ECAS 2016

sciforum

Conference Proceedings Paper

Measurements and Analysis of Polycyclic Aromatic Hydrocarbons near a Major Interstate

Dennis K. Mikel * and Viney P. Aneja

Published: 15 July 2016

North Carolina State University, Raleigh, NC 27695-8208, USA
* Correspondence: dkmikel@ncsu.edu; Tel.: +919-518-3502

Abstract: Polycyclic aromatic hydrocarbons were measured near Interstate 40, just east of Research Triangle Park, North Carolina. One hundred seven 8-h integrated samples were collected on 20 sampling days over a 2 month period in Fall 2014. The 8-h samples were collected by low flow (16.7 L/min) fine particulate samplers. The samples were analyzed using gas chromatography-mass spectrometry. Temporal distribution of the PAHs (0.1–21.6 ng/m^3 ± 9.0 std) were compared to meteorological and pollutant data collected at the near roadway station. There is a weak but significant correlation between the sum of the measured PAHs with ozone, nitrogen dioxide and nitric oxide, with the R^2 values being 0.0049, 0.0187 and 0.0788 respectively. However the p-values (α = 0.05) were 0.044, 0.002 and 0.044, which are significant. Wind rose analysis illustrated the morning hours which were predominantly southern winds, while the afternoon hours illustrated southerly and easterly winds, which suggests that the automobile traffic as the main source of PAHs. The nighttime hours wind rose shows winds from northerly and easterly direction, which are predominantly from the RDU International Airport. PAH concentration found in this study compare favorably to other research studies (0.1 to 193.6 ng/m^3) both nationally and internationally.

Keywords: Polycyclic Aromatic Hydrocarbons; PAHs; ozone; near roadway

1. Introduction

Epidemiologic research over the last 30 years has shown increases in adverse cardiovascular and respiratory outcomes in relation to mass concentrations of particulate matter (PM) ≤2.5 μm or ≤10 μm in aerodynamic diameter ($PM_{2.5}$ and PM_{10}, respectively). A number of research papers [1–5] have been published that examines the exposure and risk of Polycyclic Aromatic Hydrocarbons (PAHs) and their association with $PM_{2.5}$, PM_{10} and ultrafine particles (UFPs). Many PAHs are known carcinogens [6–8]. The US Environmental Protection Agency (EPA), whose role is to safeguard the population and the environment, has published both inhalation and oral chronic dose exposure estimates associated for PAHs [9].

A fairly new area of focus in EPA air quality research is measuring pollutants near roadways. It has been estimated that approximately 11% of households in the United States are located within 100 m of 4-lane highways or expressway [10]. In the past decade, studies have been conducted both nationally and internationally which focus on particles and gases that are emitted from mobile source exhaust from busy highways and freeways. The first major study [11] was conducted in the United States in the Los Angeles Basin. Following the Los Angeles study, a number of researchers [12–15] have found that mobile sources on freeways can be a major source of fine and ultrafine PM and PAHs have been found in the fine and ultrafine particles fractions [16–18].

This paper describes a field study that was conducted to: (1) yield 8-h integrated particle-bound PAH data from the ambient air quality station that is located near (within 15 m) a major roadway

(Interstate 40); and (2) compare and contrast the PAH data to other physico-chemical measurements (pollutant and meteorological) being collected and analyzed at this monitoring site and draw association and conclusions from that comparison.

2. Experiment

US EPA and the North Carolina Department of Environment and Natural Resources operate an air pollution monitoring station to meet the requirements for a fixed nitrogen dioxide (NO_2) near-road monitoring site. Figure 1 illustrates the location of the Research Triangle Park Near-Roadway station in relation to Raleigh, Durham and Chapel Hill, North Carolina. The inset shows the proximity of the station to the Interstate. The fence of the monitoring stations is ~15 m from the edge of the roadway. The sampling occurred between 5 September, through 6 November 2014, on a 1-in-3 day sampling schedule.

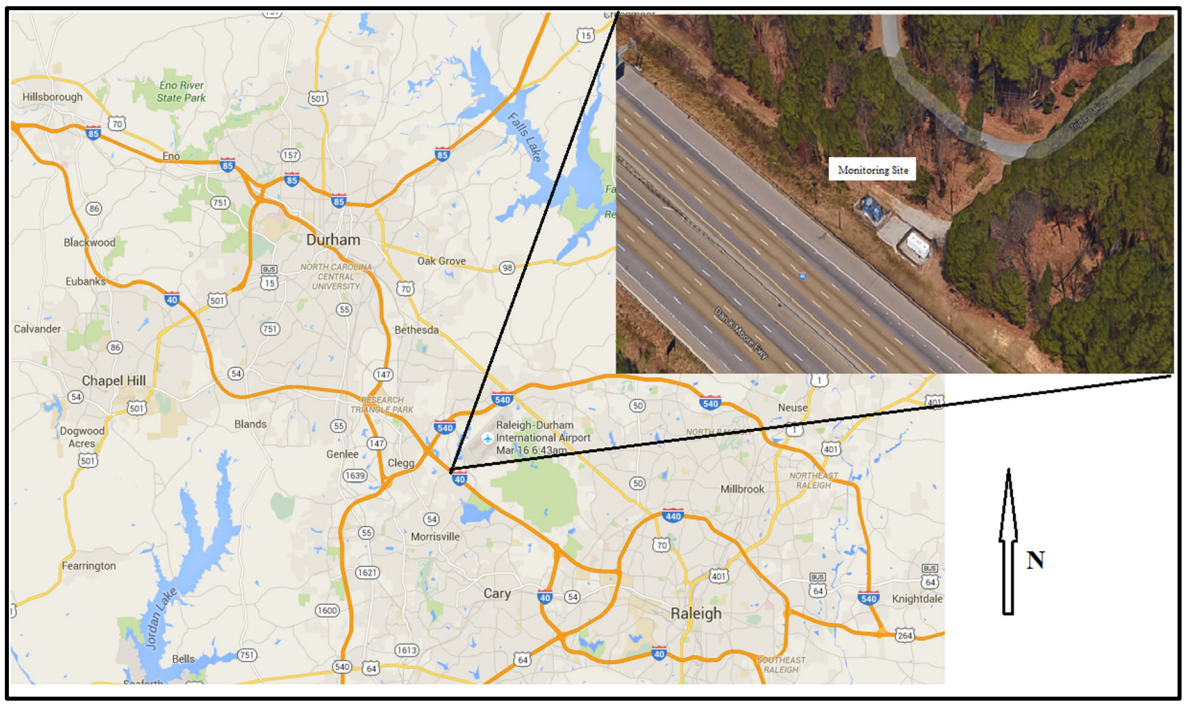

Figure 1. The monitoring location in relation to three major cities (Raleigh, Durham and Chapel Hill) in North Carolina with the insert showing the monitoring site's proximity to the Interstate.

The samples were collected using a low flow (~16.7 L/min.) sampler with a cut-point at aerodynamic size range of $PM_{2.5}$. The samplers were mounted and operated along the freeway-facing fence inside the near roadway monitoring station. The inlets were positioned above the fenceline and had direct exposure to the Interstate.

The sequential samplers were operated on three 8-h time slots. These were:

- Sampler #1: 04:00 a.m.–12:00 p.m. (morning)
- Sampler #2: 12:00 p.m.–08:00 p.m. (afternoon)
- Sampler #3: 08:00 p.m.–04:00 a.m., the next day. (nighttime)

The reasoning behind the staggered starting times was to capture the different "rush hour" commuting times between 06:00–10:00 a.m. and 04:00–08:00 p.m. on the highway. In addition, the sampling strategy allowed for the capture of the "nighttime" traffic when heavy duty diesel engines were expected to dominate the roadway.

After each sampling event, the samples were transported in a temperature controlled container to a laboratory facility on the EPA campus in Research Triangle Park, North Carolina, where they were removed from the filter cassettes, placed in petri dishes and stored in a refrigerator at ~5 °C.

In preparation for the GC-MS analysis, the filters were removed from the petri dishes and placed into 20-mL extraction vials. To each vial, 15 mL of dichloromethane was added. Each filter remained in the capped vial for 48 h. The aliquot was reduced to 2 mL using steam bath in a fume hood. After the GC-MS was tuned, 1 μL of each aliquot was injected into an Agilent 6890 Series GC System coupled with an Agilent 5973 Network Mass Selective detector equipped with a J&W Scientific/ Agilent Technologies DB-5 GC column with a helium carrier gas flow rate of 1 mL/min. The MS scan range was 50–350 mass to charge ratio (m/z). All chromatograms obtained from the samples were analyzed and cross-referenced against two mass spectral libraries in order to identify the compounds in the sample. Table 1 lists the PAHs that were examined in this study. National Institute of Standards and Technology (NIST) traceable standards for the compounds were utilized for calibrating the GC-MS.

Table 1. Compounds, CAS Numbers, Physical Characteristics.

Compound Name	CAS No.	No. of Rings	Molecular Weights
Naphthalene	91-20-3	2	**128.2**
Acenaphthene	83-32-9	3	**154.2**
Acenaphthylene	206-96-8	3	**152.2**
Fluorene	86-73-7	3	**166.2**
Phenanthrene	85-01-8	3	**178.2**
Anthracene	120-12-7	3	**178.2**
Fluorenone	206-44-0	4	**180.2**
Pyrene	129-00-0	4	**202.3**
Fluoranthene	486-25-9	4	**202.3**
Retene	483-65-8	3	**212.3**
Benzo (a) anthracene	56-55-3	4	**228.3**
Chrysene	218-01-9	4	**228.3**
Benzo (k) fluoranthene	207-08-9	5	**252.3**
Benzo (a) pyrene	50-32-8	5	**252.3**
Perylene	198-55-0	5	**252.3**
Benzo(e) pyrene	192-97-2	5	**278.4**
Dibenz (a,h) anthracene	53-70-3	5	**276.3**
Benzo (g,h,i) perylene	191-24-2	6	**276.3**
Indeno(1,2,3-cd)pyrene	193-39-5	6	**276.3**
Coronene	**191-07-1**	**7**	**300.3**

3. Results

3.1 Analysis of Traffic Patterns

The overall average daily traffic (ADT) on the 20 sample days is ~146,000 vehicles per day. The average speed of the vehicles on these days was ~70 miles per hour. The distribution of the vehicles is skewed heavily toward vehicles that are 10–30 feet in length. The next largest group (during the morning and nighttime periods) are the vehicles that are greater than 60 feet in length. The second largest group in the afternoon period was the vehicles in the <10 feet in length. Table 2 illustrates the distribution of the vehicles in the 6 different size categories.

Table 2. Distribution of the average daily traffic (ADT) for the three sampling periods.

	<10 Feet	10–30 Feet	30–40 Feet	40–50 Feet	50–60 Feet	>60 Feet	Total
Morning							
Average	1293	52,301	1759	786	388	1816	58,344
Percent	2.2%	89.6%	3.0%	1.4%	0.7%	3.1%	
Afternoon							
Average	2500	63,109	1960	901	377	1524	70,373
Percent	3.6%	89.7%	2.8%	1.3%	0.5%	2.2%	
Nighttime							
Average	251	12,692	223	125	91	788	14,169
Percent	1.8%	89.6%	1.68%	0.9%	0.6%	5.6%	

As can be seen from Table 2, ~90% of all vehicles are between 10 and 30 feet in length. The afternoon period, between 12:00 to 08:00 p.m. has the highest number of vehicles. The vehicles between 10–30 feet dominate during all three periods: 89.6%, 89.7% and 89.6%. There are some deviations in the other vehicles classes; the most significant deviation is during the nighttime period for the vehicles >60 feet in length. These vehicles account for 2%–3% of the morning and afternoon traffic, but make up 5.6% when measured against the total for the nighttime traffic.

Further analysis was performed by comparing the sum of the measured PAHs for a given 8-h period versus the average daily traffic. Figure 2 illustrates the trend plot of the sum of the PAHs versus the ADT. As can be seen from all three insets in Figure 2, the trend-lines are flat and the R-square (R^2) is very low, which indicates that there is no discernable trend between the number of vehicles on the freeway and the sum of the concentration of the PAHs. However, there is an interesting feature in this graph: there appears to be a bi-modal distribution of the traffic. Inset b of Figure 2 illustrates the weekday traffic versus the sum of the PAHs. One of the modes appears to start at 10,000 ADT and end at 20,000 ADT. There is a gap in the number of vehicles between 20,000 and 40,000. The second distribution begins at 45,000 to 80,000 ADT. Figure 2, inset c illustrates the trend plot that compares the sum of the PAHs versus the weekend traffic distribution for this study. As can be seen from inset b or c, there is no clear linear relationship for either weekend or weekday.

3.2. Analysis of PAHs Versus Meteorological Data

Wind roses were generated using the wind speed and wind direction vectors data that were collected at the monitoring location. Figure 3 illustrates the pollutant rose for the sum of the PAHs for all sampling days. As can be seen from Figure 3, the Interstate travels from Northwest to Southeast. The RDU international airport lies between Northeast to East directions. Figure 3 illustrates that the PAH originate from the North (0°), Northeast to South (180°).

Figure 4 shows the sum of the measured PAHs plotted against the wind direction vector data for the three sampling time periods: morning, afternoon and nighttime. Figure 4a shows that wind direction is from the east (90°) to south (180°). This plot suggests that the source of the PAHs is the automobile exhaust from the Interstatw. Figure 4b illustrates the winds and highest concentrations are southernly, (90°–200°), which suggests that the Interstate is the main source of the PAHs. However, Figure 4c plot illustrates the the nightime winds are from the north. This plot suggests that for the nighttime distribution, the sources of the PAHs are predominantly between 0° through 135°. This data illustrates that the airport and the traffic interchanges around it are the major contributors to the nighttime PAHs.

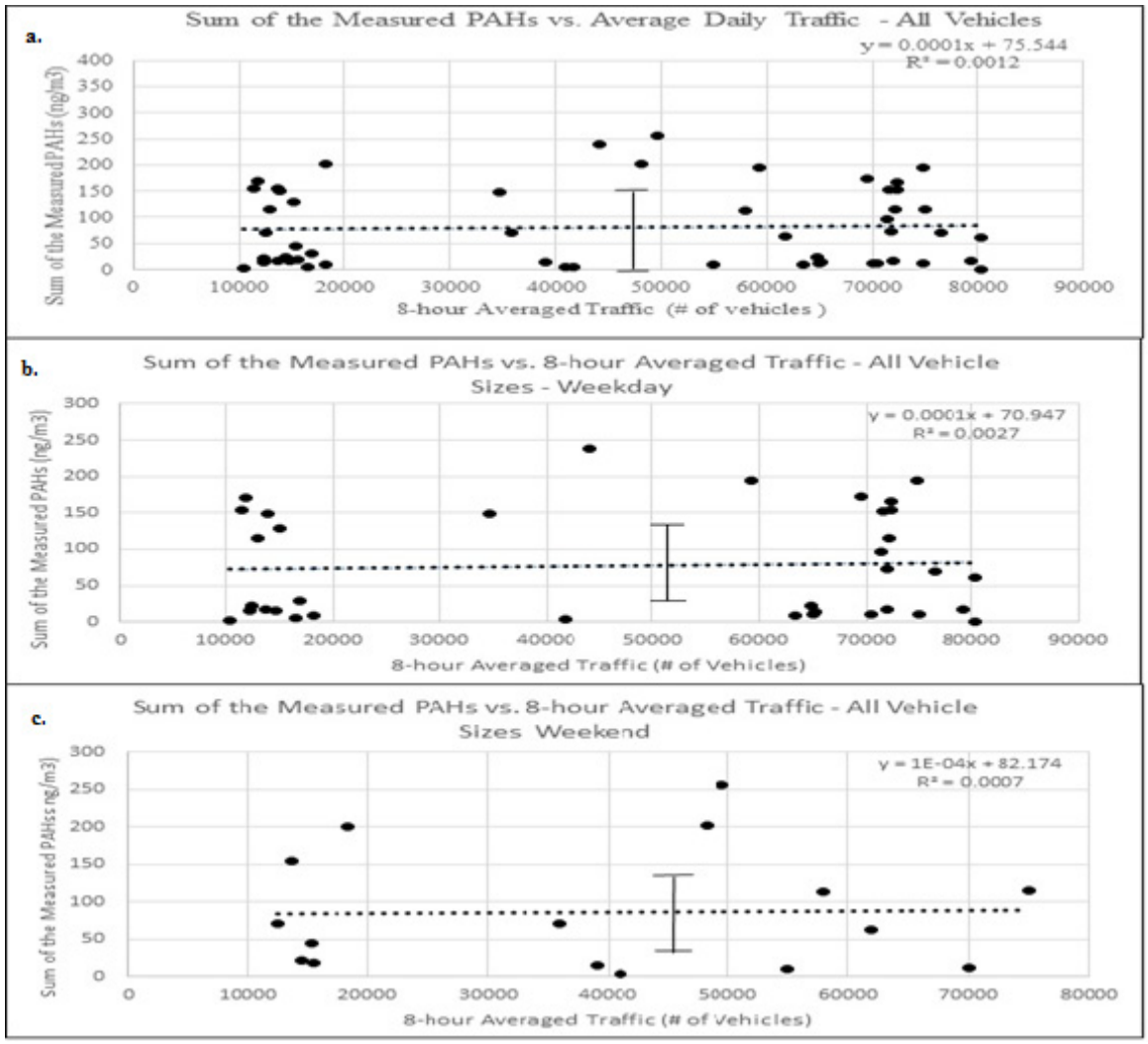

Figure 2. Trend plots of the sum of measured PAHs versus (**a**) All traffic; (**b**) Weekday traffic and (**c**) Weekend traffic (+/1 Std as indicated).

Figure 3. Pollutant Rose Representing all Sample.

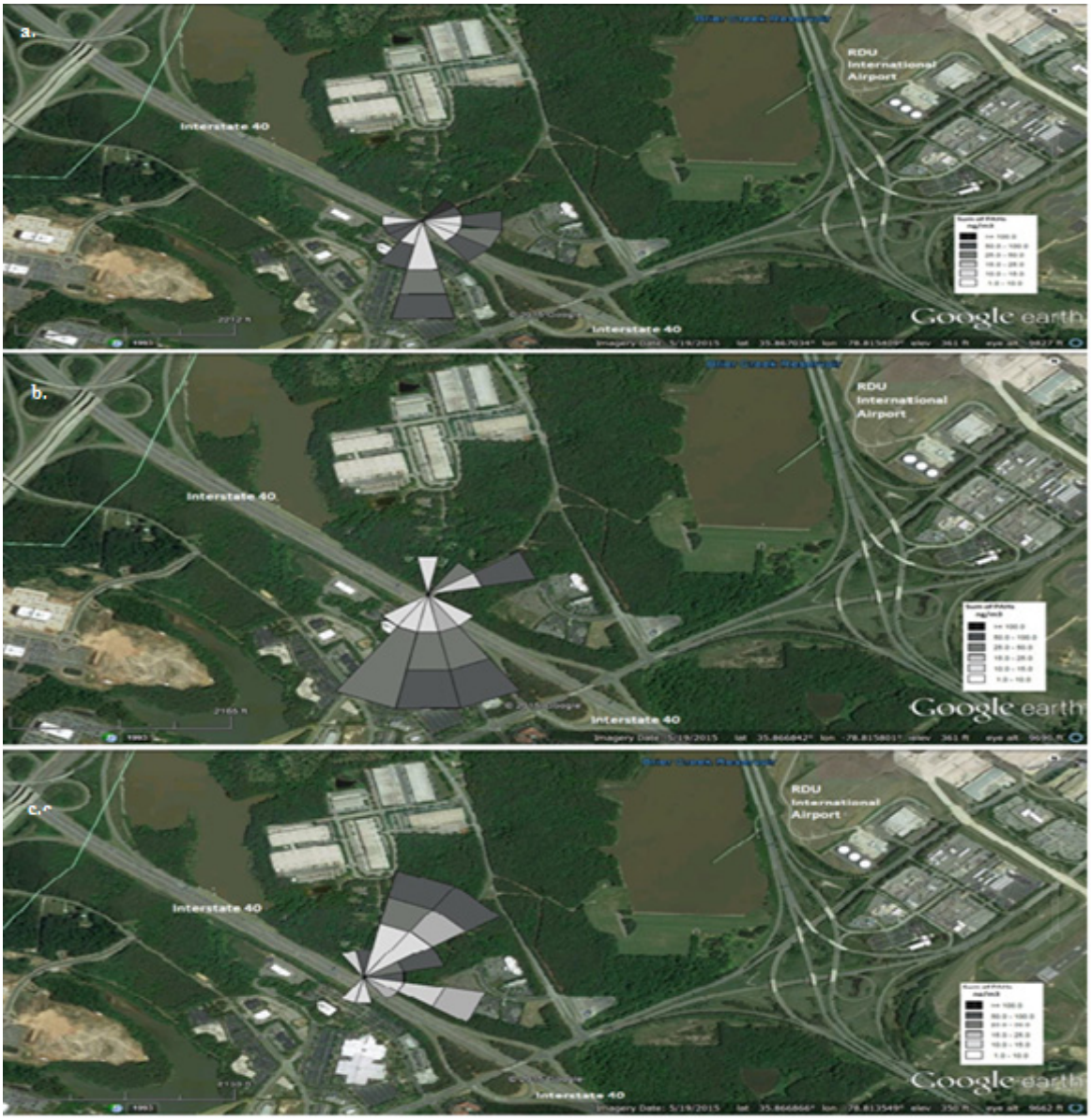

Figure 4. Pollutant Rose for (**a**) Morning; (**b**) Afternoon and (**c**) Night time 8-h Samples.

Box and whisker plots (Figure 5) were created of three PAHs that were measured in all three time periods. Inset 5a illustrates that the distribution of the Benzo (a) Pyrene (BaP) is higher in the afternoon samples than either the nighttime or morning. This suggests that the Interstate is the main source of BaP. Panels 5b and 5c show the distribution of Retene and Naphthalene. The Retene distribution is highest in the morning hours, while Naphthalene's distribution trends toward early morning and nighttime. Several papers [19–21] suggest that aircraft emissions are a major source of Naphthalene.

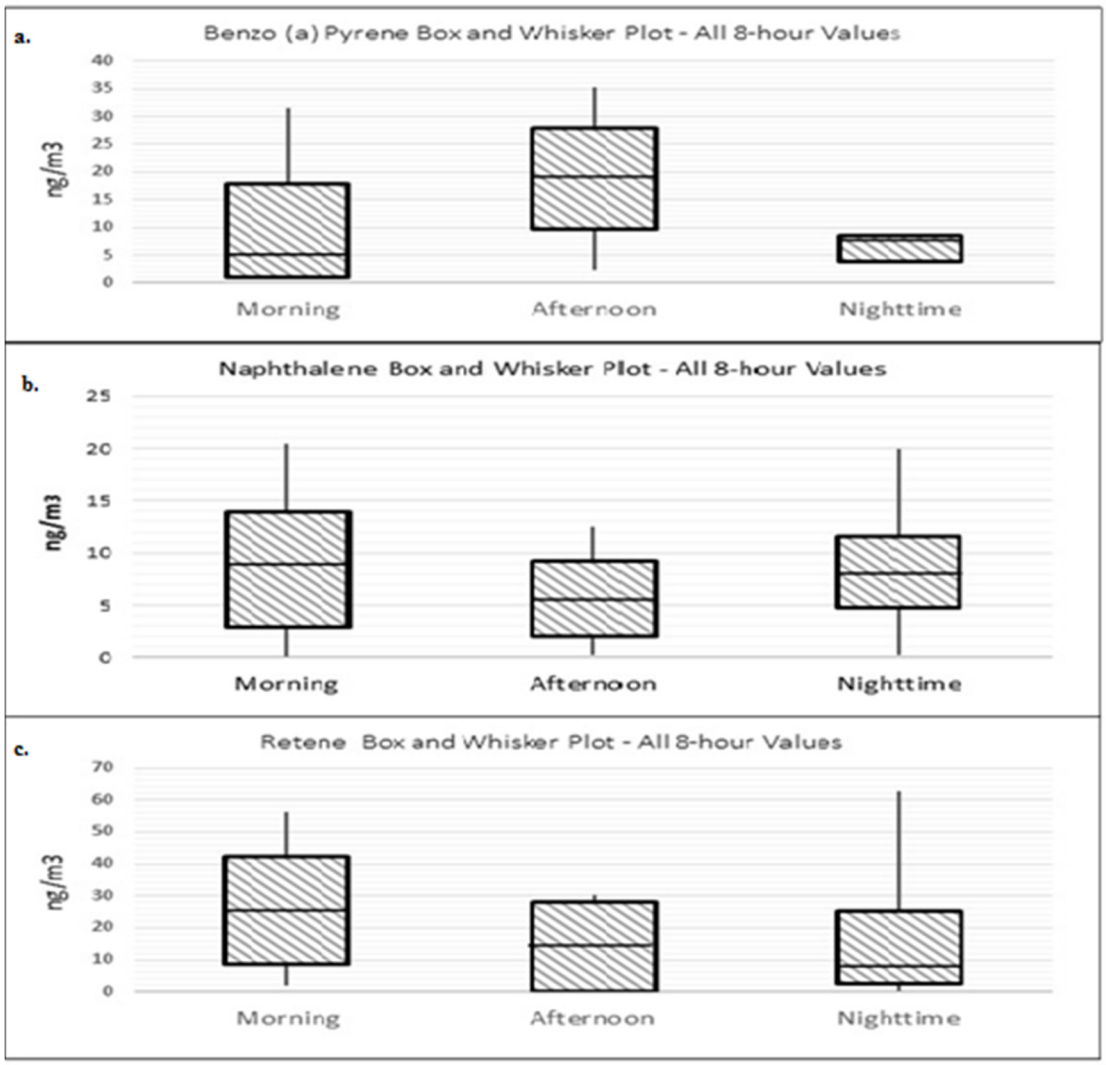

Figure 5. Box and whisker distribution plots of (**a**) Benzo (**a**) Pyrene; (**b**) Naphthalene; and (**c**) Retene.

3.3. Analysis of PAHs Versus Pollutant Data

Figure 6 illustrates the sum of the measured PAHs versus ozone (O_3), nitric oxide (NO) and NO_2. A weak correlation can be drawn between the sum of the PAHs with NO, NO_2 and ozone. Research suggests [22–28] that PAHs can react with NO, NO_2 and ozone. A significant but weak linear relationship can be seen between the PAHs and the pollutant data. Although the correlations (R^2) between the NO, NO_2 and O_3 and sum of the measured PAHs are not strong (0.0788, 0.0187 and 0.0049, respectively) there is discernable downward trend to the three graphs: as the sum of the PAHs increase the pollutants decrease. In order to determine whether there is a significant relationship between the sum of the PAHs and the pollutant gases, the p-values were calculated for the three gas pollutants against the sum of the measured PAHs. For p-test statistical analysis, if the p-value that is returned is less than 0.05 (α = 0.05), then the relationship between the two data sets is considered significant. The p-value are 0.044, 0.002, and 0.044, for ozone, NO_2 and NO, respectively, which are all less than 0.05. These findings suggest that there is a weak relationship between these two oxides of nitrogen species and ozone and that as their gas concentrations increase, the overall concentration of the PAHs decrease, suggesting that these pollutant gases are interacting with PAHs.

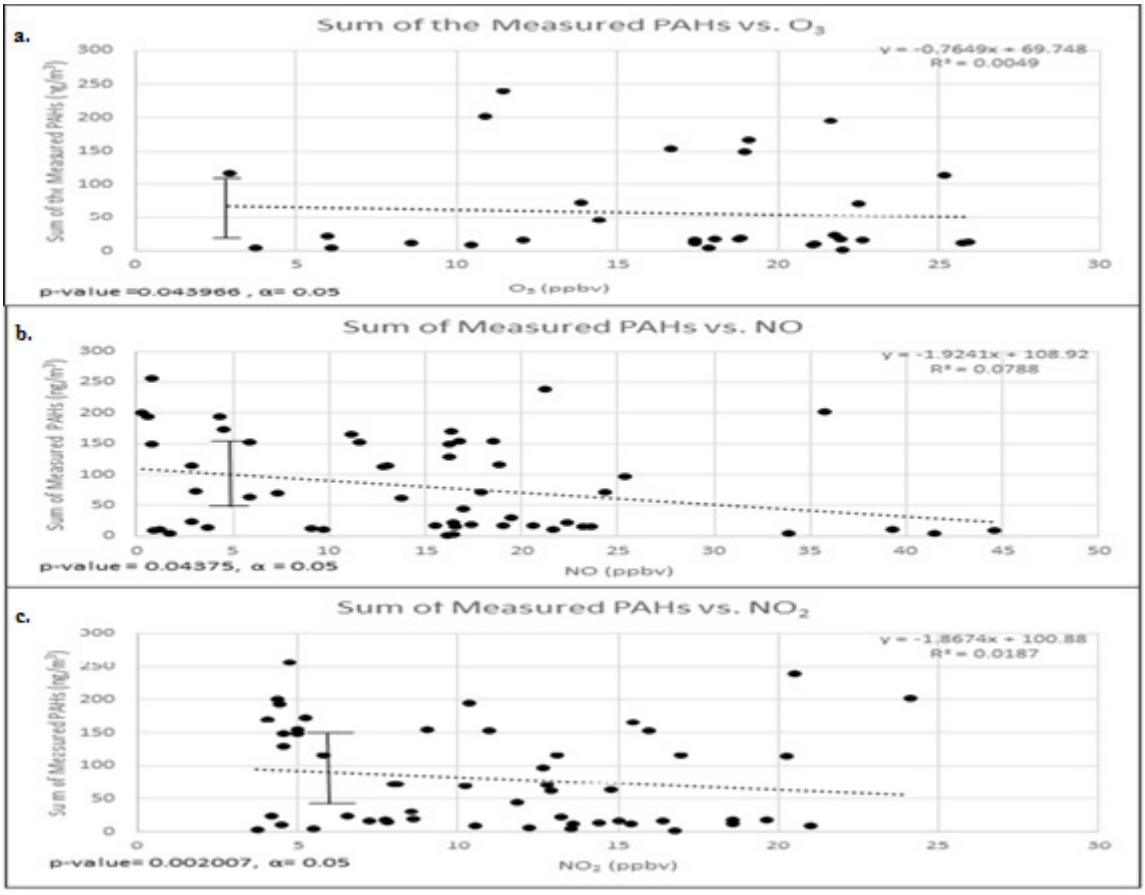

Figure 6. Sum of measured PAHs versus (**a**) ozone; (**b**) NO; and (**c**) NO2 concentration (+/1 Std as indicated).

3.4. Analysis of PAHs Versus Ultrafine Particles Counts

There appears to be a weak linear correlation with the particle number count (PNC) in the ultrafine size ranges across all bin sizes. Researchers [29] measured 10 PAHs in size segregated aerosol samples using a low-pressure impactor. They found that the distribution of the PAHs was unimodal with over 85% less than 0.12 μm in aerodynamic diameter (<120 nm). In a different location, the researchers found a secondary peak in the 0.5 to 1.0 μm range. One study [30] suggested that two PAHs, BaP and coronene. They found these two PAHs on particles less than 260 nm, with 50% being in the range of 75 to 120 nm.

This study found no clear relationship between the particle bin sizes and Sum of the PAHs. All R^2 values are low.

Table 3. Slope, Intercept and R^2 compared to the Sum of the PAHs versus number of particle in each bin.

Bin Size	Slope	Intercept	R^2
20–30 nm	**0.0803**	**982.2**	**9E-5**
30–50 nm	**−0.712**	**1277.73**	**0.0066**
50–70 nm	**−0.9278**	**978.1**	**0.0202**
70–100 nm	**−0.9172**	**914.1**	**0.0210**
100–200 nm	**−0.3449**	**979.5**	**0.0025**
=>200 nm	**0.1479**	**169.8**	**0.0153**

4. Discussion

Figure 7 illustrates the results of this study against other studies reported in the literature. Data from this research study compared well with data from other research studies [31–37]. The sum of the concentrations of PAHs in rural, suburban and urban locations range between 0.5 to 20 ng/m^3. The sum of the PAH concentrations from this study was 160 ng/m^3. A similar research study [37] performed at a busy intersection in Tainan, Taiwan, showed very high sum of the PAHs, ~667 ng/m^3.

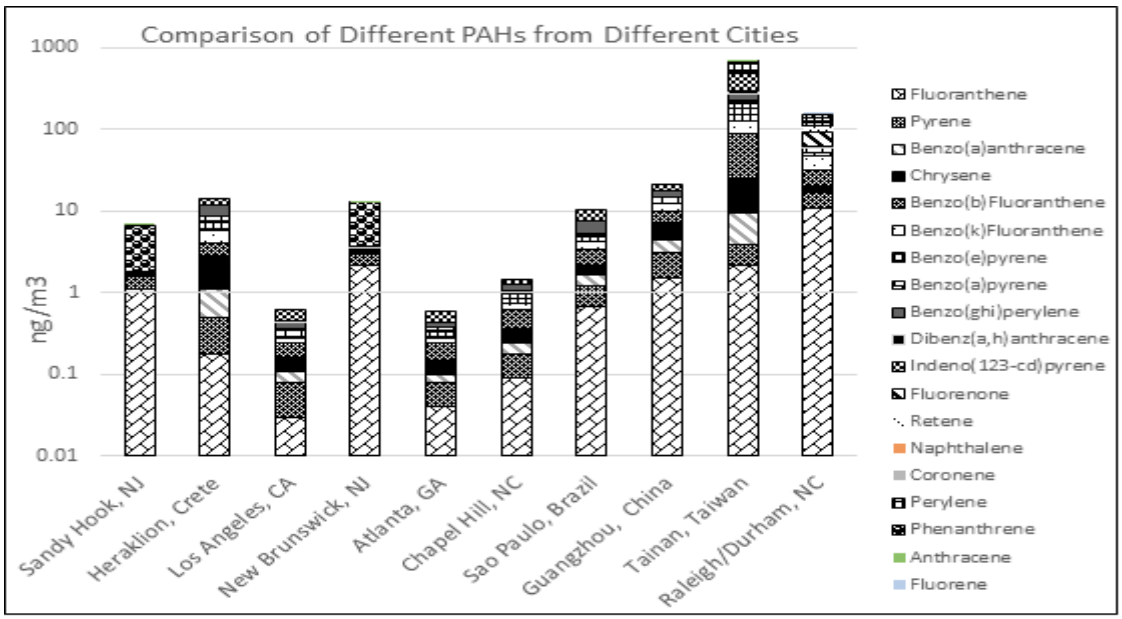

Figure 7. Comparison of study PAHs to values found in the literature.

5. Conclusions

This study provides a convenient methodology for collecting, extracting and analyzing for particle bound PAHs in three 8-h periods (morning, afternoon and nightime) within a 24-h period. The results (0.1–21.6 nanogram/cubic meter ± 9.0 std) agree with the published research literature (0.1 to 193.6 ng/m^3) both nationally and internationally. There is a weak yet significant correlation between the PAHs with atmospheric oxidants. Other results, such as the relationship of the size of vehicles to PAH trends, did not correlate well. The distribution of the PAHs varied in relationship to the time of day. For the morning and afternoon hours, the PAH sources point to the Interstate automobile emissions. During the nighttime hours, the source of the PAHs are from the North to Northeast, which suggests that the RDU International Airport and its interchanges are the major source of the PAHs.

The research studies that were encountered in the literature focused on collection, analysis and interpretation of samples that were collected for 24-h periods or longer. Some rural studies collected samples over several days in order to collect enough sample for analysis. This study illustrated that if the sampling is close to the source, PAHs can be collected in 8-h segments using low flow (~16.7 lpm) $PM_{2.5}$ samplers and source apportionment can be determined if meteorological data are available in the area.

Acknowledgments: The authors would like to thank Yang Zhang, North Carolina State University, Marine, Earth, and Atmospheric Sciences (MEAS), John Walker, EPA-Office of Research and Development (ORD), Research Triangle Park, North Carolina, Walter Robinson, Dept. Head North Carolina State University, MEAS, Sue Kimbrough, EPA-ORD, Richard Snow, EPA-ORD, Morteza Khaledi, Department Head–North Carolina State University, Chemistry Department, Danielle Lehman, North Carolina State University, Chemistry

Department–Mass Spectrometry Lab. Dennis Mikel also would like to thank the EPA-ORD for providing access to the near-roadway station and use of the $PM_{2.5}$ samplers during this study.

Author Contributions: Dennis K. Mikel conceived, designed and performed the experiment, analyzed the data and contributed reagents/materials/data analysis tools. Dennis K. Mikel and Viney P. Aneja wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

PAHs	Polycyclic Aromatic Hydrocarbons
$PM_{2.5}$	Particulate Matter ≥ 2.5 microns in aerodynamic diameter
PM_{10}	Particulate Matter ≥ 10 microns in aerodynamic diameter
UFP	Ultrafine Particulate
EPA	United State Environmental Protection Agency
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
O_3	Ozone
GC-MS	Gas Chromatography-Mass Spectrometry
NIST	National Institute of Standards and Technology
ADT	Average Daily Traffic
R^2	R-squared, the correlation coefficient of a linear equation
ng/m^3	nanograms per cubic meter
RDU	Raleigh-Durham International Airport
BaP	Benzo (a) Pyrene
μL	microliter
L pm	liters per minute
mL	millileters
nm	nanometers

References

1. Vyskocil, A.; Fiala, Z.; Chenier, V.; Krajak, L.; ; Ettlerova, E.; Bukac, J.; Viau, C.; Emminger, S. Assessment of multipathway exposure of small children to PAH. *Environ. Toxicol. Pharmacol.* **2000**, *8*, 111–118.
2. Rajput, N.; Lakhani, A. PAHs and their Carcinogenic Potencies in Diesel Fuel and Diesel Generator Exhaust. *Hum. Ecol. Risk Assess.* **2009**, *15*, 201–213.
3. Jyethi, D.S.; Khillare, P.; Sarkar, S. Risk assessment of inhalation exposure to polycyclic aromatic hydrocarbons in school children. *Environ. Sci. Pollut. Res.* **2014**, *21*, 366–378.
4. Seagrave, J.; Gigliotti, A.; McDonald, J.; Seilkop, S.; Whitney, K.; Zielinska, B.; Mauderly, J. Composition, toxicity, and mutagenicity of particulate and semivolatile emissions from heavy-duty compressed natural gas powered vehicles. *Toxicol. Sci.* **2005**, *87*, 232–241.
5. Fromme, H.; Oddoy, A.; Piloty, M.; Krause, M.; Lahrza, T. Polycyclic aromatic hydrocarbons PAH and diesel engine emission elemental carbon inside a car and a subway train. *Sci. Total Environ.* **1998**, *217*, 165–173.
6. Melendez–Colon, V.J.; Luch, A.; Seidel, A.; Baird, W. Cancer initiated by polycyclic aromatic hydrocarbons results from formation of stable DNA adducts rather than apurinic sites. *Carcinogenesis* **1999**, *20*, 1885–1891.
7. Bonner, M.; Han, D.; Nie, J.; Rogerson, P.; Vena, J.; Muti, P.; Freudenheim, J. Breast cancer risk and exposure in early life to polycyclic aromatic hydrocarbons using total suspended particulates as a proxy measure. *Cancer Epidemiol. Biomark. Prev.* **2005**, *14*, 53–60.

8. Nie, J.; Beyea, J.; Bonner, M.; Han, D.; Vena, J.; Rogerson, P.; Vito, D.; Muti, P.; Trevisan, M.; Edge, S.; et al. Exposure of traffic emissions throughout life and risk of breast cancer: The Western New York Exposures and Breast Cancer (WEB) study. *Cancer Causes Control* **2007**, *18*, 947–955.
9. Environmental Protection Agency. *Risk Assessment for Carcinogens*, 2014. Available online: http://www2.epa.gov/fera/risk-assessment-carcinogens (accessed on 15 January 2016).
10. Brugge, D.; Durant, J.; Rioux, C. Near-Highway pollutants in motor vehicle exhaust: A review of epidemiologic evidence of cardiac and pulmonary health risks. *Environ. Health* **2007**, *6*, 23.
11. Zhu, Y.; Hinds, W.; Kim, S.; Sioutas, C. Concentration and Size Distribution of Ultrafine Particles Near a Major Highway. *J. Air Waste Manag. Assoc.* **2002**, *9*, 1032–1042.
12. Sioutas, C.; Delfino, R.; Singh, M. Exposure Assessment for Atmospheric Ultrafine Particles (UFPs) and Implications in Epidemiologic Research. *Environ. Health Perspect.* **2005**, *113*, 947–955.
13. Hagler, G.; Baldauf, R.; Thoma, E.; Long, T.; Snow, R.; Kinsey, J.; Oudejans, L.; Gullett, B. Ultrafine particles near a major roadway in Raleigh, North Carolina: Downwind attenuation and correlation with traffic-related pollutants. *Atmos. Environ.* **2009**, *43*, 1229–1234.
14. Kim, S.; Shen, S.; Sioutas, C.; Zhu, Y.; Hinds, W. Size distribution and diurnal and seasonal trends of ultrafine particles in source and receptor sites of the Los Angeles basin. *J. Air Waste Manag. Assoc.* **2002**, *52*, 297–307.
15. Shi, J.; Evans, D.; Khan, A.; Harrison, R. Sources and concentration of nanoparticles ((10 nm diameter) in the urban atmosphere. *Atmos. Environ.* **2001**, *35*, 1193–1202.
16. Maciejczyk, P.B.; Offenberg, J.; Clemente, J.; Blaustein, M.; Thurston, G.; Chen, L. Ambient pollutant concentrations measured by a mobile laboratory in South Bronx, NY. *Atmos. Environ.* **2004**, *38*, 5283–5294.
17. Chen, S.-J.; Hwang, P.-S.; Hsieh, L.-T. The height variation and particle size distribution of polycyclic aromatic hydrocarbons in the ambient air. *Toxicol. Environ. Chem.* **1997**, *60*, 111–128.
18. Allen, A.G.; da Rocha, G.; Cardoso, A.; Machado, W.P.C.; de Andrade, J. Atmospheric particulate polycyclic aromatic hydrocarbons from road transport in southeast Brazil. *Transp. Res.* **2008**, *13*, 483–490.
19. Childers, J.; Witherspoon, C.; Smith, L.; Pleil, J. Real-Time and integrated measurement of potential Human exposure to particle-bound Polycyclic Aromatic Hydrocarbons (PAHs) from aircraft exhaust. *Environ. Health Perspect.* **2000**, *108*, 853–862.
20. Lai, C.-H.; Chuang, K.-Y.; Chang, J.-W. Characteristics of nano/ultrafine particle-bound PAHs in ambient air at an international airport. *Environ. Sci. Pollut. Res.* **2013**, *20*, 1772–1780.
21. Westerdahl, D.; Fruin, S.; Fine, P.; Sioutas, C. The Los Angeles International Airport as a source of ultrafine particles and other pollutants to nearby communities. *Atmos. Environ.* **2007**, *42*, 3143–3155.
22. Butler, J.; Crossley, P. Reactivity of Polycyclic Aromatic Hydrocarbons absorbed on soot particles. *Atmos. Environ.* **1980**, *15*, 91–94.
23. Feilberg, A.; Poulson, M.; Nielsen, T.; Skov, H. Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. *Atmos. Environ.* **2001**, *35*, 353–366.
24. Bamford, H.; Baker, J. Nitro-Polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the mid-Atlantic region. *Atmos. Environ.* **2003**, *37*, 2077–2091.
25. Pitts, J.N.; van Cauwenberghe, K.; Grosjean, D.; Schmid, J.; Fitz, D.; Belser, W.; Knudson, G.; Hynds, P. Atmospheric Reactions of Polycyclic Aromatic Hydrocarbons: Facile Formation of Mutagenic Nitro Derivatives. *Science* **1978**, *202*, 515.
26. Nikolaou, K.; Masclet, P.; Mouvier, G. Sources and chemical reactivity of polynuclear aromatic hydrocarbons in the atmosphere—A critical review. *Sci. Total Environ.* **1984**, *32*, 103–132.
27. Han, S-H, Oxidation Reaction with Atmospheric Molecular Oxygen at Room Temperature. *Abstract submitted to QTSM'0*2 Workshop**,** 2002**.**
28. Kormacher, W.; Mamantov, G.; Wehry, E.; Natush, D. Resistance to photochemical decomposition of Polycyclic Aromatic Hydrocarbons, Vapor-Adsorbed on Coal Fly Ash. *Environ. Sci. Technol.* **1980**, *14*, 1094–1099.
29. Venkataraman, C.; Lyons, J.; Friedlander, S. Size Distribution of Polycyclic Aromatic Hydrocarbons, and Elemental Carbon. 1. Sampling, Measurement Methods, and Source Characterization. *Environ. Sci. Technol.* **1994**, *28*, 555–562.
30. Miguel, A.; Friedlander, S. Distribution of Benzo (a) pyrene and Coronene with respect to particle size in Pasadena aerosols in the submicron region. *Atmos. Environ.* **1978**, *12*, 2407–2413.

31. Gao, B.; Yu, J.-Z.; Li, S.-X.; Ding, X.; He, Q.-F.; Wang, X.-M. Roadside and rooftop measurements of polycyclic aromatic hydrocarbons in $PM_{2.5}$ in urban Guangzhou: Evaluation of vehicular and regional combustion source contributions. *Atmos. Environ.* **2011**, *45*, 7184–7191.
32. Bourotte, C.; Forti, M.; Taniguchi, S.; Bicego, M.; Lotufo, P. A wintertime study of PAHs in fine and coarse aerosols in Sao Paulo city, Brazil. *Atmos. Environ.* **2005**, *39*, 3799–3811.
33. Li, J.; Zhang, G.; Li, X.; Qi, S.; Liu, G.; Peng, X. Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. *Sci. Total Environ.* **2006**, *355*, 145–155.
34. Eiguren-Fernandez, A.; Miguel, A.; Froines, J.; Thurairatnam, S.; Avol, E. Seasonal and spatial variation of polycyclic aromatic hydrocarbons in vapor-phase and $PM_{2.5}$ in Southern California urban and rural communities. *Aerosol Sci. Technol.* **2004**, *38*, 447–455.
35. Tsapakis, M.; Stephanou, E. Polycyclic aromatic hydrocarbons in the atmosphere of the Eastern Mediterranean. *Environ. Sci. Technol.* **2005**, *39*, 6584–6590.
36. Tsapakis, M.; Stephanou, E. Occurrence of gaseous and particulate poly-cyclic aromatic hydrocarbons in the urban atmosphere: Study of sources and ambient temperature effect on the gas/particle concentration and distribution. *Environ. Pollut.* **2005**, *133*, 147–156.
37. Shue, H.-L.; Lee, W.-J.; Lin, S.; Guor-Cheng, F.; Chang, H.-C.; You, W.-C. Particle-bound PAH Content in Ambient Air. *Environ. Pollut.* **1997**, *96*, 369–382.