	7.7	4.9	1.4	0.3	16.3
NW	0.1	2.0	4.8	3.0	0.3	0.0	10.1
Sub-totals	12.9	16.7	39.4	16.7	4.2	1.0	89.5
Calms							9.0

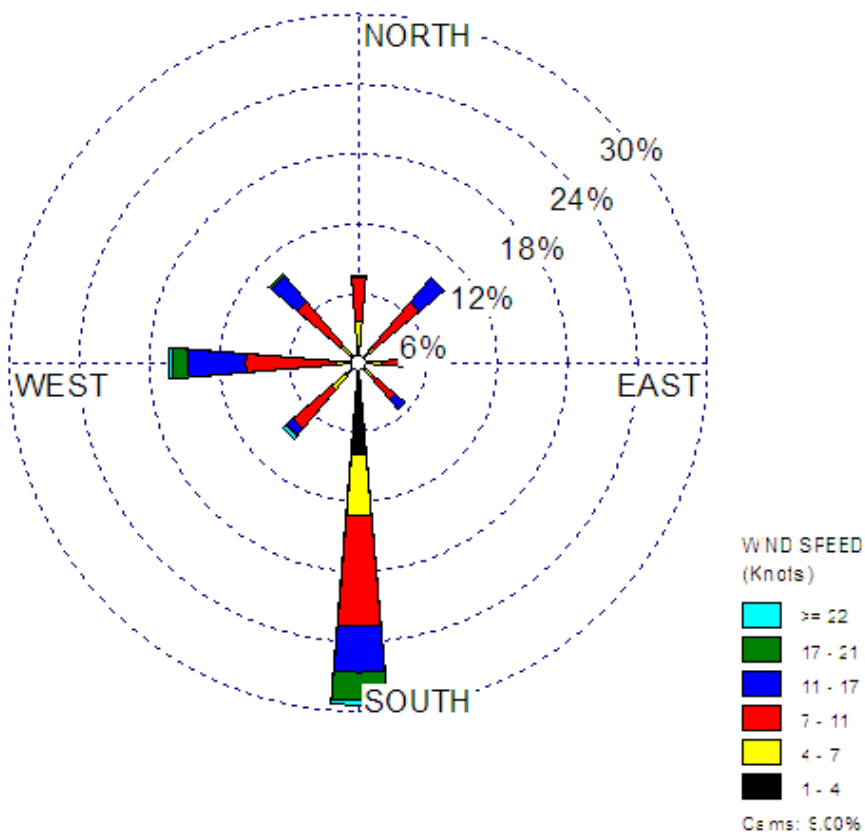


Figure 3: Wind Rose for Erie, PA during sampling period (February 1, 2005 – January 17, 2006). Erie Municipal Airport (FAA data)

3.2 Gaseous phase and particulate data

3.2.1 Comparison of sampling sites

Figure 4 compares the geometric mean concentrations of four representative PAH species (fluorene, phenanthrene, fluoranthene and pyrene) and total PAHs across the three sampling sites. Air concentrations at the City of Erie site were consistently higher for the 4 representative PAHs compared to both the suburban and Presque Isle Bay sites (Kruskal Wallace test, $X=12.16-22.65$ (range), $p \leq 0.05$). This trend was consistent across all of the 18 PAHs measured. The average measured Σ_{18} PAHs was approximately 3-fold greater at the City site compared to the other sampling locations. Additional comparisons of specific PAHs are included in Figure A-2 and Figure A-3 of the appendix.

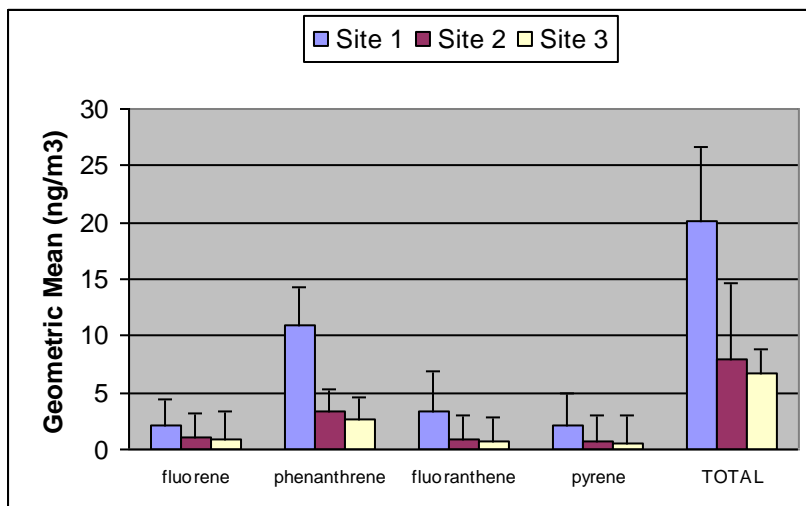


Figure 4: Comparison of the geometric means of gas/particulate concentrations among 4 representative PAHs and Σ_{18} PAHs among the three sampling sites (Site 1 = City of Erie; site 2 = suburban site and site 3 = Presque Isle site).

3.2.2 Frequency distribution of PAH species

Figure 5 shows the percentage of each individual PAHs compared to Σ_{18} PAHs for the city and suburban site. Phenanthrene was the predominant species accounting for approximately 40% of the Σ_{18} PAHs at both sites. The other predominant species included fluoranthene, fluorene and pyrene. The proportion of fluoranthene was higher (20 vs. 12%) at the City site compared to the suburban site while fluorene was lower (7.5% vs. 12 %).

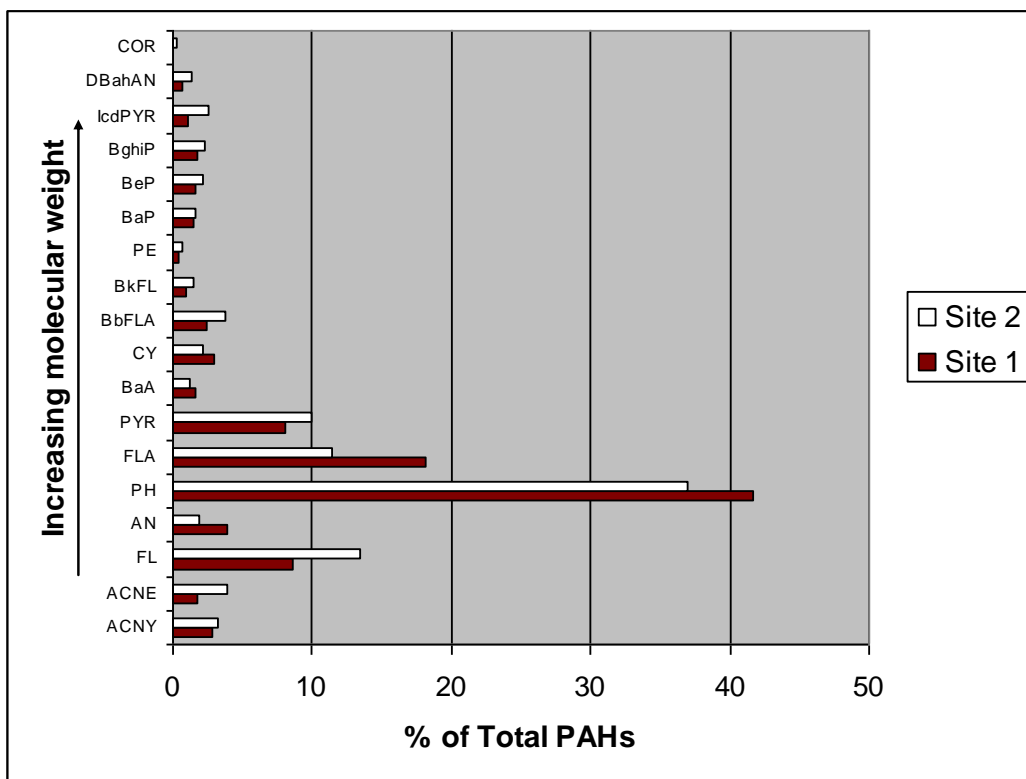


Figure 5: Comparison of PAH profiles (% of Σ_{18} PAHs) between the urban and suburban sampling sites. Data represent combined gaseous and particulate species.

3.2.3 Analysis of sampling data by season

Figure 6 shows a comparison of the total PAHs by season. The mean of total PAHs was highest in the spring for all sites followed by those in the winter. This trend was also seen in the comparisons of individual PAH species (refer to Figure A-4 of the appendix). The number of samples per site by season varied between 5 and 8.

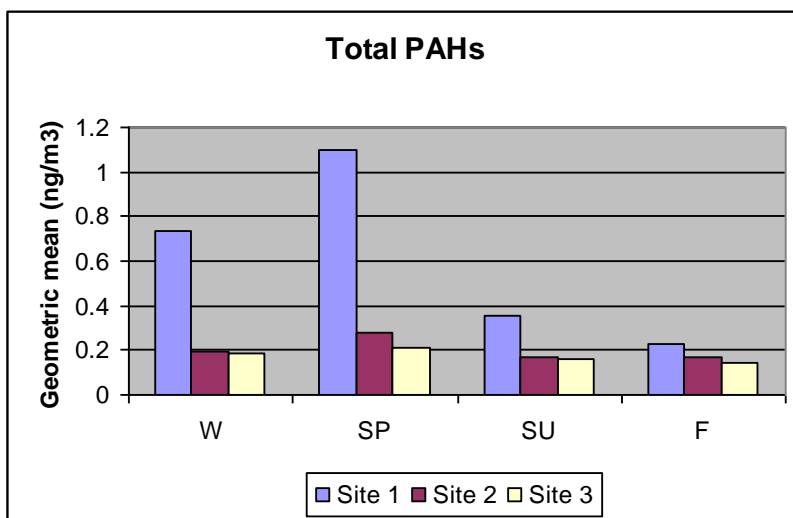


Figure 6: Comparison of the geometric means of total PAHs by season (W = winter, SP = spring, SU = summer and F = fall)

3.2.4 Comparison of sampling data to other US Cities

Table 7 shows the geometric mean of combined airborne gas/particulate PAH concentrations measured within Erie and four other US cities. Currently, there are no air concentration standards or guidelines with which to compare the various PAH species. The only alternative, therefore, is to compare data from this study with that gathered from similar urban locations within the United States. The geometric mean concentrations of the three PAH species were comparable to those of prior studies conducted within the cities of Chicago, Los Angeles, Houston and Elizabeth, New Jersey (Cotham, 1999; Naumova et al., 2002). It is, however, difficult to make strict comparisons due to differences in sampling and analytical methods, number and types of local industrial facilities and population sizes. Total PAH concentration cannot be compared between cities since there were considerable differences between the number and mixture of PAH species measured within each study.

Table 7: Comparison of the geometric means (range) of three representative PAHs measured at the City of Erie site with that from 4 U.S. cities.

	Erie, PA	Chicago, IL (Cotham,1999) ¹	Los Angeles (Naumova,2002)	Houston TX (Naumova, 2002)	Elizabeth, NJ (Naumova, 2002)
	(ng/m. ³)	(ng/m. ³)	(ng/m. ³)	(ng/m. ³)	(ng/m. ³)
phenanthrene	11.0 (0.97-59.8)	70	8.1 (0.92-25)	19 (5.4-97)	26 (6.5-60)
pyrene	2.20 (0.24-12.2)	16	1.6 (0.12-5.9)	2.3 (0.87-15)	3.6 (0.85-10)
benzo[a]pyrene	0.30 (0.06-4.07)	2.9	0.07 (0.0008-1.0)	0.03 (0.0021-0.22)	0.14 (0.045-0.53)
Population (×10 ⁶) (US Census, 2000)	0.1	2.9	3.7	2.0	0.12

¹ no range provided

3.2.5 Comparison of measured air concentration by wind direction

Sampling periods were designated as north or south depending on the prevailing wind direction during the 24-hour period. Figure 7 compares the geometric means for 4 PAH species and total PAHs when the wind was predominantly from the south verses from the north. There appears to be a slight trend in higher PAH concentrations when the predominant wind direction was from the south.

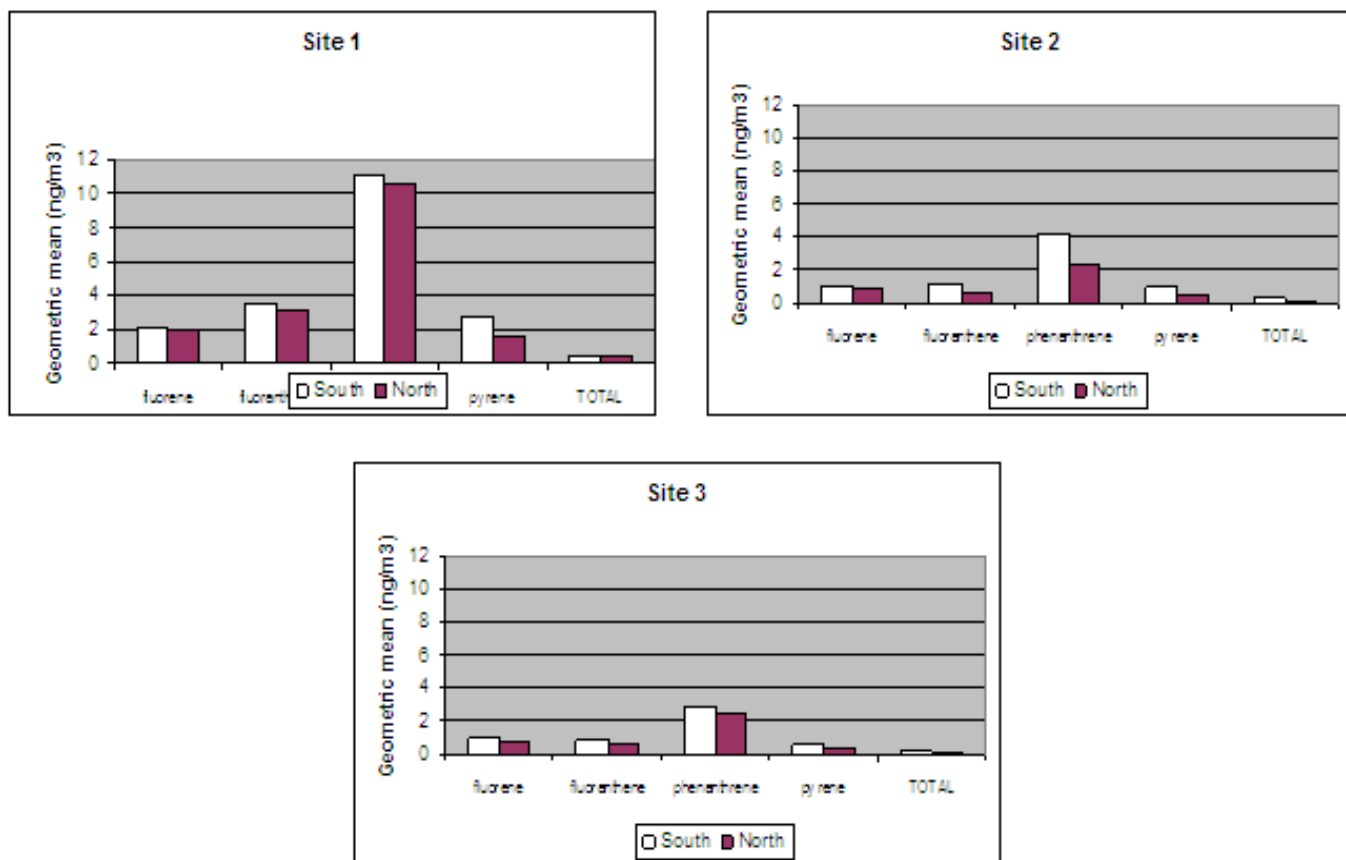


Figure 7: Comparison of target species by predominant wind direction designation

3.2.6 Comparison of sampling results to previous EPA modeled estimates

The EPA has estimated the 1996 ambient concentrations of various air pollutants for each county of the United States (EPA, 2002). These estimates are based on 1996 emissions data for various sources. The Assessment System for Population Exposure Nationwide (ASPEN) model simulates the impacts of atmospheric processes (winds, temperature, atmospheric stability, etc.) on pollutants after they are emitted. The output of this air dispersion model is an estimate of the annual average ambient concentration of each air toxic pollutant at the centroid of each U.S. census tract. For Erie county, the estimated ambient concentration for 16-total PAHs was 29.1 ng/m³ (refer to Figure 8). This compared to a value of 41.5 for the same PAHs measured within the City of Erie between 2004 and 2005. There was a slight difference between the 16 PAHs modeled by EPA and the 16 PAHs monitored in this study. In the EPA modeling benzo[e]pyrene was replaced by benzo[fluoranthene]. The modeled concentration for total 7-PAHs (benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene) was 2.3 ng/m³ for Erie county. This compares to values of 4.5 ng/m³, 1.5 ng/m³ and 1.3 ng/m³ measured within the city of Erie and two sites outside of the city.

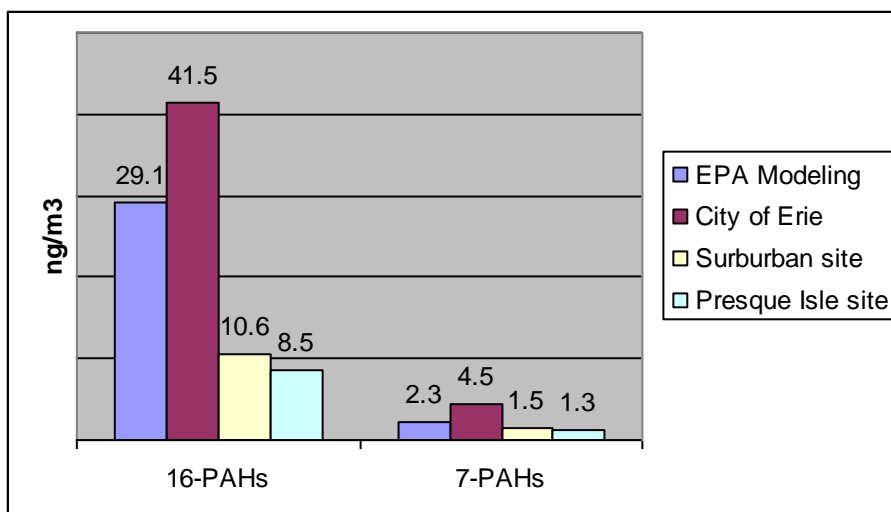


Figure 8: Comparison of modeled and measured airborne PAH concentrations within Erie County

3.3 Wet Deposition Data

There were no reportable results from the precipitation data as the measure quality objectives outlined in Table 4 were not met. There were numerous difficulties at the beginning of the study in terms of getting the appropriate flow rates. For those samples in which appropriate flow rates were obtained the concentration of PAHs was minimal with almost all levels below the MDL. It is unclear why the PAH concentrations were so low. It is suggested that either the PAHs were somehow degraded in the process of sampling, holding or analytical procedures. An alternative explanation is that for some reason, the PAHs were not desorbed properly from the resin. There were little to no PAHs found in the eluent after the resin column suggesting that the PAHs were adsorbing to the XAD resin. Based on precipitation data from other studies, it is highly unlikely that the PAH concentrations within the precipitation samples were all below the method detection limits. For example, Golumb, et al, found the mean sum of 16 PAH species within precipitation samples from the Boston area to be 720 ng/m²·cm of precipitation (Golumb, 2001).

3.4 Risk Assessment Summary

3.4.1 The Toxic Equivalency Quantity (TEQ) Analysis

PAHs occur in mixtures, the composition of which are complex and vary with the generating process. Chemicals that exert their toxicity by the same mechanism of action can have their toxicity expressed in terms of one member of that group, which is usually the most toxic species (EPA, 1993). This approach is called the Toxicity Equivalency Quantity (TEQ) Method. Conventionally, the most toxic member is assigned a relative score (normally 1) and the toxicity of the other members of the group are designated as a proportion of that value (for example 0.1 or 10%). These values are termed toxic equivalency factors (TEFs) and are

consensus-derived values obtained from multiple biological and toxicological endpoints. The toxicity of a mixture of chemicals can then be calculated by summing the concentration of each constituent multiplied by its TEF as indicated in the following formula:

$$\text{TEQ} = \Sigma\{(\text{Conc}[\text{Compound}_{1,}] \times \text{TEF}_{1,}) + \dots (\text{Conc}[\text{Compound}_{n,}] \times \text{TEF}_{n,})\}$$

where compound 1 = a particular PAH species and $\text{TEF}_{1,}$ represents its corresponding TEF (DOE, 2007).

The TEFs used within this study were gleaned from a number of different sources since EPA has designated values for only six PAH species. A summary of the TEFs by source is included in Table 8. The TEFs designated by EPA were included in the analysis when available. For those PAH species for which EPA did not designate a TEF, the factors determined by Nisbet and LaGoy were used. Three compounds (coronene, benzo[e]pyrene and perylene) did not have TEFs and, therefore, were not included in the TEQ calculation.

Table 8: Summary of TEF values from various sources and those used in the present study

Species	EPA, 1993	Thorslund, 1991	Chu and Chen, 1984	Nisbit and LaGoy, 1991	TEFs used in present study
Acenaphthylene	nd	nd	nd	0.001	0.001
Acenaphthene	nd	nd	nd	0.001	0.001
Fluorene	nd	nd	nd	0.001	0.001
Anthracene	nd	0.32	nd	0.001	0.001
Phenanthrene	nd	nd	nd	0.001	0.001
Fluoranthene	nd	nd	nd	0.001	0.001
Pyrene	nd	nd	nd	0.001	0.001
Benz[a]anthracene	0.1	0.145	0.013	0.1	0.1
Chrysene	0.001	0.0044	0.001	0.01	0.001
Benzo[b]fluoroanthene	0.1	0.14	0.08	0.1	0.1
Benzo[k]fluoroanthene	0.01	0.066	0.004	0.1	0.01
Perylene	nd	nd	nd	nd	Not included
Benzo[a]pyrene	1	1	1	1	1
Benzo[e]pyrene	nd	nd	nd	nd	Not included
Benzo[g,h,i]perylene	nd	0.022	nd	0.01	0.01
Indeno[1,2,3-cd]pyrene	0.1	0.232	0.017	0.1	0.1
Dibenz[a,h]anthracene	1	1.1	0.69	1	1
Coronene	nd	nd	nd	nd	Not included

3.4.2 TEQ Calculation and Risk Assessment

The final value of the TEQ was then compared to the inhalation unit risk as defined within the Risk Assessment and Information System database (RAIS, 2007). The provisional unit risk for benzo[a]pyrene is $0.88 \text{ (mg/m}^3\text{)}^{-1}$. The interpretation of this unit risk would be as follows: if the unit risk = 0.88 per mg/m^3 , we would expect 88 excess cancer cases (upper bound estimate) to develop per 100 people if exposed daily for a lifetime to 1 mg of the chemical in 1 m^3 of air. This value represents a provisional inhalation toxicity value developed by the National Center for Environmental Assessment (EPA, 1995).

The final TEQs calculated for each of the three sites are included in Table 9 below. The values were calculated using the 95% upper confidence level (UCL) of the mean for the lognormal distribution for each compound per site utilizing the Lands method (EPA, 1992). A copy of the specific UCL values and TEFs are included in Tables A-3 – A-5 of the Appendix.

Table 9: Summary of TEQs by site

Site	TEQ (95% UCL of the mean) (ng/m^3)
Site 1: City	1.76
Site 2: Suburban	0.72
Site 3: Presque Isle	0.69

Figure 9 summarizes the proportion that each PAH species contributed to the overall TEQ calculation for the City of Erie site. Benzo[a]pyrene (BaP) and Dibenzo[ah]anthracene (DBahAN) contributed the highest proportions (48.1% and 21.7%, respectively) to the TEQ calculation. This trend was similar for the suburban and Presque Isle sampling sites where BaP had the highest contribution followed by DBahAN (Table A-4 and A-5 of Appendix).

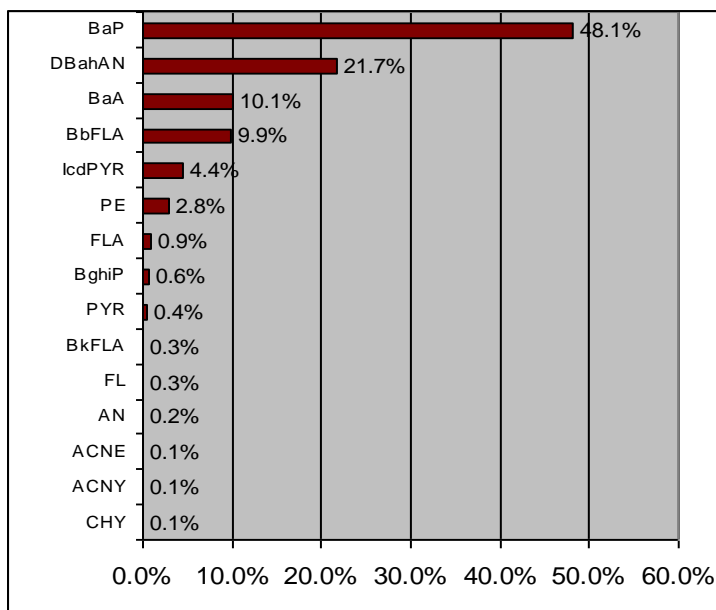


Figure 9: Proportion of contribution to the overall TEQ calculation by PAH species for City of Erie site (site 1)

3.4.3 Risk Characterization

A worst case intake for inhalation exposure was determined using the TEQ value calculated from data gathered at the City of Erie sampling site. The intake calculation for inhalation exposure was calculated for an average adult and child (ages 0-6 years). The assumption was made that the person lived and worked/resided in the City and therefore would be exposed to the same level across each day over a lifetime. The formula for the intake calculation used in the analysis was:

$$LADI_{(mg/kg-dy)} = \frac{CA \times IR \times EF \times ED}{BW \times AT}$$

The assumptions used for adults and children in order to calculate a lifetime average daily intake (LADI) are included in Table 10. Using the TEQ calculated for the City of Erie site the following intake values were determined for children and adults respectively as 5×10^{-7} to 1×10^{-7} mg/kg-day.

Table 10: Intake calculation and associated assumptions for inhalation exposure to PAHs

Parameter	Adult	Child
CA=air concentration (mg/m ³)	1.76×10^{-6}	1.76×10^{-6}
IR= Inhalation rate (m ³ /day)	20	11.66
EF=exposure frequency (days/year)	350	350
ED=exposure duration (years)	70	6
BW=body weight (kg)	70	15
Lifetime average daily Intake (mg/kg-day)	4.82×10^{-7}	1.12×10^{-7}

The inhalation slope factor for benzo[a]pyrene is $3.08 \text{ (mg/kg-day)}^{-1}$. (DOE, 2007). The excess cancer risk (point estimate) due to exposure to a specific compound is the product of the intake (lifetime average daily intake) and the cancer slope factor. Therefore, the excess cancer risk from inhalation exposure is 1.5×10^{-6} and 3.5×10^{-7} , respectively for adults and children. This is interpreted that approximately 2 excess cancers out of a population of 1 million would be expected in an adult population. Approximately four excess cancers would be expected out of a population of 10 million children due to PAH exposures via inhalation. It should be noted that these calculations include values that represents the worst case scenario and may not be representative of the general population of the City of Erie. It assumes that an individual would be exposed to the same airborne concentration of PAHS measured in this study across their entire lifetime. EPA generally considers risk estimates to be within the acceptable limits given the conservative nature of the risk estimates. It should be noted, however, that the risk estimate approach used only accounts for PAH exposures through inhalation and does not account for PAH exposures through food or drinking contaminated water.

3.4.4 Comparison to the risk-based concentration (RBC) for ambient air

The EPA has established a number of RBCs for contaminants in different media. The RBCs are generally calculated to correspond to a chemical that a person could be exposed to that would not result in a risk of cancer or other adverse health effects above a specified level of concern (generally 1 in 1 million). These values are calculated to represent assumptions covering the entire age range (both children and adults). The RBC for benzo[a]pyrene in ambient air is $6 \times 10^{-4} \mu\text{g/m}^3$. (EPA, 2007). The TEQ calculated for the City of Erie site ($1.76 \times 10^{-3} \mu\text{g/m}^3$) was above the RBC while the values for both the suburban and Presque Isle site (6.9×10^{-4} and 7.2×10^{-4}) were slightly above this value.

3.5 Dry Deposition Data

3.5.1 Particulate Fluxes

The PAHs with the highest fluxes were phenanthrene, fluoranthene, and pyrene. The other PAHs collected with the dry deposition plates were benzo[b]fluoranthene, naphthalene, benzo[e]pyrene, and chrysene. The concentrations that were below the lower calibration range ($0.1 \text{ ng}/\mu\text{L}$) but higher than the instrument detection limit were given a value of half the lower calibration range. The concentrations that were below the detection limit of the instrument were given a value of zero. The additional PAHs analyzed in this study were all below the detection limit. The sampling period varied across each of the six samples as shown in Table 11.

Table 11: Sampling time and number of days exposed

Sample No.	Sampling time (hrs)	Number of days
1	24	2
2	36	3
3	36	4
4	36	4
5	36	4
6	36	5

Table 12 lists the PAHs collected with the dry deposition plates and the descriptive statistics for each PAH found. The range of particulate Σ_{19} -PAHs fluxes measured with the dry deposition plates was 1.4-14.9 $\mu\text{g}/\text{m}^2 \cdot \text{d}$, with an average of $9.4 \pm 4.8 \mu\text{g}/\text{m}^2 \cdot \text{d}$.

Table 12: Dry Deposition Flux Data ($\mu\text{g}/\text{m}^2 \cdot \text{d}$)

Compound	Mean	S.D.	Median	Range	n
fluoranthene	2.5	1.25	2.74	3.64	6
phenanthrene	1.9	1.17	2.08	3.48	6
pyrene	2.0	1.87	1.91	5.42	6
benzo [b] fluoranthene	0.64	0.7	0.6	1.34	6
benzo [e] pyrene	0.47	0.36	0.7	0.7	6
chrysene	0.55	0.65	0.35	1.45	6
naphthalene	1.33	0.85	1.54	2.37	6

The deposition values in this study are lower than the ranges of particulate fluxes found in other similar studies as summarized in Table 13: 82-155 $\mu\text{g}/\text{m}^2 \cdot \text{d}$ (Vardar, et al., 2002), 27-229 $\mu\text{g}/\text{m}^2 \cdot \text{d}$ (Odabasi, et al., 1999), and 3.4-140 $\mu\text{g}/\text{m}^2 \cdot \text{d}$ (Franz, et al., 1998). The Vardar et al. study was done during the winter months in Chicago which may have resulted in more deposition during this period due to the temperature (Vardar, et al., 2002). Vardar et al. sampled using the dry deposition plates for two days per sample, while Odabasi et al. exposed the dry deposition plates for six days per sample. Odabasi et al. sampled from June to October (in Chicago), which may explain the large range of values found, possibly due to temperature differences. The increased sampling time may have also allowed Odabasi et al. to effectively collect enough PAHs to better quantify the results. Franz et al. sampled from November 1993 to October 1995 (in Chicago) which may explain the large range of values found. The predominant PAHs found in the study done by Vardar et al. were phenanthrene, fluoranthene, and pyrene. This was also true of the results from the present study.

Table 13: Summary of Data from PAH Dry Deposition Studies

Reference	V_p (cm/s)	F_p ($\mu\text{g}/\text{m}^2 \text{ d}$)	C_p (ng/m^3)
Present study. ¹	1.54 \pm 1.23 (0.41-3.36)	9.4 \pm 4.8 (14-14.9)	56.1 \pm 99.9 (0.94-258.3)
Vardar et al. (2002). ²	4.5 \pm 3.1 (1.1-7.8)	120 \pm 28 (82-155)	30 \pm 16 (7-55)
Odabasi et al. (1999). ²	6.7 \pm 2.8 (4.3-9.8)	144 \pm 60 (27-229)	10-48
Franz et al. (1998). ²	0.4-3.7	3.4-140	n/a

¹ Dry deposition plates with Velcro[®] surface- identified by Holsen (2004) as a potentially feasible deposition surface.

² Dry deposition plates with a greased surface.

The dry deposition particulate flux found in this study using Velcro as a surrogate surface was less than that found in other studies using greased Mylar strips. The Velcro collection technique exhibited the same pattern as in other studies, indicating that Velcro was a successful surrogate collection surface.

3.5.2 Ambient Particle Phase Concentrations

The range of particle Σ_{19} PAHs concentrations measured with the high volume air sampler was 0.94-258.3 ng/m^3 , with an average of 56.1 \pm 99.9 ng/m^3 . Table 14 lists the PAHs collected using the high volume air sampler and the descriptive statistics for each PAH found. Acenaphthene was not found above the detection limit for all six samples. The two PAHs found with the highest average concentrations were fluoranthene and benzo[b]fluoranthene. Other PAHs found with higher average concentrations were phenanthrene, pyrene, benz[a]anthracene, chrysene, benzo[e]pyrene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene. The PAHs found with high concentrations were higher molecular weight compounds with three to six rings. Similar to the dry deposition fluxes measured, fluoranthene, phenanthrene, and pyrene were found in high concentrations with the high volume air sampler.

Table 14: Ambient Particulate Air Concentration Data (ng/m^3)

Compound	Mean	S.D.	Median	Range	n
naphthalene	0.34	0.32	0.37	0.69	6
acenaphthylene	0.02	0.04	n/a	0.11	6
fluorene	0.07	0.18	n/a	0.43	6
benzo[g,h,i]perylene	1.86	1.68	1.94	4.45	6
dibenz[a,h]anthracene	0.28	0.26	0.26	0.6	6
indeno[1,2,3-cd]pyrene	1.56	1.44	1.63	3.75	6
perylene	0.22	0.28	0.12	0.69	6
benzo[b]fluoranthene	3.31	3.79	2.69	10.35	6
coronene	0.73	0.6	0.92	1.38	6

anthracene	0.2	0.2	0.2	0.53	6
fluoranthene	3.8	3.73	3.53	10.3	6
phenanthrene	1.81	1.82	1.66	5.15	6
benz[a]anthracene	1.52	1.6	1.41	4.32	6
chrysene	2.46	2.42	2.21	6.61	6
pyrene	2.44	2.25	2.27	6.27	6
benzo[e]pyrene	1.61	1.44	1.61	3.93	6
benzo[a]pyrene	1.1	0.97	1.04	2.68	6
benzo[k]fluoranthene	0.96	0.96	0.91	2.65	6

The concentrations found in this study were similar to those found in other studies: 7-55 ng/m³. (Vardar, et al., 2002), and 10-48 ng/m³. (Odabasi, et al., 1999). This wide range of values found is most likely explained by temperature variations since the lowest concentration was found at an average temperature of 18.9°C, and the highest concentration was found at 2.3°C.

3.5.3 Dry Deposition Velocities

The overall dry deposition velocities of PAHs were calculated using the dry deposition fluxes and the ambient concentrations using the following formula: $V_p = F_p / C_p$. The range of dry deposition velocities Σ_{19} PAHs was 0.41 – 3.36 cm/s, with an average of 1.54 ± 1.23 cm/s. The individual dry deposition velocities of PAHs are listed in Table 15, along with their molecular weights and descriptive statistics. The table shows that as the molecular weight of the compounds increased the average dry deposition velocity decreases.

Table 15: Individual Dry Deposition Velocities of PAHs (cm/s)

Compound	M.W.	Mean	S.D.	Median	Range	n
naphthalene	128.2	2.68	0.7	2.35	1.28	3
phenanthrene	178.2	1.78	1.31	1.39	2.44	5
fluoranthene	202.3	1.54	1.27	0.97	3.04	6
pyrene	202.3	1.02	0.42	0.87	1.06	5
chrysene	228.3	0.53	0.23	0.54	0.45	3
benzo[e]pyrene	252.3	1.1	1.23	0.53	2.55	4
benzo[b]fluoranthene	252.3	0.5	0.14	0.44	0.26	3

This value is similar to those found in other studies, but is lower than most studies with similar methods: 1.1-7.8 cm/s (Vardar, et al., 2002), and 4.3-9.8 cm/s (Odabasi, et al., 1999). The results in this study are not directly comparable to the results from other studies because of the differences in experimental procedures and estimation techniques used. The difference in the dry deposition velocities may be due to the surface used to collect the PAHs. It was established in studies by Vardar et al. and Odabasi et al. that the grease used collected not only particulate phase PAHs but also collected gas phase PAHs. Most of the PAHs found in this study were higher molecular weight compounds with lower deposition velocities. The only low molecular weight PAH found in this study was naphthalene which had an average dry deposition velocity of 2.23 cm/s. It is possible that the Velcro used here did not collect the gas phase PAHs in as high

amounts as the greased surface used in other studies, therefore, decreasing the apparent overall flux and deposition velocity.

To better understand if there was a relationship between the molecular weight of the PAHs and their dry deposition velocities a linear regression was run. Figure A-5 in the appendix shows the linear regression with each point representing a PAH from the sample periods. The results of the regression show a moderate linear relationship between the molecular weight and the dry deposition velocity of the PAHs. The R^2 value was 0.42, and the p-value was 0.002 ($n=21$), meaning that the relationship is statistically significant. A linear regression was also run using the average dry deposition velocity of each PAH found, plotted against their molecular weight. The results were statistically significant with an R^2 value of 0.93, and a p-value of 0.002 ($n=6$). These results affirm that the dry deposition velocity of PAHs is dependant upon their molecular weight, and as their molecular weight increases their deposition velocity will decrease. Dry deposition velocity values used in the linear regressions do not include particulate flux or ambient concentrations that were found below the lower calibration range of the instrument.

3.5.4 Estimate of Dry Deposition Loading of PAHs to Presque Isle Bay

The dry deposition of a compound to a water surface can be estimated through the product of the flux of the compound (mass deposited per surface area per time) by the surface area of the surface. The formula is written as:

$$A \times F_p$$

Where: A = surface area of deposition surface (m^2)
 F_p = particulate flux (kg/m^2_yr)

The surface area of Presque Isle Bay is listed as 3718 acres (15,046,212 m^2) (DEP, 2002). The average particulate flux measured in this study was 9.4 (± 4.8) $\mu g/m^2_d$ as discussed above. The range for the particulate fluxes calculated in this study varied between 1.4–14.9 $\mu g/m^2_d$ across the six sampling periods. As a result, the most likely estimated value for PAH dry deposition to PIB is 52 kg/yr. The range of the estimated dry deposition to Presque Isle Bay is 8 – 80 kg/yr.

3.6 Sources of PAHs

3.6.1 Binary ratio method of determining PAH sources

The predominant PAH compounds found during the sampling period consisted of 3- and 4-ring structures including phenanthrene, fluorene, fluoranthene and pyrene. These compounds are indicative of motor vehicle emissions and incineration, among other sources. The binary ratio method is a crude method for estimating whether sources of PAH emissions are mobile or stationary. Stationary source combustion emissions utilizing coal, oil and wood tend to have low levels of coronene relative to benzo[a]pyrene. Mobile combustion sources from diesel and petroleum tend to have high levels of benzo[ghi]perylene and coronene relative to benzo[a]pyrene (Stenberg, 1979). Table 16 summarizes the air monitoring data

gathered in this study using the binary ratio method. The ratios of the mean concentration of these PAH species at each of the three sampling sites were indicative of those predominantly from mobile sources. The two rows at the top of the table show the decision criteria. The bottom three rows show the ratios calculated from the air monitoring data by study site.

Table 16: Decision criteria for binary ratios (Hooper, et al., 1993) and summary of ratios from each of the three sampling sites

Source type	B[a]P/Cor ratio	B[a]P/B[ghi]P
Mobile	0.4 – 1.0	0.2 – 0.6
Stationary	>1.7	>0.8
Site 1: City of Erie	0.85	0.46
Site 2: Suburban	0.81	0.43
Site 3: Presque Isle	0.80	0.50

3.6.2 CMB Modelling

The goal of the chemical mass balance modelling was to determine the main sources of PAHs contributing to atmospheric PAH concentrations in the Erie area. Section 2.4 summarizes the compounds used as fitting species and the emission sources included in the model. The initial data matrix consisted of either 6 PAH species (iterations 1 and 2) or 12 species (iterations 3 through 10) and 75 samples in units of ng/m³. Various iterations of the model were run which included the entire set of sampling data (N=75) and between 3 and 6 emission sources. Table 17 summarizes the iterations by included emission sources that resulted in model convergence and greater than 50 percent of the total mass being explained by the model. This table summarizes the percentage that each source contributed to the measured PAHs as well as the percent of mass explained by the model and the associated R² value.

There was a high level of variability (i.e., range: 0 – 0.75) in the source apportionments based on the PAH species, the emissions sources and the origin of the emission data included in the model. Therefore, the results of these modeling efforts should be interpreted with caution. There are several trends that can be observed from the model output. A larger proportion of the mass was explained by the Golumb data compared to the other sources. These iterations also exhibited higher R² values (0.95) than the other iterations (0.37 – 0.78). One result that is suspect includes the high contribution of jet exhaust (75%) for iterations 1 and 2. It is highly unlikely that jet exhaust would contribute such a high proportion of airborne PAHs since the Erie airport is located between 8 and 20 kilometers from the sampling sites and represents an airport that involves a low volume of air traffic. Golumb, et al., found that jet exhaust contributed approximately 30% of the PAHs from a sampling site 12 kilometers from Boston's Logan airport, an airport with a much higher volume of air traffic compared to Erie (Golumb, 2001). The PAH fingerprint from jet exhaust may comprise one that represents a composite of PAH species actually measured in the Erie area.

It is clear that No. 2 distillate fuel did not contribute to the source apportionment since it always was eliminated from the model runs. The other source emissions showed variable contribution depending on the source used and mix of sources included in the model runs. It is difficult to elucidate the results of the wood burning data (which varied between 0 and 75% depending on the model iteration) since the emissions can vary substantially depending on the type of wood being burned and combustion temperature. Automobile emissions also showed variable contributions (0 – 57%) depending on the specific model iteration. Diesel exhaust showed moderate to high levels of contribution ranging between 2 and 49 percent. Asphalt roofing tar and asphalt manufacturing were included in the model due to the presence of an asphalt manufacturing plant located adjacent to Presque Isle Bay. The contribution from these sources varied between 0 and 60 percent. Coke oven emissions also showed variable results ranging between 0 and 48% depending on the model inputs.

In summary, with the exception of No. 2 distillate fuel, the modeling results suggest that the emission sources included in the model contribute to the airborne concentration of PAHs within the Erie area. Due to the high degree of variability obtained it is difficult to ascribe proportions to each of the emission sources. Additionally, since a low percentage of mass was explained by many of the model runs it is apparent that not all PAH sources may have been adequately included in the model. In order to better strengthen the source apportionment component of this study more sampling data that includes other compounds is recommended.

Table 17: Contribution of emission sources to PAH profiles (iteration number refers to the PAHs and sources described in Table 5)

Source	1	2	3	4	5	6	7	8	9	10
Auto exhaust 1 (Golomb, 2001)	0.24	0.25								
Diesel exhaust 1 (Golomb, 2001)	0.04	0.02								
Jet Exhaust (Golomb, 2001)	0.72	0.73								
Wood burning (Golomb, 2001)	0								0.21	
No. 2 distillate fuel (Rogge, 1997a)			0	0		0	0	0		
Wood burning 2 (Rogge, 1998)						0				0.18
Wood burning 3 (Schauer, 2001)							0			
Wood burning 4 (Khalili, 1995)								0		
Wood burning mean (2-4)			0.17	0	0.75					
Diesel exhaust 2 (Rogge, 1993)						0.32				
Diesel exhaust 3 (Schauer, 1999)							0.35		0.42	0.22
Diesel exhaust 4 (Khalili, 1995)								0.17		
Diesel exhaust 5 (Miguel, 1998)										
Diesel exhaust mean (2-5)			0.39	0.49	0.11					
Auto exhaust 2 (Rogge, 1993)						0				
Auto exhaust 3 (Khalili, 1995)							0.57			
Auto exhaust 4 (Miguel, 1998)								0	0.02	
Auto exhaust mean (2-4)			0.09	0	0.13					
Auto exhaust - NC (Rogge, 1993)			0.08	0.08		0.24		0.11		
Asphalt roofing tar (Rogge, 1997b)				0.06			0.08	0.23	0.09	
Asphalt manufacturing (ARMA, 1998)			0			0.31				0.60
Coke oven (Khalili, 1995)			0.28	0.37		0.13	0	0.48	0.26	
% mass explained	104	105	76.9	72.9	81.9	57.0	69.1	68.8	70.7	53.6
R ²	0.95	0.95	0.86	0.78	0.77	0.70	0.37	0.71	0.74	0.72

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Table A-1: Frequency distribution of wind direction for each of the 24-hour sampling periods

Sampling Date	N	NE	E	SE	S	SW	W	NW	No Wind
1-Feb-2005	12.5%	8.3%	4.2%	0.0%	16.7%	8.3%	0.0%	0.0%	50.0%
13-Feb-2005	0.0%	33.3%	37.5%	20.8%	4.2%	0.0%	0.0%	0.0%	4.2%
27-Feb-2005	4.3%	34.8%	26.1%	17.4%	17.4%	0.0%	0.0%	0.0%	0.0%
11-Mar-2005	0.0%	0.0%	0.0%	4.2%	45.8%	4.2%	37.5%	4.2%	4.2%
23-Mar-2005	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
4-Apr-2005	0.0%	0.0%	0.0%	0.0%	20.8%	8.3%	66.7%	0.0%	4.2%
16-Apr-2005	13.0%	13.0%	4.3%	0.0%	52.2%	0.0%	0.0%	4.3%	13.0%
28-Apr-2005	0.0%	0.0%	0.0%	4.2%	16.7%	16.7%	41.7%	0.0%	20.8%
13-May-2005	33.3%	0.0%	4.2%	0.0%	25.0%	0.0%	12.5%	8.3%	16.7%
25-May-2005	33.3%	0.0%	4.2%	0.0%	25.0%	0.0%	12.5%	8.3%	16.7%
5-Jun-2005	12.5%	0.0%	0.0%	0.0%	62.5%	8.3%	4.2%	12.5%	0.0%
17-Jun-2005	8.3%	0.0%	0.0%	0.0%	0.0%	0.0%	50.0%	41.7%	0.0%
29-Jun-2005	0.0%	0.0%	0.0%	0.0%	34.8%	13.0%	30.4%	17.4%	4.3%
11-Jul-2005	0.0%	0.0%	0.0%	0.0%	28.0%	0.0%	4.0%	32.0%	36.0%
23-Jul-2005	37.5%	12.5%	8.3%	0.0%	29.2%	0.0%	0.0%	0.0%	12.5%
4-Aug-2005	0.0%	4.0%	0.0%	0.0%	20.0%	32.0%	40.0%	4.0%	0.0%
16-Aug-2005	24.0%	8.0%	0.0%	0.0%	44.0%	0.0%	0.0%	4.0%	20.0%
28-Aug-2005	0.0%	0.0%	0.0%	0.0%	69.6%	13.0%	8.7%	8.7%	0.0%
9-Sep-2005	13.0%	26.1%	4.3%	13.0%	8.7%	0.0%	0.0%	0.0%	34.8%
21-Sep-2005	0.0%	0.0%	0.0%	0.0%	60.9%	8.7%	26.1%	0.0%	4.3%
3-Oct-2005	8.0%	4.0%	0.0%	0.0%	48.0%	8.0%	0.0%	8.0%	24.0%
15-Oct-2005	4.0%	0.0%	0.0%	0.0%	0.0%	12.0%	24.0%	60.0%	0.0%
27-Oct-2005	40.9%	0.0%	0.0%	0.0%	40.9%	0.0%	0.0%	4.5%	13.6%
8-Nov-2005	16.7%	12.5%	29.2%	8.3%	12.5%	16.7%	0.0%	0.0%	4.2%
20-Nov-2005	0.0%	0.0%	0.0%	0.0%	15.4%	76.9%	7.7%	0.0%	0.0%
2-Dec-2005	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	73.1%	26.9%	0.0%
14-Dec-2005	0.0%	0.0%	0.0%	95.7%	4.3%	0.0%	0.0%	0.0%	0.0%
26-Dec-2005	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	44.0%	56.0%	0.0%
7-Jan-2006	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%
19-Jan-2006	0.0%	0.0%	0.0%	0.0%	80.0%	20.0%	0.0%	0.0%	0.0%
TOTAL	7.6%	9.7%	3.9%	5.3%	29.4%	8.6%	16.3%	10.1%	9.0%

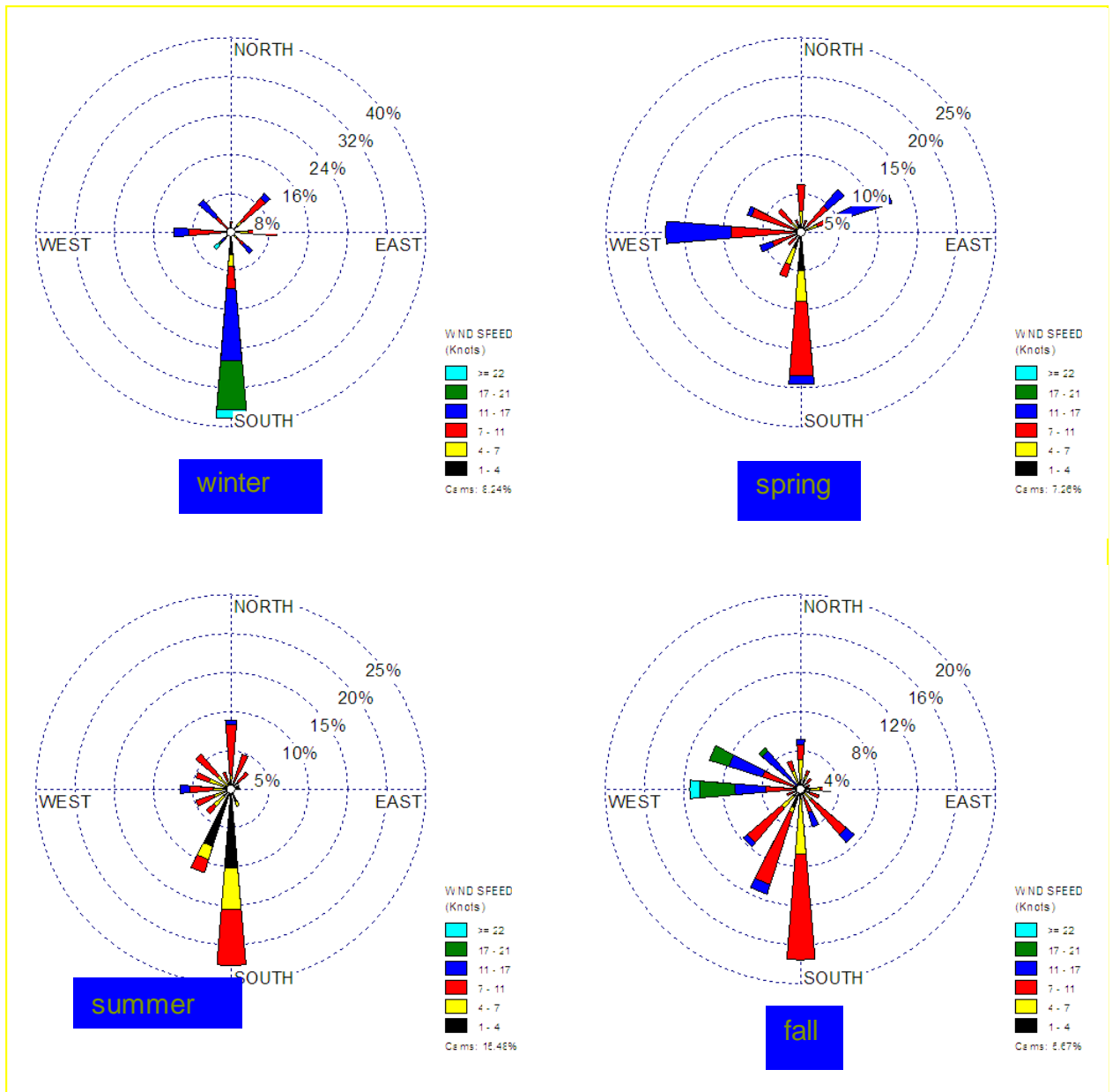


Figure A-1 wind roses for sampling periods by season. (meteorological data from Erie International airport site (NOAA)).

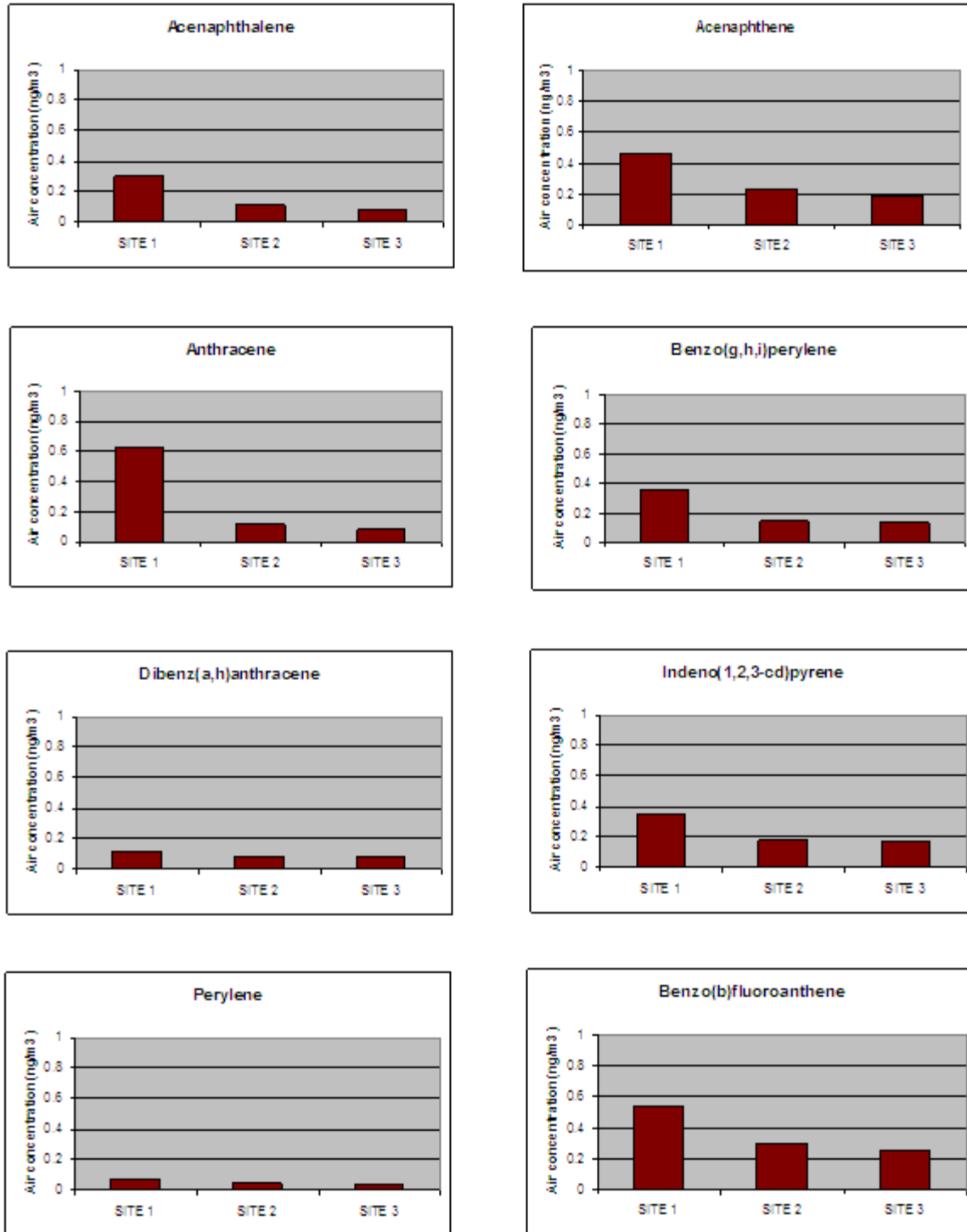


Figure A-2: Comparison of geometric means of gas/particulate concentrations by site (site 1 = City of Erie site; site 2 = suburban site; site 3 = Presque Isle site).

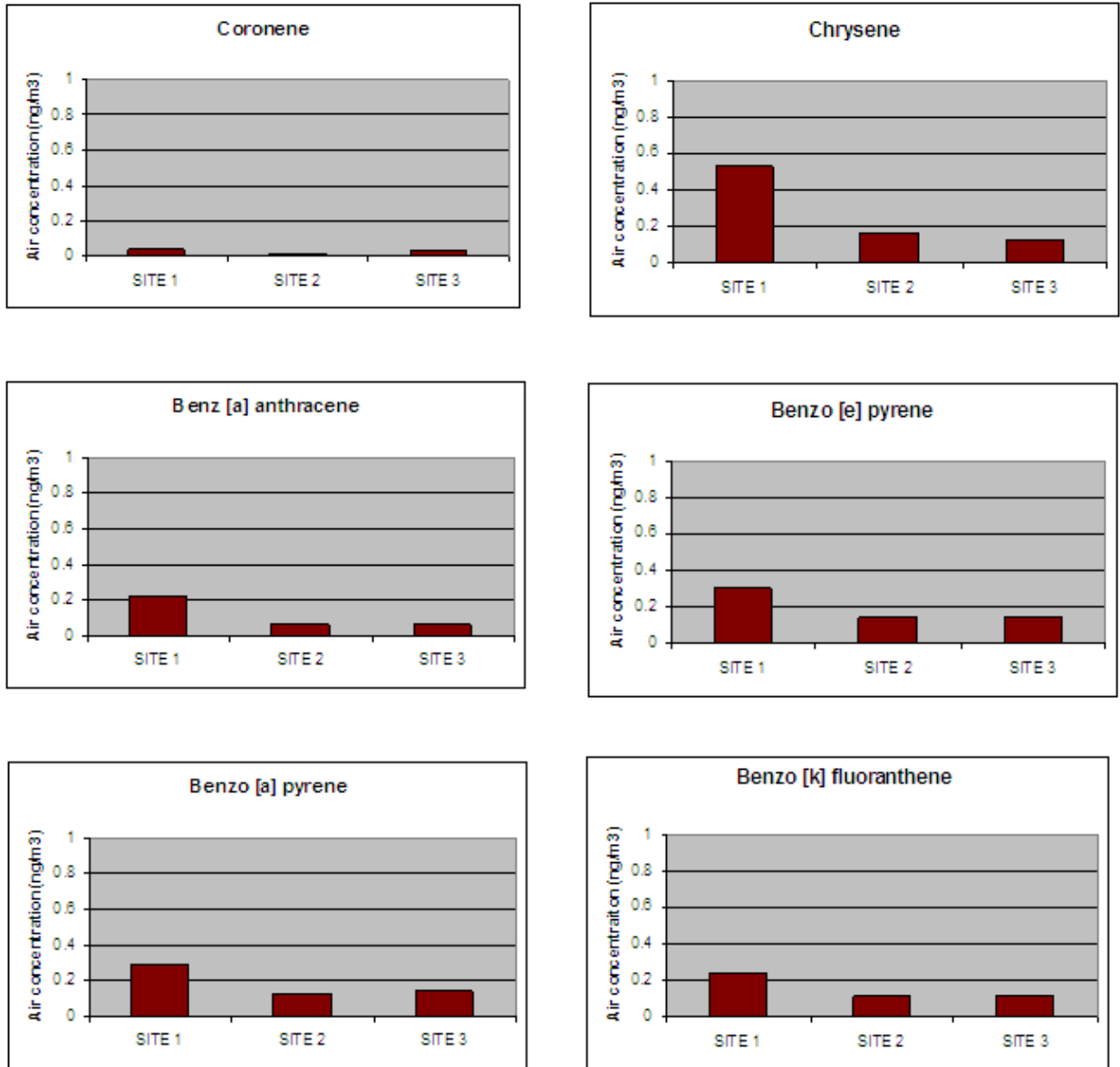


Figure A-3: Comparison of the geometric means of gas/particulate concentrations by site (site 1 = City of Erie site; site 2 = suburban site; site 3 = Presque Isle site).

Table A-2: Descriptive statistics of gas/particulate data (site 1)

Species	MEAN (SD) (ng/m ³)			MEDIAN (ng/m ³)			GEOMETRIC MEAN (GSD) (ng/m ³)			Kruskal Wallance test statistic	p-value
	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3		
Acenaphthalene	1.00 (±2.24)	0.32 (±0.93)	0.35 (±1.19)	0.32	0.12	0.10	0.30 (±4.09)	0.11 (±3.49)	0.08 (±4.14)	11.50	0.003
Acenaphthene	0.62 (±0.53)	0.38 (±0.57)	0.32 (±0.47)	0.43	0.19	0.17	0.46 (±2.16)	0.23 (±2.44)	0.19 (±2.61)	14.39	0.001
Fluorene	3.06 (±2.91)	1.39 (±1.28)	1.23 (±1.11)	1.75	0.86	0.82	2.08 (±2.41)	1.01 (±2.23)	0.85 (±2.50)	12.16	0.002
Anthracene	0.67 (±1.15)	0.23 (±0.20)	0.18 (±0.12)	0.25	0.17	0.15	0.35 (±2.76)	0.14 (±3.62)	0.14 (±2.41)	23.39	<0.0001
Phenanthrene	0.24 (±0.39)	0.14 (±0.26)	0.11 (±0.11)	0.12	0.09	0.08	0.12 (±2.94)	0.08 (±2.36)	0.08 (±2.56)	17.55	<0.0001
Fluoranthene	0.49 (±0.42)	0.28 (±0.24)	0.21 (±0.12)	0.27	0.23	0.21	0.35 (±2.26)	0.18 (±3.35)	0.17 (±2.18)	22.65	<0.0001
Pyrene	0.15 (±0.24)	0.06 (±0.04)	0.07 (±0.07)	0.09	0.07	0.05	0.08 (±3.34)	0.04 (±3.10)	0.04 (±3.25)	20.24	<0.0001
Benz(a)anthracene	1.03 (±1.70)	0.41 (±0.42)	0.39 (±0.55)	0.39	0.31	0.26	0.54 (±2.87)	0.30 (±2.10)	0.26 (±2.28)	12.47	0.002
Chrysene	0.10 (±0.15)	0.04 (±0.04)	0.04 (±0.04)	0.05	0.03	0.03	0.03 (±6.71)	0.02 (±5.28)	0.03 (±3.15)	22.13	<0.0001
Benzo(b)fluoroanthene	1.43 (±1.72)	0.19 (±0.20)	0.13 (±0.12)	0.41	0.09	0.08	0.62 (±4.02)	0.12 (±2.79)	0.08 (±2.87)	6.66	0.036
Benzo(k)fluoroanthene	6.68 (±7.47)	1.17 (±0.92)	0.88 (±0.61)	2.55	1.00	0.73	3.40 (±3.55)	0.91 (±2.09)	0.70 (±2.06)	8.45	0.015
Perylene	19.41 (±18.99)	4.16 (±2.93)	3.27 (±2.23)	9.60	3.48	2.45	11.01 (±3.29)	3.30 (±2.06)	2.64 (±1.96)	3.85	0.146
Benzo[a]pyrene	0.65 (±1.11)	0.13 (±0.18)	0.09 (±0.09)	0.13	0.08	0.08	0.22 (±4.24)	Num (±3.80)	0.06 (±2.45)	8.06	0.018
Benzo(e)pyrene	1.13 (±1.57)	0.24 (±0.29)	0.18 (±0.18)	0.33	0.17	0.16	0.53 (±3.44)	0.17 (±2.27)	0.12 (±2.50)	9.66	0.008
Benzo(g,h,i)perylene	3.55 (±3.53)	1.03 (±0.91)	0.66 (±0.46)	1.82	0.70	0.52	2.20 (±2.82)	0.75 (±2.24)	0.50 (±2.51)	12.95	0.002
Indeno(1,2,3-cd)pyrene	0.59 (±0.84)	0.21 (±0.22)	0.18 (±0.12)	0.19	0.13	0.14	0.30 (±2.98)	0.14 (±2.48)	0.14 (±1.95)	6.09	0.048
Dibenz(a,h)anthracene	0.56 (±0.90)	0.17 (±0.13)	0.18 (±0.14)	0.24	0.13	0.17	0.30 (±2.74)	0.12 (±2.37)	0.14 (±2.27)	2.47	0.290
Coronene	0.38 (±0.46)	0.16 (±0.15)	0.16 (±0.14)	0.22	0.09	0.12	0.23 (±2.59)	0.11 (±2.43)	0.11 (±2.37)	1.76	0.416

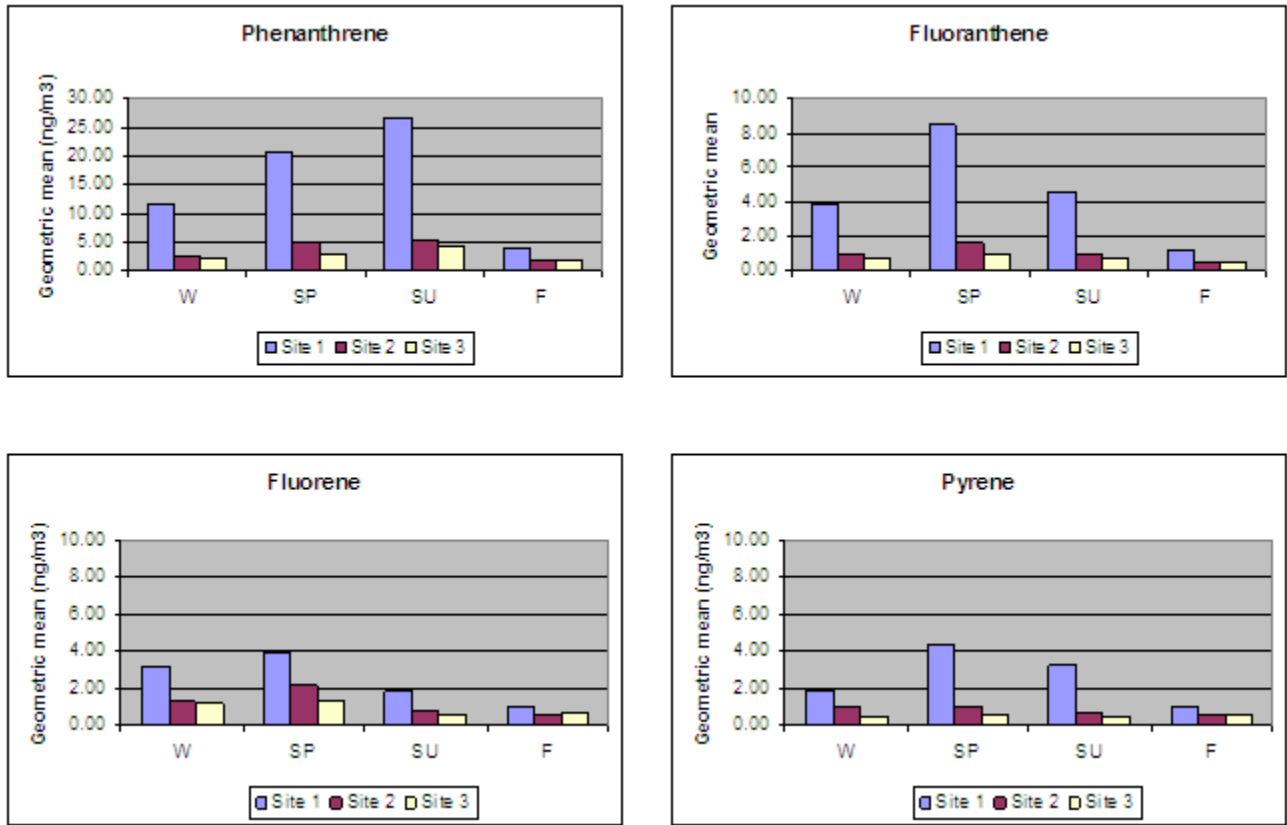


Figure A-4: Comparison of the geometric means by site and season

Table A-3: TEF summary for City Data

Compound	UCL (normal) (ng/m ³)	UCL (lognormal) (ng/m ³)	TEF	Adjusted UCL based on TEF (ng/m ³)	Percent of total TEQ
acenaphthylene	1.77	1.95	0.001	0.002	0.1%
acenaphthene	0.80	0.87	0.001	0.001	0.0%
fluorene	4.06	4.64	0.001	0.005	0.3%
benz [g,h,i] perylene	1.05	0.97	0.01	0.010	0.6%
dibenz [a,h] anthracene	0.37	0.38	1	0.380	21.7%
indeno [1,2,3-cd] pyrene	0.66	0.77	0.1	0.077	4.4%
perylene	0.23	0.32	NA	.	.
benzo [b] fluoranthene	1.67	1.74	0.1	0.174	9.9%
coronene	0.17	2.13	NA	.	.
anthracene	2.03	3.94	0.001	0.004	0.2%
fluoranthene	9.29	16.10	0.001	0.016	0.9%
phenanthrene	26.97	49.87	0.001	0.050	2.8%
benz [a] anthracene	1.07	1.78	0.1	0.178	10.1%
chrysene	1.70	2.38	0.001	0.002	0.1%
pyrene	4.91	7.04	0.001	0.007	0.4%
benzo [e] pyrene	0.88	0.98	NA	.	.
benzo [a] pyrene	0.88	0.84	1	0.844	48.1%
benzo [k] fluoranthene	0.54	0.60	0.01	0.006	0.3%
		TEQ		1.76	

Table A-4: TEF summary for PAH data from suburban site

Compound	UCL (normal) (ng/m ³)	UCL (lognormal) (ng/m ³)	TEF	Adjusted UCL based on TEF (ng/m ³)	Percent of total TEQ
acenaphthylene	0.64	0.48	0.001	0.000	0.1%
acenaphthene	0.58	0.52	0.001	0.001	0.1%
fluorene	1.84	2.02	0.001	0.002	0.3%
benz [g,h,i] perylene	0.29	0.68	0.01	0.007	1.0%
dibenz [a,h] anthracene	0.23	0.18	1	0.177	24.6%
indeno [1,2,3-cd] pyrene	0.37	0.78	0.1	0.078	10.8%
perylene	0.08	0.15	NA	.	.
benzo [b] fluoranthene	0.56	0.56	0.1	0.056	7.8%
coronene	0.06	0.40	NA	.	.
anthracene	0.26	0.33	0.001	0.000	0.0%
fluoranthene	1.50	1.67	0.001	0.002	0.2%
phenanthrene	5.24	6.07	0.001	0.006	0.8%
benz [a] anthracene	0.11	5.88	0.1	0.110	15.3%
chrysene	0.35	0.35	0.001	0.000	0.0%
pyrene	1.35	1.52	0.001	0.002	0.2%
benzo [e] pyrene	0.28	0.33	NA	.	.
benzo [a] pyrene	0.21	0.28	1	0.277	38.4%
benzo [k] fluoranthene	0.21	0.25	0.01	0.003	0.3%
		TEQ		0.719	

Table A-5: TEF summary for PAH data from Presque Isle site

Compound	UCL (normal) (ng/m³)	UCL (lognormal) (ng/m³)	TEF	Adjusted UCL based on TEF (ng/m³)	Percent of total TEQ
acenaphthylene	0.76	0.56	0.001	0.001	0.1%
acenaphthene	0.48	0.49	0.001	0.000	0.1%
fluorene	1.62	2.05	0.001	0.002	0.3%
benz [g,h,i] perylene	0.22	0.31	0.01	0.003	0.4%
dibenz [a,h] anthracene	0.15	0.19	1	0.192	27.7%
indeno [1,2,3-cd] pyrene	0.25	0.33	0.1	0.033	4.8%
perylene	0.09	0.15	NA	.	.
benzo [b] fluoranthene	0.58	0.54	0.1	0.054	7.8%
coronene	0.06	0.14	NA	.	.
anthracene	0.17	0.24	0.001	0.000	0.0%
fluoranthene	1.09	1.26	0.001	0.001	0.2%
phenanthrene	4.05	4.46	0.001	0.004	0.6%
benz [a] anthracene	0.13	0.15	0.1	0.110	15.9%
chrysene	0.24	0.29	0.001	0.000	0.0%
pyrene	0.83	1.22	0.001	0.001	0.2%
benzo [e] pyrene	0.22	0.24	NA	.	.
benzo [a] pyrene	0.23	0.29	1	0.288	41.5%
benzo [k] fluoranthene	0.21	0.24	0.01	0.002	0.4%
		TEQ		0.693	

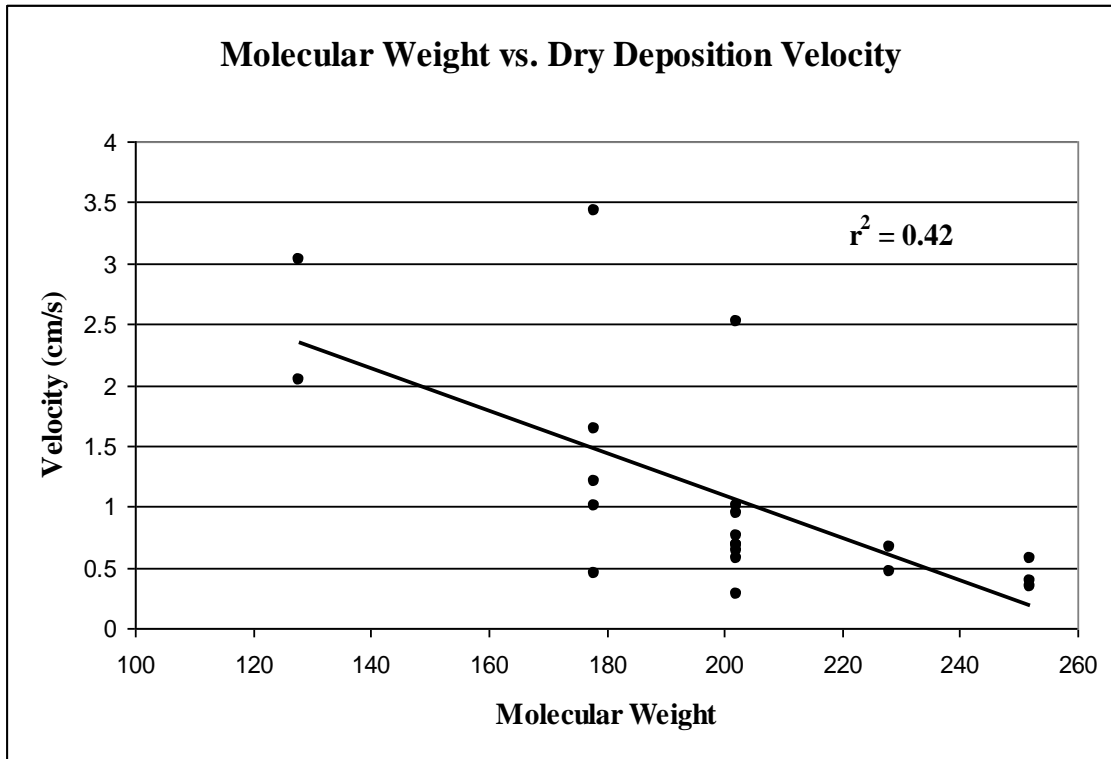


Figure A-5: Regression of Molecular Weight vs. Dry Deposition Velocity

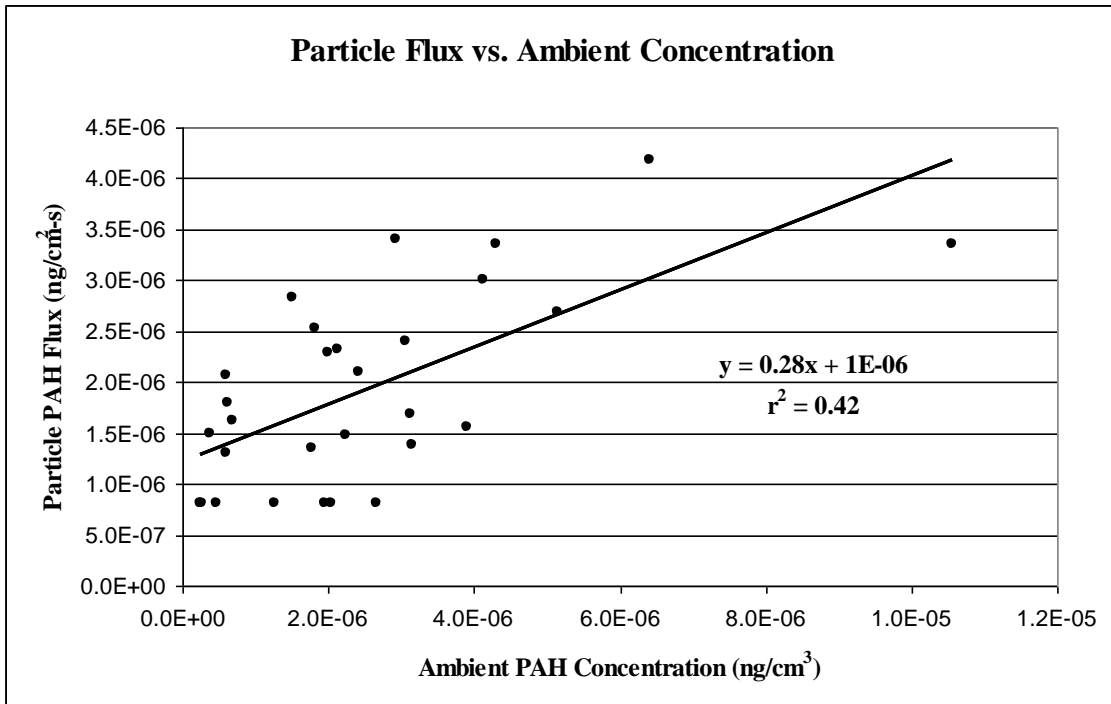


Figure A-6: Regression of Particle PAH flux vs. Ambient PAH concentration