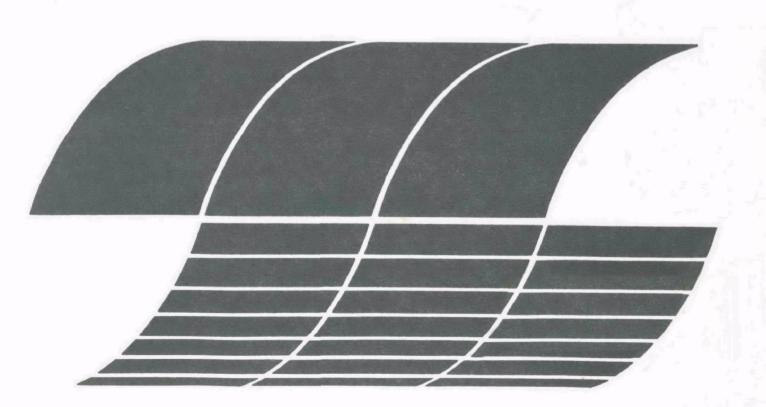


POM Source and Ambient Concentration Data: Review and Analysis

Interagency Energy/Environment R&D Program Report



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POM Source and Ambient Concentration Data: Review and Analysis

by

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Abstract

Polycyclic organic matter (POM) is an unregulated class of pollutants which is a potential candidate for regulatory action as outlined in Section 122a of the Clean Air Act Amendments of 1977.

Source and ambient concentration data for POM have been reviewed and analyzed. Based on the literature reviewed, POM data were summarized and the sampling and analytical techniques were critiqued and evaluated against state-of-the-art technology. The objective was to determine the scientific and engineering credibility of a previously established POM data base by an evaluation of the sampling and analytical techniques employed. POM is an unregulated class of pollutants which is a potential candidate for regulatory action as outlined in Section 122a of the Clean Air Act Amendments of 1977.

It can be concluded that sampling techniques contain uncertainties that limit the usefulness of these data in an environmental assessment of POM. These uncertainties include the possibility of the incomplete capture of POM during emission sampling, the chemical degradation of the collected sample during both emission source and ambient sampling, and the unproven reliability of benzo(a)pyrene as an indicator of total POM from emission sources or in ambient media.

The uncertainty may be compounded by losses during analysis. Also, since it is not feasible to quantify all the POM which may be present in an environmental sample, the number of POM reported will reflect the scope of the analytical strategy and the limitations of the analytical technique employed. Existing POM data are sufficient, however, to document its source dependence and variability, as well as to verify its occurrence in air, soil, and water.

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ABBREVIATIONS AND SYMBOLS

B(a)P - Benzo(a)pyrene B(e)P - Benzo(e)pyrene

BSO - Benzene soluble organics
ECD - Electron capture device

EVC - Equilibrium vapor concentration

FID - Flame ionization detection

GC - Gas chromatography

GC/FID - Gas chromatography/Flame ionization detection

GC/MS - Gas chromatography/mass spectrometry
HPLC - High pressure liquid chromatography

LC - Liquid chromatography

MS - Mass spectrometry

PAH - Polynuclear aromatic hydrocarbons

PNA - Polynuclear aromatics

PNAH - Polynuclear aromatic hydrocarbons

POM - Polycyclic organic matter

SASS - Source analysis sampling system

TLC - Thin layer chromatographyTSP - Total suspended particulate

UV - Ultraviolet

XEOL - X-ray excited optical luminescence

l = liter

m³ = cubic meters

ng = nanograms

μg = micrograms

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1.0 INTRODUCTION

The Clean Air Act Amendments of 1977, Section 122a, directed the Administrator of the Environmental Protection Agency (EPA) to review all available relevant information and determine whether or not emissions of "... polycyclic organic matter into the ambient air will cause, or contribute to, air pollution which may reasonably be anticipated to endanger public health." An affirmative determination would require POM to be listed under one of the following sections: Section 108 (a)1, Air Quality Criteria and Control Techniques, Section 112(b)(1)(a), National Emission Standards for Hazardous Air Pollutants, or Section 111(b)(1)(a), Standards of Performance for New Stationary Sources.

The determination of whether to list POM and the selection of the most suitable control option involves a thorough assessment of possible health effects, emission sources, and ambient air levels. The procedure requires, as a first step, a summary of the existing situation. Such an assessment should include an evaluation of the state-of-the-art in monitoring and control technology and an estimate of the environmental impact. As pointed out by the August 3, 1978 Science Advisory Board report on POM, the environmental assessment of POM requires an in-depth analysis of the scientific credibility of the data. It is the purpose of this report to evaluate the sampling and analytical methodologies employed in the determination of ambient levels and source emissions of POM and to determine the utility of the data in the EPA decision-making process.

2.0 SUMMARY

A large source of data reflecting an international interest in the occurrence of polycyclic organic matter in air, soil, and water has been created (see Appendix A). Polycyclic organic matter (POM) is a generic term applied to a group of fused-ring organic compounds, members of which have been proven to be animal carcinogens. In general, POM refers to those organic compounds consisting of two or more fused aromatic rings. The rings may either be comprised totally of carbon atoms or may contain hetero atoms of nitrogen, oxygen, and sulfur, in addition to other ring substituents.

POM is subdivided into two categories on the basis of the atomic constituents of the ring structures. These categories are polycyclic aromatic hydrocarbons and heterocyclic polynuclear aromatics. The former category contains those compounds with all-carbon skeletons. Alternative names for this category include polynuclear aromatic hydrocarbons (PNAH), polynuclear aromatics (PNA), and aromatic hydrocarbons. The latter category, the least studied of the two, includes the aza arenes, the oxa arenes, and the thia arenes.

Due to the large possible number of ring combinations and substituent permutations, the theoretical number of POM can run into the millions. However, only 249 were listed in the 1962 Bureau of Mines Bulletin on coal carbonization products (1), and only approximately 100 have been identified in a single ambient air sample (2).

Analytical techniques involved in the quantification of POM have evolved from simple fluorescent techniques to computerized gas chromatography/mass spectrometry (GS/MS). Most techniques have yielded conservative data which are thought to be correct within an order of magnitude. The main advances in analysis have been concerned with improved resolution increasing the number of identifiable compounds.

Sampling technology has been slower to advance. Historically, sampling for atmospheric polycyclic organic matter has been limited to the collection of particulates on filter surfaces where losses of POM can occur through the desorption of POM from particulate captured on the filter surface, and through chemical rearrangement. The rate of this loss varies from compound to compound and with the ambient concentrations of other oxidants. Recent studies

have shown that benzo(a)pyrene [B(a)P] may be one of the more reactive forms of POM (3). Its seemingly facile reaction with atmospheric pollutants as well as with filter surfaces casts doubt on its usefulness as an indicator of total POM.

During direct emission source sampling, losses can increase significantly as the concentration of oxidants and temperature at which the sample is taken increases. Emission estimates based on particulate sampling techniques have been shown to be low by a factor of from 2 to 200 (4). Sampling techniques employing impingers and solvent filled bubble trains offer substantial improvement over particulate sampling. Advanced techniques using sorbent resins to trap the vapor phase of POM have increased accuracy by a factor of 2 to 200 over particulate sampling alone, but still do not account for POM losses through chemical rearrangement (4). Emission estimates still may be low by as much as a factor of 2 to 3.

Because uncertainties in sampling and analytical techniques may in some cases have significant impact on reported data, caution should be exercised in the interpretation and use of such data. Insufficient information concerning geography, meteorology, distribution and type of potential sources, as well as control technology, if any, also restricts reliable comparisons of data. In addition, the apparent reactivity of B(a)P under normal sampling conditions coupled with the variability of B(a)P/POM ratios in ambient mixtures and the declining trend in the measured B(a)P concentrations makes the use of B(a)P as a reliable indicator of total POM highly questionable. It is therefore a conclusion of this study that historical data be viewed as being semiquantitative with regard to their utility in EPA decisionmaking.

The following conclusions may also be drawn regarding POM in the environment. POM as found in the environment is largely the result of incomplete combustion. Natural sources of POM include forest fires and volcanoes. These sources, coupled with the possibility of bacterial synthesis, can be considered to produce a natural background of POM. Anthropogenic sources are a consequence of the direct combustion of coal, petroleum, petroleum derivatives, and wood for industrial applications, power generation, transportation, and domestic space heating. Additional man-made sources include burning coal refuse banks, incineration, agricultural burning, and prescribed forest burning.

POM is emitted to the atmosphere as a component of particulate matter. The atmosphere serves as a reservoir for storage and decomposition as well as a medium for transport. Ultimately atomspheric POM is either decomposed or deposited on exposed surfaces. POM deposited on soil may be decomposed, taken up by plants, leached into the groundwater, or washed into waterways. POM enters the aquatic environment through direct atmospheric deposition, runoff, and industrial effluents. It may be degraded, buried in sediments, or transported to the ocean. (Measured ambient POM concentrations are contained in Appendix A.)

POM is removed from the environment through a variety of mechanisms. Photochemical degradation is probably the chief source of destruction of POM in the aquatic and atmospheric environment. Chemical oxidation is significant near the source but decreases in importance as atmospheric concentrations of oxidants decrease. Microbial degradation appears to dominate in soil.

An evaluation of the literature indicates that efforts should be made to: (1) determine the relative abundance of POM in the vapor state under ambient conditions, (2) establish the rates and the mechanism by which degradation occurs during both ambient and source sampling, and (3) establish and expand the applicability of a single POM or a group of POM as an indicator for total POM on a source-by-source basis.

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3.0 SAMPLING FOR POLYCYCLIC ORGANIC MATTER

The first step in determining the magnitude of a potential health or environmental hazard is the collection of a qualitatively and quantitatively representative sample. Regardless of the accuracy and precision of the subsequent analytical technique, the data generated, and ultimately, the decisions based on those data will be no more reliable than the sample collected for analysis. Sample collection is particularly significant when working at trace levels such as with polycyclic organic matter.

After surveying the literature it may be concluded that:

- 1. Emission factors based on particulate sampling techniques incorporating sorbent resins in the sampling train are quantitatively more accurate than those relying solely on particulate collection. Accuracy may be improved by as much as a factor of 2 to 100 depending upon the emission source.
- 2. High volume samplers have been demonstrated to be an accurate method for sampling total suspended particulates in the atmosphere. However, present ambient particulate sampling methods do not take into consideration potential for loss of POM in the vapor phase, the desorption of POM from particulate matter, or molecular rearrangements of POM on the particulate surface. Consequently, the accuracy of the various techniques may vary from sample to sample by as much as a factor of 2.
- 3. Present water sampling methods utilizing sorbent resins appear to be quantitatively accurate for low levels of POM.
- 4. No data exist by which to evaluate soil sampling techniques. However, those techniques which avoid contamination appear to be quantitatively accurate.

3.1 DIRECT EMISSION SOURCE SAMPLING

It is widely accepted that POM results from the incomplete combustion of organic matter in a reducing atmsophere and is found, as such, in association with emissions from combustion sources. These emission sources are generally categorized as either mobile or stationary (1). Mobile sources are related to transportion. Their emissions are comprised of diesel and gasoline exhausts. Stationary sources pertain to heat and power generation, refuse burning, and industrial applications.

The collection techniques employed in sampling these sources can be categorized as either direct or indirect, depending on the characteristics of the individual source. Mobile sources and the ducted products of large-scale stationary sources lend themselves to direct sampling techniques. In general, these sources are characterized by high temperature, high gas velocity, and in some cases heavy particulate loading (2).

A number of systems have been designed for use in direct emission source sampling. A basic component of these systems is the inclusion of a device to trap particulates. Since the amount of particulate matter collected is a function of design and differs from system to system, EPA Method 5 has been adopted as a standard for particulate analysis (2) and has become the basis of much of the POM data.

In order to obtain a representative sample by Method 5, a point must be selected in the duct that is free of obstructions and projections that might cause undesirable turbulence. Temperature, particulate mass distribution, and average gas velocity are determined, and a sample is drawn at the same velocity as the gas stream being sampled, i.e., isokinetically, in order to prevent particulate bias (2). The sample is pulled through a glass-lined, heat resistant probe to a dry collection box and passed through a filter. The filter is rated at 99.7 percent efficiency for 0.3 µm dioctyl phthalate particles and is relatively inert to chemical reaction. The temperature in both filter and probe are kept above 121°C to prevent condensation. Particulate matter, and any associated POM, is defined to be the material removed during cleanup from the filter and from the walls of the probe and nozzle (2).

Measuring POM concentration by means of particulate sampling procedures assumes that the POM is either in the form of condensed particulates or adsorbed onto condensed particulate at the sampling temperature. However, depending on the temperature and the nature of each source, POM at the sampling point is likely to exist as a vapor or a liquid, as well as being adsorbed onto a solid substrate. At the sampling temperature prescribed by Method 5, the concentration of POM in the vapor phase may be significant. Pupp $\underline{\text{et}}$ $\underline{\text{al}}$. (3) theorized that direct particulate sampling for flue gases and vehicle exhausts would miss a concentration of POM equal to the equilibrium vapor pressure concentration (EVC) of the pollutant (3). The EVC is defined as the concentration of compound present as a vapor in equilibrium with that

compound as a solid. The EVC is temperature dependent, and for a pure compound it increases with increasing temperature (see Table 3-1).

Gas velocity as well as temperature may affect the vapor state of POM by influencing the vaporization rates of the POM already trapped on the filter surface. High temperatures increase the rate of vaporization resulting in greater loss of POM per unit volume of emission sampled at lower gas velocities than at higher velocities (3). These factors can become significant where POM contained in the fractionated particulate and in the material adhering to the nozzle, probe, and filter surface are exposed during long periods of sampling to elution by hot exhaust gases. Losses have been recorded by Commins and Lawther (4) for pure benzo(a)pyrene deposited on a glass fiber filter and subjected to various flows of laboratory air at 100°C. At 0.3 liters per minute for 4 hours, approximately 60 percent of benzo(a)pyrene was recovered from the filter surface. When the temperature of the air was elevated to 170-200°C, total loss of benzo(a)pyrene was reported after 5 minutes of treatment.

A substantial loss of POM could, therefore, be anticipated when sampling for long periods of time at stack temperatures or at the temperature prescribed by Method 5. However, adsorption onto a solid appears to modify the rate of loss. Rondia (5) measured the loss of several types of POM deposited onto a granulated carbon surface and exposed to air currents at various temperatures. Substantial losses of the higher weight POM occurred at 100°C, and after 20 minutes at 130°C, only 59 percent of the total benzo(a)pyrene was recoverable. The rate of loss increased with decreasing particulate size and increasing temperature and air velocity.

Various attempts have been made to minimize POM losses by trapping the vapors in impingers, solvent filled bubblers, and cold traps (1,2). The most recent innovation was developed by Jones et al. (6). Method 5 was tested against a modified version of Method 5 consisting of a nozzle, probe, filter and cooled resin cartridge (TENAX) to trap organics in the vapor phase. The results indicated that total POM as measured by Method 5 could be low by as much as two orders of magnitude, depending on the fuel source (see Table 3-2). The closest agreement in measurements showed Method 5 results to be low by a factor of 2.5.

TABLE 3-1. CALCULATED EQUILIBRIUM VAPOR CONCENTRATIONS IN $\mu g/1000 \text{ m}^3$ FOR POM UNDER VARYING TEMPERATURE CONDITIONS

	-10°C	25°C	30°C	50°C	93°C	130°C
Pyrene	580	7.6 x 10 ⁴	1.40 x 10 ⁵	9.0 x 10 ⁵	6.3 × 10 ⁷	9.4 x 10 ⁸
Benz(a)anthracene	3.4		2.8×10^{3}			
Benz(a)pyrene			1.6 x 10 ²			
Benz(e)pyrene	0.15	7.8 x 10 ¹	1.6 x 10 ²	1.8×10^{3}	4.3×10^{5}	1.4×10^{7}
Benzo(k)fluoranthene	0.013		3.0×10^{1}		_	
Benzo(ghi)perylene	1.8×10^{-3}	1.6	3.4	48	1.8 x 10 ⁴	7.6×10^5
Coronene	1.8 x 10 ⁻⁵	:	0.058	ļ		

Reference 3

TABLE 3-2. COMPARISON OF TOTAL POM COLLECTION TECHNIQUES: EPA METHOD 5 VS. MODIFIED EPA METHOD 5 EMPLOYING A SORBENT RESIN

Source	Total POM (ug/m ³) collected by Method 5	Total POM (µg/m ³) collected by modi- fied Method 5
Oil fired boiler (Residual oil)	4.2	55.2
Oil fired boiler (Residual oil)	0.15	12.2
Burner (Natural gas)	0.55	1.3
Carbon black manufacturing operation (effluent)	56.5	124

Reference 6 (Adapted)

In order to accommodate the phased approach/cost effective methodology of the EPA environmental assessment program at the Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, a new high-volume, particulate sampling train has been developed along the lines proposed by Jones et al.(6). The Source Assessment Sampling System (SASS) employs triple cyclones and a glass fiber filter all maintained at 205°C for particulate fractionation and particulate capture. This is followed by a sorbent resin cartridge maintained at 20°C for capture of organics in the vapor phase (7). The resin, XAD-2, has been selected for use in the SASS train because it shows a greater volumetric and weight capacity than does TENAX (8).

POM quantifications based on SASS train sample collections are not yet available for evaluation. Based on evaluations of the collection characteristics of the sorbent resin alone (8), it is not unreasonable to expect quantitative recovery of POM in both the particulate and the vapor stages. However, potential losses as a result of chemical oxidation of POM adsorbed on the particulate, adsorbed on the resin surface, or present in the vapor phase have not been evaluated.

The extent of losses through rearrangement has not been clearly established. Jones <u>et al</u>. (6) compared the results from POM analysis from samples taken by Method 5 with a sorbent resin after the impinger system, and by Method 5 with the resin situated immediately after the filter ahead of the impinger system. EPA Method 5 with the adsorbent located after the impinger system collected 1.4 $\mu g/m^3$ of POM and the system employing a filter immediately followed by the adsorbent collected 12.2 $\mu g/m^3$ POM. The difference of approximately one order of magnitude between the two resin collection techniques was attributed to losses via chemical reactions with oxidants produced by the fuel.

In a series of automotive exhausts sampling validation experiments, Spindt (9) examined several variations in the filter/sorbent resin sampling system. In one test, using a sampling configuration similar to Jones' method, B(a)P was both injected into the sampling line and deposited in the sorbent trap. A sample of an automotive exhaust gas was drawn through a probe maintained at 176.7°C followed by a glass fiber filter and a resin cartridge at 4.5°C. Less than 50 percent of the B(a)P injected into the system and only

20 percent of that deposited on the sorbent resin was recovered. When the system was modified to include an air dilution of the sample, and C^{14} B(a)P was injected into the system, 50 percent of the radioactive tracer was recovered from the lines and filters, 2.2 percent was found in the sorbent trap, and 21.5 percent was recovered as degraded products at various points in the system. The remaining B(a)P was not detected. Spindt concluded that most of the injected B(a)P reacted with constituents of the exhaust gas (9).

Factors influencing the rate of degradation appear to be the concentration of POM in the vapor phase (9), the concentration of oxidants (10), the reactivity of the specific POM, and the spectra and intensity of electromagnetic radiation (11). Since limited information exists on the nature and concentration of POM degradation products produced during a typical sampling run, it is impossible to accurately quantify the loss of POM attributable to chemical rearrangement. However, it appears loss can sometimes exceed 50 percent, or a factor of 2, for total POM as measured by benzo(a)pyrene.

3.2 INDIRECT EMISSION AND AMBIENT AIR SAMPLING

The physical state of POM in ambient air is determined in part by the amount of particulate generated by the source. Natusch and Tomkins (12) contend that the extent of POM adsorption onto particulate is proportional to the frequency of collision of POM molecules with available surface area, resulting in preferential enrichment of smaller diameter particulates. areas of high particulate concentrations, such as the stack of a fossil fuel power plant, one would expect nearly quantitative adsorption of the POM onto particulates. As particulate concentration decreases, as in internal combustion engines, one would expect to find more POM in the condensed phase. general, the largest concentration of POM per unit of particulate mass will be found in the smaller diameter aerosol particulates. As seen in Table 3-3, tests utilizing particulate sizing techniques on urban aerosols have demonstrated that as much as 75 percent of the total benzo(a)pyrene adsorbed onto particulate matter can reside on particulates with diameters less than 2.3 μm (15,16,17,18).

Sampling for POM in ambient air and from indirect emission sources has relied heavily upon the collection of the suspended particulates. The main-

TABLE 3-3. DISTRIBUTION OF B(a)P ON PARTICULATES OF VARYING SIZE

Ref.	l acation	Particle size in µM									
nei.	Location	≤1.1	1.1	2.0	3.3	4.6	7.0	<7.0			
15	Green Bay, WI µg/1000 m ³ % distribution	2.9 29%	1.1		.2	2.0 20%		2.7 27%			
16	Toronto (avg. 4 sites) µg/1000 m ³ % distribution	0.077 44%	0.047			0.050					
17	Ontario µg/1000 m ³ % distribution	1.08 85%			0.10						
18	Pittsburgh µg/1000 m ³ % distribution			1.4 6%			0. 4%				

TABLE 3-4. VAPOR PRESSURE FOR SEVERAL POM AT 25°C

Compound	Number of rings	Vapor pressure in Torrs
Anthracene	3	1.95 x 10 ⁻⁴
Phenanthrene	3	6.80 x 10 ⁻⁴
Benzo(a)anthracene	4	1.10 × 10 ⁻⁷
Pyrene	4	6.85 × 10 ⁻⁷
Benzo(a)pyrene	5	5.49×10^{-9}
Benzo(e)pyrene	5	5.54 x 10 ⁻⁹
Benzo(k)fluoranthene	5	9.59 x 10 ^{-11*}
Benzo(ghi)perylene	6	1.01×10^{-10}
Coronene	7	1.47 × 10 ⁻¹²

^{*}Benzo(k) fluoranthene is a non-alternant compound containing a single resonant pentacyclic ring structure.

Reference 3 (Adapted)

stay of the National Air Surveillance Network (NASN) program, indirect emission sampling methods, and many individual research projects has been the high volume sampler. The sampler consists of a filter assembly and a vacuum pump housed under a cover shelter. Air is drawn through the filter at a flow rate of 40 to 60 CFM (1.13 to 1.70 m^3/min). Particulate matter is entrained on the filter surface through impaction, interception, adsorption, electrostatic deposition, or infiltration (19).

The accuracy of the high volume sampler depends upon the consistency of the flow rate. Filter clogging can substantially reduce the flow rate and cause as much as 50 percent deviation from the true particulate average. However, when operated according to standard methods, the high volume sampler has repeatedly proven its reliability. The precision of off-the-shelf samplers testing the same air space has been demonstrated to be \pm 5 percent at the 95 percent confidence level (20,21,22).

The high volume sampler samples with nearly 100 percent efficiency for particulate matter greater than 0.3 μm in diameter. When operated at the maximum flow rate, it obtains a representative portion of the atmosphere with a suspended particulate loading as low as 0.1 $\mu g/m^3$ (19).

As in emission source sampling, the location of the sampling point is crucial in both indirect emission and ambient sampling. A site should be selected with regard to the spatial distribution of the emission sources, the population density, the size of the area, the topography, and prevailing meterological conditions (23). A sample taken from a single point cannot necessarily be considered representative of an area (24,25). Several sites must be selected to compensate for topography and meteorology, as well as to delineate the geographical population variability.

The frequency of sample collection is also important. The influence of meteorology, the effect of topography, and the variations in the productivity of the sources combine to determine the most desirable sampling frequency. Daily samples yield the most accurate information. The accuracy decreases as the time interval between samples is increased. For particulate sampling, the minimum frequency of 24 hours once every 6 days has been recommended for an initial air quality survey. This would yield approximately a \pm 90 percent variability from the annual mean at the 70 percent confidence level (23). The

extent to which this can be applied to POM sampling is not known. Although POM has been shown to correlate with the benzene soluble organic fraction (BSO) of the total suspended particulate (TSP), a correlation between the BSO and TSP has not been established. It has not been demonstrated, therefore, that a statistically significant particulate sampling program can yield statistically significant POM data.

The actual applicability of filter samplers in general to POM sampling is subject to question. As in direct emission source sampling, it appears that losses of POM might occur as a result of desorption, failure to collect vaporphase POM, and chemical rearrangements of POM on the filter surface. Rondia (5) studied desorption and concluded that such losses were related to the vapor pressure of the individual POM, the physical state of the POM, i.e., condensed liquid versus adsorbed solid, and the velocity of air and air temperature during sampling.

Vapor pressures have been calculated for only a few types of POM, but have proven to be significant (see Table 3-4). A POM mixture placed on filter paper and allowed to stand for 30 days at room temperature showed substantial losses of fluoranthene and pyrene, approaching 75 percent of the initial concentration of each. Some loss of benzo(a)pyrene was recorded but no loss was demonstrated for 1,12-benzoperylene (5).

The effect of the physical state on POM stability has received limited attention. Volatility has been theorized to decrease as a consequence of POM being trapped in the interior of the particulate during particulate formation (9). For pure POM mixtures adsorbed onto surfaces, volatility has been shown to increase with increased surface area. Rondia (5) demonstrated that for a fixed set of temperature and air flow conditions, the volatilization decreased with increasing particulate size; higher losses were recorded for fine smoke particulates than for granulated (100 mesh) carbon particles.

Under ambient sampling conditions, it appears that POM losses are less dependent upon temperature variations than upon variations in the velocity of the air passing through the sampled POM. Stenburg et al. (26) demonstrated that the difference in POM attributed to temperature variation when collected from a split exhaust stream—one side cooled to 15.5°C and the other to 32°C—were well within the realm of experimental error. Rondia (5) depos—

ited benzo(a)pyrene and 1,12-benzoperylene on a tared dish and subjected them to temperatures ranging from 100°C to 140°C. Analyses were made every hour for four hours and only at 140°C did losses of benzo(a)pyrene become substantial. POM contained in smoke particulate was analyzed, and when all other conditions were held constant and only the temperature was varied from "laboratory conditions" to 50°C, the results showed no significant trends that could be attributed to temperature losses (5).

Commins (27), however, demonstrated that a substantial loss of POM in a given sample could be attributed to variations in the velocity of the air drawn through the sample (see Table 3-5). The effect was summarized by Pupp et al. (3). He concluded that losses occurring as a consequence of a low-volume, long-term sampling might approach the equilibrium vapor concentration of the respective forms of POM. Such losses would be governed by the rate of sublimation during high volume sampling, and the total loss of POM under such conditions would be less than that occurring during low volume sampling.

The existence of a POM vapor phase has been postulated by several researchers; however, the extent to which POM is found in the vapor phase under ambient conditions has not been conclusively determined. It has been theorized by Pupp et al. (3), that the EVC of pure POM, such as benzo(a)pyrene, is significant and that, barring surface adsorption effects, larger quantities of POM could be found in ambient air than are found associated with particulate matter.

Miguel and Friedlander (28) attempted to verify this by sampling 6 m^3 of an urban aerosol (Pasadena, California) with a high volume glass fiber filter backed by two cold traps in series. Although calculations based upon the EVC for benzo(a)pyrene indicated that 165 times as much of this POM would be contained in the vapor phase than in the annual geometric average reported for Los Angeles, California, none was detected. Since the detection limit of the thin layer chromatography/spectrophotofluorometric analysis technique employed in this experiment was 0.05 ng, it was estimated that the amount of B(a)P escaping collection was less than 0.08 ng/ m^3 .

Vapor-phase benzo(a)pyrene was also tested for by Commins and Lawther (4) by drawing 81.6 m 3 of filtered urban air over a 30 day period through a Dreschel bottle containing pure paraffin as a solvent. Tests for fluorescence at

TABLE 3-5. DEGRADATION OF POM ON SMOKE SAMPLES UNDER VARIOUS TEST CONDITIONS (ug/100 m³)

	TARTOOS	TEST CONDITIONS	(μg/100 m /	
РОМ	Initial a analysis	Analysis after 3 week	3 week @ 0.3 l/min	3 week @ 0.3 d 1/min & 50°C
Fluoranthene	30.9	19.5	7.4	7.2
Phenanthrene	14.0	5.9	4.1	2.9
Benzo(e)pyrene	5.8	7.1	3.9	5.6
Pyrene	23.7	15.6	3.2	3.4
Benzo(ghi)perylene	6.6	6.0	6.3	5.5
Benzo(a)pyrene	20.0	19.1	19.0	16.6
Anthanthrene	2.3	2.5	1.6	2.0

Reference 27 (Adapted)

^aInitial analysis of POM contained in smoke sample.

^bAnalysis of unextracted smoke sample after three weeks storage under laboratory conditions.

 $^{^{\}text{C}}\text{Analysis}$ of POM contained on smoke sample held at laboratory temperatures after 3 weeks of exposure to 0.3 ℓ/min of clean air.

 $[^]d\mbox{Analysis}$ of POM contained in smoke sample held at 50°C after 3 weeks exposure to 0.3 $\mbox{g/min}$ of clean air.

regular intervals did not produce any evidence of benzo(a)pyrene. Bunn \underline{et} \underline{al} . (29) sampled an urban aerosol using a sorbent resin column in parallel with a standard high volume sampler. Laboratory analysis of the sample fraction showed that substituted as well as unsubstituted dicyclic POM were collected on the resin, but tricyclic POM and greater were found only in the particulate fraction (see Table 3-6). In addition, Pellizzari \underline{et} \underline{al} . (30) using a TENAX column especially designed to sample vapor phase organics reported no forms of POM larger than naphthalene in the vapor phase when sampling urban air.

A distinction should be made between POM in a true vapor state and POM contained in the smaller diameter aerosol particulates. Krstulovic <u>et al</u>. (31) sampled three areas in Rhode Island using a filter backed with a polyurethane foam plug. The filter was rated at 98 percent efficiency for particles $\geq 1.0~\mu m$. Since efficiency for collecting smaller particulates decreases with decreasing particulate diameters, significant amounts of POM were found on the polyurethane plug (see Table 3-7). The results of the test were inconclusive for demonstrating the presence of POM in the vapor phase.

DeWeist and Rondia (32) sampled for benzo(a)pyrene in a coking region of Belgium and found substantial seasonal variations even though there was no apparent change in the productivity of the source. In a series of wintertime experiments with filters heated from -2° C to 28° C, they were able to duplicate the seasonal trends in B(a)P. They concluded that those trends were probably due to volatilization and/or chemical reactions catalyzed by trace metals.

Since the loss of vapor phase POM appears to be negligible when sampling ambient air at high velocities and at ambient temperatures, the most likely explanation for the losses appears to be via chemical rearrangement. Lane and Katz (10) experimented with POM under varying conditions of illumination and ozone concentrations. Under conditions of zero illumination, which would duplicate the illumination levels encountered inside a high volume sampler, the half-life of three POM was found to decrease substantially with increasing concentrations of ozone (see Table 3-8). Benzo(a)pyrene, which has been used as the indicator for total POM showed particularly significant losses. The initial rate of disappearance was extremely rapid and was theorized to be dependent on the exposed surface area. Multilayering on the particle and the accumulation of POM in the interstices of the particulates modified the rate of disappearance to 1.5 percent per hour after the initial rapid reaction.

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TABLE 3-6. VAPOR PHASE POM: COLLECTED CHARACTERISTICS OF STANDARD HIGH VOLUME SAMPLER BACKED BY SORBENT RESINS

Compound	Tenax-GC	XAD-2	Hi-Vol Particulate
Naphthalene	Х	Х	ND
Methylnaphthalene	X	χ	ND
Anthracene	ND	ND	х
Fluoranthene	ND	ND	Х
Pyrene	ND	ND	X
Benzofluorene	ND	ND	x
Methylchrysene	ND	ND	Х
Benzofluoranthene	ND	ND	х
Benzpyrene	ND	ND .	Х

Reference 29

X - POM detected.

ND - POM not detected.

TABLE 3-7. VAPOR PHASE POM: COLLECTION EFFICIENCY OF 130 µm FILTER BACKED WITH A POLYURETHANE FOAM PLUG (µg/1000 m³)

Compound	Prov Filter	idence ^a Plug	King: Filter	ston ^b Plug	Narraganse Filter	tt Bay ^C Plug
Naphthalene	248	100.7	31.1	27.9	3.18	4.91
Phenanthrene	337.7	5.6	46.6	4.9	4.9	6.4
Fluoranthene	1,249.8	281.3	-	165.4	159.4	-
Benzo(a)pyrene	29.7	-	-	3.5	4.2	-
1,2,3,4-Dibenz- anthracene	806.4	3,709.2	102.5	-	-	29.7

Reference 31

^aProvidence, RI - industrialized area

^bKingston, RI - urban area

^CNarragansett Bay, RI - remote area

TABLE 3-8. VARIATIONS IN POM HALF LIFE UNDER DARK CONDITIONS AT DIFFERENT LEVELS OF ATMOSPHERIC OXIDANTS (Ozone)

Ozone ppm	B(a)P	В(Ь)F	B(k)F
0.19	0.62	52.7	34.9
0.70	0.4	10.8	13.8
2.29	0.3	2.9	3.3

Reference 10 (Adapted)

TABLE 3-9. POM LOSSES AS A RESULT OF THE STORAGE OF UNEXTRACTED SMOKE SAMPLES

Compound	Concentration	Percent loss	
	Initial	l yr later	Tercent 1033
Fluoranthene	225	18	92
Pyrene	328	38	88
Benzo(a)pyrene	111	76	32
Benzo(e)pyrene	71	55	23
Anthanthrene	70	55	21
Benzo(ghi)perylene	252	226	10
Coronene	142	140	1 .

Reference 27 (Adapted)

Later work by Katz et al. (33) using simulated smog conditions in which $\rm SO_{_X}$ and $\rm NO_{_X}$ were drawn through a filter using benzo(a)pyrene, demonstrated that the degree of degradation was greater with $\rm NO_{_X}$ than it was with $\rm SO_{_X}$. The rate was greater still when the two pollutants were combined in the presence of ozone.

It appears possible, therefore, for the chemical decomposition during ambient sampling to exceed 35 percent over a 24-hour period (10). Korfmacher \underline{et} \underline{al} . (11) showed that such losses for benzo(a)pyrene might run as great as 50 percent. The rate could be higher depending upon the substrate surface and the ambient oxidant concentration. Consequently, it is not unreasonable to expect sample concentrations to be low by as much as a factor of 2 due to chemical reactions involving POM entrained on the filter.

3.3 WATER SAMPLING

POM is found in water in both solid and liquid fractions. Sampling techniques for water-borne POM have varied from grab sampling to the use of sorbent resins. Grab samples must be viewed with suspicion due to the adsorption of POM onto container surfaces. The POM loss under these conditions is dependent on the POM concentration and composition of the container. Losses as high as 77 percent for benzo(ghi)perylene in glass have been reported (34).

Sorbents such as TENAX-GC (35), XAD-2 (36,37), and polyurethane foam (34,38) have been tested and shown to be capable of quantitative recovery for B(a)P and other forms of POM at low concentrations spiked into water samples. A field monitoring unit has been proposed by Basu and Saxena (34) that employs polyurethane foam plugs. The monitor consists of a pumping unit, a thermostatic water circulator, polyurethane foam columns, a temperature sensor, and a flow meter. When operated at $62 \pm 2^{\circ}C$ and at a flow rate of 240 mL/min, it has demonstrated an ability to quantitatively recover POM in distilled water, tapwater, and raw river water (38).

3.4 SOIL SAMPLING

POM in soil is found in association with decaying organic matter, microorganisms, or bound to mineral surfaces. Typically samples are collected with coring or spading techniques. There are no indications that special techniques other than those which prevent sample contamination are required. Although it is not possible to accurately evaluate soil sampling methodologies at this point, it would appear that current soil sampling allows qualititative recovery of POM. Errors, however, could be anticipated in the extraction of POM tightly bound to soil particles prior to analysis.

3.5 STORAGE

Organic compounds in general are subject to losses due to photodecomposition, adsorption, vaporization, thermal decomposition, and chemical reaction during storage (39). Substantial losses have been demonstrated for POM when held for a year prior to analysis (see Table 3-9). In order to minimize such losses, has been recommended that samples be extracted and stored in the dark in glass containers and at subzero temperatures (39).

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4.0 ANALYTICAL TECHNIQUES

A variety of analytical techniques are currently being used to determine POM concentrations in environmental samples. A review of the literature would indicate that:

- 1. Hundreds of POM compounds may be present in environmental samples. The number of POM compounds reported for a given sample may vary substantially, thus reflecting the limitations of the specific analytical technique used.
- 2. Agreement between POM concentrations obtained using different analytical techniques can be expected to be no better than an order of magnitude.
- 3. Quantitative data for POM concentrations will generally be less than actual concentrations.

Quantitative analysis of an environmental sample for POMs can be accomplished in a variety of ways. Two currently used techniques for POM analysis are outlined in Table 4-1 (1,2). These examples represent two of the hundreds of methods for POM analysis found in the literature. Basically all methods for POM analysis share a common format of six distinct steps: (1) extraction, (2) concentration, (3) enrichment, (4) resolution, (5) identification, and (6) quantification. There is, however, no standard technique for POM analysis, and significant variations in methods exist for each of these six steps.

Few studies have been published comparing the effectivenes of different techniques for POM analysis. Establishing the effectiveness of any one method is therefore difficult. Results from both intralaboratory and interlaboratory studies indicate that POM concentrations obtained using different techniques can generally be expected to agree within an order of magnitude (3,4,5,6,7). In one intralaboratory study, food and soot samples were analyzed. For most POM compounds, results agreed within a factor of five, but reports varied substantially in the number of POMs found in the sample. Other interlaboratory comparisons indicate that results can be expected to agree within a factor of two for POM test mixtures. Test mixtures are solutions containing POM standards and do not approach the complexity of environmental samples (8,9). For intralaboratory comparisons of two methods for POM analysis, agreement within a factor of two is common (see Table 4-2).

New Method for B(a)P Analysis	Method Used by National Bureau of
for National Air Surveillance Network	Standards for POM Analysis in the
Samples	Marine Environment
SAMPLE Soxhlet extraction with cyclohexane EXTRACTED ORGANICS IN DILUTE SOLUTION Kuderna Danish Concentrator CONCENTRATED SOLUTION Thin layer chromatography on 20% acelated cellulose developed with ethanol/CH ₂ Cl ₂ PARTIALLY RESOLVED POMS Perkin-Elmer MPF-3 Fluorescence spectrophotometer Scan at excitation wavelength: 388 nm for B(a)P 434 nm for anthracene IDENTIFICATION OF B(a)P AND ANTHRACENE Read at emission wavelength: 430 nm for B(a)P 470 nm for anthracene QUANTITATIVE DATA ON B(a)P AND ANTHRACENE 98.9 ± 5% recovery reported for samples spiked with B(a)P	SEAWATER OR MARINE SEDIMENT Dynamic headspace sampling NONVOLATILE ORGANICS Liquid chromatography Precolumn coupled to a µBondapak C18 analytical column POM SEPARATED FROM MATRIX High pressure liquid chromatography µBondapak NH2 solid phase POM RESOLVED BY RING NUMBER Reversed phase high pressure liquid chromatography POM ALKYL HOMOLOGUES RESOLVED UV absorption and fluorescence emission spectroscopy Gas chromatography/mass spectrometry IDENTIFICATION AND QUANTIFICATION OF NUMEROUS POM

Reference 1

Reference 2

TABLE 4-2. POM ANALYSIS USING DIFFERENT ANALYTICAL TECHNIQUES

Reference	Tochniques compand	Sample	Results	
number	Techniques compared	medium	B(a)P	Other POM
3	Thin layer chromatography/ fluorescence	Water	42.7 ng/2	137.5 ng/l av
	Gas chromatography/flame ionization detector		77.1 ng/£	154.9 ng/l av
	High pressure liquid chromatog- raphy/ultraviolet absorption	Pitch	53 μg/l 45 μg/l	
4	Gas chromatography/flame ionization detector	Air Filter	74.5 μg/l av 59 μg/l av	
	Gas chromatography/flame ionization detector	Dust	5.35 μg/g 6.05 μg/g	9.2 μg/g av 6.8 μg/g av
5	Column chromatography/ultra- violet absorption	Standards in solvent	(% Recovery) 90.0% 80.5%	(% Recovery) 91.7% 77.7%
	Seven different thin layer chromatography methods	Spiled	55.8%-100.4% av	
6	Gas liquid chromatography/ flame ionization detector	Spiked air samples	82.5%	
	Column chromatography/ultra- violet absorption-fluorescence		75.6% av	
_	Gas chromatography/ultra- violet absorption	Spiked	92%	95.5% av
7	Gas chromatography/mass spectroscopy	soot	105%	110.5% av

4.1 EXTRACTION

Thorough extraction of POM from a sample is necessary if the amount of POM available for analysis is to represent the quantity sampled. Air and water samples contain POM tightly bound to particulate matter, and in samples of vegetation or food, POM may be complexed with protein (10). Only a percentage of the POM concentration will be reported unless a rigorous extraction procedure is used. The most commonly employed method has been Soxhlet extraction. The sample is placed in a Soxhlet apparatus with organic solvent and refluxed for several hours. Benzene and cyclohexane have achieved widespread use, but other solvents have also been used, including methanol, methylene chloride, acetone, tetrahydrofuran, hexane, pentane, ether, isooctane, chloroform, and mixtures of two or more of these solvents. However, the effectiveness of some of these solvents in achieving good POM recovery may be questionable (11,12).

Ultrasonic extraction, an alternative to using the Soxhlet apparatus, involves mechanical disruption of the sample with ultrasonic vibrations (13,14). This method allows for faster extraction than with the Soxhlet apparatus, although there is controversy over which is the more effective.

4.2 CONCENTRATION

After extraction of a sample, the POM is contained in a dilute solution. Usually, the solution must be concentrated before further analysis is possible. Although evaporative methods, such as the use of Kuderna-Danish apparatus, rotary evaporator, or nitrogen stream, can concentrate the solvent mixture effectively, significant quantities of POM may be lost if evaporation is not done carefully. This applies especially to the more volatile tricyclic and tetracyclic POM compounds (9).

Two extraction methods do not employ large quantities of solvents, making a concentration step unnecessary: thermal stripping, a method in which POM is removed from the sample by heating it to 300°C, and vacuum sublimation, in which samples are heated under reduced pressure. These methods may offer good results but have not yet achieved widespread use (15).

4.3 ENRICHMENT

A typical laboratory sample contains less than 2 percent polycyclic organic matter. An enriched mixture containing a higher percentage of POM is

obtained by concentrating the POM separated from other compounds using either chromatographic techniques or solvent partitioning.

Liquid chromatography (LC) has achieved widespread use for the separation of POM from other components. A variety of LC techniques have been used differing in the choice of solvents (mobile phase), column packings (solid phase), and number of stages. Numerous solvents and solvent mixtures have been employed, including pentane, hexane, cyclohexane, isooctane, benzene, chloroform, methylene chloride, ether, isopropanol, toluene, methanol, and water. Alumina or silica gel are generally used as column packings.

Thin Layer Chromatography (TLC) has also been used for enriching POM in a sample. As with LC, a variety of organic solvents have been used for the mobile phase. Silica gel, alumina, and acelated cellulose are commonly used solid phases. In addition to enriching a sample, initial resolution of the individual POM compounds can also be accomplished with TLC; for example, Daisey and Leyko separated POM from a sample and obtained three POM fractions. Effective separation of the B(a)P and B(e)P isomers was achieved, making subsequent resolution of the individual forms of POM relatively easy (16).

High pressure liquid chromatography (HPLC) is the newest chromatographic method to be applied to POM analysis. HPLC is very versatile partly because of the availability of numerous solid and mobile phases. Certain HPLC columns have been shown to effectively enrich the POM and resolve the POM mixture into individual compounds, and may significantly reduce the time needed for analysis.

With any technique, some loss of POM from the sample can be expected to occur during enrichment. POM may bind irreversibly to chromatographic surfaces or undergo chemical photooxidative decomposition, if the sample is exposed to light.

Another technique for enrichment is liquid-liquid extraction, i.e., solvent partitioning. This method has not been used as much as TLC or LC but offers some advantages. Multistep partition schemes involving extraction with nitromethane, cyclohexane, and dilute acid and base solutions have been shown to enrich samples while dividing POMs into acid, basic, and neutral fractions (17). The literature is not conclusive on which solvents are best suited for solvent partitioning. Dimethylformamide and dimethylsulfoxide have been reported to be superior solvents for this method (15).

4.4 RESOLUTION

Once the POM mixture has been separated from the matrix, the individual POM compounds must be resolved. Many POM compounds exist as isomers having the same number of fused rings and possessing similar chemical properties which makes them difficult to isolate. Since different isomers can exhibit very different biological effects, their resolution is extremely important. For example, benzo(a)pyrene is an active carcinogen and its isomer benzo(e)-pyrene is nonactive. Other isomers that can be difficult to separate include benz(a)anthracene, chrysene and triphenylene, benzo(b)fluoranthene and benzo-(k)fluoranthene, and benzo(ghi)perylene and anthanthrene (18).

Resolution of POM with methyl substitutions from parent compounds is also difficult. Since each parent compound may have numerous possible substitution sites, the number of possible derivatives is enormous, particularly if disubstituted and polysubstituted structures are considered. For example, benz(a)-anthracene can be difficult to separate from numerous similar compounds, including chrysene, triphenylene, 12 possible methyl derivatives, and 66 possible dimethyl derivatives (see Figure 4-1).

7-12 Dimethylbenz(a)anthracene

Triphenylene

Figure 4-1. A structural comparison of 7,12-dimethylbenz(a)anthracene benz(a)anthracene, chrysene, and triphenylene

Once again, separation is especially important because of the different biological effects these compounds may have. Although 7,12-dimethylbenz(a)anthracene is a highly active carcinogen, other methyl substituted benz(a)anthracenes are only moderately active or nonactive.

In experiments concerned only with quantifying B(a)P or a limited number of POM compounds, LC or TLC methods are also used for resolution. Many methods including those employing LC and TLC for separating and resolving POMs have been proposed as tentative standard methods for air pollution analyses. However, other techniques are capable of greater resolution of POM mixtures into individual compounds.

Gas chromatography (GC) is the most effective method for resolving POM. Resolution of air and cigarette smoke samples into over a hundred POM compounds can be achieved with GC methods. Both capillary and packed GC columns have achieved extensive use for POM analysis. Capillary columns are considered more effective than packed columns for resolving POM, but early problems with column fabrication, coating, and short column life made packed columns easier to use (15).

HPLC is rapidly becoming a popular method for POM analysis. Resolution of POM compounds can be accomplished relatively quickly and cheaply using HPLC, but may be incomplete. Mass spectral analyses of single HPLC fractions can indicate the presence of more than one type of POM (17). However, HPLC is the most powerful tool for the resolution of high molecular weight POM compounds possessing volatilities too low for GC application (19).

4.5 IDENTIFICATION

Initial identification of POM compounds can be made based on LC, TLC, or GC retention values. For LC, POM identification is based on elution order. POM compounds on a TLC plate have a characteristic color and migration index $(R_{\mathbf{f}})$. Identification using GC is based on retention times. Confidence in the identification is enhanced when an internal standard is run and retention values are measured relative to the standard.

Detection devices measuring UV absorption, UV fluorescence, or mass spectra (MS) are used to identify or verify identifications of POMs. UV absorption is a commonly used method. Each POM compound has a unique spectra making positive identification of POM compounds possible in principle. However, significant overlap exists between the spectra for many POM compounds. With limited instrumental resolution, identification may not be possible in practice.

UV fluorescence offers advantages in sensitivity over UV absorption. Identification of picogram quantities of POM has been claimed. Also, differences in absorption and emissions wavelengths can be used to identify POM (15).

Mass spectra are extensively used for POM identification. Capillary GC/MS is generally accepted as the most powerful tool for the identification of trace levels of POM. Even with this technique, however, identification of each component in a sample containing hundreds of POM compounds is not feasible. Some unknown compounds may be identified by analyzing POM standards and comparing results. Presently, standards can be purchased for some priority pollutant POMs including 1,2-benzanthracene, benzo(a)pyrene, 3,4-benzofluoranthene, 11,12-benzofluoranthene, and chrysene (20). The lack of standards has limited the ability of researchers to elucidate the POM components of a sample.

4.6 QUANTIFICATION

Once a POM compound has been identified, quantitative data can be obtained. The accuracy of such data is dependent on the efficiency of each step of the analysis procedure. Care must be taken to minimize loss of POM during analysis. Confidence in the analytical technique is also enhanced when samples are spiked with known amounts of POM and good recoveries are reported.

Many methods are available for quantifying POM concentrations (see Table 4-3). UV absorption, UV fluorescence, flame ionization detection (FID), and mass spectroscopic (MS) methods are the most commonly used techniques for POM quantification. Results obtained by these methods appear comparable (see Table 4-2) (2,9,21,22,23,24,25,26).

Originally the most commonly employed technique, UV absorption continues to be popular for POM analysis. The method is familiar and available to many investigators. Problems can develop, however, due to significant overlap of spectra between POM compounds. A new method for the analysis of POM absorption spectra may aid in interpreting data by producing more distinct spectral peaks. This method treats the spectrum as a curve and plots the second derivative of the expression for the curve. Further experimentation with second derivative analysis will determine its applicability to POM analysis (27). UV absorption methods do not offer the sensitivity achieved with UV fluorescence.

TABLE 4-3. DETECTION DEVICES FOR POM ANALYSIS

Detection Method	Advantages	Limitations
UV Absorption	Familiar method useful for routine analysis.	
UV Fluorescence	Excellent sensitivity.	quantification dif- ficult. a
Flame Ionization Detector (FID)	Possess the widest range of linear response	Nonselective response. Good resolution necessary.
Electron Capture Detector (ECD)	B(a)P response disting guishable from B(e)P.C	Sample must be free of impurities.
Mass Spectrometry (MS)	The most sophisticated tool for POM quantification.	Expensive for routine analysis.
Shpol'skii Effect	Increased selectivity over room temperature fluorescence.	
X-ray Excited Optical Luminescence (XEOL)	Require no resolution once the POM fraction is isolated. 1, g, h	Relatively new methods which have not achieved widespread use.
Synchronous Lumines- cence	FUM Traction is isolated.	·
Sensitized Fluorescence	Requires no expensive equipment or special training.	Limited estimation of total POM.

aReference 15 (Adapted)

^bReference 21 (Adapted)

^CReference 2 (Adapted)

dReference 9 (Adapted)

e_{Reference 22} (Adapted)

fReference 23 (Adapted)

g_{Reference 24} (Adapted)

hReference 25 (Adapted)

¹Reference 26 (Adapted)

Fluorescence detectors have shown the capacity for detecting POM in picogram to nanogram quantities. UV absorption and fluorescence methods were the major choices for POM quantification until the application of GC for the resolution of POM mixtures.

Flame ionization detectors (FIDs) can be coupled to GC for POM analysis. GC/FID is well suited to analysis of environmental samples for POM, since it gives both good sensitivity and a wide range of linear response. GC/FID allows for accurate POM quantification over a range of seven orders of magnitude (21). FID response, however, is nonselective, and accurate data are dependent on complete GC resolution. A more selective response can be achieved with electron capture devices (ECDs). ECDs are rarely used for environmental POM analysis since the relatively weak POM response can be completely obscured by sample contaminants such as organosulfur (4). GC-mass spectrometers are the most sophisticated devices used for POM analysis. Because MS data can be extremely complex, computer analysis of results can aid in the interpretation and quantification of POM data.

The above methods are best suited to POM analysis once POM compounds have been resolved. Because of the difficulties involved with resolution, methods employing X-ray Excited Optical Luminescence (XEOL), Shpol'skii fluorescence effects, and synchronous luminescence are being developed to give quantitative POM data without prior resolution.

A fluorescence spot test has been developed for the estimation of POM concentrations. This method requires no sophisticated equipment. It is based on the sensitization of the inherent fluorescence of POM. POM fluorescence can be greatly enhanced, i.e., sensitized, in the presence of trace amounts of naphthalene. The fluorescence of a sample extract plus naphthalene can be compared visually under an ultraviolet lamp to the fluorescence of naphthalene and the sample alone, and total POM concentrations can then be deduced. This method can be used for detection of POM in picogram (10^{-12} g) quantities and is reported to be accurate within a factor of ten. This method may provide a useful screening method for environmental samples to determine if more specific and elaborate analysis is warranted (26).

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5.0 DATA SUMMARY

There exists a large data base dealing with POM in air, water, and soil which reflects the international interest in POM over the past 25 years (see Appendix A). The accuracy of this data base is not known. It is generally considered to be semiquantitative, with the measured POM concentrations best categorized as being high, medium, or low.

In order to grasp the semiquantitative nature of the data, a useful approach might be to consider it with respect to the recommended phased sampling and analytical strategy proposed by Process Measurements Branch of IERL at RTP (1). At Level 1 of this 3-phase approach, no special emphasis is placed on obtaining a statistically representative sample. The sampling and analysis are designed to show within broad general limits the presence or absence of a pollutant and its approximate concentration. The target accuracy is specified to be within a factor of 3. In order to give that accuracy, both sampling and analytic methods must have a precision better than a factor of 2.

After reviewing the literature it can be concluded that POM emission factors and POM emission estimates based on particulate collection techniques alone do not fall within the bounds of a Level 1 assessment. SASS train analysis is thought to give an order of magnitude increase in accuracy in some cases but still does not consider POM losses arising from chemical rearrangements on the filter surface and in the gas phase eluted from the particulate. Thus, while the available data are inadequate to demonstrate the efficiency of the method, indications are that the SASS train data will give comparable Level 1 accuracy when sampling for POM

Ambient POM estimates based on particulate sampling also contain a high degree of uncertainty. Assuming losses arising from failure to collect the vapor phase and from desorption to be negligible, the chief source of error apparently lies in chemical degradation of POM on the filter surface. The extent to which this occurs is a function of the filter composition and the oxidant concentrations in the ambient air, the physical characteristics of the POM and its carrier substrate, and the individual chemical characteristics of the POM under investigation (see Section 5.1). The accuracy of the estimate can also be expected to decrease when using a single POM such as benzo(a)-

pyrene as an indicator for total POM. Ambient estimates of POM concentrations appear to be less accurate than specified for a Level 1 evaluation.

Water sampling using resins and soil sampling appears to be accurate within a factor of 2. At low concentrations of POM quantitative errors in the extraction and analytical portion of the determinations are probably the largest source of uncertainty. Water and soil values, however, can be considered to meet Level 1 requirements.

Although the direct application of these data to the EPA decisionmaking processes should be restricted, they can serve to trace out the route of POM through the environment.

5.1 POM IN THE ATMOSPHERE

Polycyclic organic matter in the atmosphere originates as pyrolysis products formed during combustion. It can be concluded that:

- 1. Normal background ambient air concentrations for POM in remote areas appear to be ≤ 0.2 nanograms/m³. Urban atmospheric levels may be 10 to 100 times higher.
- 2. Atmospheric POM concentrations as indicated by ambient B(a)P appear to be declining and are considered significantly less than the levels recorded 10 years ago.
- 3. Chemical and photochemical oxidations function to remove POM from the atmosphere. The rate of removal is a function of light intensity and duration, concentration of atmospheric oxidants, chemical properties of the individual POM, and interaction with the carrier substrate.
- 4. Neither long- nor short-term studies using benzo(a)pyrene as an indicator of total POM are reliable for quantitative estimates. Underestimations of total POM result from the failure to consider B(a)P's apparent rapid decomposition rate as well as the variable B(a)P/POM ratios in ambient air. The quantity of POM generated by a source varies with the efficiency of the combustion process and the quantity of fuel used (2).

In general, it is thought that combustion efficiency is the primary factor. Inefficient combustion sources such as residential space heaters tend to emit higher amounts of POM than do the better controlled, more efficient sources such as utility boilers. These factors are reflected by B(a)P emission estimates based on emission factors (see Table 5-1). The concentration

TABLE 5-1. ESTIMATED BENZO(a)PYRENE EMISSIONS IN METRIC TONS/YR

Source	Minimum	Intermediate	Maximum	Date
Coal-Fired Power Plants	0.31	0.46	0.77	1974
Coal-Fired Industrial Boilers	0.047	0.057	19	1973
Coal-Fired Residential Furnaces	0.096	26	740	1972
Other Solid Fuel Burning Sources				
Domestic StovesResidential Fireplaces	52	73	110	1975
Oil-Fired Intermediate Boilers	1			
 Industrial Boilers Commercial/Institutional Boilers 	0.23	0.37	0.68	1973 1973
Oil-Fired Residential		19		19/3
Furnaces	0.89	0.98	2.0	1973
Gas-Fired Intermediate Boilers				
. Industrial Boilers		0.021		1973
. Commercial/Institutional Boilers		0.61		1973
Gas-Fired Residential Furnaces	0.12	0.43	1.5	1973
Petroleum Catalytic Cracking	ŀ			
 Fluid Catalytic Cracking Thermofor Catalytic 	0.000022	0.00023	0.0024	1977
Cracking	0.0000015	0.0012	0.035	1977
. Hondriflow Catalytic Cracking	0.0044	0.0048	0.0048	1977
Coke Production	0.050	110	300	1975
Asphalt Production				
. Saturators	0.00035	0.0044	0.017	1976
. Air Blowing . Hot Road Mix	0.0014	0.0044	0.025	1976 1976
Other Industrial Processes				
. Iron and Steel Sintering . Chainlink Fence	0.022	0.63	41	1977
Lacquer Coating . Carbon Black Production	0.039	0.087	0.087	1976
Incinerators				
MunicipalCommercial	0.0031	0.027	0.24 4.7	1974 1972

TABLE 5-1. (Continued)

Source	Minimum	Intermediate	Maximum	Date
Agricultural & Forest Fires				
Bagasse BoilersForest Fires	9.5		0.0061 127	1973 1976
Burning Coal Refuse Banks	280		310	1972
Mobile Sources				
Automobile (gasoline)Automobile (diesel)Trucks (diesel)Rubber Tire WearMotorcycles	1.5 0.0064 0.075 0	2.7 0.013 0.13 5.6	3.3 0.031 6.2 11	1975 1975 1975 1977 1975

Reference 3. Range of estimates based on multiplying the B(a)P emissions factor times the most recent national production or consumption figures.

TABLE 5-2. B(a)P EMISSIONS FROM HEAT GENERATION AS A FUNCTION OF COMBUSTION EFFICIENCY

Source	Wood (µg/kg)	Coal (µg/kg)	0il (µg/%)	Gas ₃ (µg/m³)
Residential furnaces <210,000 Btu/hr	17,000	3,500	2.2	. 2
Intermediate and industrial boilers <30 x 10 ⁶ Btu/hr	-	0.93	1.1-32	0.6-7.6

Reference 3

of POM inherent in the composition of the fuel is of lesser importance. Although fossil fuels have been shown to possess substantial amounts of POM as a consequence of formation or processing techniques, the combustion of coal, gas, or oil do not necessarily produce a higher POM level than wood (see Table 5-2).

POM is emitted to the atmosphere as a liquid-solid particulate suspension, i.e., an aerosol. The chemical composition is a complex mixture reflecting combustion characteristics of each individual source or the dominance of a single type of source such as the coking ovens of Birmingham, Alabama, or the vehicular traffic of Los Angeles, California (see Table 5-3). As the mixture moves through the air, its composition may be altered by mixing, dilution, and chemical reactions. The transport through the atmosphere is governed by the aerosol's residence time and windspeed. The residence time is dependent on the size of the particulate and has been reported to be on the order of 35 to 80 hours in winter and 100 to 200 hours in summer (5). POM from emission sources is generally contained within the lower 2 km of the atmosphere, and POM concentrations can generally be expected to decrease with distance from the source (5). For benzo(a)pyrene the decrease has been reported to be best described by a double logarithmic function curve (6).

Those conditions that favor reduced residence times in winter, e.g., decreased vertical mixing, also tend to favor long-range transport of aerosols. Monitoring studies by Lunde and Bjorseth (7) have shown that POM can be transported up to 1000 km. A 20-fold increase in local concentrations in Norway was measured in the winter when winds were from the direction of industrial Western Europe. The phenomenon was not detected during the summer.

Given the possibility of long-range transport, it is not surprising, then, that nonzero atmospheric POM levels have been found in remote areas. Since it is impossible to separate the contributions of natural sources from those originating from the dispersal of anthropogenic aerosols, it is reasonable to accept the remote levels as being indicative of background concentrations (see Table 5-4).

Urban and industrial centers are characterized by much higher levels of POM, which for a specific site may run as much as 10 to 100 times as great as remote levels. Urban POM levels as measured by B(a)P have been shown not to

TABLE 5-3. POM CONCENTRATION REFLECTING THE DOMINANCE OF A SINGLE SOURCE

POM Concent	rations in	Los Angeles	Air (ng/m ³):	Automotive	Source
Compound	Site 1	Site 2	Site 3	Site 4	Average
Pyrene	2.0	1.4	3.8	0.16	1.8
Benz(a)anthracene	1.1	0.8	3.1	0.04	1.3
Benzo(e)pyrene	3.0	1.8	3.2	0.09	2.0
Benzo(a)pyrene	1.1	0.5	3.5	0.03	1.3
Fluoranthene	1.9	0.8	3.4	0.12	1.6
Benzo(ghi)perylene	9.2	4.2	7.1	0.21	5.2
Coronene	6.4	3.2	2.8	0.20	3.2

Reference 4

POM Concentr	ations in B	irmingham, A	labama Air (ng/m ³): Cok	ing Source
Compound	Site 1	Site 2	Site 3	Site 4	Average
Pyrene	4.6	10.8	9.1	2.5	6.8
Benz(a)anthracene	5.3	21.2	14.5	3.4	11.1
Benzo(e)pyrene	7.6	26.1	15.0	5.6	13.6
Benzo(a)pyrene	9.0	35.8	20.5	6.0	17.8
Fluoranthene	4.9	11.2	10.8	2.6	7.4
Benzo(ghi)perylene	9.5	22.4	15.3	7.9	13.8
Coronene	2.7	3.8	3.5	2.7	3.2

Reference 3

TABLE 5-4. ANNUAL AMBIENT B(a)P CONCENTRATIONS AT NASN STATIONS (ng/m³)

	1966 ^a	1970 ^a	1976 ^b	1977 ^b
Honolulu	-	-	0.02	0.05
Chicago	-	-	0.53 ^C	0.21 ^c
Montgomery	-	•	0.26	0.04 ^c
New Orleans	-	-	0.24	0.18
Baltimore	-	-	0.51	0.32
Detroit	-	-	1.1	0.42 ^c
New York	-	-	1.0	0.47 ^C
Youngstown	-	- -	1.4	1.2
Bethlehem	-	· -	0.33	0.15
Philadelphia	-	-	0.98	0.45
Chattanooga	-	-	0.27	0.66
Average for NASN urban stations	4.6	2.2	0.5 ^a	0.28 ^b
Average for 3 NASN remote stations	0.5	0.2	0.ļ ^a	<u>.</u>

^aReference 3

bReference 8

^CBased on 3 quarters reported

relate to city size, but rather to the nature and degree of industrial and public activities, types and relative quantities of fuels consumed, degree of regulation exercised by authorities over emissions, volume of vehicular traffic, and extent to which photochemical and other reactions occur (9).

These levels are a product of large-scale and/or massed combustion sources, and have been observed to coincide with the presence of an inversion layer, steady winds from the direction of the combustion source, and the onset of winter. Temperature inversions limit the movement of air masses and prevent the dispersal of atmospheric pollutants. Adamek (10) found benzo(a)-pyrene levels to be 117 to 350 percent higher than average during inversions. Gordon (11) demonstrated that B(a)P levels would vary inversely with the height of the inversion layer and found a linear relationship between the two.

As in long range transport, wind direction will also have an important effect on local POM levels. Adamek compared wind direction and atmospheric B(a)P levels and found B(a)P to increase when the wind was from the direction of urban centers. Unlike wind direction, windspeed does not appear to exert any significant effects on POM levels. In three separate studies comparing windspeed and B(a)P concentrations, no significant correlation was detected (10,11,12).

Two pronounced trends have been observed to occur in POM concentrations. The first is the pronounced seasonal variation in POM concentrations, which has been demonstrated in many areas (see Table 5-5). Higher levels of benzo-(a)pyrene occur in winter coinciding with increased particulate concentration and increased particulate surface area (14). The effect is assumed to be a result of increased combustion of home space heaters and local meteorology. The second trend has been a long-term decrease in ambient benzo(a)pyrene. Between 1966-1976 an approximate 84 percent decrease from an annual average median concentration of 3.2 ng/m^3 to 0.5 ng/m^3 was reported for 32 of the reporting NASN urban stations. The decrease has been characterized by a lessening of the seasonal variations in urban POM levels and a decline in remote POM levels. This has been attributed to the decrease in the residential usage of coal for space heating and restrictions on outdoor incineration.

As long as particulate is suspended in the atmosphere, POM adsorbed onto its surface will be degraded. Degradation pathways include photooxidation by ultraviolet light and chemical oxidation by ozone, peroxides, NO_{x} or SO_{x} (see

TABLE 5-5. VARIATIONS IN SEASONAL AVERAGES OF B(a)P CONCENTRATIONS (µg/1000 m³)

Reference	Location	Yr.	Summer	Winter
13	Toronto	1972-73	12.6	17.1
3 3 3 3	Belfast Dublin Oslo Helsinki	1962-63 1962-63 1962-63 1962-63	9 3 36 42	51 23 103 53
10	Canadaaverage of 10 towns	1971-72 1972-73	0.50 1.2	0.71 0.85
10	Welland, Canada	1971-72 1972-73	6.0 5.53	11.6 4.76
3	URBAN USAaverage of 10 NASN sites	1958-59	1.96	24.6

TABLE 5-6. HALF-LIVES IN HOURS FOR DEGRADATION OF POM BY MAJOR ENVIRONMENTAL OXIDIZERS

	RO2ª	Singlet oxygen	Ozone ^C (water)	Ozone ^d (air)	Chlorine ^e	но <mark>:</mark> f
Anthracene	3.8 x 10 ⁴	5			A11	All
Dimethylanthracene	0	.05			have	have
Phenanthrene Pyrene	2×10^8 2.4×10^5		0.68	5.6 x 10 ²	half-	half-
Perylene	3.8×10^4				lives	life
Benzopyrene	2.4 x 10 ⁵	5	1.05	8.7×10^2	<.5 hr	of
Benzanthracene		10	0.45	3.7×10^2		approxi-
Dimethylbenzanthracene		<5				
Dibenzanthracene		<5	0.42	3.4×10^2		mately
Dimethyldibenzanthracene		0.02	0.17	$<1.4 \times 10^2$		10 hr

^aSame for air. Alkyl peroxy radical.

^bSame for air.

 c_{10}^{-4} M.

 $^{^{}d}_{2} \times 10^{-9} \text{ M.}$ $^{e}_{10}^{-5} \text{ M.}$

f_{Hydroperoxy} radical.

Reference 15.

Table 5-6) (15). Laboratory simulations of POM degradations give conflicting results depending upon the concentration of atmospheric oxidants and the light source used for illumination. Lane and Katz (16) took great care in simulating both illumination and ambient pollutant levels, and determined that benzo(a)pyrene was more rapidly degraded in both light and dark conditions than benzo(k)fluoranthene and benzo(b)fluoranthene (see Table 5-7).

The quantity of POM contained in ambient atmosphere is of great interest. Lao et al. (17) identified over 100 compounds in a single air sample (see Table 5-8). Obviously, an analysis of the total POM in an atmospheric sample is prohibitively time-consuming and much too costly to be employed on a routine basis. An estimate of the total POM based on routinely analyzed B(a)P, however, does not consider B(a)P's facile reactivity with atmospheric pollutants and sunlight. Neither does it consider the variation in B(a)P to POM ratios from source to source and with the application of source specific control technology. These factors become extremely important in trying to interpret the significance of the declining trend of B(a)P from 1966 to 1976 (18).

5.2 POM IN THE AQUATIC ENVIRONMENT

Conclusions about POM in the aquatic environment are general in nature due to limitations in the available data base. It may be concluded, however, that:

- 1. POM enters the aquatic system from four major sources: (a) atmospheric deposition; (b) urban and rural runoff; (c) industrial and municipal effluent; and (d) oil seeps and spills.
- 2. POM is only slightly soluble in water. Consequently a significant percentage of POM in the aquatic system would be found adsorbed onto particulate matter.
- 3. Natural water systems act as a reservoir for POM. POM is transported through these reservoirs as particulates or adsorbed onto sediment and can be expected to accumulate in areas of biological significance, e.g., lakes, reservoirs, and estuaries.
- 4. Primary removal of POM from the aquatic environment is through photochemical reactions and bacterial degradation.

TABLE 5-7. HALF LIVES IN HOURS OF SELECTED POM IN SIMULATED DAYLIGHT, a SUBJECTED TO VARYING CONCENTRATIONS OF ATMOSPHERIC OXIDANTS (ozone)

0zone	Benzo(k)fluoranthene	Benzo(a)pyrene	Benzo(b)fluoranthene
0.0	14.1	5.3	8.7
0.19	3.9	0.58	4.2
0.70	3.1	0.20	3.6
2.28	0.9	0.08	1.9

Reference 16

^aQuartzline lamp.

Dihydro-benzo[a]anthracene Biphenv1 Octahydro-phenanthrene and dihydro-chrysene, and dihydro-triphenylene octahydro-anthracene Dihydro-fluorene Benzo[alanthracene, chrysene, and triphenylene Dihydro-fluorene Tetrahydro-methyl-benzo[a]anthracene, Methyl-biphenyl chrysene, and triphenylene Methyl-biphenyl Dihydro-methyl-benzo[ghi] Benzindene Benzindene fluoranthene Fluorene Methyl-benzo[a]anthracene Dihydro-phenanthrene Methyl-triphenylene Dihydro-anthracene Methyl-chrysene 2-Methyl-fluorene β,β'-Binaphthyl 1-Methyl-fluorene Dihydro-methyl-benzo[k&b] 9-Methyl-fluorene fluoranthenes and Phenanthrene dihydro-methyl-benzo Anthracene [a&e]pyrenes Benzoquinoline Methyl-β,β'-binaphthyl Benzoquinoline Dimethyl-benzo[a]anthracene Acridine and triphenylene Fluorene carbonitrile Dimethyl-chrysene Benzo[j]fluoranthene
Benzo[k]fluoranthene and Fluorene carbonitriled Methyl-phenanthrene benzo[b]fluoranthene Methyl-anthracene Methyl-benzo[k]fluoranthene and Ethyl-phenanthrene and methyl-benzo[b]fluoranthene dimethyl-phenanthrene Ethyl-phenanthrene and Benzo[a]pyrene, benzo[e]pyrene ethyl-anthracene Pervlene Ethyl-anthracene and 3-Methyl-cholanthrene dimethyl anthracene Methyl-benzo[a]pyrene and methyl-benzo[e]pyrene Octahydro-fluoranthene Octahydro-pyrene o-Phenylene-fluoranthene Dimethyl-benzo[k]fluoranthene and Dihydro-fluoranthene Dihydro-pyrene dimethyl-benzo[b]fluoranthene Fluoranthene Dimethyl-benzo[a]pyrene and Dihydro-benzo[a]fluorene and dimethyl-benzo[e]pyrene 1,2,3,4-Dibenzanthracene dihydro-benzo[b]fluorene Pyrene 2,3,6,7-Dibenzanthracene Benzo[b]chrysene and Dihydro-benzo[c]fluorene Dihydro-benzo[c]fluorene o-phenylenepyrene Benzo[a]fluorene Benzo[b]fluorene and Picene and benzo[c]tetraphene Benzo[ghi]perylene and benzo[c]fluorene anthanthrene Methyl-fluoranthene Methyl-o-phenylene-fluoranthene Methyl-dibenzanthracene Methyl-pyrene Methyl-pyrene Methyl-benzo[b]cyrysene and Trimethyl-fluoranthene and methyl-benzo[c]tetraphene trimethyl-pyrene Methyl-o-phenylene-pyrene Trimethyl-fluoranthene and and methyl-picene Methyl-benzo[qhi]perylene trimethyl-pyrene Dihydro-benzo[c]phenanthrene and methyl-anthanthrene Dihydro-benzo[c]phenanthrene Coronene Benzo[c]phenanthrene and Dibenzpyrene hexahydro-chrysene Benzo[ghi]fluoranthene Dihydro-benzo[a]anthracene, dihydro-chrysene, and dihydro-triphenylene

POM can enter the aquatic systems via a number of routes. Surface waters near a source of urban and industrial aerosols will receive a substantial amount of POM through atmosphere fallout and precipitation. Runoff following heavy rains will result in POM-containing soils, road and tire dust, exhaust condensation, and other materials containing POM being washed into storm sewers and ditches (19). Municipal and industrial effluents discharging into waterways will further increase POM loadings (20)(see Table 5-9). Concentrations of benzo(a)pyrene as high as 27,000 μ g/ ℓ have been found in some untreated industrial effluent (21). In addition, oil seeps, spills, and discharges add to the POM concentration. Sullivan (22) estimated that 10 to 20 metric tons of B(a)P entered the oceans each year as a result of petroleum discharges.

The effect of POM in the aquatic world is determined by its solubility: the more soluble the POM the better the chances of its being incorporated into biological systems. The solubility will vary depending upon the POM in question, but it is generally quite low. Solubilities in water of most POM consisting of three or more rings is reported to be less than 10^{-10} M (15). Theoretically, solubility can be enhanced through micellular mechanisms involving surfactants such as detergents, biopeptides, and alkaloids. extent to which such enhancement occurs in nature is not known. However, it is generally felt that major environmental transport will be in the form of condensed particulate or adsorbed onto particulate. McGinnes and Snoeyink (23) studied two representative POMs, benzopyrene and benzanthracene, and proposed that POM would not occur significantly in solution but would be either adsorbed onto a surface or in the form of a condensed particle. In the latter case, it would adsorb onto the first available surface and remain there until decomposed, biologically assimilated, or dissolved in an organic nonpolar solvent.

In an adsorbed state, transport through the aquatic environment is governed by the physical laws of sedimentation. Since sedimentation and resuspension occur as a function of flow rate, an accumulation of POM would be expected to occur in placid areas such as lakes and reservoirs. The riverborne particulate, however, would eventually work its way to the ocean where deltas and estuaries have proven to be efficient traps for suspended matter. Particulate retention in these areas is enhanced by inshore and alongshore

TABLE 5-9. POM IDENTIFIED IN SEVERAL U.S. SURFACE WATERS ($\mu g/\ell$)

Source	B(a)P	Total POM
Monongahela @ Pittsburgh, PA	0.04	0.60
Ohio River @ Huntington, WV	0.006	0.058
Ohio River @ Wheeling, WV	0.21	1.59
Delaware River @ Philadelphia, PA	0.04	0.35
Lake Winnebago @ Appleton, WI	0.0006	0.007

Reference 20

TABLE 5-10. DECOMPOSITION OF POM BY BACTERIA FOUND IN NATURAL WATER SYSTEMS

Nongrowth POM	Growth substrate	Nongrowth POM percent remaining after 4 weeks
Pyrene	Naphthalene Phenanthrene	36.7 47.2
Benzo(a)pyrene	Naphthalene Phenanthrene	83.5 38.3
1,2-Benzanthracene	Naphthalene Phenanthrene	58.3 33.8
1,2,5,6-Dibenzanthracene	Naphthalene Phenanthrene	92.7 32.9

Reference 29

currents which combine to restrict suspended matter into continental shelf areas. It has been estimated that 90 percent of the river-borne particulates accumulate in this region where they can undergo continuous resuspension and transport via wave action and currents (24).

POM has been shown to follow the same general trends. Sedimentation has been demonstrated by high POM levels which have been measured in lake beds. River-borne concentrations of POM have been shown to increase following rainfall events indicating that scouring of sediments may be occurring as a result of increased river flow. The possibility of containment of POM on the continental shelf is shown by Mallet who has identified POM in coastal waters both adjacent to and remote from human areas and habitats (25). Additional work by DeLima-Zanghi (26) showed that coastal plankton contained significant amounts of B(a)P, whereas those plankton taken from the high seas were not contaminated.

Removal processes of POM from the aquatic world include evaporation, photochemical oxidation, sedimentation, and microbial oxidation. Evaporation appears to remove dicyclic POM and, to a limited extent, tricyclic POM. It has been demonstrated to be effective with naphthalene, but less so with anthracene and fluoranthene which are significantly less volatile (27). Photochemical oxidations of POM in water occur as a result of direct photolysis involving oxygen and photosensitized reactions via intermediate substances. Sensitivity varies from compound to compound and appears to be a function of molecular weight, ring structure, and physical state. Half-lives have been shown to increase with increasing molecular weights, and linear polycyclics are more sensitive than their bent isomers (28). In general, photochemical oxidations in water systems appear slower than in air because of the presence of fewer types of oxidizing species. The primary oxidizers in natural water have been identified as alkylperoxy and hydroperoxy radicals as well as singlet oxygen (15).

The effect of the physical state on decomposition was studied by McGinnes and Snoeyink (23). Benzo(a)pyrene as a condensed particulate was shown to decompose rapidly under normal daylight conditions; the rate of decomposition and endpoint were governed by the size of the particle. For particles of $1.5~\mu m$ in diameter, the reaction exhibited first order kinetics until 55~to

65 percent of the total B(a)P was decomposed at which point the process ceased, leaving a residual. The residual was not affected by an increase in radiant energy. Apparently the decomposition products formed a protective barrier around the residual B(a)P preventing it from reaction. It was postulated that a residual would remain in particulate greater than 0.4 μ m in diameter.

Particulate benz(a)anthracene did not exhibit this effect. Although it did require a threshold value of sunlight, once the threshold value was attained, the particulate decomposed completely. No residual was detected, presumably due to the solubility of the decomposition product.

The adsorption of POM onto a surface can modify the rate of reaction. Adsorption onto Kaolinite clay, a particulate commonly found in natural water systems, was shown to enhance the rate of decomposition presumably by increasing the surface area. In addition, the reaction proceeded to completion for both benzo(a)pyrene and benzo(a)anthracene.

In an experiment using an ecosystem enclosure treated with POM-enriched crude oil, Lee et al. (27) determined that as much as 50 percent of C^{14} benzo-(a)pyrene might be degraded via photochemical reactions. The rate of degradation was postulated to be dependent upon the intensity of the ultraviolet radiation, the duration of exposure, and physical state. McGinnes and Snoeyink (23) stated that sufficient ultraviolet energy is produced on a cloudy day to decompose benzo(a)anthracene and benzo(a)pyrene in turbid streams. Lee et al. (27) concluded that the first five meters depth is the most important region of photochemical reactions. Other studies have shown that the ultraviolet radiation zone can extend to a depth of 25 to 30 meters in clear water and to a depth of 18 cm in highly turbid rivers (28).

The duration of POM exposure to sunlight is also important in the decomposition of POM. In estuarine waters, the duration of exposure is partially a function of particulate sedimentation and resuspension. It has been estimated that sediment a few millimeters deep is recycled through the water column on a daily basis and that sediment approximately 2 cm deep is recycled annually. Particulates less than $0.5~\mu m$ in diameter have been estimated to reside in the water column between 200 and 600 years. It has also been estimated to take 500 to 1000 years to bury a single layer of particulate, and, consequently, any associated POM on the continental shelf (24).

Degradation of POM in water can also occur by bacterial action. Bacteria may act directly upon POM contained in a sediment or upon a metabolite produced by marine fauna. Such metabolites typically contain trans-diols substituted on intact polynuclear rings. The rate and degree of decomposition by bacteria is apparently influenced by the degree of solubility, membrane permeability, and enzyme specificity (29). Mixed bacterial cultures taken from natural water systems have been shown to grow on naphthalene, phenanthrene, and to a limited extent, anthracene. POM with larger ring structures could not be utilized directly as a growth substrate. Benzo(a)pyrene, pyrene, 1,2-benzanthracene, and 1,2,5,6-dibenzanthracene were slowly decomposed over a 4-week period only in the presence of naphthalene and phenanthrene (see Table 5-10) which served as a carbon source (29).

Although restricted by the ring size and the degree of alkylation, bacterial degradation presents the ultimate means of removing POM from the environment. POM is attacked forming cis-diol products and eventually results in ring cleavage and the generation of ${\rm CO}_2$ and water (30).

5.3 POM IN SOIL AND GROUNDWATER

Polycyclic organic matter has been identified in soil and in underlying groundwater. Conclusions are:

- 1. The preponderance of POM in soil probably results as a consequence of atmospheric deposition from both natural and anthropogenic combustion sources.
- A natural background has been hypothesized to exist and may originate in part from bacterial synthesis.
 - POM contained in soil can be taken up by plant tissues.
- 4. POM can be incorporated into groundwater by leaching. Sanitary landfills might be a major source of future contamination.
- 5. POM in soil is decomposed by photochemical and microbial action. Bacterial processes appear to be the most important.

POM in soil originates from the deposition of atomspheric aerosols of both anthropogenic and natural combustion sources. As many as 30 different POM have been identified in soil samples (31). Studies of airports (32,33) oil refineries (34), highways (35), and process works (34) have demonstrated that concentrations of POM resulting from anthropogenic activities decrease

with the distance from the source and with the soil depth (see Table 5-11). Highest levels have been found on the surface within 50 m of the source, and elevated concentrations have been measured as far away as 5 km. In areas remote from man, the relationship appears to be different. In these remote areas, concentrations of POM appear to be independent of soil depth (36).

The extent to which natural sources such as forest fires and volcanic activity contribute to POM levels is unknown. It is believed that these sources combined with a postulated bacterial biosynthesis account for an apparent background of $1-10 \mu g/kg$ benzo(a)pyrene in soil (34).

POM in the soil may be incorporated into the food path by adsorption into vegetative and plant matter, leached into groundwater, buried in sediments, or degraded. The quantity of POM absorbed by plant tissues has been found to be less than, but parallel to, the POM concentration in contiguous soils. Food crops such as carrots and potatoes have been observed to contain benzo(a)-pyrene when grown in contaminated soil (37,38). The highest concentrations were found in the first few millimeters of the root's surface. In addition, both carrots and potatoes demonstrated the capability of absorbing POM through the roots and translocating it to other tissues (39).

POM has been identified in groundwater and as such may constitute a natural background for surface waters (see Table 5-12). It has been postulated that POM levels in groundwater are a consequence of atmospheric deposition and bacterial synthesis during groundwater formation, infiltration from already contaminated surface waters, and leaching from solid waste disposal sites (see Table 5-13).

Removal of POM from soil occurs through photolytic oxidation and bacterial degradation. Pyrene adsorbed onto garden soil and exposed to ultraviolet radiation at 32° C has been shown to undergo chemical rearrangements resulting in the formation of diones and diols (44). As in water, the ultimate removal of POM is through microbial actions (29). The rate of destruction is dependent on the size of the ring structure, the degree of condensation, and the number of and location of ring substituents. For POM greater than 4 rings, an alternate carbon source is required for co-metabolism. Bacterial cultures using phenanthrene as a carbon source were shown to degrade more than 50 percent of the B(a)P, 30 percent of the pyrene, and 27 percent of the 1,2-benz-

TABLE 5-11. VARIATION OF B(a)P CONCENTRATION WITH DISTANCE FROM SOURCE EMISSION $(\mu g/kg)$

Reference	Location	Distance from source in meters				
		Source	≤ 50	51-250	251-500	501-1500
33	Airport†	400	64	46	17	1.3
34	Oil refinery	12,000			1,200	-120
35	Highway* (in town) (rural)	176 120	100	6 -	21 15	5

^{*}Total POM $\mu g/kg$ +Maximum values

VARIATION OF B(a)P CONCENTRATION IN SOILS NEAR EMISSION SOURCES AS A FUNCTION OF DEPTH

Reference	Location	Depth in cm.				
-		0-10	11-30	31-50	51-150	
35	Hungary - forest soil*	3.5	2.5	2.0	1.6	
34	Oil refinery* - USSR 500 m from refinery* 1,500 m from refinery*	11,900 1,200 120	14,530 1,120 190	13,530 81 8	540 2 .5	
33	Airport - USSR*	64.3	32.0	-	-	
34	Farmland - USSR*	8.2	5.0	-	-	
34	Soils treated with sha tar - USSR*	l le 238	25	-	-	

^{*}Maximum values

TABLE 5-12. POM IDENTIFIED IN GROUNDWATER ($\mu g/\ell$)

Reference	Location	B(a)P	Total POM
20	Champaign, IL	Not detected	0.007
20	Elkhart, IN	0.004	0.02
20	Fairborn, OH	0.0003	0.003
40	Germany (maximum values)	0.0007	0.013
41	Germany (average at 12 locations)	0.0004	0.04
42	Germany (average of 3 locations)	0.02	

TABLE 5-13. POM LEVELS FOUND ADJACENT TO A STEEL WASTE SANITARY LANDFILL (ppb)

Location	POM concentration (ppb)		
Well at highest elevation of landfill	3		
Well at below landfill	<3		
Surface water at site	11		
Downstream, surface water	<3		
Seepage spring	3-30		

Reference 43.

anthracene contained in a test solutions over a 4-week period (29). In other laboratory studies, microfauna have been shown to destroy as much as 70 percent of the benzo(a)pyrene in a soil sample (45). In soils containing as much as 30,000 mg/kg of B(a)P, bacterial degradation has been credited with 50 to 70 percent removal (34).

Bacterial decomposition appears to be restricted to the upper portions of the soil. Under anerobic conditions such as may occur below the soil's surface, degradation may not occur (45). Benzo(a)pyrene has been identified at depths of 17 m below the surface, corresponding to a geologic age of 100,000 years.

5.4 POM IN THE FOOD PATH TO MAN

There are numerous studies in the international literature dealing with POM concentrations in food for human consumption. Caution is advised when attempting to generalize such data from one country to the next. While similarities exist, the principal dietary constituents, growing conditions and the processing and preparation techniques may differ substantially enough to cause misinterpretation of the data. A review of the literature leads to the following conclusions:

- 1. POM may be introduced into food at several points along the food path. In general, microorganisms, plants, and invertebrates tend to accumulate higher levels of POM than do vertebrates. Although POM is lipid soluble and is readily incorporated into a biological system, no evidence of irreversible bioaccumulation in fatty tissues has been documented.
- 2. POM levels in ambient air and to a lesser extent POM levels in soil contribute to the total POM found in and on crops. POM levels in water are amplified in some foods derived from aquatic systems.
- 3. Variations in industrial control techniques, degree of urbanization, growing conditions, processing procedures, and preparation methods will affect POM contained in food.

Due to the high lipid solubility and increased aqueous solubility via lipids and molecules, POM appears to be readily incorporated into biological systems. It can therefore be expected to enter the food chain at any trophic level. In aquatic environments, POM may enter through absorption and/or

ingestion. Algae and other organisms have demonstrated the ability to absorb POM directly from the surrounding waters (46). In turn, algae and particulate matter containing POM may be ingested by filter feeders. Mollusks, especially mussels, have demonstrated high POM concentrations when grown in contaminated water. Significant levels of benzo(a)pyrene have been identified in mussels found in remote areas the Greenland coast (47). In areas where measurable amounts of POM have been identified in the water, concentrations in algae and invertebrates are found to be as much as 200 times higher than that recorded in the water (15).

In terrestrial plants, POM levels appear to be a function of ambient POM concentration, length of exposure, and surface characteristics of the plant. In root vegetables, benzo(a)pyrene has been identified in carrots grown in soil containing a known amount of benzo(a)pyrene and in potatoes grown in soil treated with shale oil for erosion control (34). High levels in above ground crops have been linked with ambient air concentrations (grain, kale), large surface areas (kale), waxy surface (plum), and length of growing season (tomatoes) (38,48).

POM may enter higher trophic levels, i.e., vertebrates, through inhalation and ingestion. The extent to which it may concentrate has not yet been adequately documented. In one study cows, pigs, chickens, and ducks were fed a daily diet of 10 mg benzo(a)pyrene for an unspecified period of time. Less than 0.26 μ g/kg of B(a)P was found in the muscle fat and liver, 0.007 μ g were found in eggs, and cow's milk contained 0.10 μ g/ ℓ (49). Gorelova and Di-kun (50) could find only traces of B(a)P after the administration of an unspecified amount in these same test animals.

Polycyclic organic matter may also be added to food during some processing and preparation steps. Heat treatment with smoke, sterilization in the canning process, fumes from grain dryers, food additives, and cooking can all contribute to increased POM levels in food.

The smoking process can result in substantial increases in POM levels in meat and fish. This is particularly important in Europe where up to 40 percent of the meat products and 15 percent of the fish catch are smoked (51). In America where the trend is toward chemical preservation and liquid smoke flavoring, smoking is rarely used for food preservation (52). The Food and

Drug Administration (FDA) has tested liquid smoke for benzo(a)pyrene and found none to be present. However, B(a)P can be found in the residue from which liquid smoke is distilled in concentrations up to 3,800 $\mu g/g$ (53).

Since food additives have numerous applications in the food processing industry, they are a potential source of POM. Food additives include chemical residuals which may or may not be added directly to the food itself. Hydrocarbon solvents are a potential additive when used in the extraction of vegetable oil. European workers have reported POM in technical grade hexane (54). Since hydrocarbon solvents are a potential food additive when used in the extraction of edible oils, they have been examined by the Food and Drug Administration. In a survey of commercial grade hexane from 11 plants involved in the processing of edible oils and related products, of the 15 solvents tested only nine solvents contained traces of pyrene, fluoranthene, anthracene, and phenanthrene and at levels of less than 0.35 $\mu g/\ell$ (53).

Mineral oils, when used in the canning of meats and in the manufacture of bread, may also become a food additive. Concentrations of mineral oil in bread can go as high as 1500 ppm. Analyses of mineral oils by the Food and Drug Administration have shown that the oils conform to the current standards that restrict total POM at such levels to less than 0.05 μ g/ ℓ (53).

POM has also been identified in carbon black stabilized polyethylene plastics and petroleum-based waxes (54,55,56). To determine the possibility of POM migration into food from paraffin waxes, the Food and Drug Administration has analyzed 290 different waxes. Approximately one-fifth of the samples contained POM above 0.01 $\mu g/g$, but none were carcinogenic (53).

Canned food may contain POM as a result of the heat sterilization procedure during processing. The contents are heated to at least 120° C to insure sterilization, but higher temperatures are reached next to the surface of the can and may promote POM production (57).

At temperatures greater than 400°C, fatty acids, glycerides, cholesterol, carotenes, and other compounds found in food can form POM. Temperature dependent effects on benzo(a)pyrene production have been demonstrated by heating starch in the absence of air at two different temperatures. At 370° - 390° C, 7 µg of B(a)P/g of starch were formed as opposed to 1700 µg B(a)P/g of starch at 650° C (58). These temperatures are commonly reached during cooking where

the surface of bread can reach 400° C while baking, and boiling fats reach $400-600^{\circ}$ C (59).

Fumes from the heat source may contain POM which may be deposited on food surfaces. Bread baked in wood stoves show elevated POM levels over bread baked in an electric oven. Elevated POM levels are also seen in charbroiled meat, where POM is produced by pyrolysis of grease drippings and is subsequently deposited on the surface of the meat through smoke condensation (60,61)

Preparation of food items can also be responsible for decreased levels of POM in fresh produce. Washing fruits and vegetables can lower B(a)P concentrations as much as 10 percent and peeling has been shown to reduce B(a)P levels in potatoes (37).

Work has been done by the FDA to determine the amount of POM in a total diet composite sample (see Table 5-14). Typically a composite contains 82 items of food and drink in a quantity sufficient to provide a two-week intake of food for a 16-19 year-old boy. The composite is prepared in the following manner: About 25 items from a typical market basket require such processing as frying, boiling, peeling, trimming, or washing. Bones, peelings, stems, and other nonedible portions are discarded, but meat drippings are saved and included in the composite. Those foods normally eaten raw are divided into portions, and part are prepared and part are left uncooked. After preparation, weight adjustments are made for losses during processing and the foods are weighed in predetermined proportions before homogenization and analysis (62).

Using European data, Borneff estimated the yearly intake of POM through food to approach 4.15 mg. This represents a 3 to 4 mg of POM intake from fruits, vegetables and bread, 0.10 mg from fats and oils, and 0.05 mg from meat and drinking water (19). These estimates are significantly higher than the USFDA estimates, possibly reflecting national differences in environmental conditions and in food preparation.

TABLE 5-14. POM DETECTED IN A TYPICAL U.S. TOTAL DIET COMPOSITE SAMPLE

Category	POM detected	Quantity of POM (µg/kg)	Yearly Intake (µg/kg)
MEATS, FISH, POULTRY			
Roast beef, ground beef, pork chops, pork sausage, chicken, fish, canned fish, luncheon meat, liver, eggs, frank-furters - 3,916 g	Pyrene, fluoran- thene	<2	<204
ROOT VEGETABLES			
Carrots, onions - 383 g	Pyrene, fluoran- thene	<2	<19
DAIRY PRODUCTS			
Fresh milk, evaporated milk, nonfat dry milk, ice cream, cottage cheese, processed cheese, natural cheese, butter - 12,403 g	Pyrene, fluoran- thene	<2	<646
OILS, FATS, AND SHORTENINGS			
Shortenings, peanut butter - 539 g	Pyrene fluoran- thene, benzo(a)- pyrene, benzo(k)- fluoranthene, benzo(b)fluoran- thene, benzo(e)- pyrene, benzo(ghi)- perylene, benzo(a)- anthracene, phenan- threne	<0.5	<7
BEVERAGES			
Tea, coffec, cocoa, soft drinks, water - 16,855 g	Pyrene, fluoran- thene	<2	_<878 <1,754 μg/kg Total

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APPENDIX A

Appendix A is comprised of five sets of bar graphs presenting POM concentrations measured in air, water, and soil. The graphs are a compilation of the data gathered during the review phase of this project. They are international in scope. No effort has been made to screen the data on the basis of the sampling and analysis technique employed for collection. They are intended only to demonstrate the range and variability of POM occurring in the environment. Each value is referenced enabling the user to return to the original reference for data of particular interest.

All the graphs are similar in construction. The end point of each bar indicates the concentration of a specific POM as reported in the reference indicated by a lower case alphabetic character. Diagonal cross hatching is used when the POM concentrations have been converted to common units of measure to facilitate comparison. Standard units are $\mu g/1000 \text{ m}^3$ for air, $\mu g/2$ for water, and $\mu g/kg$ for soil. The structures of the individual POM compounds have been included for convenience.

The first three graphs contain air data categorized as urban or rural. (The individual references should be consulted for a more exact definition of urban and rural.) Due to the large number of benzo(a)pyrene determinations, urban B(a)P has been separated from the other urban POM reading.

Water data are contained in the fourth series of graphs. POM levels identified in river, lake, ground, and marine waters are included.

The fifth set of graphs give POM levels in soil. The soil categories include rural, urban, and industrial soil.

BENZO(a)PYRENE CONCENTRATIONS IN μ g/1000 m³

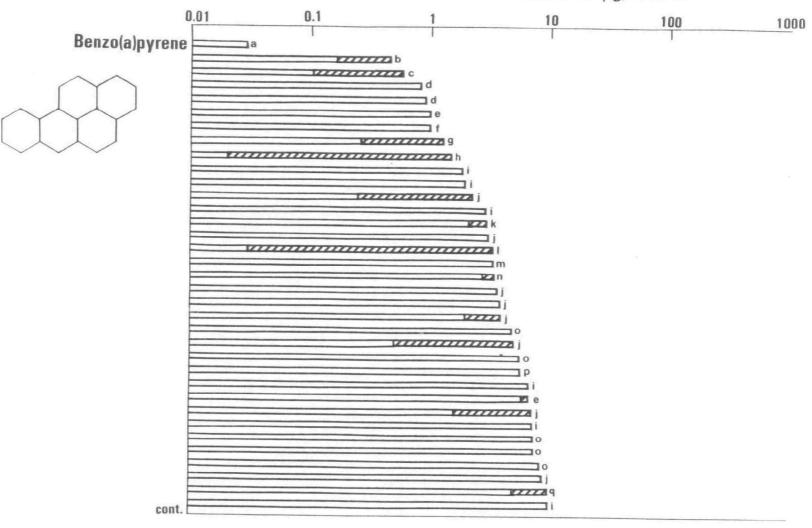


Figure A-1. Ambient concentration of benzo(a)pyrene in urban air in $\mu g/1000~\text{m}^3$. Each line represents specific reported values. Diagonal lines indicate ranges.

BENZO(a)PYRENE CONCENTRATIONS IN μ g/1000 m³

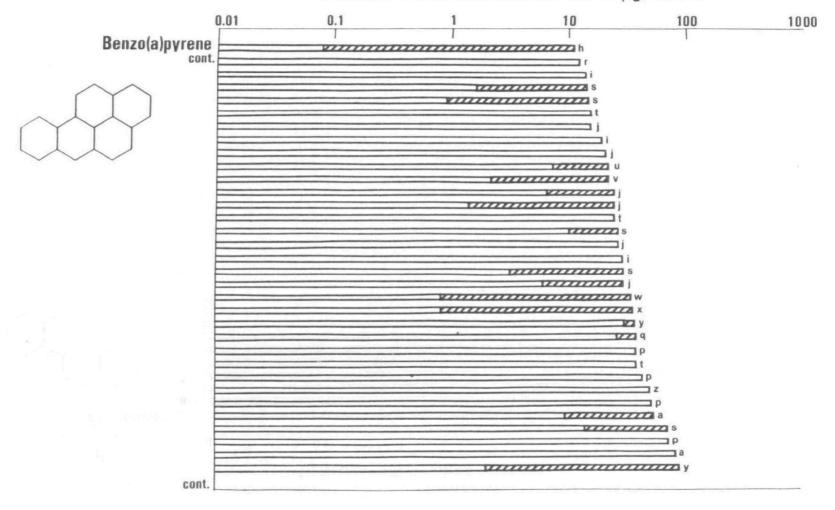


Figure A-1. Ambient concentration of benzo(a)pyrene in urban air in $\mu g/1000~m^3$. Each line represents specific reported values. Diagonal lines indicate ranges.

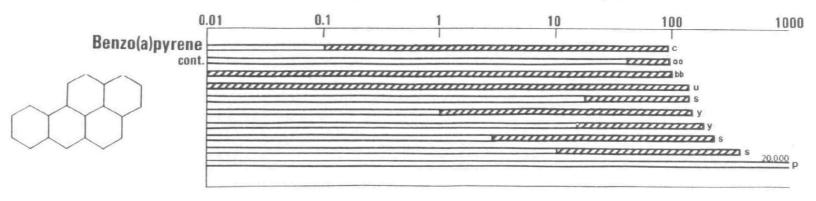


Figure A-1. Ambient concentration of benzo(a)pyrene in urban air in $\mu g/1000$ m³. Each line represents specific reported values. Diagonal lines indicate ranges.

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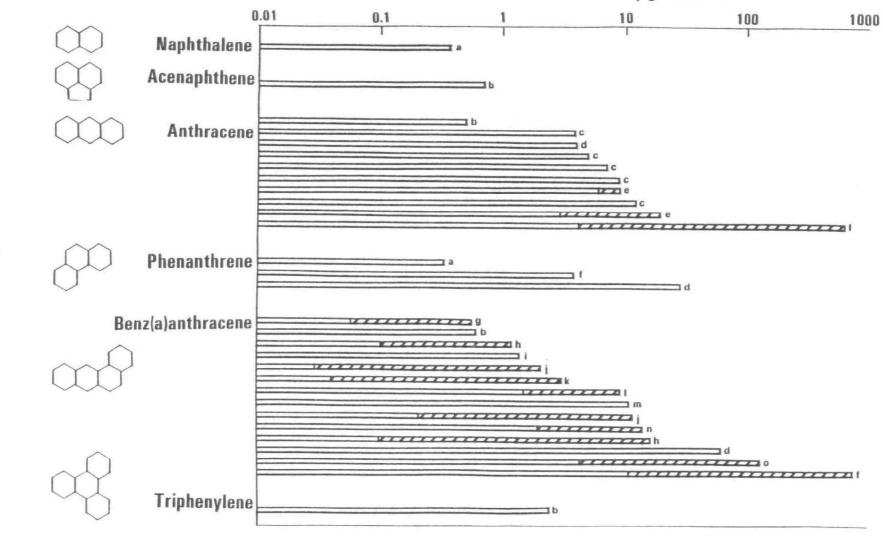


Figure A-2. Ambient concentration of POM in urban air in $\mu g/1000$ m³. Each line represents a reported value. Diagonal line indicates ranges.

Figure A-2. Ambient concentration of POM in urban air in µg/1000 m³. Each line represents a reported value. Diagonal line indicates ranges.

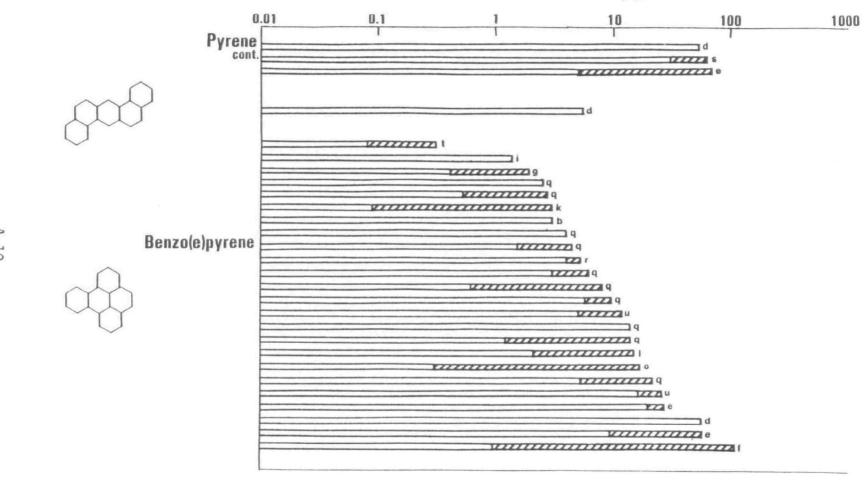


Figure A-2. Ambient concentration of POM in urban air in µg/1000 m³. Each line represents a reported value. Diagonal line indicates ranges.

POM CONCENTRATIONS IN $\mu g/1000~m^3$ 0.01 0.1 100 1000 Perylene mm t Naphtho(1,2,3,4-def)chrysene Anthanthrene

cont.

Figure A-2. Ambient concentration of POM in urban air in $\mu g/1000$ m 3 . Each line represents a reported value. Diagonal line indicates ranges.

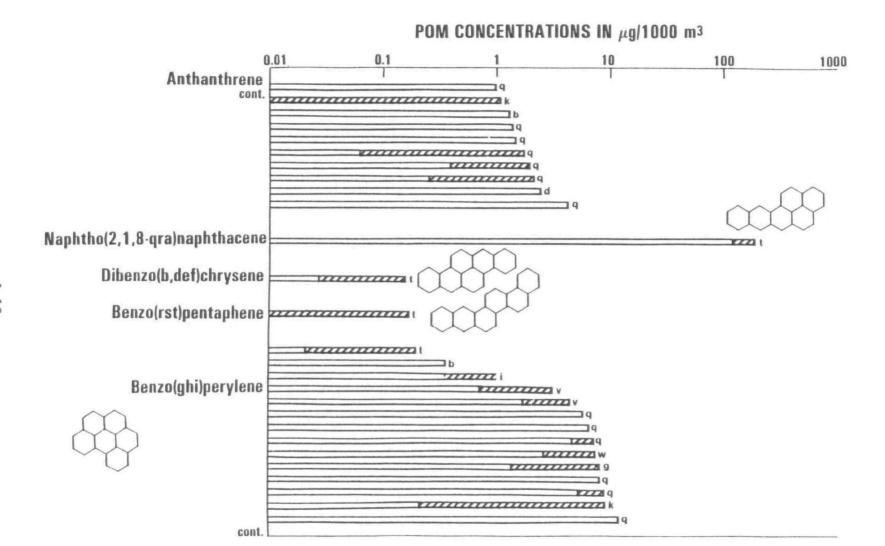


Figure A-2. Ambient concentration of POM in urban air in $\mu g/1000~m^3$. Each line represents a reported value. Diagonal line indicates ranges.

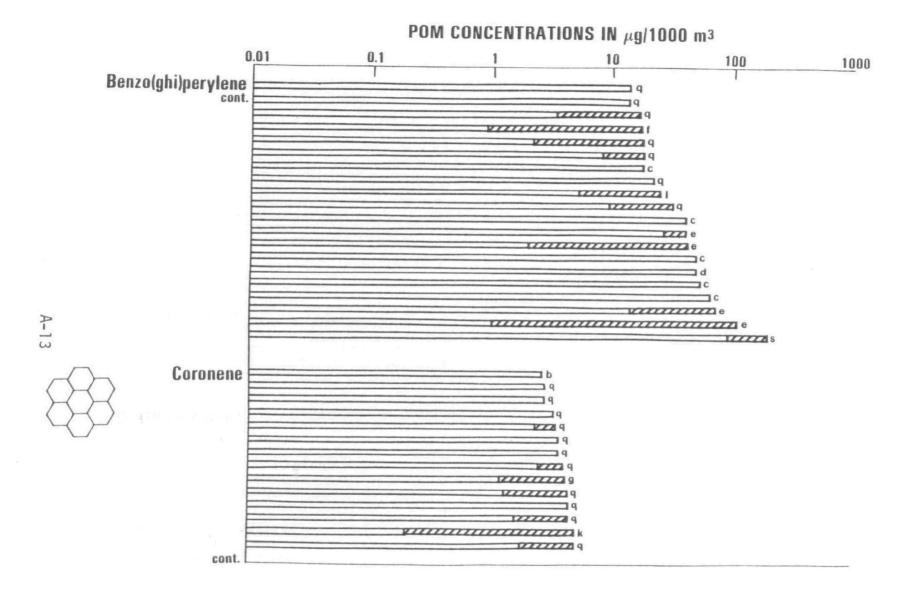


Figure A-2. Ambient concentration of POM in urban air in $\mu g/1000~m^3$. Each line represents a reported value. Diagonal line indicates ranges.

POM CONCENTRATIONS IN $\mu g/1000 \text{ m}^3$

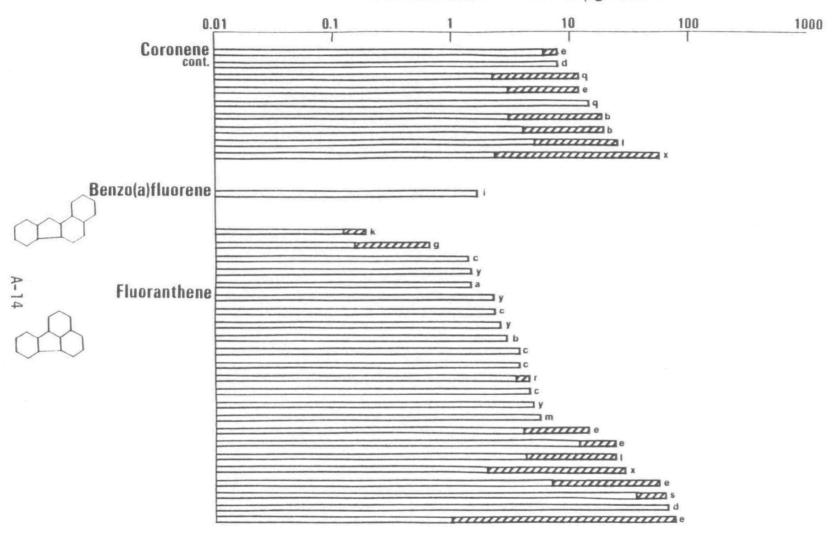


Figure A-2. Ambient concentration of POM in urban air in $\mu g/1000~m^3$. Each line represents a reported value. Diagonal line indicates ranges.

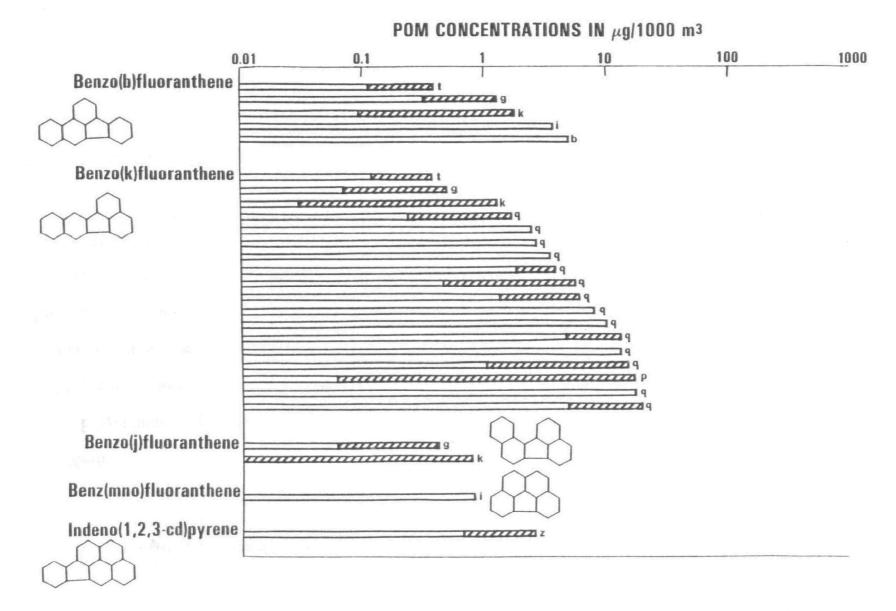


Figure A-2. Ambient concentration of POM in urban air in $\mu g/1000$ m³. Each line represents a reported value. Diagonal line indicates ranges.

POM CONCENTRATIONS IN µg/1000 m³

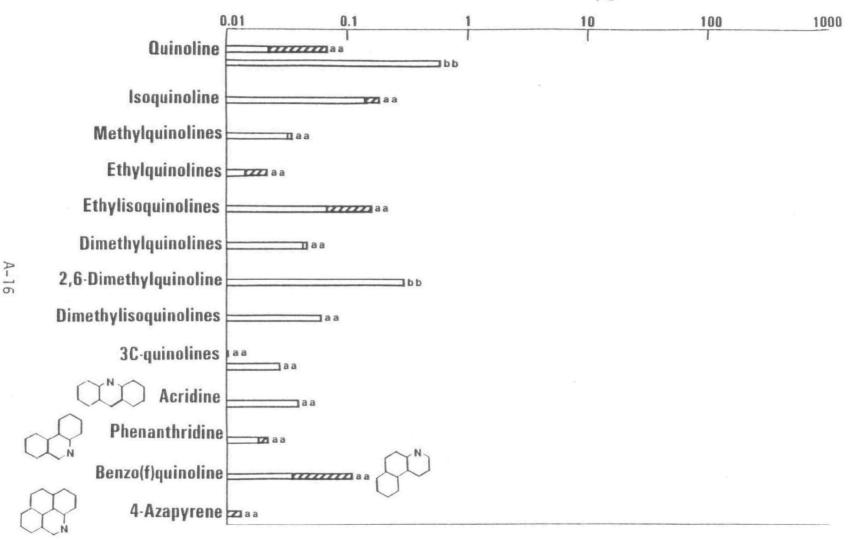
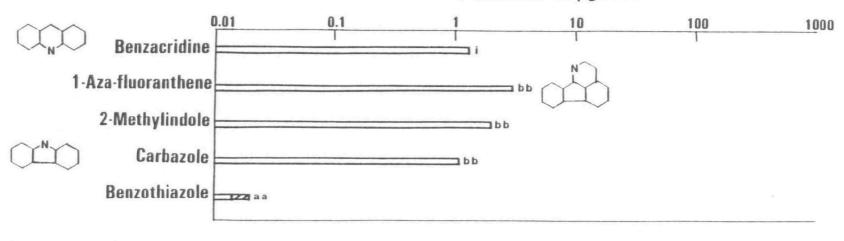


Figure A-2. Ambient concentration of POM in urban air in $\mu g/1000~m^3$. Each line represents a reported value. Diagonal line indicates ranges.

POM CONCENTRATIONS IN µg/1000 m³



7

Figure A-2. Ambient concentration of POM in urban air in $\mu g/1000~m^3$. Each line represents a reported value. Diagonal line indicates ranges.

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Figure A-3. Ambient concentration of POM in rural air in $\mu g/1000~\text{m}^3$. Each line represents a specific reported value. Diagonal indicates range.

Figure A-3. Ambient concentration of PCM in rural air in $\mu g/1000~m^3$. Each line represents a specific reported value. Diagonal lines indicate ranges.

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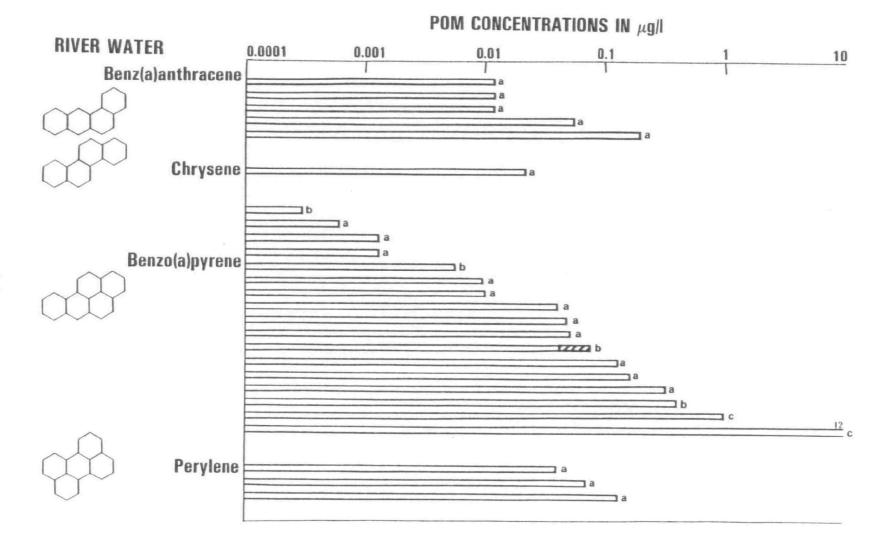


Figure A-4. Ambient concentration of POM in various forms of water in $\mu g/\ell$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATIONS IN $\mu \mathbf{g} / \mathbf{I}$

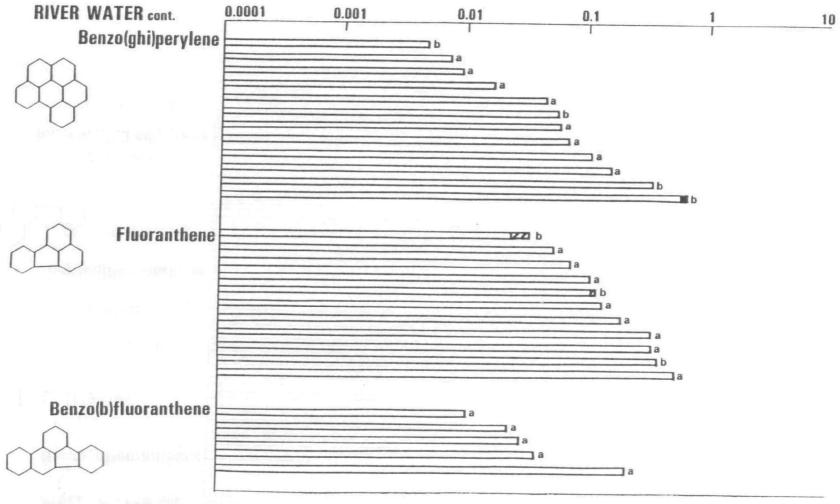


Figure A-4. Ambient concentration of POM in various forms of water in $\mu g/\ell$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATIONS IN μ g/I

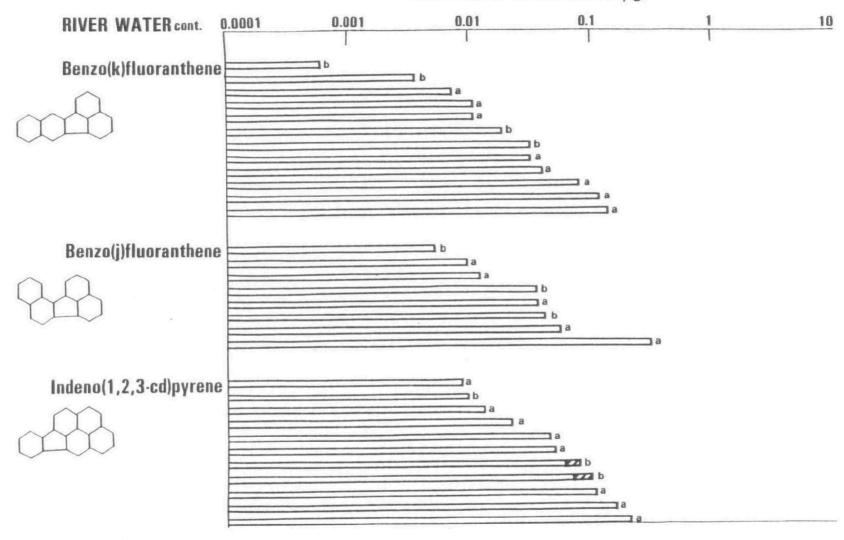


Figure A-4. Ambient concentration of POM in various forms of water in $\mu g/\ell$. Each line represents a specific reported value. Diagonal lines indicate ranges.



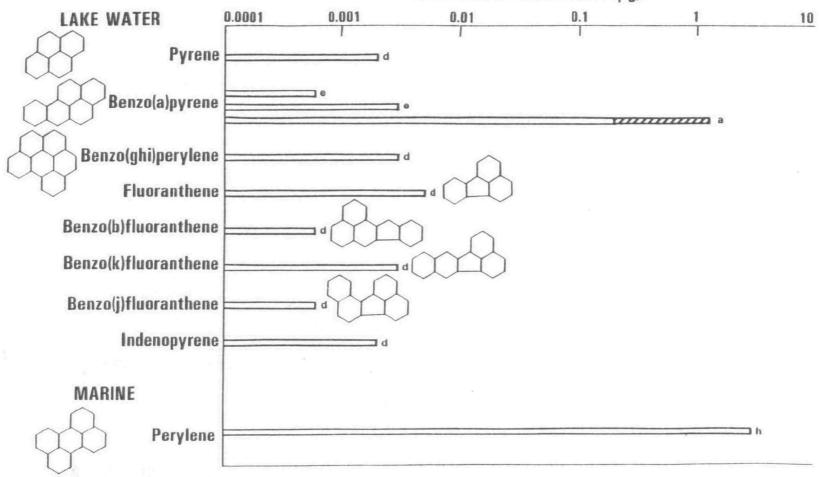


Figure A-4. Ambient concentration of POM in various forms of water in $\mu g/\ell$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATIONS IN $\mu g/I$

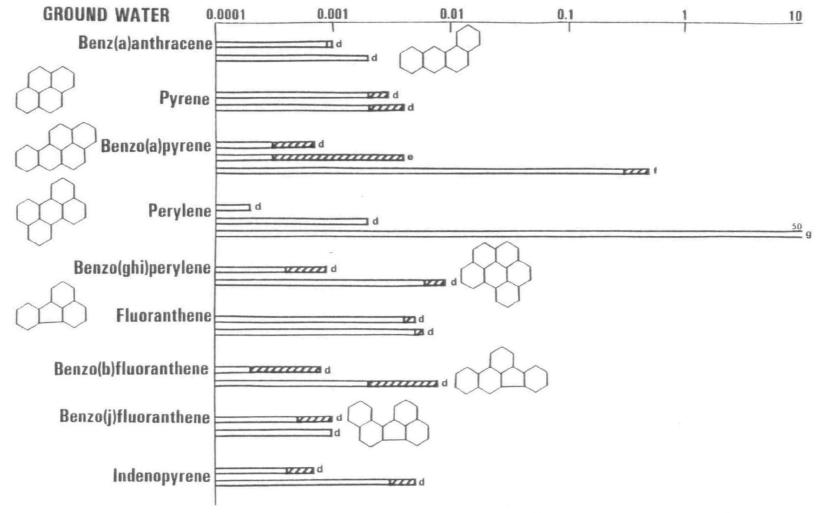


Figure A-4. Ambient concentration of POM in various forms of water in $\mu g/\ell$. Each line represents a specific reported value. Diagonal lines indicate ranges.

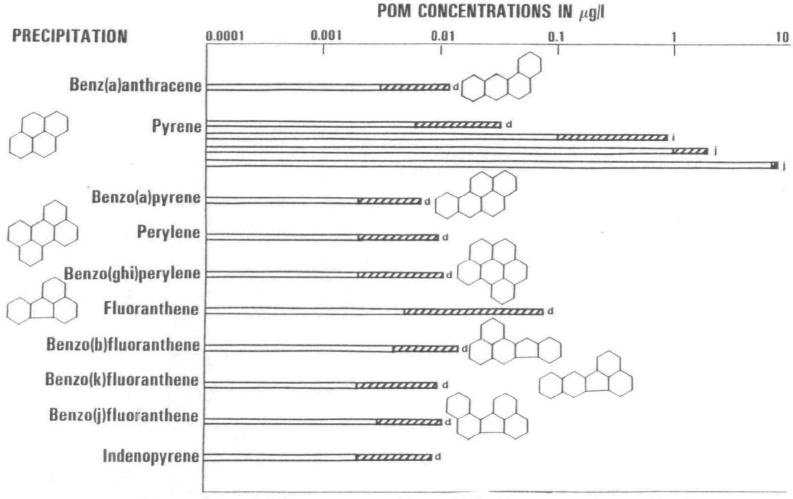


Figure A-4. Ambient concentration of POM in various forms of water in $\mu g/\ell$. Each line represents a specific reported value. Diagonal lines indicate ranges.

REFERENCES - POM IN WATER

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POM CONCENTRATION IN $\mu g/kg$

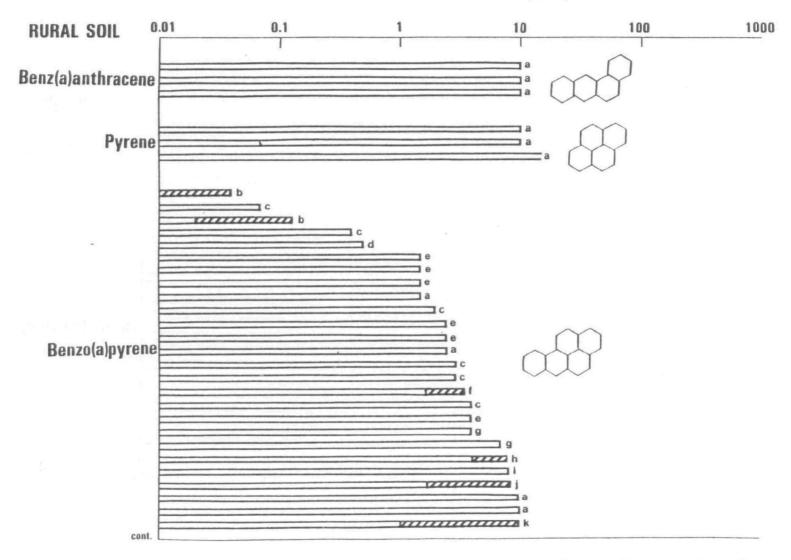


Figure A-5. Ambient concentration of POM in various soil types in $\mu g/kg$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATION IN $\mu g/kg$

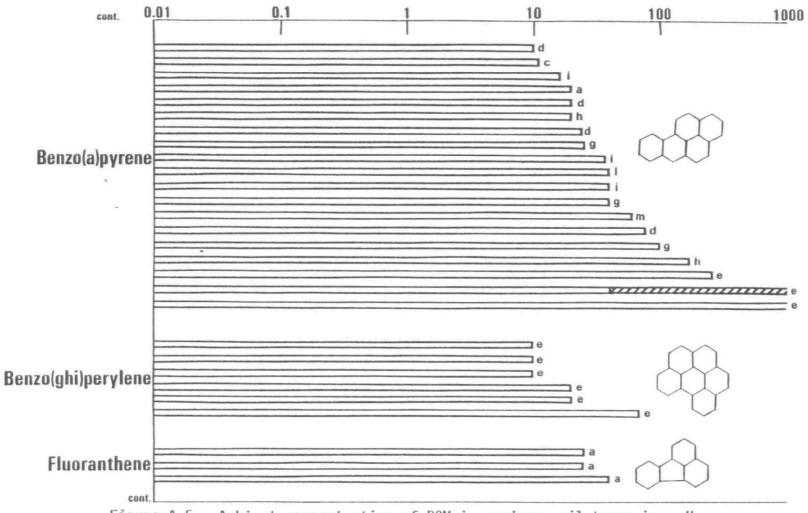


Figure A-5. Ambient concentration of POM in various soil types in $\mu g/kg$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATIONS IN $\mu g/kg$

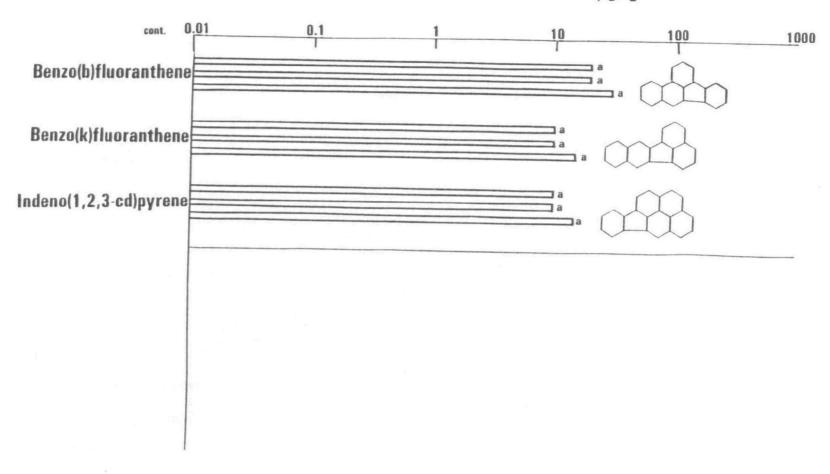


Figure A-5. Ambient concentration of POM in various soil types in $\mu g/kg$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATIONS IN µg/kg

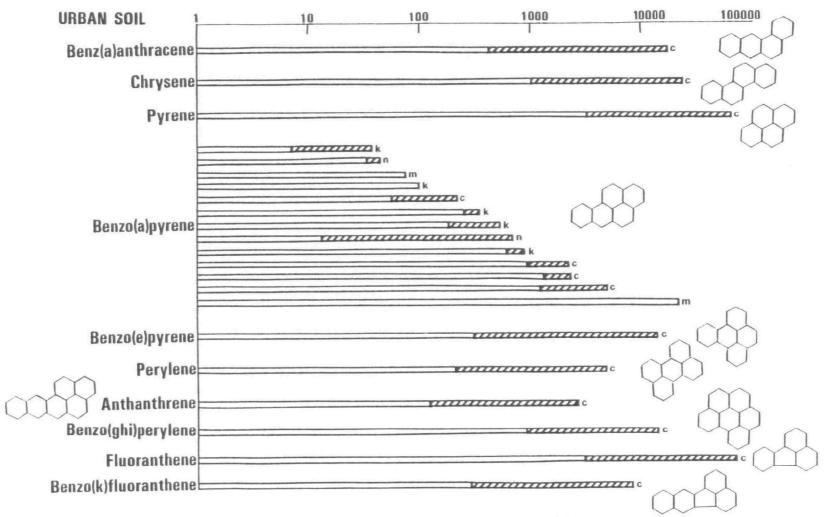


Figure A-5. Ambient concentration of POM in various soil types in $\mu g/kg$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATIONS IN µg/kg

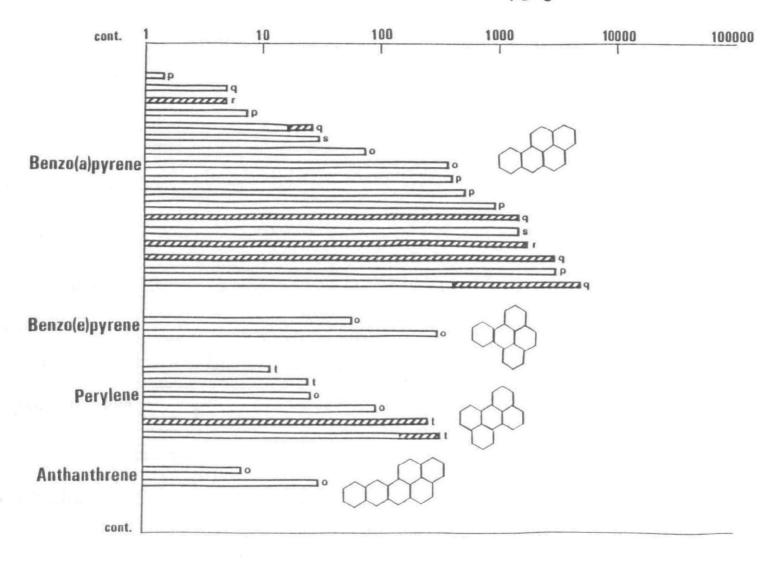


Figure A-5. Ambient concentration of POM in various soil types in $\mu g/kg$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATIONS IN µg/kg

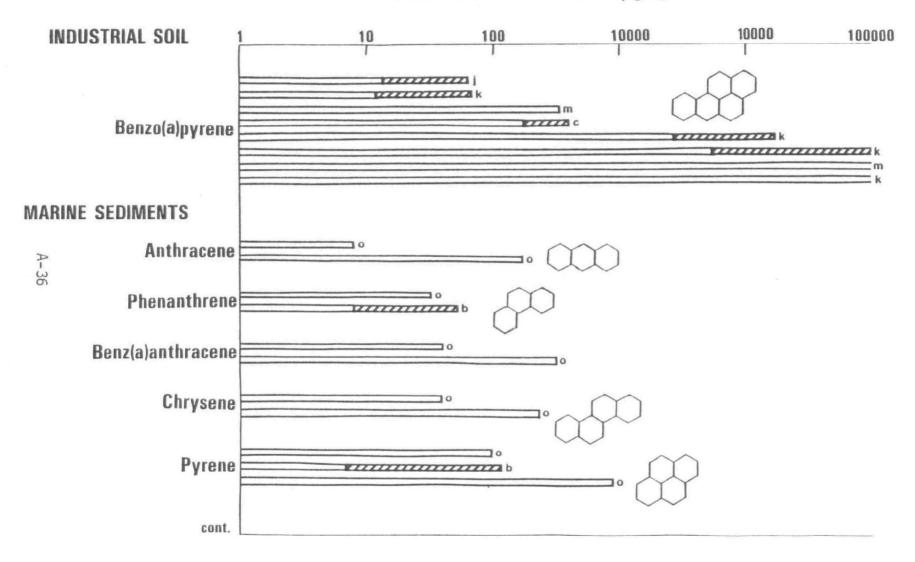


Figure A-5. Ambient concentration of POM in various soil types in $\mu g/kg$. Each line represents a specific reported value. Diagonal lines indicate ranges.

POM CONCENTRATIONS IN $\mu g/kg$

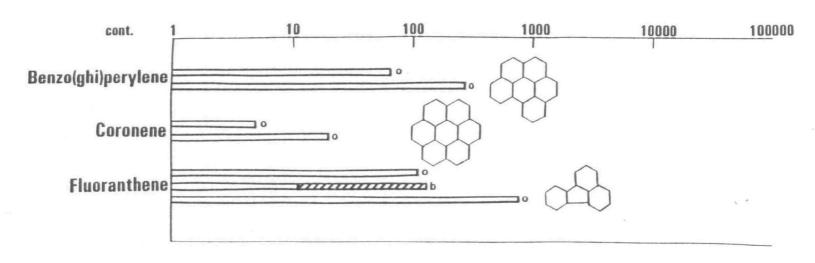


Figure A-5. Ambient concentration of POM in various soil types in $\mu g/kg$. Each line represents a specific reported value. Diagonal lines indicate ranges.

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APPENDIX B - BIBLIOGRAPHY

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15. SUPPLEMENTARY NOTES IERL-RTP project officer is John O. Milliken, Mail Drop 63, 919/541-2745.

16. ABSTRACT The report gives results of an analysis of source and ambient concentration data for polycyclic organic matter (POM). Based on the literature reviewed, POM data were summarized and the sampling and analytical techniques were critiqued and evaluated against state-of-the-art technology. The objective was to determine the scientific and engineering credibility of a previously established POM data base by an evaluation of the sampling and analytical techniques employed. (POM is an unregulated class of pollutants which is a potential candidate for regulatory action as outlined in Section 122a of the Clean Air Act Amendments of 1977.) It was concluded that sampling techniques contain uncertainties that limit the udesfulness of these data in an environmental assessment of POM. The uncertainties include the possibility of the incomplete capture of POM during emission sampling, the chemical degradation of the collected sample during both emission source and embient sampling, and the unproven reliability of benzo(a)pyrene as an indicator of total POM from emission sources or in ambient media. The uncertainties may be compounded by losses during analysis. Also, since it is not feasible to quantify all the POM which may be present in an environmental sample, the number of POMs reported will reflect the scope of the analytical strategy and the limitations of the analytical technique employed.

17. KEY WO	PRDS AND DOCUMENT ANALYSIS	
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS c. COSATI Field/Group	
Pollution Pyrenes Polycyclic Compounds Organic Compounds Sampling Analyzing	Pollution Control 13B Stationary Sources 07C Polycyclic Organic Matter 14B Benzo(a)pyrene	
Assessments 18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified 22. PRICE	