Human exposures to PAHs: an eastern United States pilot study

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Abstract

Personal exposure monitoring for select polycyclic aromatic hydrocarbons (PAHs) was performed as part of the National Human Exposure Assessment Survey (NHEXAS) Pilot Study in Baltimore, MD and in four surrounding counties (NHEXAS-Maryland). An objective of this effort was to establish environmental exposure estimates for non-scripted subpopulations involved in their normal activities. Participants, children and adults (ages 13-84) were randomly selected from urban, suburban, and rural areas near Baltimore. Twenty-four hour PM_{10} sample collections (~5.8 m^3) were performed using personal environmental monitors (PEMs). Monitoring was performed for 47 households and 6 sampling Cycles during 1995-1996. A total of 233 personal air samples were available from the participants with eight PAHs speciated (e.g., chrysene, benzo(a)pyrene) as well as an aggregate grouping (total carcinogenic PAHs). Results indicate that ~50 % of the selected samples had detectable concentrations for 3 to 5 of the individual PAHs depending upon spatial setting. Noted differences were observed between exposure concentrations from individuals living in rural areas as compared to urban/suburban environments. Mean benzo(a)pyrene concentrations were observed to be 0.10 ng/m^3 across the entire sampling population. This represented a value well below the World Health Organization's (WHO) 1.0 ng/m^3 ambient air guideline for this PAH.

Introduction

The National Human Exposure Assessment Survey (NHEXAS) Pilot Studies were a series of human exposure surveys conducted in several geographical settings in the United States (U.S.). Field sample collections began in 1995 and were completed in 1997. The goals for such an effort have been reported (Buck et al. 1995; Lebowitz et al. 1995; Pellizzari et al. 1995). These studies were performed in selected locations in Maryland, Arizona and the Mid-West. Each study varied in cohort size from approximately 80 (Maryland) to 500 (Mid-West) individuals by locality. The studies focused on estimating individual exposures for subject populations living a non-scripted (real-world) lifestyle. The NHEXAS-Maryland participants were statistically selected with respect to gender, residential setting (urban, suburban, rural) and other factors (Buck et al. 1995). A repeated measures study design involving a variety of pollutant classes and media was employed and involved monitoring for pesticides, particulate matter (PM), and PM components (elements) among others for this cohort. Air, house dust, yard soil, drinking water, blood, urine and duplicate-diet food collection were incorporated into the various sampling schemes. Specific analyses associated with personal exposures or biomarker levels of such pollutants as lead, chlorpyrifos, and copper among others associated with NHEXAS-Maryland have been reported (Egeghy et al. 2005; MacIntosh et al. 1999; MacIntosh et al. 2001; MacIntosh et al. 2000; Pang et al. 2002; Pang et al. 2001; Ryan et al. 2000; Ryan et al. 2001). Echols et al., (Echols et al. 1999) have published on the time activities and demographics of this participant population.

One of the primary goals of this overall effort was to document the status and trends of human exposures to pollutants of potential health concern. One pollutant class of interest was the polycyclic aromatic hydrocarbons (PAHs). Certain PAHs have been identified as known or suspected human carcinogens (e.g, benzo(a)pyrene) and are known to have multiple environmental sources (IARC 1983; Luch 2005). The IARC report describes their sources ranging from environmental tobacco smoke (ETS), automotive exhaust, coke oven emissions, and other combustion-related processes**.** Personal exposure concentrations linked to such sources have been reported (Binkova et al. 1995; Watts et al. 1994; Williams et al. 1997; Williams et al. 1999). While PAHs are common in the ambient environment, limited historical information has been available concerning non-occupational PAH concentrations and the variability of potential human exposures to this pollutant class.

Some of the objectives of the NHEXAS-Maryland PAH Pilot Study (hereby referred to as the "study") were to:

- quantify individual personal exposures to PAHs and determine the variability of these exposures from a repeated measures (longitudinal) data collection scheme,
- examine the inter-and intrapersonal variability in the relationship between personal PAH exposures based upon exposure factors (e.g, geographical setting), and
- evaluate the methodologies used to collect field samples and perform laboratory analysis.

Particulate matter air samples collected during the study were to be analyzed for a number of PAH species and comparisons drawn between various sampling scenarios (settings). This paper reports a summary of the environmental findings.

Methods

Study design

Details concerning the overall NHEXAS-Maryland study (MacIntosh et al. 2001; MacIntosh et al. 2000; Ryan et al. 2001) have been reported. This design employed a random sample collection protocol with a repeated-measure approach. Retention of the participants over a one-year period was attempted. Rural, suburban, and urban census tract stratification of the study population was a primary feature. Census tracts included in the recruiting were then secondarily stratified by being either predominantly minority (e.g., African-American) or predominantly non-minority (Caucasian). Recruitment was performed in four Maryland counties and the city of Baltimore. Only one individual per household was enrolled in the study population. A depiction of the study area is shown in Figure 1**.** In brief, as of the 2000 Census, the City of Baltimore represented a mixture of both urban and suburban locations having a predominantly African-American population. Both Baltimore County and the Anne Arundel locations were characterized as being a mixture of urban and suburban neighborhoods and being predominantly Caucasian in population. Queen Anne's and Talbot counties were rural in nature and also predominantly Caucasian in population distribution. Personal environmental monitoring during six monitoring sessions (Cycles) for select PAHs took place from September 1995 to September 1996. These were defined as Cycle 1 (Sept 21-Dec 20, 1995), Cycle 2 (Jan 15-Feb 25, 1996), Cycle 3 (Feb 26- April 20, 1996), Cycle 4 (April 22-June 14, 1996), Cycle 5 (Jun 27-Jul 27, 1996)

and Cycle 6 (Jul 29-Sep 18 th, 1996). Pang et al. (Pang et al. 2001) have described the individual sample collection periods.

Echols et al., (Echols et al. 1999) have reported a complete description of the participant demographics. A total of 79 participants were enrolled, of which 62% were female. Age of participants ranged from 13 to 84 years with a mean of 45. The majority of enrollees were between the ages of 25 and 64 (81%). Nearly 80% of the study population was Caucasian. African-Americans represented only 19% of the participant distribution. It should be noted that the statistics immediately above on minority/non-minority status differed significantly from census estimations where African-Americans were the overall dominant overall population group. This is because enrollment was not associated with a census-based (racial) population requirement. Potential participants living in a given study area were contacted randomly (based on their address) without regards to race. Households from suburban census tracts were the most highly represented (55.7%). Only 16.5% of the population lived in rural areas. The distribution of the analyzed samples from the rural, suburban and urban participants was 21, 52, and 27%, respectively. High school and college graduates made up 46.8 and 43.0%, respectively, of the overall study population. Nearly 88% of the participants had annual household incomes greater than $20,000 ($15,500 being the recognized U.S. household poverty level at that time).

Personal air monitoring was performed using 4 liter per minute battery-powered samplers equipped with PM_{10} personal environmental monitors (PEMs- MSP Inc, Minneapolis, MN). Numerous uses of these personal monitors and their subsequent gravimetric analysis have been reported (Rodes et al. 2001; Williams et al. 2003; Williams et al. 2000). Personal monitoring for PAHs using approaches similar to those employed here have been reported (Binkova et al. 1995; Watts et al. 1994; Williams et al. 1997; Williams et al. 1999). Environmental PAH methods employed for another NHEXAS-related study, the Minnesota Children's Pesticide Exposure Study (MNCPES), have been reported (Clayton et al. 2003; Lobscheid and McKone 2004). Participants were requested to wear monitors positioned in their breathing zones for a 24-hr period which would equate to an air sample of ~ 5.8 m^3. They were asked to wear the monitor continuously except while sleeping, changing of clothes or bathing. During such times they were asked to maintain the monitor in close proximity (e.g., on a bedroom night stand).

Laboratory analysis

While more than 400 possible personal monitoring attempts could have occurred over the lifetime of the study based upon enrollment, a smaller number was actually performed. This was the result of some participants choosing not to consent to personal monitoring while still participating in other aspects of the study. In addition, a small percentage (< 5 % of the collected personal air samples were voided due to quality assurance reviews (e.g., pump malfunction, run duration). Finally, a decision was made to analyze only the personal air samples for participants that had coincidental (matched) collections of blood, urine, soil and other select NHEXAS specimens to leverage study resources. This ultimately resulted in a total of 233 personal air samples available for PAH analysis. These filter samples were received by the US EPA in late 1999 and then maintained at -30^{o}C in the dark while awaiting laboratory processing which was completed in 2000. Impact of storage on PAH degradation of particulate matter filter samples in like manner to that described above have reported losses typically well under 12% for periods as long as 12 years (Ambe and Mukai 1997; Cimberle et al. 1983) for benzo(a)pyrene. Even so, it is acknowledged that some minor PAH degradation might have occurred in the current samples between collection and analysis dates.

Eight PAHs were selected for recovery and analysis (Table 1). These PAHs are recognized as known or suspected human carcinogens (IARC 1983). PAH recovery from each filter was performed by three sequential 10 ml dichloromethane sonication extractions in borosilicate 15-mL vials equipped with Teflon lined caps. The total filter extract was reduced in volume to 5 mL under a stream of purified nitrogen gas. Each extract was then filtered (0.45 μm) for extraneous particles and then placed under a gentle stream of nitrogen gas. Solvent reduction was continued just to the point of dryness at which reconstitution was performed using 0.5 mL of chromatography-grade acetonitrile (Burdick and Jackson, Muskegon, WI) to facilitate chemical analysis.

High pressure liquid chromatography with fluorescence detection (HPLC-FL) was conducted using a 20 μl volume of each reconstitute injected onto a 5 μm Supelcosil LC-PAH column (4.6 mm x 25 cm – Supelco, Bellefonte, PA) maintained @40^{o}C. Descriptions of this approach have been previously reported (Watts et al. 1994; Williams et al. 1997). A solvent delivery system (Waters 510, Waters Corp, Milford, MA) along with a Hewlett-Packard LS-40 (Hewlett-Packard, Santa Clara, CA) or Waters 470 programmable fluorescence detector was employed for analyte separation and detection. Isocratic elution was performed using helium degassed 10:90 (v/v) H_2O/ACN at 1.5 mL/min. Each injection was performed in duplicate, with the means used in analyte concentration

187 determination. Precision error of repeated injections was very low. As an example, precision error was routinely ≤
188 10 % for all PAHs when injection concentrations were ≥ 0.01ng/μL. Analytical runs of field samples and blanks
189 (method and solvent) were performed with calibration and audit samples interspersed throughout. Linear calibration
190 curves made up of a minimum of 4 (0.07 to 0.58 ng/μL) or 6 (0.0005 to 0.50) points were employed and repeated
191 three times over a normal 24-hr analysis run to establish the resulting algorithm for processing unknowns. Excellent
192 linearity was established with the lowest R^2 value reported for any single PAH for any single calibration event being
193 ≥ 0.985. The vast majority of calibrations resulted in coefficients ≥ 0.999 being established for all PAHs.
194
195 ***Fluorescence detection***
196 A time-programmable, wavelength-variable fluorescence detector was used to monitor for the PAHs. The
197 strengths and limitations of this approach have been reported (Watts et al. 1994; Williams et al. 1994; Williams et al.
198 1997; Williams et al. 1999). Table 1 presents the excitation and emission wavelengths chosen to optimize individual
199 PAH detection and specificity. The PAHs ranged from the four benzene-ringed benzo(a)anthracene to the much
200 larger indeno(1,2,3-cd)pyrene possessing six aromatic rings. Typical detection statistics are reported in Table 1.
201 The instrument limit of detection (ILOD) ranged from 0.1 to 6.8 pg/μL dependent upon each PAH. This was the
202 ability of the instrument itself to detect the PAHs of interest at a minimum of 2 times the signal/noise ratio. The
203 environmental limit of detection (ELOD), representing the average environmental concentration needed during a
204 24-hr sample collection to allow detection following normal sample processing, was typically on the order of 0.01-
205 0.08 ng/m^3. This value was used as a relative benchmark of overall analytical sensitivity but not employed to
206 actually censor data. Both the ILOD and ELOD were determined to vary on a day by day basis as a function of
207 fluorescence lamp intensity and solvent quenching effects.
208
209 ***Quality assurance***
210 A total of 10 filter sets spiked at three levels of concentration (0.1, 1.0, 10 ng/filter) were prepared and used
211 to determine analyte recovery. One set was analyzed during each analysis run. Over thirty method blanks were
212 incorporated into the analyses. A National Institute of Standards and Technology reference PAH mix (NIST-1647c)
213 was used to audit the analytical system for calibration performance. Values in Table 2 provide a description of the
214 mean data quality indicators concerning filter blanks, audit sampless, recovered filter spikes and NIST comparisons.

Filter blanks (>10 % of the analysis population) routinely had less than 0.3 pg/µL of an individual PAH present.. This was equivalent to 150 pg/filter or a corresponding environmental PAH concentration of approximately 0.025 ng/m^3 for a nominal 24-hr sample. Audit samples interspersed throughout the HPLC runs were observed to yield agreement ranging from 99 to 103% versus the calibration samples. Comparison of the NIST 1647c samples challenged against our calibration curve indicated agreement errors ≤ 9.3%. Filter spikes yielded mean recoveries ranging from 78% (benzo(a)pyrene) to 94% (benz(b)fluoranthene). No correction of field data was performed as a result of the laboratory control findings.

Statistical analysis

SAS version 9.2 (Statistical Analysis System, Cary, NC) was used in the data analysis. PAH pollutant concentrations detected above their ILOD were used without change. Non-detected PAHs (all those below the ILOD) were assigned a value of 0.0 ng/m^3 to allow for their incorporation into analyses such as those involving univariate data descriptions. The percentage of the sample population having an individual PAH concentration above the respective ELOD was calculated by stratum as a general indication of the environmental concentrations observed during the field monitoring effort and the utility of the overall analytical approach. Values established were the simple ratios of the number of samples having a PAH with a concentration above the ELOD versus the total sample population (N=233), treated as a percentage.

Because the overall sample population distribution varied greatly by monitoring location (stratum), additional data treatment was required. A sample population-weighted least squares mean approach was employed. Least squares means were generated using a mixed model approach controlling for repeated measurements and adjusting for interactions between the repeats and the locations. Minority status was determined not to be a significant determinant in the development of the model and was also found to be confounded by location. It should be recognized that the NHEXAS population did not represent the minority census distributions of the study areas and thus any findings concerning minority status could be misrepresentative and therefore are not reported further. Components of the final model included the monitoring session (Cycle), participant identifier within a given stratum, stratum, and a Cycle/stratum interaction term. A covariance test was conducted on the resulting model. Box plots defined by individual PAH and stratum were obtained as well as Spearman correlations between the various PAHs. The boxes in these plots represent the interquartile range and the line is the median value. The

whiskers are the minimum and maximum values within a confidence interval based on a 1.5 times the interquartile range and values outside of the confidence interval are marked as asterisks. The weighted approach was used in the development of cumulative PAH exposure distribution plot estimates for individual PAH and select groupings to establish the percentage of the sample populations having potential PAH exposures above certain reported levels of health concern.

Results and discussion

A typical representation of HPLC response to a blank, field sample and calibration sample is shown in Figure 2. Both benzo(ghi)perylene and indeno(cd)pyrene often had the poorest peak resolution in the isocratic scheme employed. Summary personal PAH exposures across all strata are presented in Table 3. The majority of these concentrations were determined to be ≤ 0.10 ng/m^3. Since environmental concentration of dibenzo(a,h)anthracene were low, assignment of 0.0 ng/m^3 for those values below the ELOD resulted in calculated mean values for this PAH falling below the ELOD. It was not unusual for 30% or more of the overall sampling population to have a given PAH concentration below the detection limit (Table 4), especially for samples associated with the rural stratum.

The magnitude and variability of individual PAH exposures by strata are presented in Figure 3. The box and whisker plots depict the interquartile range with medians for each PAH represented. Even though the interquartile range was often relatively small (e.g., benzo(a)pyrene concentrations between 0.0 and ~ 0.5 ng/m^3 for suburban subpopulations), personal exposure events with concentrations well above the 100th percentile were often observed. These possibly reflect the impact of human activity patterns and unknown environmental exposure factors on personal PAH exposure for one or more participants. The suburban and urban exposures typically exceeded those observed for rural participants.

Figure 4 provides cumulative distribution function plots (cumulative percent) of representative PAHs and also the summed totals across the various strata. The plots reveal that there is little difference between personal benzo(a)pyrene exposures for any of the stratum at the 50th percentile. It is not until approximately the 90th percentile that the urban population approaches exposure values of 1 ng/m^3 for this PAH, a human health guideline value first established in Europe (WHO 1987). Further comparisons presented in Table 5 comparing stratum-weighted least squares mean estimates, reveal that only the rural and urban strata were close to being statistically

different in mean total PAH concentrations ($p = 0.07$). Participants from Cycle #2 (winter 1996) had much higher exposures to total carcinogenic PAHs in comparison to all other Cycles (Figure 5). It should be noted that personal monitoring was not conducted for the first four weeks of this Cycle due to field support issues. In addition, a heavy snowfall (~ 30 inches) in the area disrupted the normal manner in which participants were sampled. Both of these events severely impacted the total number of participants involved in the monitoring for this time period and therefore likely affected the resulting weighted statistics in comparison to the other Cycles.

Spearman correlations between the various PAHs from urban stratum monitoring are presented in Table 6 as an example of PAH relationship characteristics. As a whole, correlations (R) between most of the PAHs generally exceeded 0.60. Benzo(a)pyrene and indeno(cd) pyrene were often found to be highly correlated with the other PAHs. Dibenzo(a,h) anthracene comparisons with the other PAHs generally resulted in very poor correlation ($R < 0.2$), probably impacted by the large number of samples observed to have environmental concentrations below the detection limit for this PAH.

Even though findings from this study have their limitations, this pilot effort was able to obtain probability-based exposure data involving an environmental pollutant of high interest (PAH). Urban participants would appear to have had higher personal PAH exposures than participants living in rural areas that might have been even further resolved if a larger sampling population had been involved. Suburban and urban participants were observed to have similar exposures. Source apportionment has not been performed on this sample population and therefore no suggestion as to the PAH sources impacting the various monitoring strata is possible. Personal exposure to IARC-listed or suspected carcinogenic air pollutants were often observed here at concentrations well below 1 ng/m^3. The US EPA has not established national air quality standards or safe reference concentrations for any of the PAHs discussed. However, the World Health Organization (WHO 1987) first suggested an ambient air standard of 1 ng/m^3 for benzo(a)pyrene. The European Union has issued a directive to its collective members substantiating this same annual guideline (European Commission 2011). If applied to the exposure findings from the current study, less than 10% of the NHEXAS-Maryland participants across all strata would be expected to meet or exceed this standard. Even so, the cited standard is ambient-based and the subpopulations studied here would surely have had unknown PAH exposure sources from non-ambient sources (e.g., environmental tobacco smoke, cooking aerosols, mobile sources). Such a consideration suggests that ambient levels were probably even less of an impact than the current distribution functions would indicate.

299 . Studies conducted in the New York City area associated with the Columbia Center for Children's
300 Environmental Health (CCCEH) have reported on a variety of PAH exposure issues involving a number of cohorts
301 (Miller et al. 2004; Narvaez et al. 2008; Rosa et al. 2011). Although the reported CCCEH studies lacked a true rural
302 component, a number involved personal exposure monitoring and therefore provide an opportunity for comparison
303 with the findings from the current study. Narvaez et al., (2008) reported total personal PAH exposures involving a
304 cohort of pregnant minorities during 1998 through 2006. They summed the same PAHs as those we report. They
305 observed annual mean averages ranging from approximately 16 ng/m^3 (1998) to 2.5 ng/m^3 (2006) with a pronounced
306 decrease in concentration in the latter years. Our mean personal concentration of 0.7 ng/m^3 was lower than even
307 their 2006 data year but this included our values associated with the rural locations. Even when we examined data
308 from only our urban and suburban locations, potentially more spatially comparable to those in the CCCEH studies,
309 our maximum total PAH concentration from any single personal monitoring event never exceeded 13.2 ng/m^3.
310 Miller et al., (2004) determined that environmental tobacco smoke (ETS) exposures did not impact total personal
311 carcinogenic PAH exposures which averaged 3.6 ng/m^3 from a cohort of more than 300 women monitored during
312 their third trimester of pregnancy. They reported ETS exposures via questionnaire response. Questions pertaining to
313 ETS exposures associated with our pilot study were collected but have yet to be incorporated into any analysis.
314 There has not been a systematic examination of PAH concentrations in the US. Wilson and Chuang (1991)
315 conducted an eight home pilot study involving indoor air monitoring. A larger cross-sectional study involving
316 indoor and outdoor PAH concentrations associated with 125 California homes have been described (CARB 1994).
317 They reported night time mean benzo(a)pyrene concentrations of 0.77 and 0.44 ng/m^3, respectively. In addition,
318 Morgan et al., (2004) performed indoor and outdoor PAH air monitoring in a recent study involving a total of 257
319 North Carolina and Ohio preschool children. They reported median benzo(a)pyrene indoor (0.08 ng/m^3) and
320 outdoor (0.09 ng/m^3) concentrations very similar to the mean personal value (0.10 ng/m^3) we observed in the
321 Maryland cohorts. The NHEXAS-related MNCPES analyses revealed median personal and outdoor benzo(a)pyrene
322 exposures of 0.07 and 0.01 ng/m^3, respectively.
323 A number of European and Asian studies have reported much higher environmental levels than those
324 reported above or from the current study. Annual mean benzo(a)pyrene concentrations in European urban areas
325 have been reported in the 1 to 10 ng/m^3 range (WHO, 2000). A personal monitoring study performed in Krakow,
326 Poland (Edwards et al. 2010; Jedrychowski et al. 2003) has reported personal benzo(a)pyrene concentrations of 12

ng/m^3. Additional work by this group on a cohort involving 344 pregnant, non-smoking women reported mean total carcinogenic PAH concentrations of ~39 ng/m^3. This was a value more than 50 fold higher than that we observed. Coal and refuse burning are believed to have been the primary combustion sources associated with these exposures. Traffic police officers in Beijing, China were exposed to winter-time estimates of 82.1 ng/m^3 of benzo(a)pyrene (Liu et al. 2007). Police officers in Florence, Italy working in high density traffic areas, were estimated to have benzo(a)pyrene exposures ranging from 4.1 to 1.8 ng/m^3 depending upon observed traffic density (Perico et al. 2001).

Our pilot study represented an attempt to investigate personal PAH exposures in a randomized cohort. The sampling scheme allowed for a general comparison of personal exposures between rural, urban and suburban scenarios. Even so, these exposure estimates should not be considered fully transferrable to other localities due to the limited geographical area of the study design. The overall sample size was also limited and many PAHs were often determined to be present at concentrations below the analytical detection limit. Olson et al., (2008) have suggested that environmental concentrations of PAHs in urban areas of the U.S. are often so low that use of low flow rate personal monitoring might result in many measurements being below analytical detection limits. However, obtrusiveness and additional participant burden by use of larger monitors must be recognized as severe study handicaps in attempts to reduce measurement uncertainty in future efforts. Accurate measurements are needed if PAHs are to be used as organic markers in efforts to determine particulate matter sources. The methodology employed here (HPLC-FL) provided a relatively low cost means of obtaining PAH data with a high degree of daily laboratory output but might not have been able to provide the degree of specificity/detectability needed for source apportionment requirements. More expensive, but more informative gas chromatograph/mass spectroscopy (GC/MS) techniques have recently been used to overcome some of these considerations (Morgan et al. 2004; Olson et al. 2008). Even using such techniques it would appear that it might be difficult to establish personal PAH exposure distributions accurately for some settings.

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Table 1. Excitation/emission wavelengths and detection characteristics

PAH	Excitation (nm)	Emission (nm)	Retention time (min)	ILOD[a] (pg/µl)	ELOD[b] (ng/m^3)
Benzo(a)anthracene	265	380	5.1	0.1-1.0	0.01-0.15
Chrysene	265	380	5.7	0.1-0.8	0.01-0.07
Benz(b)fluoranthene	290	430	7.4	0.3-5.0	0.03-0.40
Benz(k)fluoranthene	290	430	8.6	0.2-1.7	0.01-0.15
Benzo(a)pyrene	290	430	10.4	0.2-1.3	0.02-0.11
Dibenzo(a,h,)anthracene	298	440	12.4	0.4-6.8	0.08-0.59
Benzo(g,h,i)perylene	302	500	15.0	0.1-2.7	0.01-0.23
Indeno(cd)pyrene	302	500	16.1	0.3-3.5	0.01-0.30

[a]instrument limit of detection. Subject to change daily as function of fluorescence lamp intensity and quenching factors

[b]environmental limit of detection. Subject to change daily as a function of fluorescence lamp intensity and quenching factors

Table 2. Mean quality assurance summary

PAH	Filter blank pg/µl	%QC sample[a] calibration agreement	% spike[b] recovery (± STD)	% NIST1647c[c] agreement error
Benzo(a)anthracene	0.2	99	87 ±12.8	8.7
Chrysene	0.1	102	85 ±12.1	8.6
Benz(b)fluoranthene	0.2	102	94 ±17.9	5.1
Benz(k)fluoranthene	0.1	102	81 ±11.1	6.0
Benzo(a)pyrene	0.1	101	78 ± 7.7	9.3
Dibenzo(a,h,)anthracene	0.2	102	85 ±11.3	8.4
Benzo(g,h,i)perylene	0.1	103	83 ± 7.4	2.5
Indeno(cd)pyrene	0.1	102	83 ±10.1	5.0

[a]Direct comparison of a secondary QC sample analyzed during the run sequence to assess the validation of the daily calibration curve

[b]Represents recovery of spiked solutions of a known PAH coated upon 37 mm Teflon filters, allowed to dry and then recovered by dichloromethane via sonication. Values represent mean % recoveries associated with all of the combined 0.1, 1.0, and 10 ng filter spikes recoveries combined and their overall standard deviation.

[c]Comparison of NIST-prepared PAH standards versus the in-house prepared calibration samples.

Table 3. Observed PAH concentrations across all strata and participants

PAH	Mean[a] ng/m^3	STD ng/m^3	Minimum[b] ng/m^3	Maximum[b] ng/m^3
Benzo(a)anthracene	0.17	0.59	0.01	4.3
Chrysene	0.08	0.30	0.01	2.8
Benz(b)fluoranthene	0.09	0.21	0.03	1.3
Benz(k)fluoranthene	0.04	0.08	0.01	0.5
Benzo(a)pyrene	0.10	0.25	0.02	1.6
Dibenzo(a,h,)anthracene	0.01	0.03	0.08	0.4
Benzo(g,h,i)perylene	0.15	0.64	0.01	7.0
Indeno(cd)pyrene	0.10	0.28	0.01	21.0
Mean total carcinogenic	0.73	1.92	0.18	13.2

[a]Estimates established from the entire subject population (N= 233). Samples below the detection limit were valued at 0.0 ng/m^3 in the calculations.

[b]Minima and maxima values represent the lowest or highest daily concentration observed for any sample from all participants and strata

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Table 4. Percentage of samples with PAH concentrations above the detection limit

PAH	Total %	Rural %	Suburban %	Urban %
Benzo(a)anthracene	67.4	59.2	72.7	63.5
Chrysene	67.4	49.0	73.5	69.8
Benz(b)fluoranthene	65.7	47.0	71.1	69.8
Benz(k)fluoranthene	71.2	53.1	76.9	74.6
Benzo(a)pyrene	70.8	42.9	76.9	80.9
Dibenzo(a,h,)anthracene	24.5	14.3	33.1	15.9
Benzo(g,h,i)perylene	67.0	59.2	69.4	68.3
Indeno(cd)pyrene	59.2	51.0	58.7	66.7

Detection limit (ELOD) defined in Table 1. N= 233 total samples across all stratum.

Table 5. Testing for differences of total carcinogenic PAH by stratum

Variable 1	Variable 2	Difference estimate	SE	DF	t-value	p-value
rural	suburban	-0.66	0.53	149	-1.26	0.21
rural	urban	-0.99	0.55	149	-1.82	0.07
suburban	urban	-0.32	0.37	149	-0.86	0.39

The difference estimate is the least squares mean concentration difference (ng/m^3) between variable 1 and variable 2.

539 Table 6. Spearman PAH correlations across the urban stratum

	B(a)A	Chrysene	B(b)F	B(k)F	B(a)P	Db(ah)A	B(ghi)P	I(cd)P
B(a)A	1	0.74	0.62	0.55	0.59	0.02	0.47	0.63
Chrysene		1	0.81	0.72	0.77	0.02	0.55	0.76
B(b)F			1	0.87	0.67	0.07	0.69	0.79
B(k)F				1	0.78	0.08	0.71	0.81
B(a)P					1	-0.05	0.52	0.75
Db(ah)A						1	0.17	0.13
B(ghi)P							1	0.66
I(cd)P								1

540 Benzo(a)A= benz(a)anthrance, B(b)F= benzo(b)fluoranthene, B(k)F= benzo(k)fluoranthene, B(a)P = benzo(a)pyrene,
541 Db(ah)A= dibenzo(ah)anthracene, B(ghi)P=benzo(ghi)perylene, I(cd)P=indeno(cd)pyrene.
542

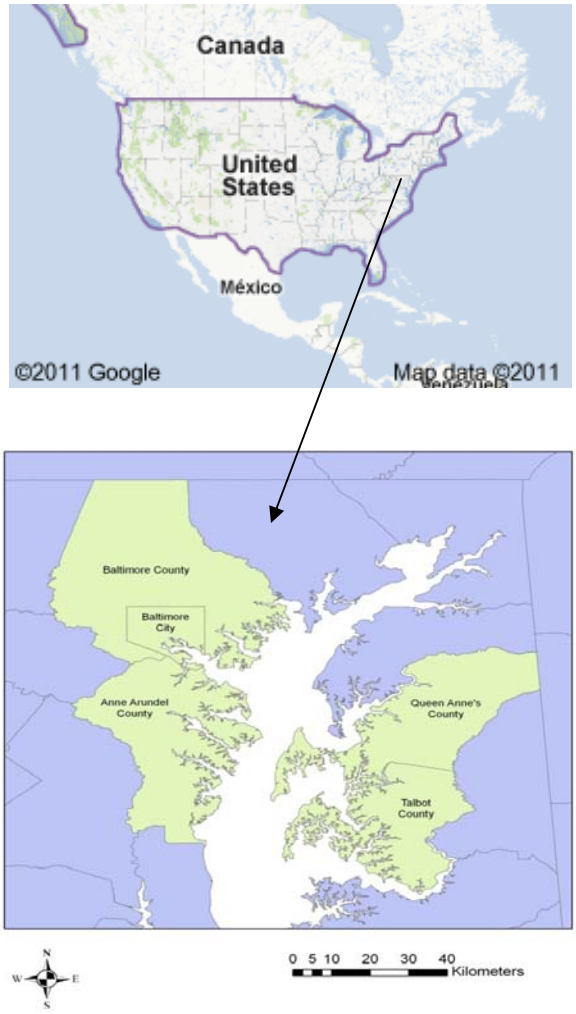

Figure 1. NHEXAS Maryland study areas.

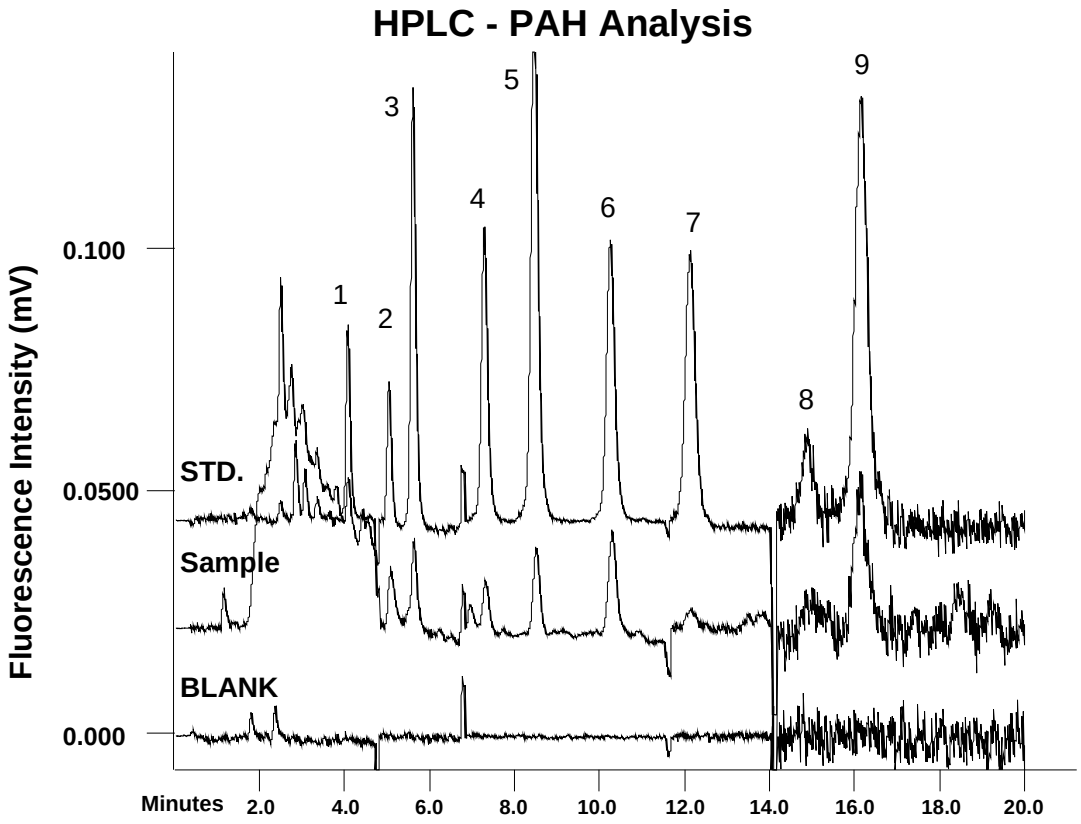

Figure 2. Chromatographic examples of a calibration sample, an unknown, and a method blank.

1=pyrene, 2=benz(a)anthracene, 3=chrysene, 4=benz(b)fluoranthene, 5=benz(k)fluoranthene, 6=benzo(a)pyrene, 7=dibenz(ah)anthracene, 8=benzo(ghi)perylene, 9=indeno(cd)pyrene.

A change in plotting attenuation at the 14.0 minute mark is responsible for the increased signal noise depicted in the plots. Pyrene was a component of the calibration sample but not incorporated into the results presented in this summary.

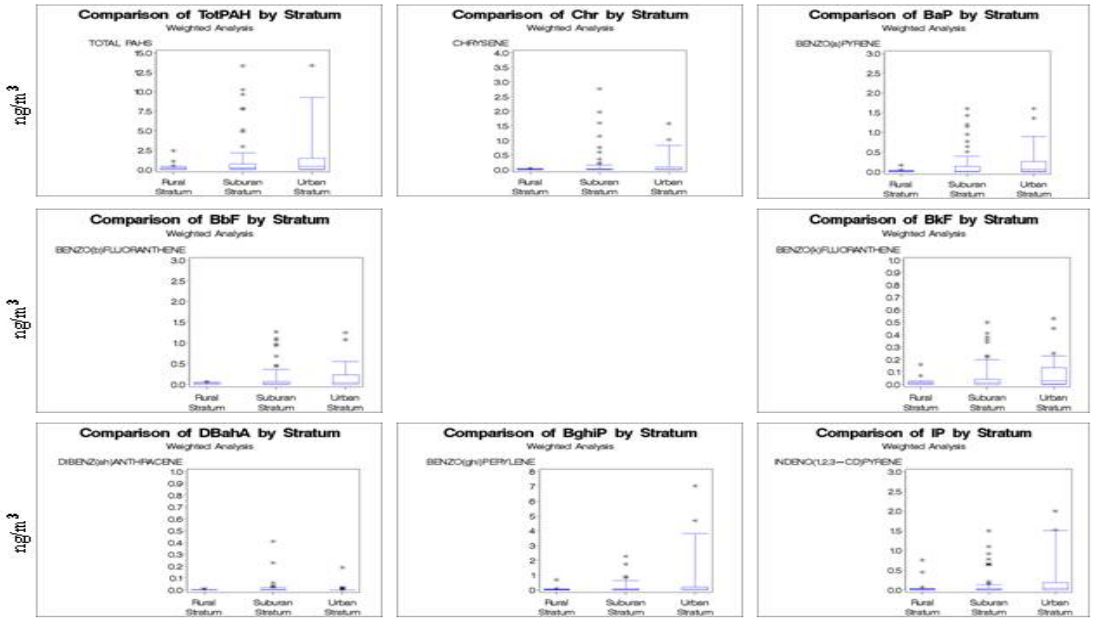

Figure 3. Comparison of select PAH exposures (ng/m^3) by stratum. Rural, suburban and urban sampling locations indicate the various personal monitoring subpopulations being compared. Concentrations depicted are in units of ng/m^3.

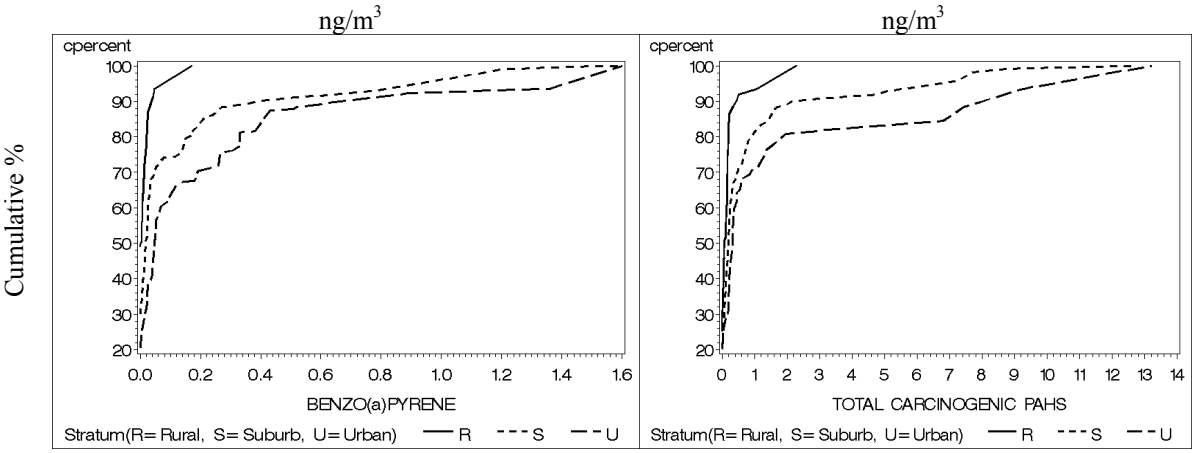

Figure 4. PAH exposure distributions across the various stratum as a function of cumulative percentage. The Y-axis depicts the population distribution percentage with the X-axis indicating the PAH concentration in units of ng/m^3.

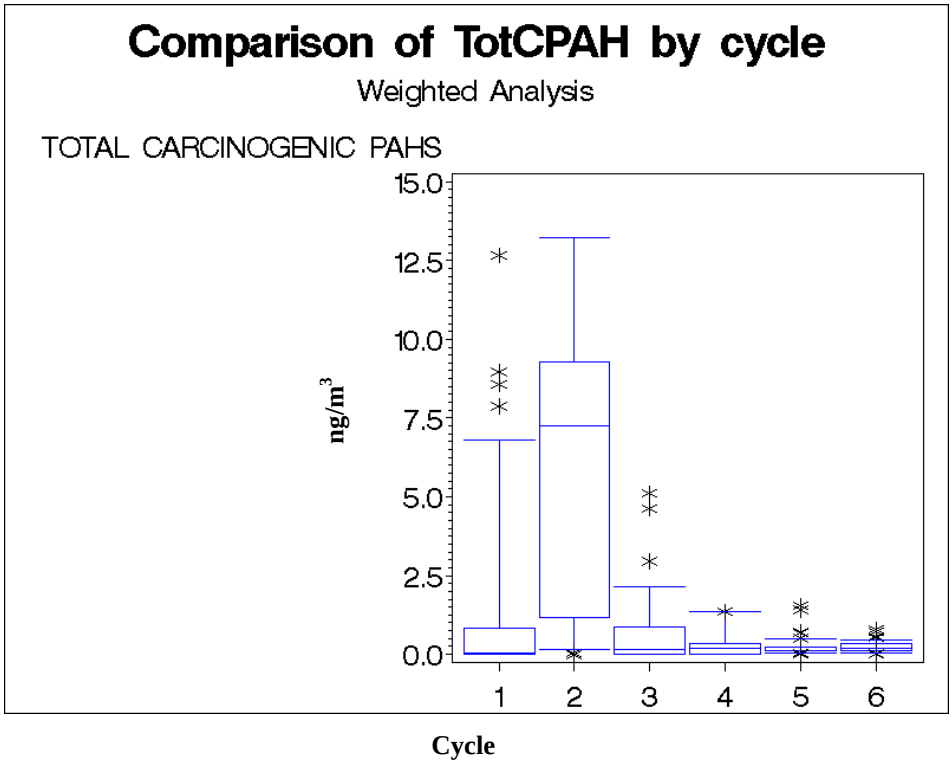

Figure 5. Distribution of total carcinogenic PAH (ng/m^3) by Cycle. The winter 1996 session (Cycle #2) was significantly impacted by a cold weather event.