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Atmospheric Polycyclic Aromatic Hydrocarbons: An Aspect of Air Pollution in Fairbanks, Alaska

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ABSTRACT. Quantitative analysis of atmospheric polycyclic aromatic hydrocarbons (PAH) in Fairbanks, Alaska revealed significant levels of representative components. A fairly constant PAH pattern was observed throughout the winter of 1976-77, and the absolute PAH level correlated with air stagnation. Consideration of relative levels of individual PAH components reveals vehicular emissions as the major source but also provides evidence for contributions from power plant emissions. Fairbanks' PAH levels approach those of major cities in more moderate climates, and this situation emphasizes the importance of air quality problems in development of the Arctic.

RÉSUMÉ. A Fairbanks en Alaska, suivant des analyses quantitatives d'hydrocarbures aromatiques polycliques dans l'atmosphere, des teneurs significatives de composés representatifs, etaient atteintes preques constamment pendant l'hiver 1976 - 1977. Le teneur PAH absolue correspondait à une air stagnant. L'examen des teneurs relatives de composés PAH, pris individuellement, indique que les emissions par échappement des voitures sont la source principale mais qu'aussi certainement il y a eu une part d'emission, provenant de la centrale electrique. Les teneurs en PAH à Fairbanks approchent celles des grandes cités sous des climats plus temperés; cette constatation attire l'attention sur l'importance des problémes de qualite de l'air, liés à la mise en exploitation de l'Arctique. Traduit par Alain de Vendegies Aquitaine Co. of Canada.

INTRODUCTION

Although Fairbanks, Alaska is a settlement of only about 60,000 people (within 30 km of city center) in the midst of a pristine area, it has had air quality problems for some time (Oliver and Oliver, 1949; Robinson *et al.*, 1957; Benson, 1965; 1969; Holty, 1973; Jenkins *et al.*, 1975). In fact, in recent winters ambient carbon monoxide levels have regularly exceeded the standards (9 ppm, 8h average) set by the United States Environmental Protection Agency.

While previous studies have dealt with inorganic atmospheric pollutants (including ice fog), carbon monoxide, and total hydrocarbons (e.g. Winchester *et al.*, 1967; Holty, 1973; Jenkins *et al.*, 1975), there are no data of levels of polycyclic aromatic hydrocarbons (PAH). The PAH's are products of incomplete combustion and are of concern because of their carcinogenic (Falk *et al.*, 1964; Heidelberger, 1976) and mutagenic (Miller and Miller, 1971) properties. The same combination of high fuel consumption and stagnant wintertime air which leads to other air quality problems forbodes high PAH

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levels. Thus a study of atmospheric PAH levels in Fairbanks was undertaken as a case study in what appears to be an increasing problem as man populates the Arctic.

MATERIALS AND METHODS

Chemicals (and PAH Abbreviations)

Cyclohexane, benzene, and dichloromethane were distilled prior to use. Carbon disulfide (spectrograde) was used as supplied.

PAH standards (fluoranthene, FLU; phenanthrene, PHE; pyrene, PYR; chrysene, CHY; benzo[a]pyrene, BAP; benzo[e]pyrene, BEP; perylene,PER; and benzo[ghi]perylene, BGP) were purchased and used without further purification.

Thin Layer Chromatography

Preparative thin layer chromatography (TLC) was performed on 20 x 20 cm plates of 0.25 mm Silica Gel 60 (E.M. Reagents). The plates were developed with benzene:cyclohexane (3:2) for one hour.

Standard Solution

A solution of PAH standards (10-20 μg/mL of each component) was prepared in carbon disulfide. An internal standard of 2.0 μg/mL of biphenyl was added for calibration.

Gas Chromatography

Gas chromatographic analysis (GC) was accomplished with a Varian 1200 gas chromatograph (flame ionization detector) fitted with a ⅛ in. o.d. x 2 m stainless steel column packed with 2% Dexsil 300 on 60/80 mesh Chrom G AW DMCS. The column temperature was held at 160° C for 2 minutes, programmed from 160° C to 280° C at 4° C/min, then maintained at 280° C for 20 min. Peak areas were quantified with a Columbia Scientific Industries Model CSI 38 digital integrator or by planimetry.

Gas Chromatography — Mass Spectrometry

Gas Chromatography — mass spectrometry (GC/MS) was accomplished with a Hewlett Packard 5700A gas chromatograph interfaced to a Hewlett Packard 5930A mass spectrometer (electron impact ionization) and a Hewlett Packard 5933A data system. The gas chromatograph was fitted with a 53 m capillary porous layer open tubular (PLOT) glass column coated with OV-101. The column temperature was programmed from 120° C to 280° C at 8° C/min and the final temperature maintained for 16 min.

PAH Analysis

Airborne particulate samples (provided by the Fairbanks North Star Borough Environmental Services Department) from 6 m above street level at

the center of Fairbanks (6th and Cushman) were collected on glass fiber filters by high volume samplers. The dessicated filters were stored in the dark at —15° C until used.

The filters were extracted overnight (Soxhlet apparatus) with 300 mL cyclohexane and the extract concentrated by distillation to *ca.* 25 mL. The remaining solvent was removed *in vacuo,* nitrogen introduced, and the residue taken up in 1.0 mL dichloromethane. Following preparative TLC, the PAH band (visualization at 366 nm) was scraped and the hydrocarbons eluted by stirring with 30 mL dichloromethane for 30 min. Filtration, followed by solvent distillation and concentration *in vacuo* provided a PAH sample. A 2.0 mL portion of internal standard (biphenyl, 2.0 μg/mL) was added and the volume reduced to *ca.* 0.2 mL under a stream of nitrogen. Replicate samples of 1.0 μL were analyzed by GC and GC/MS.

Air Quality Data

Carbon monoxide (CO) and suspended particulate matter (SPM) levels for sampling days were determined by the Fairbanks North Star Borough Environmental Services Department by standard methods. Temperature inversion strengths were estimated from 2 A.M. soundings taken by the National Weather Service at the Fairbanks Airport.

RESULTS AND DISCUSSION

Analytical Procedure

Analysis of the standard PAH mixture by a modification of the procedure of Lao *et al.* (1973) indicated that all components were separated by gas chromatography with the exception of benzo[a]pyrene and benzo[e]pyrene. Quantitative analyses of standard solutions which were subjected to the entire extraction and cleanup procedure demonstrated recoveries of individual components ranging from 55-86% with the less volatile components recovered more efficiently.

PAH Composition

A set of 21 randomly selected samples collected in the period of November 1976 through April 1977 was analyzed for PAH composition. The Fairbanks area was covered with snow except for small cleared areas until April and the sampling period corresponds to the season during which air pollution problems are normally encountered. The results of these analyses are presented in Table 1. All PAH standards were found in quantifiable concentrations except perylene, which has been omitted from the Table.

The concentrations of the six standard PAH's of Table 1 represent about 70% of the PAH's found by GC/MS, so it is convenient for discussion to define Total PAH as the sum of the concentrations of the six standards. The concentration of each PAH can then be defined as a percentage of the total,

TABLE 1. Atmospheric PAH Levels (ng/m³) in Fairbanks

Date[a, b]	PHE	FLU	PYR	CHY	BAP & BEP	BGP	SUM OF SIX PAH
11-08-76(w)	0.1	1.8	1.8	3.3	—	3.7	10.7
12-08-76(w)	0.9	7.4	9.3	8.3	4.4	4.2	34.5
12-20-76(s)	11.3	29.0	28.9	29.2	9.6	8.3	116.3
12-26-76	21.6	20.2	23.4	21.5	10.2	8.1	105.0
01-01-77	2.2	8.6	12.0	18.1	9.6	8.3	58.8
01-07-77(s)	1.2	9.0	10.5	10.8	4.8	6.9	43.2
01-13-77	0.7	5.3	13.0	3.6	3.4	5.0	31.0
01-25-77(s)	1.4	10.1	15.9	41.6	14.3	17.8	101.1
01-31-77(w)	0.8	2.8	15.0	2.7	1.7	2.9	25.9
02-12-77	5.1	20.7	31.6	24.8	7.5	16.3	106.0
2-18-77(s)	0.2	1.9	2.5	4.9	2.4	3.9	15.8
02-24-77(s)	4.2	24.1	39.8	44.7	20.7	21.2	154.7
03-02-77(w)	0.6	1.3	2.0	1.6	1.0	2.4	8.9
03-08-77(w)	—	0.5	0.7	17.5	0.9	1.9	21.5
03-14-77(w)	—	4.3	7.0	28.0	4.1	4.9	48.3
03-20-77	0.7	2.1	2.2	3.5	1.0	1.4	10.9
03-26-77	—	1.6	1.9	2.3	0.3	1.2	7.3
04-02-77	0.1	1.0	0.8	0.6	0.4	0.5	3.4
04-08-77	0.6	1.9	7.6	2.6	1.5	2.4	16.6
04-19-77	0.4	0.7	0.8	0.6	0.6	0.7	3.8
04-25-77	0.3	0.5	0.4	0.7	0.4	0.6	2.9
Mean	2.9	7.4	10.8	12.9	4.9	5.8	44.1
Minimum	0.1	0.5	0.4	0.6	0.3	0.5	2.9
Maximum	21.6	29.0	39.8	44.7	20.7	21.2	154.7

a. The designations (s) and (w) indicate days with strong and weak inversions, respectively. All other days exhibited inversions of intermediate strength.

b. Sampling dates were during the normal work week except: Saturdays (01-01-77, 02-12-77, 03-26-77, 04-02-77) and Sundays (12-26-76, 03-20-77).

as summarized in Table 2. The mean percentage compositions given in Table 2 all show large standard deviations, but all components except phenanthrene (which suffers from poor recovery in extraction) show normal distributions when plotted on normal-probability paper (Volk, 1958). Thus the PAH concentrations are linearly related, and a relatively constant PAH pattern exis5s in Fairbanks' air.

TABLE 2. Average composition of a six component mixture of atmospheric PAHs in Fairbanks. Abundances in individual PAHs are given as percentages of the mixture.

PAH	Mean	Standard Deviation
PHE	5.4	4.9
FLU	16.5	6.0
PYR	24.4	11.9
CHY	28.4	16.1
BAP & BEP	10.7	3.6
BGP	15.9	6.6

TABLE 3. PAH pattern comparisons. The concentrations are standardized to fluoranthene (FLU).

Source	PHE	FLU	PYR	BAP & BEP	BGP	PER	CHY	Reference
Fairbanks	0.39	1.00	1.46	0.66	0.78	*a*	1.74	This Work
Automobile exhaust	0.37	1.00	1.45	0.27	0.68	*a*	*b*	Hangebrauck *et al.*, 1967
Automobile exhaust	3.19	1.00	1.51	0.21	0.35	*b*	0.30	Grimmer and Böhnke, 1972
Truck exhaust	1.0	1.00	1.63	0.18	0.40	0.02	*b*	Hangebrauck *et al.*, 1967
Coal-fired power plant	*a*	1.00	1.00	1.44	*a*	*a*	*b*	Cuffe and Gerstle, 1969
Coal-fired power plant	*b*	1.00	2.10	1.0	*a*	*a*	*b*	Hangebrauck *et al.*, 1967
Small coal furnaces	1.03	1.00	0.69	0.43	0.21	0.03	*b*	Hangebrauck *et al.*, 1967
Open burning	*a*	1.00	1.10	0.35	0.10	*a*	*b*	Hangebrauck *et al.*, 1967

a The compound either was not detected in the sample or its concentration was below the level of quantitative determination.

b Compound was not reported.

This relationship was further confirmed by plotting the concentration of each component against fluoranthene (FLU) for all samples in Table 1. A proportional relationship was established for each PAH/FLU ratio (see first entry, Table 3) with correlation coefficients ranging from 0.72 to 0.93. In each plot the slope of the regression line is nonzero with 99% confidence. Thus two lines of data analysis suggest that, whatever the sources, relatively constant proportions of PAH components are being injected into the atmosphere.

PAH Sources

Potential sources of PAH in the Fairbanks area include power plants, residential heating units, refuse incineration (primarily the municipal waste disposal facility several kilometers from the sampling site), and motor vehicles. Some insight into the actual PAH sources can be obtained from comparison of the average Fairbanks PAH pattern with patterns reported from potential sources. The data of Table 3 reveal that the Fairbanks PAH pattern resembles that of vehicular exhaust (ignoring the conflicting published data for PHE) except for the high levels of BAP/BEP and CHY observed in Fairbanks. While the requisite data for CHY are absent, it is apparent that emissions from a coal-fired power plant can supply the increased BAP/BEP levels observed.

Correlation of PAH Levels with Meteorological Parameters

With a defined set of PAH sources near the city center, it becomes obvious that the airborne PAH levels are a function of total PAH emission and atmospheric mixing volume. Assuming that total PAH emissions were approximately constant during the sampling period (due to relatively constant traffic patterns), the atmospheric mixing volume becomes the crucial factor. Analysis of the mixing volume is, in turn, a function of "inversion strength." We defined "strong inversions" as those characterized by a temperature gradient of equal to or greater than 7° C in the first 100 m from the surface and weak inversions by a gradient of less than 1° C in the first 100 m at the 2 A.M. sounding. The five sampling days with strong inversions had Total PAH levels ranging from 15.8 - 154.7 ng/m^3 with a mean of 86.2 ng/m^3. The lowest PAH level associated with a strong inversion was observed on a day (Feb. 18, 1977) which became unusually windy after the 2 A.M. sounding and which was characterized by the National Weather Service as a day with "excellent" dispersion conditions. The six sampling days with weak inversions had Total PAH levels ranging from 8.9 - 48.3 ng/m^3 with a mean of 25.0 ng/m^3. The mean PAH level during strong inversions differs significantly from the mean PAH level during weak inversions at the 95% confidence level.

Establishment of a correlation of PAH levels with inversion strength led us to examine the relationship between PAH level and the concentration of carbon monoxide. Carbon monoxide is known locally to be a product of vehicular combustion, with ambient atmospheric concentrations related to inversion strength (MacKenzie and Arnold, 1973). Correlation of atmospheric carbon monoxide concentrations with Total PAH levels by regression analysis gives a linear fit with a correlation coefficient of 0.58 (significantly nonzero at the 99% confidence level). This "low" correlation coefficient is thought to be primarily due to scatter in the data, as depicted in Fig. 1. The scatter is probably the result of three factors: 1) the carbon monoxide is produced almost exclusively by vehicles while the PAH levels also come from coal-fired power plants which emit little carbon monoxide; 2) carbon monoxide levels were monitored at 3 m whereas PAH levels were monitored at 6 m, with resulting increases in mixing volume and importance of power

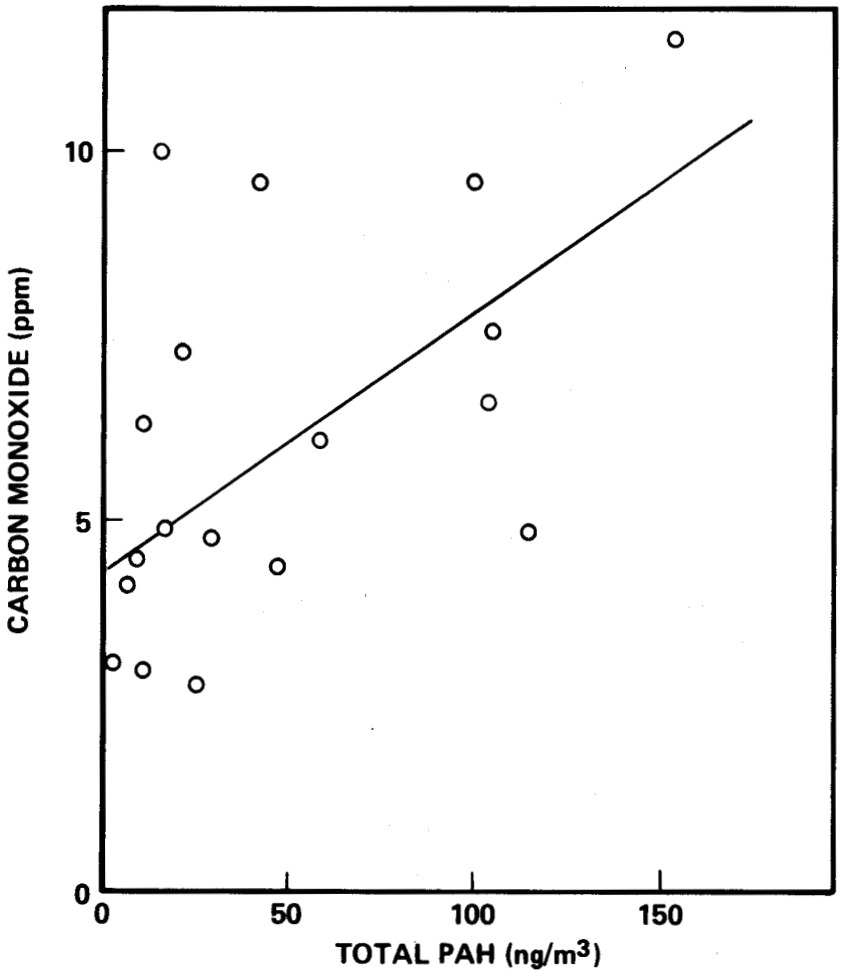

FIG. 1. Ambient carbon monoxide level (24 h average) *vs.* Total PAH in Fairbanks atmosphere.

plant stack effluents; 3) carbon monoxide dispersion is governed by diffusion whereas PAH is dependent upon diffusion, sedimentation, and coagulation as a result of association with particulate matter (Pierce and Katz, 1975a).

Seasonal Variations of PAH Levels

An interesting aspect of air quality in Fairbanks is the high particulate level observed during early spring, assumed to be the result of dust generated during removal of winter snowcover (MacKenzie and Arnold, 1973). This assumption receives verification from analysis of Total PAH/SPM ratios observed on a seasonal basis (Table 4). The data of Table 4 are consistent with the idea that as the dirt and gravel roads around Fairbanks dry out in spring and as wind levels increase, the particulate load rises while the PAH concentrations diminish.

TABLE 4. Monthly mean PAH composition of suspended particulate matter (SPM).

Month	SPM (ug/m^3)	Total PAH (ng/m^3)	PAH/SPM (ppm)
December 1976	87.1	85.3	979
January 1977	48.0	52.0	1080
February 1977	78.7	92.2	1170
March 1977	55.5	19.4	350
April 1977	178.6	6.7	38

TABLE 5. PAH content of urban air (ng/m^3).

City	PHE	FLU	PYR	CHY	BAP	BEP	PER	BGP	Reference
Rome[a]		1.0-18.0	0.4-17.0	0.4-39.0	0.4-14.6	0.2-10.5			Zoccolillo *et al.*, 1972
Budapest[b]	10	10.4	20.6	71.5	26.8	15.2	11.0	8.6	Kertész-Sáringer and Morlin, 1975
New York[a]					0.1x 9.4				Colucci and Begeman, 1971
New York[b]	0.36	1.1	1.05	1.6	1.15	1.4	0.1	0.9	Dong *et al.*, 1976
Los Angeles[a]		0.15-0.68	0.23-1.24	0.26-1.57	0.17-1.27	0.42-1.96	0.06-0.22	1.35-8.25	Gordon, 1976
Toronto[a]					0.16-0.47	0.08-0.31	0.03-0.14	0.02-0.21	Pierce and Katz, 1975a
College Park, MD[b]		4.1	5.2	4.8	3.2	4.6		3.9	Fox and Staley, 1976
Pittsburgh[b]			4.5		6.6	11.0			DaMaio and Corn, 1966
Fairbanks[b]	2.9	7.4	10.8	12.9[c]	4.9[c]		[d]	5.8	This work

[a] Range of reported values.
[b] Mean value reported.
[c] Isomeric mixture of BAP and BEP.
[d] Below detection limit.

Comparison of PAH Levels in Fairbanks with Other Cities

Comparisons of the winter PAH levels in Fairbanks with those observed in some major metropolitan areas are presented in Table 5. While detailed comparisons are ill-advised because of differences in sampling procedures and

analytical methods, it is clear that the levels of these pollutants in Fairbanks approach those observed in much more populated centers in more moderate climates. Thus the analysis of PAH levels in Fairbanks emphasizes the air quality problems of the arctic environment enunciated by others (e.g. Holty, 1973; Benson and Rizzo, 1979).

CONCLUSIONS

Analyses of PAH patterns in the Fairbanks atmosphere indicate that they result from a combination of vehicular emissions and power plant effluents. While the contributions of vehicles have long been considered important pollution sources, this appears to be the first clear indictment of power plants for pollutants other than ice fog.

During winter, the PAH levels are correlated with total particulate levels. However, the increase in particulates observed with the loss of snowcover in spring is not associated with a rise in PAH. Thus these additional particulates do not appear to be related to combustion emissions.

Because of problems associated with high fuel consumption and air stagnation, winter PAH levels in the Fairbanks atmosphere approach those of much larger communities in more moderate climates. Thus PAH levels indicate that air quality may well be a determining factor in further development of the Arctic.

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