

Statistical analysis of the Los Angeles data indicate that the geometric mean carbon monoxide concentration (18) was 10 ppm with 90% confidence limits of 4–25 ppm. The largest daily maximum hourly average CO concentration reported was 37 ppm.

Assuming that the hydrocarbon mixture used in this investigation (Table IV) is representative of the Los Angeles atmosphere, the effect of reducing the carbon monoxide concentration from the geometric mean given above to zero, by whatever means, would be small. The NO₂ formation rate would be reduced about 14% while the ozone yield would be unaffected. Thus, based on the data of this investigation, the effect of carbon monoxide on photochemical smog formation would be negligible, in accord with the conclusion of Dodge and Bufalini.

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Dependency of Polynuclear Aromatic Hydrocarbon Content on Size Distribution of Atmospheric Aerosols

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■ An examination was made of the dependency of polynuclear aromatic hydrocarbon (PAH) content on the particle size distribution of atmospheric suspended particulate matter. Ambient aerosols were collected in specific time periods during 1972 and 1973 using size-fractionating cascade impactors (Anderson "Hi-Vol" samplers) at five sites in Toronto, Ont. Collected particulate matter was extracted with benzene in a Soxhlet apparatus. Eight PAH's and two oxygenated arenes were separated by thin-layer chromatography and identified and analyzed by absorption and fluorescence spectrophotometry. The efficiency and accuracy of the procedures involved were studied. The size distribution of PAH-containing particulates followed approximately a log-normal relationship for suburban and rural sampling sites with the majority of PAH content associated with particles below 3.0 μm diameter. Significant variations were discovered in PAH content between downtown-urban, urban, suburban, and rural areas. PAH concentration in submicron particles increased during the winter months.

Polynuclear aromatic hydrocarbons (PAH) and related polycyclic arenes are known to be widely distributed in the atmospheric environment. Some of these compounds are carcinogenic for experimental animals and have been associated with the incidence of various types of cancer in man.

Since the majority of PAH compounds are adsorbed on particulate matter, the great increase in the potential carcinogenic effect of such compounds as benzo(a)pyrene by incorporation with substantially inert particulate matter of small size is believed to be brought about by transport through the upper respiratory tract into the bronchioles and alveoli of the lungs (1).

At present, progress in control of air pollution by atmospheric particulate matter is evaluated by calculating the total weight of material collected by standard high-volume sampling techniques (2). However, it is important to realize that the total weight of particulate collected is a cumulative total of the fractional contribution of all particulate sizes composing the heterogeneous, polydisperse aerosol that is present in the atmosphere. Because the content of PAH's and other suspected carcinogens has been determined almost exclusively on the basis of separation and analysis of organic matter obtained from the above type of sampling system, no assessment of the PAH content with respect to size of particles in an aerosol can be made.

Technological advances toward increased burning efficiency of fossil fuels and on control techniques of particulate and gaseous emissions from stack effluents and transportation sources will lead to a decrease in the amount of large, nonrespirable particle emissions but may also lead to an increase in the number of particles in the respirable size range. Respirable particles may be defined as those

particles with aerodynamic diameter below 5.0 μm that are deposited in the human respiratory tract (3). Hence, from an inhalation health aspect, it is important to determine the amount of potential carcinogenic material associated with the particles in an aerosol that may be inhaled and deposited in the respiratory tract.

Particle size distributions of various trace inorganic materials have been measured by Lee et al. (4), Natusch et al. (5), and Gladney et al. (6). There is presently little information on the particle size or mass distribution of PAH in an aerosol. In one study (7), more than 75% of the weight of selected PAH's was associated with aerosol particles less than 2.5 μm in diameter. However, Thomas (8) has shown that the amount of benzo(a)pyrene per unit weight of soot obtained from the combustion of various fuels was constant for all particle sizes. In this paper, the size distributions of chrysene, benz(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, perylene, benzo(ghi)perylene, anthanthrene, coronene, 7-H-benzo(de)-anthracene-7-one, and phenalen-1-one are examined in relation to sampling location and seasonal variations.

Experimental

Sample Collection. Suspended particulate matter was collected at five locations in the Toronto, Ont., area. The locations may be described as follows: (1) York University, a northern suburban-rural area, (2) Evans Ave., a southwestern suburban area, (3) south of the Toronto International Airport, a rural area near the MacDonald-Cartier Freeway, (4) Bathurst St., a northern suburban area, and (5) College St., a downtown urban area.

Aerosol samples were collected during 1972 and 1973 by five-stage Anderson Hi-Vol cascade impactors. The first four stages of the sampler comprise the fractionating head, while the fifth stage is a backup filter positioned between the fractionating head and a standard Hi-Vol air sampler [for a more detailed description of the sampler, see Burton et al. (9)]. At a flow rate of 20 cfm (566 l/min) the sampler fractionates suspended particulate matter into five aerodynamic size ranges according to the calculated 50% cutoff diameters given in Table I. Calibration with a synthetic aerosol and field evaluation of this sampler has recently been carried out (9).

The fractionators were carefully assembled with fiber glass collection media (pH 6.5) and installed on the Hi-Vol samplers. Originally, fiber glass collection media at pH 11.0 were used. However, sulfate production in the presence of sulphur dioxide increased the weight of collected particulates to yield invalid samples (9). The flow rates were adjusted with variable voltage transformers and measured with oil manometers. Sampling time varied between 24 and 48 hr, depending on the atmospheric particulate loading of the sampling location. Before and after each sampling period, the filters were conditioned at constant relative humidity ($50 \pm 2\%$) and temperature ($22 \pm$

2°C) for 24 hr and weighed to obtain the total weight of collected particulate matter. The particulate-laden filters were placed in a Soxhlet extractor, and the organic matter was extracted with 250 ml of spectrograde benzene for 8 hr. The organic matter was filtered and reduced to a volume of 50 ml by flash evaporation at a temperature below 40°C . The remaining benzene was carefully evaporated under a stream of dry nitrogen at room temperature. The residue was dissolved in a known amount of benzene and stored in the cold and dark until analysis was performed.

Analytical Technique. The standard PAH's were purified through recrystallization and thin-layer chromatography on cellulose acetate where necessary. All solvents employed were of spectrograde quality. Estimations of PAH content in organic matter, in airborne particulates, and in volume of air sampled were carried out with the aid of internal standards and calibration curves for each compound investigated.

Isolation of the PAH's contained in the organic matter was accomplished through the use of neutral aluminum oxide thin-layer plates ($20 \times 20 \times 0.1$ cm) as the stationary phase with a mixture of pentane: ether (19:1, v/v) as the mobile phase by the ascending method of development in a sandwich chamber (Brinkmann, Model 116C; minimum volume chamber that saturates rapidly). Favorable results were obtained with this type of chamber since the necessity of letting the chamber equilibrate for $1\frac{1}{2}$ -2 hr prior to development was eliminated. Also, better resolution of PAH's was achieved for a shorter time of development.

Aliquots of the various extracts were added 1.5 cm from the bottom of the thin-layer plate. Pure samples of PAH's were added to the origin of the same plate to be used as internal standards. After the solvent was allowed to rise to a height of 15 cm in the chamber, the developed chromatogram was dried and viewed under a long-wave ultraviolet light source. The fluorescent areas of internal standards and corresponding areas of the PAH's isolated from the organic matter were marked and the absorbent, containing standard and unknown, was removed from the plate. The desired PAH's were eluted with 20-30 ml of hot spectrograde dichloromethane. The solvent was then evaporated under dry nitrogen at room temperature and the residue taken up in a specific volume of spectrograde toluene.

Luminescence measurements were carried out at room temperature on a Farrand Mki spectrofluorometer equipped with a high intensity Xenon arc lamp, grating monochromators for wavelength selection in both excitation and emission spectra, a RCA 1P28 photomultiplier tube and a Heath strip chart recorder. Wavelength resolution was achieved with the aid of slits varying in width from 1-20 nm. Both excitation and emission spectra were recorded at a scanning speed of 75 nm/min.

In sufficiently dilute solutions and in the absence of interfering substances, fluorescence emission intensity is a linear function of concentration. For all analytic work, calibration curves were determined in conditions exactly the same as those encountered in the analysis. Beer's law was obeyed for PAH concentrations below 10^{-5} mol/l. Samples of PAH were efficiently degassed by displacing dissolved oxygen with dry nitrogen prior to luminescence analysis.

Determination of the benzo(a)pyrene [BaP] and benzo(k)fluoranthene [BkF] content present in both the internal standards and organic matter was accomplished using the method of Dubois and Monkman (10). Other members of the benzopyrene series—i.e., benzo(e)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, and benzo(g)-

Table I. Aerodynamic Size Range of Suspended Particulate Matter Collected with Anderson Hi-Vol Cascade Impactor

| Stage no. | Size range, μm |
|----------------|---------------------------|
| 1 | ≥ 7.0 |
| 2 | 3.3-7.0 |
| 3 | 2.0-3.3 |
| 4 | 1.1-2.0 |
| 5 ^a | ≤ 1.1 |

^a Stage 5 is the backup filter (8×10 in. glass fiber).

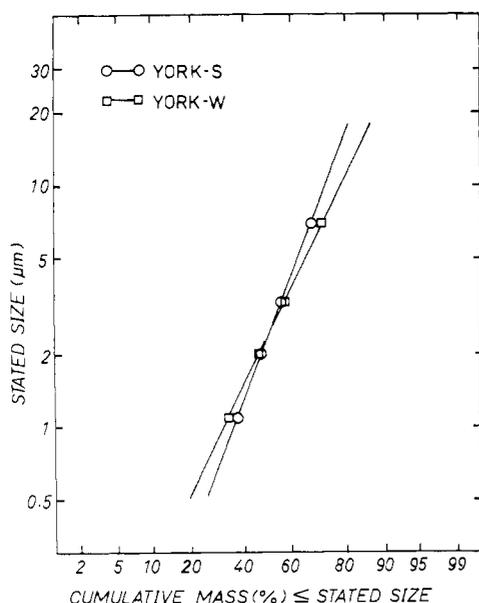


Figure 1. Least squares plot of average cumulative mass of suspended particulate matter for York site (summer—S, winter—W, 1972)

hi)fluoranthene, did not interfere with the luminescence measurements of BaP and BkF.

Two ring carbonyls, 7-H-benz(*de*)anthracene-7-one and phenalen-1-one were extracted from samples of atmospheric particulate matter using benzene ($93 \pm 4\%$) and isolated by thin-layer chromatography ($91 \pm 2\%$) with aluminum oxide and pentane:chloroform (3:2, v/v). Luminescence measurements were carried out at room temperature in concentrated sulfuric acid.

Results and Discussion

Sample Collection. The common technique for representing the particle-weight distribution of an aerosol calls for a determination of the relationship between the cumulative mass of the collected particulate matter and the size of that particulate matter (11). This is accomplished by plotting the logarithm of the effective cutoff diameter (ECD) for each stage on the ordinate as a function of the cumulative mass, expressed as a percent, less than or equal to the ECD at each stage on the abscissa. In practice, log-probability paper is used.

Since the particle sizes of most suspended particulate matter follow approximately a normal logarithmic distribution, the mass median diameter (MMD) is found at the 50% mass cumulative point. The geometric standard deviation (σ_g), which is roughly equivalent to the slope of the distribution curve, provides an indication of the particle dispersion on the range of particle sizes in an aerosol. The value is estimated from the ratio of the 84% value of particle size to the 50% value of the particle size. Figure 1 is a least squares plot of the average cumulative mass of suspended particulate matter in relation to particle size for the York sampling station. Data indicated that the suspended particulate matter was well described by a log-normal function as indicated by the linearity of the calculated size distribution. The size distribution curves were also used to determine the percentage of particulate mass, less than or equal to a selected size. The actual concentration of particles less than or equal to a selected diameter was determined from the product of the percentage of the cumulative mass for that fraction and the total aerosol concentration.

Data presented in Table II include the total mass concentration, MMD, σ_g , and the percentage of particles in the respirable size range for the five sampling sites in Toronto, Ont., including sampling periods representative of both winter and summer seasons. Unfortunately, no winter samples for the Evans or MacDonald Cartier stations were available. The geometric mean values for each station, together with the geometric standard deviations, were calculated using standard techniques. In this case, the geometric standard deviation represents the spread of the values over the number of samples analyzed and, hence, gives an indication of the degree of variability for different sampling periods. The mean mass concentration varied from a low of $67 \mu\text{g}/\text{m}^3$ in the relatively clean air of the rural-suburban areas to a high of $108 \mu\text{g}/\text{m}^3$ in sub-urban-metro areas. However, the mass concentration for all stations displayed a significant fluctuation from the mean values. The MMD's and σ_g 's appear to be dependent upon the sampling location and time of year. In most cases, at least 50% of the aerosol mass was associated with particles less than or equal to $3.0 \mu\text{m}$.

Analytical Technique. Sensitivity and Accuracy. All quantitative data were secured with the aid of internal standards under reproducible conditions (internal standard is defined as a compound that is subjected to exactly the same treatment as the unknown compound being investigated). The efficiency of extraction of enriched par-

Table II. Data Obtained with Anderson Impactors at Five Different Sites in Toronto, Ont.

| Sampling station | Sampling period | No. of samples | Geometric mean \pm geometric standard deviation | | MMD, μm | σ_g | Concn, $\leq 1.0 \mu\text{m}$, % | Concn, $\leq 3.0 \mu\text{m}$, % |
|-------------------|-------------------|----------------|---|--|--------------------|----------------|-----------------------------------|-----------------------------------|
| | | | Mass concn, $\mu\text{g}/\text{m}^3$ | | | | | |
| York | 24/06/72–28/07/72 | 10 | 78.0 ± 25.8 | | 2.3 ± 0.6 | 10.8 ± 1.5 | 34.2 ± 2.0 | 54.1 ± 1.8 |
| York | 31/01/72–31/03/72 | 15 | 67.2 ± 18.3 | | 2.4 ± 0.4 | 6.2 ± 1.1 | 31.0 ± 1.6 | 54.5 ± 2.0 |
| Evans | 22/05/73–29/05/73 | 6 | 92.8 ± 23.1 | | 3.1 ± 0.5 | 6.8 ± 1.1 | 26.0 ± 2.1 | 51.2 ± 2.0 |
| MacDonald-Cartier | 14/05/73–20/05/73 | 12 | 68.7 ± 37.5 | | 2.7 ± 0.7 | 7.9 ± 2.4 | 32.0 ± 1.4 | 51.0 ± 2.0 |
| Bathurst | 30/06/73–24/07/73 | 4 | 108.1 ± 17.3 | | 1.5 ± 0.5 | 20.1 ± 2.5 | 40.7 ± 0.9 | 57.2 ± 1.3 |
| Bathurst | 15/12/73–29/01/74 | 3 | 107.4 ± 25.9 | | 4.3 ± 0.2 | 9.4 ± 0.5 | 28.2 ± 0.5 | 44.2 ± 0.7 |
| College | 30/06/73–24/07/73 | 4 | 105.4 ± 23.7 | | 1.8 ± 1.2 | 16.1 ± 4.5 | 36.2 ± 1.0 | 54.7 ± 2.6 |
| College | 15/12/73–27/02/74 | 5 | 78.8 ± 22.8 | | 3.4 ± 0.4 | 13.5 ± 0.4 | 30.2 ± 0.7 | 46.3 ± 0.9 |

ticulate matter and recovery of PAH's by Soxhlet extraction with benzene ranged from 95–100% with a relative standard deviation of $\pm 3\%$. Reduction in the volume of organic matter using flash evaporation with subsequent drying using a stream of dry nitrogen at room temperature did not lead to any loss of PAH content through either evaporation or decomposition. Recoveries of standard PAH's using alumina thin-layer chromatography varied from 94–98% with a relative standard deviation of ± 2 to $\pm 4\%$. The spectroscopic procedure itself appeared to be highly sensitive and accurate. The lower limit of detection and measurement of a standard BaP solution of 2.0 ng/ml was achieved with a deviation of less than 1%. The limiting factor in the analysis of PAH appeared to be the efficiency and reproducibility of the extraction and separation procedures used prior to luminescence analysis. Corrections of up to $5 \pm 3\%$ for extraction and $6 \pm 4\%$ for separation, elution, and analysis were applied for estimation of PAH content. Because of the very small concentration of PAH's in the atmosphere, it was not possible to analyze individual samples. Particulate samples, corresponding to a specific stage of the Anderson sampler and hence size fraction of aerosol collected, were combined and extracted as a group. As a result, average values of PAH concentration were obtained for aerosol samples collected over a period of several particulate sampling periods and, thus, any variation in PAH content within the specified sampling period could not be determined. However, monthly and seasonal variations were obtained. All data reported below were averaged over multiple determinations and have been corrected for the losses reported above.

PAH-Size Distribution. Data on the PAH-size distribution of three representative PAH's, expressed in relation to μg PAH/g particulate and in relation to ng PAH/1000 m^3 air, are presented in Tables III and IV, respectively. The values reported are averages of multiple determinations on the same sample and, in this case, the standard deviations reported represent the degree of reproducibility of the analysis procedure.

By comparing Tables III and IV, it is observed that the MMD values are different for the same aerosol sample. However, it must be remembered that the values are based on two different parameters—data in Table III are obtained with respect to weight of particulate matter collected whereas data in Table IV are obtained with respect to volume of air sampled. During atmospheric sampling, the volume of air passing through each stage of the sampling device is the same, but the amount of particulate matter collected on each stage will be different. Hence, the amount of PAH appears to be different depending upon the frame of reference that is chosen. Most data on concentration of toxic trace species are expressed as a mass per volume of air sampled.

The PAH content with respect to particle size of the suspended particulate matter followed approximately a log-normal distribution for three of the five sampling sites—i.e., York, Evans, and MacDonald Cartier. However, the distribution curves were significantly nonlinear for the Bathurst and College sampling stations. The total PAH concentration tended to be highest in the urban areas, while the rural-suburban areas exhibited the lowest concentration. In general, the MMD values for the PAH-containing aerosols were larger at the York station than at the Evans or MacDonald-Cartier stations, indicating a relatively smaller amount of PAH's in the respirable size range. This is supported by the fact that only 6–14% of the PAH content at York was associated with particles of diameter $\leq 1.0 \mu\text{m}$, whereas 40–60% PAH content for the same particle size was found at the other two stations. All geometric standard deviations (σ_g) were small, denoting a narrow distribution of PAH content in the particle size investigated.

The lack of linearity in the PAH-size distribution curves for both the Bathurst and College sampling sites indicated that the PAH content was significantly influenced by the presence of specific emission sources different from those present at the other sampling sites. The percent mass of BaP for each stage of the Anderson sampler with respect to volume of air sampled (i.e., size frac-

Table III. Data on PAH Content with Respect to Weight of Particulate Matter Collected at Five Different Sites in Toronto, Ont.

(μg PAH/g particulate)

| Sampling station | Sampling period | Compound | Total ^a concn | MMD, μm | σ_g | Concn, $\leq 1.0 \mu\text{m}$, % | Concn, $\leq 3.0 \mu\text{m}$, % |
|-------------------|-----------------------|----------|--------------------------|--------------------|------------|-----------------------------------|-----------------------------------|
| York | 24/06/72– 28/07/72 | BaP | 12.6 | 2.4 | 2.2 | 14 | 62 |
| | | BkF | 11.2 | 2.7 | 1.9 | 6 | 56 |
| | | Per | 7.4 | 2.8 | 1.9 | 8 | 56 |
| York | 31/01/72– 31/03/72 | BaP | 17.1 | 1.6 | 2.5 | 30 | 76 |
| | | BaF | 17.4 | 1.8 | 2.4 | 22 | 72 |
| | | Per | 10.1 | 1.6 | 2.6 | 28 | 78 |
| Evans | 22/05/73– 29/05/73 | BaP | 11.2 | 1.4 | 3.3 | 40 | 70 |
| | | BkF | 13.4 | 1.4 | 4.1 | 40 | 71 |
| | | Per | 4.6 | 1.8 | 2.7 | 29 | 68 |
| MacDonald-Cartier | 14/05/73– 20/05/73 | BaP | 4.8 | 0.9 | 5.1 | 56 | 78 |
| | | BkF | 5.2 | 0.8 | 5.4 | 58 | 79 |
| | | Per | 1.9 | 1.0 | 4.9 | 54 | 74 |
| Bathurst | 30/06/73– 24/07/73 | BaP | 39.8 | | | | |
| | | BkF | 41.7 | | | | |
| | | Per | 14.3 | | | | |
| Bathurst | 15/12/73– 29/01/74 | BaP | 41.0 | | | | |
| | | BkF | 46.2 | | | | |
| | | Per | 15.6 | | | | |
| College | 30/06/73– 24/07/73 | BaP | 24.9 | | | | |
| | | BkF | 24.0 | | | | |
| | | Per | 11.8 | | | | |
| College | 15/12/73– 27/02/74 | BaP | 65.0 | | | | |
| | | BkF | 64.4 | | | | |
| | | Per | 37.2 | | | | |

^a Reproducibility of PAH concentration is $\pm 6\%$ for BaP, $\pm 5\%$ for BkF and Per.

Table IV. Data on PAH Content with Respect to Volume of Air Sampled at Five Different Sites in Toronto, Ont.

(Ng/1000 m³ air)

| Sampling station | Sampling period | Compound | Total ^a concn | MMD, μm | σg | Concn, ≤1.0 μm, % | Concn, ≤3.0 μm, % |
|-------------------|-----------------------|----------|--------------------------|---------|------|-------------------|-------------------|
| York | 24/06/72- 28/07/72 | BaP | 127.1 | 2.6 | 2.6 | 15 | 56 |
| | | BkF | 115.8 | 2.9 | 2.8 | 14 | 54 |
| | | Per | 72.1 | 2.7 | 2.7 | 15 | 54 |
| York | 31/01/72- 31/03/72 | BaP | 238.2 | 1.2 | 4.2 | 46 | 76 |
| | | BkF | 250.8 | 1.1 | 3.8 | 47 | 78 |
| | | Per | 135.6 | 1.2 | 3.5 | 42 | 78 |
| Evans | 22/05/73- 29/05/73 | BaP | 216.8 | 1.0 | 5.3 | 46 | 70 |
| | | BkF | 263.7 | 0.9 | 6.2 | 52 | 72 |
| | | Per | 69.5 | 1.1 | 6.1 | 46 | 68 |
| MacDonald-Cartier | 14/05/73- 20/05/73 | BaP | 112.7 | 0.3 | 11.7 | 70 | 82 |
| | | BkF | 125.6 | 0.3 | 12.0 | 72 | 84 |
| | | Per | 34.6 | 0.5 | 10.9 | 68 | 80 |
| Bathurst | 30/06/73- 24/07/73 | BaP | 831.3 | | | | |
| | | BkF | 907.9 | | | | |
| | | Per | 148.2 | | | | |
| Bathurst | 15/12/73- 29/01/74 | BaP | 850.2 | | | | |
| | | BkF | 961.7 | | | | |
| | | Per | 172.4 | | | | |
| College | 30/06/73- 24/07/73 | BaP | 389.6 | | | | |
| | | BkF | 389.6 | | | | |
| | | Per | 174.8 | | | | |
| College | 15/12/73- 27/02/74 | BaP | 716.5 | | | | |
| | | BkF | 767.8 | | | | |
| | | Per | 305.9 | | | | |

^a Reproducibility of PAH concentration is ±6% for BaP, ±5% for BkF and Per.

tion of BaP-containing particulate matter) for all five sampling locations is presented in Figure 2.

Significantly different variations in the benzo(a)pyrene content were recorded for different sampling sites. The York site had a maximal amount of BaP for stage 3 (2.0-3.3 μm) whereas the Evans and MacDonald-Cartier sites exhibited the greatest concentration of BaP for stage 5 (≤1.1 μm) during the summer sampling period. However, during the winter sampling period at York, the BaP content significantly increased for particle sizes below 1.0 μm. This indicates that, during the winter period, PAH content was associated primarily with smaller particles than during the summer period. The same relationship holds for several other PAH's analyzed at this station.

The College St. station, in general, showed the same BaP distribution for both winter and summer samples, although the PAH concentration for particles collected during winter was very much higher than the PAH content for the summer. Also, during the winter period, most of the PAH content was associated with particles less than 1.0 μm and greater than 7.0 μm. At least 50% of the BaP content was found in particles of diameter greater than 7.0 μm at the Bathurst location during the summer sampling period, while only approximately 25% was found in particles of size less than 1.0 μm. However, during the winter sampling period this distribution was essentially reversed—i.e., 50% of the BaP mass was associated with particles less than 1.0 μm and only 25% associated with particles greater than 7.0 μm. It is interesting to note that although the PAH content increased significantly for the winter season at most sampling locations, the PAH content at the Bathurst site remained essentially constant.

For all of the test sites, approximately 85-90% of the total PAH content with respect to volume of air sampled was associated with particles less than 5.0 μm diameter for the winter sampling period, while 70-85% was associated with the same size fraction for the summer sampling period. These values are essentially in agreement with the values reported by DeMaio and Corn (7) for aerosol samples collected in Pittsburgh but are slightly lower than the

concentrations reported by Kertész-Sáinger et al. (12) for the same size of particles collected in Budapest. It is evident that the dependency of PAH content on size and, perhaps, on the type of particle found in the aerosol, varies significantly with sampling locations, season, and relevant emission sources.

Seasonal Effects on PAH-Size Distribution. It is generally accepted that the gross concentration of PAH's is lower in the summer months than the winter months (13). To determine any seasonal effects on the PAH-size distribution, samples of organic matter, representative of summer and winter suspended particulate levels at the York station, were quantitatively measured for the presence of the following PAH's: chrysene, benz(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, perylene, benzo(ghi)perylene, anthanthrene, and coronene. Size distribution curves for each compound followed approximately a normal logarithmic distribution with significant differences between the summer and winter sampling periods. Com-

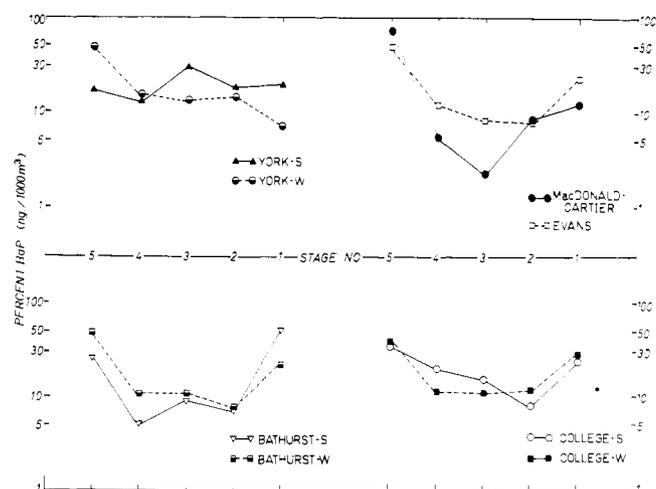


Figure 2. Percent mass of benzo(a)pyrene in relation to stage number for the five sampling sites

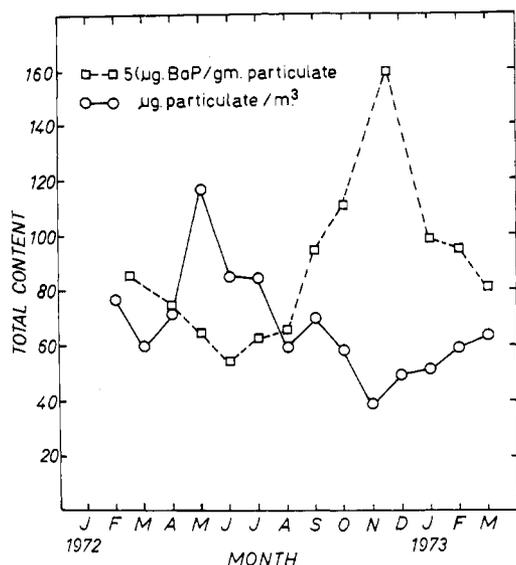


Figure 3. Monthly change in total concentration of particulate matter and total benzo(a)pyrene content (X5)

parison of the total PAH content, MMD, σ_g , and respirable PAH content in relation to weight of particulate matter for both sampling periods is given in Table V.

The total PAH content for the summer period ranged from anthanthrene with the lowest concentration of approximately 2 $\mu\text{g/g}$ particulate to benzo(ghi)perylene with the highest concentration of 20 $\mu\text{g/g}$ particulate. Chrysene, benzo(a)pyrene, and benzo(k)fluoranthene had approximately the same concentration as did coronene and perylene. The total concentration of PAH's were higher for the winter period by a factor of 65–75%.

The MMD's of all PAH's were lower in the winter than in the summer, indicating that the PAH's were associated with a smaller range of particles of relatively large average diameter in summer but with a larger size range of particles of relatively small average diameter in winter. This conclusion is borne out by the fact that the MMD's for PAH's in summer are larger than the MMD's for PAH's in

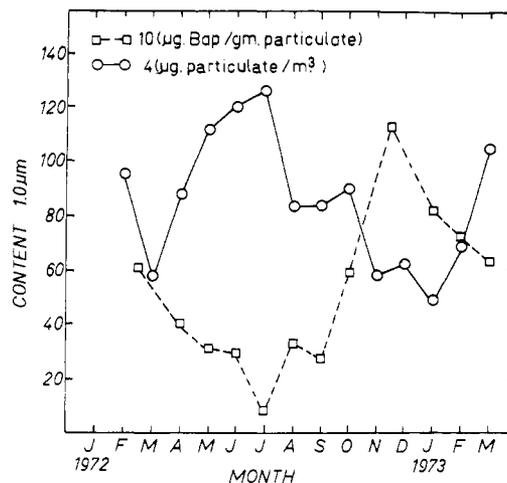


Figure 4. Monthly change in submicron concentration of particulate matter (X4) and submicron benzo(a)pyrene content (X10)

winter, while the σ_g 's for PAH's in winter are larger than the σ_g 's for PAH's in summer (Tables III, IV, V).

During the summer period, 6–23% of the total PAH content was found in particulates with diameter $\leq 1.0 \mu\text{m}$, while particles of diameter $\leq 3.0 \mu\text{m}$ contained 56–70% of the total PAH content. Hence, during the colder winter months the PAH content increased substantially for the smaller respirable particles found in the suspended particulate matter.

Comparison of the monthly particulate matter concentration in the air with the amount of PAH associated with that particulate matter indicated a more marked change in the content of PAH than in the amount of airborne particulates. A one-year study of the amount of three representative PAH's: benzo(a)pyrene, benzo(k)fluoranthene, and perylene, was carried out for the particulate matter collected at the York sampling station and is presented in Figures 3 and 4 (data shown for BaP only). The amount of

Table V. Seasonal Effects on PAH-Size Distribution at York Site, Toronto, Ont. (μg PAH/g particulate)

| Compound | R _B | Sampling period ^a | Total concn | MMD, μm | σ_g | Concn, $\leq 1.0 \mu\text{m}$, % | Concn, $\leq 3.0 \mu\text{m}$, % |
|----------------------|----------------|------------------------------|----------------|--------------------|------------|-----------------------------------|-----------------------------------|
| Chrysene | 1.19 | S | 11.6 \pm 0.5 | 2.7 | 1.9 | 7 | 56 |
| | | W | 17.5 \pm 0.8 | 1.6 | 2.9 | 33 | 72 |
| Benz(a)anthracene | 1.09 | S | 11.3 \pm 0.5 | 2.4 | 2.1 | 12 | 62 |
| | | W | 22.2 \pm 0.4 | 1.6 | 3.2 | 35 | 70 |
| Benzo(a)pyrene | 1.0) | S | 12.6 \pm 0.7 | 2.4 | 2.2 | 14 | 62 |
| | | W | 17.1 \pm 0.9 | 1.5 | 2.9 | 35 | 74 |
| Benzo(k)fluoranthene | 0.99 | S | 11.2 \pm 0.5 | 2.7 | 1.9 | 6 | 56 |
| | | W | 17.4 \pm 0.8 | 1.4 | 3.1 | 38 | 74 |
| Perylene | 0.95 | S | 7.4 \pm 0.3 | 2.8 | 1.9 | 8 | 56 |
| | | W | 10.1 \pm 0.5 | 1.6 | 2.3 | 30 | 76 |
| Benzo(ghi)perylene | 0.85 | S | 20.2 \pm 1.0 | 2.0 | 2.3 | 23 | 69 |
| | | W | 31.1 \pm 1.5 | 1.2 | 3.3 | 43 | 78 |
| Coronene | 0.40 | S | 8.2 \pm 0.5 | 2.5 | 2.0 | 9 | 59 |
| | | W | 12.3 \pm 0.7 | 1.4 | 3.1 | 37 | 74 |
| Anthanthrene | 0.78 | S | 1.8 \pm 0.1 | 2.4 | 2.2 | 14 | 61 |
| | | W | 2.6 \pm 0.1 | 1.3 | 3.0 | 40 | 78 |
| Benzanthrone | 0.67 | S | 30.5 \pm 1.8 | 2.6 | 2.1 | 9 | 56 |
| | | W | 39.1 \pm 2.3 | 1.6 | 3.3 | 35 | 70 |
| Perinaphthanone | 0.37 | S | 26.5 \pm 1.6 | 3.0 | 1.9 | 4 | 50 |
| | | W | 15.9 \pm 1.0 | 2.0 | 2.6 | 22 | 66 |

^a S, York (24/06/72–28/07/72). W, York (31/01/72–31/03/72). R_B, distance traveled by compound with respect to benzo(a)pyrene.

Table VI. Ratio of Benzo(k)fluoranthene and Perylene to Benzo(a)pyrene Found in Particulate Samples Collected at York Site

| Month | Total content | | Content $\leq 1.0 \mu\text{m}$ | |
|----------|---------------|---------|--------------------------------|---------|
| | BkF/BaP | Per/BaP | BkF/BaP | Per/BaP |
| 1972 F-M | 1.02 | 0.59 | 1.14 | 0.53 |
| A | 1.01 | 0.37 | 1.09 | 0.43 |
| M | 0.88 | 0.20 | 1.06 | 0.16 |
| J | 0.93 | 0.23 | 1.14 | 0.18 |
| J | 1.13 | 0.67 | 1.01 | 0.47 |
| A | 0.82 | 0.37 | 0.67 | 0.34 |
| S | 1.59 | 0.36 | 1.78 | 0.38 |
| O | 1.16 | 0.37 | 1.21 | 0.39 |
| N-D | 0.93 | 0.43 | 1.00 | 0.27 |
| 1973 J | 0.99 | 0.46 | 1.18 | 0.37 |
| F | 1.00 | 0.52 | 1.16 | 0.38 |
| M | 1.01 | 0.62 | 1.10 | 0.47 |

BkF and Per may be calculated by multiplying the concentration of BaP found in Figures 3 and 4 by the appropriate ratios found in Table VI for each sampling period.

Figure 3 indicates that the total amount of particulate matter in the air (i.e., sum of all size fractions) was highest during the early summer and then decreased to a minimal value during the winter. However, the total content of benzo(a)pyrene with respect to weight of particulate matter followed the opposite pattern. The highest value for the total benzo(a)pyrene content was recorded for the early winter period while the lowest value was recorded for the early summer period. Hence, it is apparent that the increase in benzo(a)pyrene content during the early winter months was not due to an increased amount of particulate matter but, instead, to an increased amount of benzo(a)pyrene adsorbed in the particulate matter.

Essentially the same pattern was observed for submicron particles in the sampled aerosols as indicated in Figure 4. An increase in the particulate concentration of particles $\leq 1.0 \mu\text{m}$ was observed during the early summer months with a decrease in the early winter months. Maximal values for the benzo(a)pyrene content associated with particles $\leq 1.0 \mu\text{m}$ diameter were recorded during early winter while minimal values were recorded during early summer. In this case, there is a more dramatic increase in the PAH content of submicron particles between summer and winter as opposed to the total PAH content. The percent mass of the various PAH's in the respirable size range calculated from the size distribution data was higher during the winter than the summer, as indicated in Table V. As a result, the MMD's were lower for this time period.

Size Distribution of Heterocyclic Arenes. There are some indications that PAH's are degraded in the atmosphere by photooxidation, by reaction with atmospheric oxidants, and by reaction with sulfur oxides (14). Reactions may be particularly facile when the compounds are adsorbed on particulate matter, such as soot, with the likely reactions of hydrocarbons being the production of oxygenated compounds. Such oxygenated derivatives as 7-H-benz(de)anthracen-7-one (benzanthrone) and phenalen-1-one (perinaphthanone) are found in urban air and the oxygenated fraction of air extracts seem to be carcinogenic (15). Concentrations of both compounds were determined and appear in Table V. Size distribution curves followed approximately the same pattern as did the curves for PAH—i.e., a normal logarithmic distribution. The

MMD for each compound decreased for the winter period while the σ_g increased. The content of these two oxygenated arenes also significantly increased in respirable particles during the winter.

Conclusion

The content of polynuclear aromatic hydrocarbons has been examined in relation to the size of suspended particulate matter found in the air of five different locations in Toronto, Ont. The polycyclics investigated were found to be highly dependent upon the size of the atmospheric aerosol with the greatest concentration being the respirable size range. Studies have also shown that the content of heteroaromatics is also size dependent. Seasonal variations in the PAH content were also found to be quite size dependent.

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