

THE U.S. EPA LAKE MICHIGAN URBAN AIR TOXICS STUDY: AMBIENT AIR MONITORING AND ANALYSIS FOR POLYCYCLIC AROMATIC HYDROCARBONS

AA13

Jane C. Chuang
Dave B. Davis
Michael Kuhlman
Battelle
Columbus, Ohio

Gerald J. Keeler
University of Michigan
Ann Arbor, Michigan

Nancy K. Wilson
Gary F. Evans
U.S. EPA, Atmospheric Research and
Exposure Assessment Laboratory
Research Triangle Park, North Carolina

ABSTRACT

The U.S. EPA Lake Michigan Urban Air Toxics Study (LMUATS) was conducted at four sampling sites in and around Lake Michigan in July and August 1991. This paper addresses the portion of the study that dealt with ambient air monitoring and analysis for polycyclic aromatic hydrocarbons (PAH). The PS-1 medium volume sampler was equipped with a quartz fiber filter in series with a XAD-2 cartridge to collect total PAH. Ambient air was sampled over a 12-h period at a nominal flow rate of 4 cfm. Parallel sampling was conducted at one site to determine the overall precision of the sampling and analytical methods used in this study. The corresponding filter and XAD-2 samples were combined and extracted with dichloromethane (DCM). The DCM sample extracts were analyzed by gas chromatography/mass spectrometry (GC/MS) to determine target PAH. The validation of the sampling and analytical methods for ambient monitoring of PAH, quality control/quality assurance procedures, and ambient PAH concentration profiles from the LMUATS are discussed.

INTRODUCTION

Section 112(m) of the 1990 Clean Air Act Amendment (CAAA) requires a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants to the Great Lakes, as well as to other large lakes and coastal waters. It is suggested that a significant portion of the toxic contaminants found in the Great Lakes are deposited from the atmosphere. However, there are insufficient data, at present, to estimate reliably the magnitude and importance of the input to the lakes from atmospheric deposition of most air toxics.¹ In addition, the selection of monitoring sites (e.g., inland versus shoreline versus open lake siting) is critical to this assessment. It is also unknown how much of the air toxics in the air over the lakes originates from sources near (within 20 km) the lake shoreline versus sources farther upwind. Therefore, studies are needed to determine the dynamics of air toxics transport over and deposition into the Great Lakes.

As part of the initial phase of the studies, the U.S. EPA Lake Michigan Urban Air Toxics Study (LMUATS) was conducted in the summer of 1990 to monitor various chemical classes of air toxics in and around the Lake Michigan area. The four LMUATS sampling sites included three sites on land: (1) downtown Chicago, at the Illinois Institute of Technology (IIT), representing input from an urban complex, (2) Kankakee airport, a site upwind of IIT, and (3) South Haven, a site along the eastern side of Lake Michigan. The fourth sampling site was on the research vessel RV Laurentian, representing over-the-water input; the Laurentian was used for monitoring air toxics along the western shore of Lake Michigan at least 10 mi offshore from Chicago. The main objective of the LMUATS was to collect representative air samples and provide accurate measurements of air toxics at these four sampling sites.

In the LMUATS, polycyclic aromatic hydrocarbons (PAH) are one of the compound classes of air toxics monitored at the four sampling sites. Many PAH found in ambient air are potent carcinogens, mutagens, or both.²⁻⁴ We have conducted several studies to develop and evaluate sampling and analytical methods for both indoor and outdoor monitoring of PAH.⁵⁻⁸ This methodology has been successfully employed in several small-scale field studies⁹⁻¹¹ and was also utilized in the LMUATS.

In this paper, we summarize the validation of sampling and analytical methods for ambient air monitoring of PAH, the utilization of quality control/quality assurance procedures for the LMUATS, and the ambient PAH concentration profiles from the four sampling sites of the LMUATS.

EXPERIMENTAL SECTION

Sampling Procedures

The PS-1 samplers (General Metal Works, Cleves, Ohio) were located at each designated sampling site. The sampling module consisted of a quartz fiber filter (104 mm QAST, Pallflex, Putnam, CT) and XAD-2 (Supelco, Bellefonte, PA) trap to collect both particle-bound and vapor-phase PAH. The cleaning and preparation procedures for quartz fiber filters and XAD-2 traps are detailed elsewhere.⁶ In the breakthrough study, the PS-1 sampler was equipped with a quartz fiber filter and two XAD-2 traps in series. The first XAD-2 trap was spiked with 2 μg of each naphthalene- d_8 , phenanthrene- d_{10} , pyrene- d_{10} , benz[a]anthracene- d_{12} , chrysene- d_{12} , benzo[e]pyrene- d_{12} , and benzo[a]pyrene- d_{12} prior to sampling. Then air was sampled for 24 hours at a nominal flow rate of 5 cfm at Columbus, Ohio. Two tests were conducted and the average sampling temperatures were 72°F and 94°F.

In the LMUATS, the clean filters and XAD-2 traps were prepared at Battelle and sent to each sampling site. A standard operation procedure for loading, operating, and unloading of PS-1 samplers was prepared for the field sampling team. At the beginning of the field sampling, an experienced Battelle technician went to the South Haven Site and demonstrated the proper sample handling procedure to minimize any possible field contamination and ensure the integrity of the collected samples. The PS-1 sampler equipped with quartz fiber filter in series with an XAD-2 cartridge was used to collect total PAH. Ambient air was sampled over a 12-hr period at a nominal flow rate of 4 cfm. The collected samples were stored in the dark at 0°C before they were sent back to Battelle for analysis. Sampling data sheets containing necessary sampling information (e.g., sample I.D. code) were filled out by the field operators for each set of filter and XAD-2 samples and were sent back with samples.

Analytical Procedures

The filter and XAD-2 samples from the breakthrough study were extracted separately. The corresponding filter and XAD-2 samples from LMUATS were combined and extracted with dichloromethane (DCM). The DCM extract was concentrated by Kuderna-Danish (K-D) evaporation. The concentrated DCM extract was analyzed by GC/MS in electron impact (EI) mode to determine target PAH. A Finnigan TSQ-45 GC/MS/MS operated in GC/MS mode was employed. Data acquisition and processing were controlled by an INCOS 2300 data system. The MS was operated in the selected ion monitoring (SIM) mode. Peaks monitored were the molecular ions and characteristic fragment ions of

the target analytes. The GC column was a DB5 fused silica capillary column (30 m x 0.25 mm; 0.25 μ m film thickness, Supelco). The GC temperature was held at 70°C for 2 min, and then programmed to 290°C at 8°C/min. Identification of target analytes was based on correct molecular ions, correct fragmentation ions, and their GC retention times relative to that of the corresponding internal standards (phenanthrene-d₁₀ and/or 9-phenylanthracene). Quantification of target analytes was based on the comparison of the respective integrated ion current responses of target ions to that of the corresponding internal standard, with average response factors generated from analyses of standard solutions.^{9,10}

RESULTS AND DISCUSSION

In the breakthrough study, the recoveries of the seven spiked perdeuterated PAH on the first XAD-2 trap after 24 hours ambient sampling ranged from 80% for pyrene-d₁₀ to 100% for phenanthrene-d₁₀ from both tests. We did not find any spiked perdeuterated PAH on the second XAD-2 traps from both tests. Therefore, there is no evidence of breakthrough of the spiked PAH compounds to the second trap. This finding is in agreement with our previous studies⁵ when only one XAD-2 trap was used and quantitative recoveries were obtained. We also measured the native, non-spiked, PAH in the XAD-2 traps. The ratios of the concentrations of native PAH on trap 2 to trap 1 ranged from <0.01 (pyrene) to 0.05 (phenanthrene). In most cases, the levels of native PAH found in the second traps were either similar to or even lower than those found in the field blank. These results demonstrated that the detection of the native PAH in the second trap is at background levels and is not associated with sampling or breakthrough. Based on these results, we do not anticipate any serious breakthrough problems would occur when the PS-1 sampler with a quartz fiber filter in series with one XAD-2 trap is used to collect ambient PAH.

In the LMUATS at the South Haven Site, duplicate PS-1 sampling was carried out for 3 days. The results of duplicate samples were used to determine the overall precision of sampling and analysis methods. The measured total PAH concentrations were in good agreement between the duplicate samples. The mean relative standard deviations ranged from 1.3% for dibenzo[a,h]anthracene to 14% for fluoranthene. Field blanks from each sampling site were also prepared and analyzed the same way as the samples. The results showed that some 2- to 4-ring PAH and benzofluoranthene were present in the field blanks. The amounts of PAH found in the field blanks are about two to five times higher than those in the laboratory blanks. The field blanks were handled identically to the actual samples, including loading and unloading of the PS-1 sampler, except that no air was drawn through the field blank modules. Therefore, somewhat higher PAH on the field blanks compared to the laboratory blanks is not surprising. The amounts of individual PAH found in the field blanks represent 0.3-4% of the average total amounts of these PAH in the samples from the IIT site. Because the loadings of PAH in the samples from the other three sites were lower than that from the IIT site, these background levels were about 2-30% of the average PAH loadings in the samples from these three sites. Note that the actual air volumes sampled ranged from 50 m³ to 120 m³. The total PAH loadings in the samples varied depending upon the sample volumes. As a result, the levels of phenanthrene, anthracene, fluoranthene, and pyrene found in the field blanks accounted for approximately 30% of these PAH loadings in samples with low sample volumes. The field blank levels for all other PAH accounted for lower percentages in all samples.

Table I summarizes the minimum, maximum, and average background-corrected concentrations observed at the four sampling sites for each target PAH. The most abundant PAH found in ambient air was naphthalene and the least abundant target PAH was either anthracene or cyclopenta[c,d]pyrene. Highest average ambient concentrations of all target PAH were found at the IIT site. At this site, the average concentrations ranged from 0.22 ng/m³ of cyclopenta[c,d]pyrene to 530 ng/m³ of naphthalene. Note that the average concentrations of some known carcinogens, such as benzo[a]pyrene and indeno[1,2,3-c,d]pyrene, at this urban site were approximately ten times higher than at the other three

sites. In general, ambient concentrations for other target PAH at the IIT site were also significantly higher than those at the other three sites except that naphthalene, acenaphthylene, and retene showed some regional concentration patterns. The higher PAH concentrations at IIT may arise from mobile source emissions and stationary sources nearby. Among the other three sites, the average ambient concentrations from the same sampling days were generally higher at R/V Laurentian than those at the Kankakee and South Haven sites, and average levels at South Haven were generally the lowest among these three sites. We are still in the process of data analysis incorporating the meteorological data, in an attempt to understand the atmospheric transport and deposition of PAH to Lake Michigan.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. The overall precision of the sampling and analysis methods for PAH monitoring ranged from 1.3% (dibenzo[a,h]anthracene) to 14% (fluoranthene) for duplicate PS-1 samples from parallel sampling.
2. The PAH concentration profiles revealed that the highest average ambient concentrations were observed at the IIT site for all the sampling dates.
3. There are temporal variations observed at each sampling site. Further data analysis to incorporate meteorological data is necessary in an attempt to understand the atmospheric transport and deposition of PAH to Lake Michigan.

REFERENCES

1. W.M. Strachan and S.J. Eisenreich, International Joint Commission Workshop report, Scarborough, Ontario, 1986, published May 1989.
2. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans; International Agency for Research on Cancer: Lyon, France, 1983, 32(1), pp 95-447.
3. G. Motykiewicz, J. Michalska, J. Szeliga, and B. Cimander, "Mutagenic and clastogenic activity of direct-acting components from air pollutants of Silesian industrial region," Mutat. Res. 204:208-296 (1988).
4. S. Salomaa, J. Tuominen, E. Skytta, "Genotoxicity and PAC analysis of particulate and vapor phases of environmental tobacco smoke," Mutat. Res. 204:173-183 (1988).
5. J.C. Chuang, S.W. Hannan, and N.K. Wilson, "Field comparison of polyurethane foam and XAD-2 resin for air sampling for polynuclear aromatic hydrocarbons," Envir. Sci. Technol. 21:798-804 (1987).
6. J.C. Chuang, M.W. Holdren, M.R. Kuhlman, and N.K. Wilson, "Methodology of indoor air monitoring for polynuclear aromatic hydrocarbons and related compounds," Proc. of the 1989 Int. Symp. on Measurement of Toxic and Related Air Pollutants Pub. VIP-13, Pittsburgh, PA, 1989, pp 495-501.
7. J.C. Chuang, M.R. Kuhlman, and N.K. Wilson, "Evaluation of methods for simultaneous collection and determination of nicotine and polynuclear aromatic hydrocarbons in indoor air," Envir. Sci. Technol. 25:661-665 (1990).

8. N.K. Wilson, J.C. Chuang, and M. R. Kuhlman, "Sampling Polycyclic Aromatic Hydrocarbons and Related Semivolatile Organic Compounds in Indoor air," Indoor Air, 4, in press (1991).
9. J.C. Chuang, G.A. Mack, J.R. Koetz and B.A. Petersen, Pilot study of sampling and analysis for polynuclear aromatic compounds in indoor air. N.K. Wilson, Project Officer, Report, EPA/600/4-86/036. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1985.
10. J.C. Chuang, G.A. Mack, J.W. Stockrahm, S.W. Hannan, C. Bridges, and M.R. Kuhlman, Field evaluation of sampling and analysis for organic pollutants in indoor air. N.K. Wilson, Project Officer, Report, EPA/600/4-88/028. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1988.
11. J.C. Chuang, G.A. Mack, M.R. Kuhlman, N.K. Wilson, "Polycyclic aromatic hydrocarbons and their derivatives in indoor and outdoor air in an eight-home study," Atmos. Environ. 25B(3):369-380 (1991).

Table I. Ambient concentration (ng/m³) for target compounds.

Compound	IIT ^(a)			Kankakee ^(b)			South Haven ^(b)			R/V Laurentian ^(c)		
	min	max	avg	min	max	avg	min	max	avg	min	max	avg
Naphthalene	160	840	530	7.8	960	330	11	230	64	15	420	120
Acenaphthylene	1.7	14	4.8	0.02	6.7	2.6	0.16	1.0	0.51	0.42	3.8	1.4
Acenaphthene	4.0	130	56	0.07	3.4	1.8	0.50	1.8	1.0	0.40	8.1	2.3
Fluorene	7.0	130	54	0.16	6.5	3.7	1.3	7.8	3.3	2.4	16	7.2
Phenanthrene	17	430	170	1.8	14	8.0	1.9	8.9	4.6	1.3	31	11
Anthracene	0.44	18	7.6	<0.01	1.4	0.30	0.06	0.23	0.13	<0.01	0.78	0.27
Fluorenone	1.5	23	12	0.27	2.0	1.0	0.27	2.0	0.84	0.30	2.4	1.1
Retene	0.21	0.92	0.58	0.03	0.53	0.27	0.16	0.76	0.42	0.21	1.3	0.57
Fluoranthene	3.9	110	47	0.49	7.1	2.1	0.65	3.7	1.5	0.53	8.8	3.2
Pyrene	2.4	55	24	0.20	5.2	1.1	0.27	1.8	0.75	0.23	5.2	1.6
Benz[a]anthracene	0.29	8.9	3.0	0.01	2.7	0.25	<0.01	0.57	0.12	0.01	1.2	0.26
Chrysene	0.53	13	5.2	0.03	2.8	0.33	0.03	1.3	0.28	0.03	2.5	0.62
Cyclopenta[c,d]pyrene	0.08	0.63	0.22	<0.01	0.11	0.03	<0.01	0.18	0.04	<0.01	0.52	0.09
Benzofluoranthenes	0.80	33	10	0.06	5.1	0.58	0.04	2.6	0.50	0.06	3.7	0.92
Benzof[e]pyrene	0.25	9.1	2.8	0.03	1.4	0.17	0.03	0.74	0.15	0.03	1.0	0.25
Benzof[a]pyrene	0.29	15	3.0	0.02	2.5	0.26	0.02	0.69	0.13	0.02	0.80	0.25
Indeno[1,2,3-c,d]pyrene	0.37	10	3.9	0.06	2.3	0.30	0.04	1.3	0.24	0.04	1.6	0.41
Dibenzo[a,h]anthracene	0.20	3.2	1.4	0.08	0.76	0.19	0.02	0.60	0.15	0.03	0.58	0.21
Benzof[g,h,i]perylene	0.43	8.0	3.3	0.04	1.7	0.23	0.03	1.0	0.19	0.03	1.4	0.33
Coronene	0.26	3.9	1.4	0.02	0.34	0.13	0.02	0.31	0.08	0.03	0.43	0.16

(a) Data are from 16 tests (daytime sampling) performed at 7/16/91-7/24/91, 7/29/91, 7/31/91, 8/2/91-8/8/91.

(b) Data are from 21 tests (daytime sampling) performed at 7/12/91, 7/16/91-7/24/91, 7/29/91, 7/31/91, 8/2/91-8/9/91; duplicate tests performed at 8/7/91-8/9/91.

(c) Data are from two samplings (daytime versus nighttime) of each of the following sampling dates: 7/11/91, 7/23/91, 7/24/91, 8/6/91, and 8/7/91; one daytime sampling at 7/12/91; and one nighttime sampling at 8/5/91.