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Project Summary

Review of Sampling and Analysis Methodology for Polynuclear Aromatic Compounds in Air from Mobile Sources

C. C. Chuang and B. A. Petersen

The objective of this program was to review and recommend test compounds and sampling and analysis methods for a future EPA study of polynuclear aromatic hydrocarbons (PAH) in microenvironments.

A literature survey was performed by a computer search of nine data bases: Chemical Abstracts (1967-1983), Enviroline (1971-1983), Pollution Abstracts (1970-1983), APTIC (1966-1978), NTIS (1964-1983), Engineering Index (1970-1983), BIOSIS (1970-1983), Excerpta Medica (1970-1983), and Medline (1970-1983). Additional materials representing state-of-the-art practice were also reviewed.

Review of PAH profiles in ambient air indicated that concentrations of PAH were generally higher in winter than summer and varied with climate and between sampling sites within an urban area. Levels of several PAH were found to be proportional to traffic density. Studies of the biological activity of ambient air samples showed that some PAH and their nitrated derivatives are extremely carcinogenic and mutagenic. The following compounds were determined to be the most prevalent and mutagenic or carcinogenic in ambient air and were recommended for the future EPA study: phenanthrene, pyrene, cyclopenta(c,d)pyrene, benzo(a)-pyrene, dibenz(a,h)anthracene, 1-nitropyrene, fluoranthene, benz(a)anthracene, benzo(e)pyrene, benzo(g,h,i)perylene, coronene, and 3-nitrofluoranthene.

In the review of PAH sampling methods, collection of both gaeous and particulate-bound PAH was determined to be necessary to accurately characterize health effects of PAH in ambient air. Most studies have used filters to sample particulate-bound PAH and adsorbents to collect vapor phase PAH. The major sampling problems encountered in these studies were PAH losses due to volatilization and reactivity. A modified high volume (Hi-Vol) sampler which can remove large particulates (>10 μm) and collect both particulate and vapor phase PAH was recommended for the EPA study.

Both screening and analytical methods for PAH determination were reviewed. Luminescence techniques, thin layer chromatography, ultraviolet (UV) spectroscopy, and a fluorescence spot test have been successfully applied in previous PAH screening studies and were recommended for the EPA study. For PAH analysis, combined gas chromatography/mass spectrometry (GC/MS) with either electron impact or negative ion chemical ionization was found to provide higher sensitivity and specificity than other techniques reviewed and was recommended for the future study.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Methods Development Branch is developing sampling and analytical methodology for an experimental study of human exposure to polynuclear aromatic hydrocarbons (PAHs) and PAH derivatives in ambient air within microenvironments, emphasizing those which originate from mobile sources. The form and concentration in which these PAH materials appear in microenvironments are matters of increasing interest and importance because of the increasing use of diesel powered vehicles. Of particular concern is the presence of nitrated PAHs in diesel exhaust. PAHs, especially pyrene, have been reported to react readily with nitrogen oxides to form nitrated derivatives, which are powerful direct acting mutagens. Both the PAHs and nitrogen oxides are present in combustion emissions; thus the formation of nitroaromatics in these emissions or in subsequent atmospheric reactions is possible. In recent studies conducted by Battelle Columbus Laboratories, nitrated PAHs have been identified in urban air particulate samples. Reliable sampling and analytical techniques need to be established before potential effects of PAHs and PAH derivatives on the environment can be assessed.

The specific objectives of this project were to survey and review the current knowledge of PAHs found in ambient air and to use the results of the review to develop a design and analytical methodology for an experimental study of human exposure to PAH found in ambient air within microenvironments.

The first phase of this project is a review of the available literature to determine:

- Sampling and analysis methodology for PAHs in ambient air.
- Specific PAH compounds and subclasses of the PAHs that are potentially most important because of their long-term health risk.
- PAH profiles from specific mobile sources that can be used to relate the PAH concentrations in air to those sources.

Procedure

A literature survey was performed by a computer search of nine data bases:

Data Base	Years Searched
Chemical Abstracts	1967-1983
Enviroline	1971-1983
Pollution Abstracts	1970-1983
APTIC	1966-1978
NTIS	1964-1983
Engineering Index	1970-1983
BIOSIS	1970-1983
Excerpta Medica	1970-1983
Medline	1970-1983

Because the citations obtained from Chemical Abstracts listed only the authors and topics, a manual search of the abstracts of those topics of interest was performed. To collect information that might have been missed in the computer search, a manual review was also conducted of other sources considered to represent current state-of-the-art practice, such as handbooks, manuals, and research reports published by the USEPA and recognized professional organizations. Over 1000 citations were obtained as a result of both computer and manual searching. Abstracts and citations considered most relevant to the subject area were reviewed and divided into two subsets, sampling methods and analysis methods, for further evaluation. Photocopies of some important articles were obtained to allow for a more critical review than abstracts alone provided

Results

The results of this review are presented in these three sections of the report:

- PAH profiles and biological activity from ambient air samples,
- Sampling methodology for the collection of PAHs, and
- Chemical analysis methodology.

The relative importance of PAHs that are found in ambient air and that originate from mobile sources, in terms of their long-term health risk, is addressed in the first section. Sampling, analytical and screening methodologies for the measurement of PAHs and PAH derivatives that may be suitable for a USEPA proposed experimental study are identified and evaluated in the other two sections These methodologies will be used to guide the development of an experimental pla for a human exposure study.

Conclusions and Recommendations

Several important characteristics o PAH profiles in ambient air and thei biological activity have been identified i this review. PAH concentrations in ambi ent air vary widely and in general ar higher in winter than in summer. Th concentrations of PAH compounds als vary between sampling sites within a urban area and vary with climate. How ever, levels of several PAHs such a cyclopenta(c,d)pyrene, benzo(g,h,i)pery lene, and coronene are directly propor tional to traffic density. These compound can be used, therefore, as indicators t identify the origin of mobile source con tamination within microenvironments Based on these characteristics, suc compounds should be considered fo monitoring in the EPA experimental study

Several carcinogenic and mutagen PAHs and PAH derivatives found i ambient air should also be investigated i the EPA study. Benzo(a)pyrene, benzo fluoranthenes, cyclopenta(c,d)pyrene an dibenz(a,h)anthracene are known carcino gens and therefore should be considere important compounds to be monitored i the future study.

Nitropyrenes and nitrofluoranthene are potent direct-acting mutagens an have been identified in both ambient a and automobile exhaust. Dinitropyren and hydroxynitropyrene are two materia with the highest mutagenicity known t date and have been found in mobil source emissions. While these two com pounds have not yet been found i ambient air, they will probably be found i microenvironments polluted by thes sources

Based on the available information, th following PAH compounds are potentia candidates to be monitored in the EP experimental study. phenanthrene, flu oranthene, pyrene, benz(a)anthracene cyclopenta(c,d)pyrene, benzo(e)pyrene benzo(a)pyrene, benzo(g,h,i)perylene, di benz(a,h)anthracene, coronene, 1-nitro pyrene, 3-nitrofluoranthene, benzofluo ranthenes, and indeno(1,2,3-c,d)pyrene Monitoring for the above species woul provide a general characterization of PA concentration in ambient air The meas urement of these compounds can be use to assess the PAH profile in a wide variet of microenvironments, including thos containing emissions from mobile an stationary sources. Furthermore, th

same compounds can be used to assess the PAH concentration within residential sites. For this application, it would be highly desirable to correct for PAH contributed by tobacco smoke. This correction can be made, if a correlation exists between PAH compounds and several tobacco smoke products such as quinoline and isoquinoline. If such a correlation exists, then an adjustment of the PAH concentration due to tobacco smoke can be made. Thus, by including tobacco smoke marker compounds in the list of compounds to be monitored, residences and work places can be included as microenvironments.

Sampling methods used in the EPA future study must collect representative samples of potentially harmful PAHs in ambient air and must also minimize sampling losses frequently encountered with PAHs. PAHs exist in vapor and particulate phases in the atmosphere, and most particle-bound PAHs are found in the submicron range. These small particles also produce a major percentage of the mutagenic activity of airborne particulate matter. Both the vapor and respirable particle-bound PAHs should be considered for collection, and an appropriate sampling and analysis system should be designed for the experimental study.

PAH losses in sampling are mainly due to volatilization and reactivity with NO_2, O_3, and UV radiation. Volatilization of PAHs cannot be avoided, but can be minimized by the use of back-up traps in the sampling system for collection of vapor phase material. Some reactive PAHs are believed to undergo atmospheric reaction, such as nitration, to convert PAHs to nitro PAHs. Erroneous results will occur if these reactions continue during the sampling and analysis procedure. In general, reactivity mechanisms of PAHs in the atmosphere are not well defined, and a simple solution to eliminate reactivity losses in sampling has not yet been demonstrated. A device to remove O_3 and NO_2 prior to particle sampling should be considered to minimize this degradation.

The recommended sampling device for the EPA experimental study is a modified Hi-Vol sampler. With a properly designed sampler inlet, a modified sampler can remove larger particles (>10 μm) before passage of the air sample through the collection system. The collection system should consist of a filter medium to collect particulate matter and a solid sorbent cartridge to trap vapors. Proper sampling procedures need to be designed and validated to avoid volatilization losses and reduce reactivity problems.

The procedures to be developed should consider the following parameters:

- Sampler configuration
- Sampling time
- Sampling temperature
- Sampling flow rate
- Filter face velocity
- Frequency of samples
- Quantity of sample necessary for measurement

Once ranges have been established, the operation of samplers can be optimized for the specific site selected.

Rapid screening methods for PAHs identified in this review include a sensitized spot test, UV spectroscopy, TLC with fluorescence and/or UV detection, and luminescence techniques.

Several analytical techniques such as HPLC with UV and/or fluorescence detection, GC/FID, and GC/MS have been used successfully to measure PAHs in ambient air and can be considered for the EPA experimental study. The HPLC technique is very sensitive and less expensive than the GC/MS technique. It may be possible to determine PAHs using HPLC methods without sample cleanup. If so, it may be possible to perform HPLC analyses in the field. No reference has been found describing the use of synchronous fluorescence (SF) detection with HPLC for the determination of PAHs in air. This technique offers several advantages in terms of improved sensitivity and specificity. Therefore, development and evaluation of SF detection with HPLC is also suggested for the future study. It should be noted that single column GC or HPLC analyses employing single detectors do not give unambiguous results, and confirmation of these analytical results with specific techniques such as GC/MS is necessary.

Capillary column GC/FID has been demonstrated to be useful as a routine analytical tool for PAH determinations. A sample cleanup procedure is required to remove the interference from aliphatic hydrocarbons. Few analytical methods for detection of nitro PAHs are reported in the literature. The negative ion CI GC/MS technique is very sensitive, but requires the use of expensive and sophisticated equipment. Therefore, less expensive methods such as GC and/or HPLC techniques should be developed and evaluated for the determination of nitro compounds in the future study. In the future EPA experimental study—for the most important sample types, which demonstrate unusually high mutagenicity and/or carcinogenicity—more sophisticated analytical techniques (such as EI GC/MS and NCI GC/MS) will be required to provide a more complete chemical characterization.

C. C. Chuang is with Battelle Columbus Laboratories, Columbus, OH 43201, and B. A. Petersen is with SCIEX, Inc., Worthington, OH 43085.
***Nancy K. Wilson** is the EPA Project Officer (see below).*
The complete report, entitled "Review of Sampling and Analysis Methodology for Polynuclear Aromatic Compounds in Air from Mobile Sources," (Order No. PB 85-227 759/AS; Cost: $10.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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