Figure 3. Sample chromatograms comparing the shape of the backflush peak with a gasoline sample

mode. The last column gives the concentration necessary to produce a peak height of one division and therefore represents (approximately) the minimum detectable concentration. For the two-carbon hydrocarbons, these concentrations are around 1-2 $\mu g/m^3$, values comfortably below those found in lightly polluted air. Sensitivity is no problem for methane. The propane peak was much broader than the two-carbon compounds because this was recorded in the backflush mode. It was, of course, correspondingly smaller in height. Even so, propane gave a backflush peak sharper (not surprisingly) than the ambient air peak. Use of this sensitivity, as listed in Table I, would have given concentration values far too small. Since the principal components of the backflush peak are gasoline hydrocarbons, an actual gasoline sample was used to prepare a calibration comparison. It is noteworthy that the peak width is about the same for gasoline and ambient air. For gasoline the minimum detectable concentration was much higher than for propane, about 100-200 $\mu g/m^3$. No attempt was made to estimate the precision of the methods. In the absence of obvious malfunction, there was little change in calibration fac-

tors. Accuracy would doubtless have been improved by integration of these backflush peaks. This was not possible in the present program, so peak heights were read by hand and entered into punch cards. Five hydrocarbon peaks were measured on each chromatogram and four chromatograms were taken per hour each day, yielding 960 measurements. Availability of data on punch cards made possible extensive manipulation of the data. For example, joint distributions were tabulated as in Table II. This shows the distribution of C_3^+ (the backflush peak) plus ethene and acetylene against the acetylene concentration. With a few exceptions a good correlation is evident. An occasional high C_3^+ value may be attributed to a chance spill of gasoline or some other organic substance near the analyzer.

Ambient air samples give a sharp peak just ahead of, but almost completely separated from, the methane peak. (The scale of the chromatograms in Figures 2 and 3 is too small to show it.) It is not an electronic spike or a pressure pulse, because it is delayed about 20 s after valve switching, is well shaped as a chromatographic peak, and varies in size from sample to sample. It is hard to imagine what would pass through this column faster than methane and yet give response in a flame detector. One hypothesis is that a portion of the carbon monoxide is reduced to methane by the flame support hydrogen just ahead of the flame. Reduction of the CO to CH_4, intentionally and quantitatively, might be possible with this system.

Literature Cited

(1) Eggertsen, F. T., Nelsen, F. M., *Anal. Chem.*, **30** (6), 1040-3 (1958).
(2) Stephens, E. R., Burleson, F. R., *J. Air Pollut. Control Assoc.*, **19** (12), 929-36 (1969).
(3) Stephens, E. R., Coordinating Research Council Summary Report CAPA 5-68, NTIS Accession No. PB 230, 993/AS, 1973.
(4) Stephens, E. R., *Am. Soc. Test. Mater., Spec. Tech. Publ.*, **No. 653**, 365 (1978).

Comparative Distribution of Eight Polycyclic Aromatic Hydrocarbons in Airborne Particulates Collected by Conventional High-Volume Sampling and by Size Fractionation

Morris Katz* and Cecilia Chan

Centre for Research on Environmental Quality, T-115 Steacie Science Building, York University, 4700 Keele Street, Toronto, Ontario M3J 2R3, Canada

■ Airborne particulate samples were collected by a conventional high-volume sampler and by an Andersen cascade impactor on 3 to 5 days in each month over a period of 1 year at two sampling sites in Hamilton, Ontario, a city containing a large concentration of iron and steel manufacturing facilities. Eight individual polycyclic aromatic hydrocarbons (PAHs) were separated and analyzed quantitatively by thin-layer chromatography and fluorescence spectrophotometry, using internal standards. The size-fractionated samples contained much higher amounts of the soluble organic extracts than the corresponding extracts in the high-volume samples. Substantially higher levels of PAHs were also found in the cascade impactor samples. Data are presented on the distribution of the weight PAHs in five size classification ranges, seasonal influences on PAH levels, and comparisons of the much higher Hamilton PAH levels over corresponding concentrations reported for New York City and Los Angeles.

Ambient air levels of polycyclic aromatic hydrocarbons (PAHs) are of concern because of their potential for adverse biological effects, including transformation of some of these substances to mutagens and carcinogens by mammalian microsomal enzyme systems. Their occurrence in the environment, chemistry, and metabolism have been reviewed in a recent publication (Gelboin and Ts'o (1)). PAHs are universal products of the combustion of fossil fuels and are present in emissions from many other stationary and mobile combustion sources, including those from coke production, incineration of refuse, and combustion of gasoline and diesel by vehicles. These substances also are readily synthesized in nature and

are distributed widely in air, water, soil, and biological tissue. The more volatile hydrocarbons, up to the tricyclic stage, may occur largely in the gaseous state in the atmosphere, but the tetracyclic, pentacyclic, and higher molecular weight members are associated with and are transported by airborne particulate matter (1). Various aerosol deposition mechanisms, including dry deposition, rainout, and washout, result in the contamination of water, soil, and food by PAHs.

Since the majority of PAH compounds are adsorbed on airborne particulate matter (2), their potential carcinogenic effect on human health depends largely on the extent to which these compounds are distributed in the respirable size range below about 7-μm diameter. Only particles smaller than this size can be transported through the upper respiratory tract into the bronchioles and alveoli of the lungs (3). In a study of the dependency of 10 PAH compounds on size distribution of aerosols at sites in Toronto, Canada, Pierce and Katz (4) found that about 85–90% of the total PAH content was associated with particles less than 5.0 μm in diameter for the winter sampling period, while 70–85% were associated with this size fraction during the summer sampling period. Substantially similar values were reported by De Maio and Corn (5) for particulate samples collected from the air in Pittsburgh.

The general practice in routine analysis of PAHs involves the collection of airborne particulates by means of high-volume samplers, using fiber glass filters in sheets of 20 × 25 cm and air sampling rates of 1.2 to 1.7 m³/min over a period of 24–48 h. This procedure yields aerosol samples that vary widely in diameter from less than 0.5 to more than 30 μm. Such samples from 121 stations in the U.S. National Air Surveillance Network (NASN) were analyzed routinely for benzo[a]pyrene (BaP) from 1966 to 1970. A special study was also made of 40 NASN sites in order to examine BaP concentration trends from 1966 to 1972 (6). However, this filtration method may result in substantial losses of tetracyclic and pentacyclic compounds at ambient temperatures, including BaP, due to their equilibrium vapor concentrations and the high sampling airflows over long periods (7, 8). Other investigators have proposed the use of glass fiber filters impregnated with glycerin tricaprylate (9) or the use of porous polymer beads, such as Tenax GC, a 2,4-diphenyl-p-phenylene oxide polymer, as a backup adsorbent filter downstream from the fiber glass filter, in order to increase the sampling efficiency of volatile species (8, 10, 11).

Some PAHs, including BaP, undergo comparatively rapid oxidation or photodecomposition after irradiation with simulated sunlight in the presence of ozone, in dynamic flow chambers. Such decomposition effects were observed by Thomas et al. (12) with BaP adsorbed on soot, by Tebbens et al. (13) with BaP and perylene in irradiated smoke, and by Lane and Katz (14) for the rapid decrease in half-lives of BaP, benzo[b]fluoranthene, and benzo[k]fluoranthene, after irradiation with a Quartzline lamp that simulated closely the spectrum of sunlight.

Experimental

Collection of Suspended Particulate Matter. The present study was undertaken to determine the differences in concentration of eight PAH compounds in samples collected by the usual high-volume method and in particulates collected at much lower flow rates of about 0.57 m³/min by means of the Andersen cascade impactor, which classifies particles in five size ranges from less than 1.0 to over 7.0 μm in diameter. This sampler has been described by Burton et al. (15). The study area was Hamilton, Ontario, a highly industrialized city of about 350 000 population. It is the center of the largest concentration of iron and steel manufacturing facilities in Canada, containing the usual configurations of
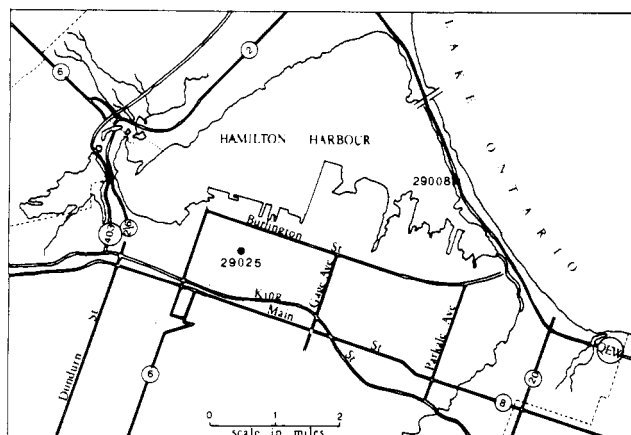

Figure 1. Geographic location of sampling stations 29008 and 29025 in Hamilton, Ontario

coke ovens, blast furnaces, and basic oxygen converters. Other major sources of particulate pollution consist of combustion products of fossil fuels and emissions from motor vehicles.

Hamilton was chosen because an earlier investigation by Katz, Sakuma, and Ho (16) of the concentrations of 10 PAH compounds in the air of Toronto, Hamilton, Sarnia, and Sudbury, Ontario, using conventional high-volume samplers, had indicated that Hamilton air contained the highest level of these compounds. Particulate samples were collected at two sampling stations, as shown on the map, Figure 1, and designated as station 29008 (North Park, west-central) and station 29025 (Barton-Wentworth). On the International Grid, station 29008 is located at an Easting of 05984 and Northing of 47927, whereas 29025 is at an Easting of 05939, Northing 47900. The iron and steel complexes and other heavy industry are located along the waterfront of Hamilton Harbour. Particulate emissions from these industries would be transported to station 29008 by southwest winds and to a lesser extent by west winds, whereas corresponding emissions would be carried to station 29025 mainly by northwest winds with contributions from fluctuating north-northeast winds.

Two sets of particulate samples were collected over 24-h periods at each site, during 3 to 5 days in each month, over the yearly period from June 1977 to May 1978. At station 29008, cascade impactor samples were collected in each month of the above yearly period, while high-volume samples were also collected in each month from January to May 1978. At station 29025, high-volume samples were obtained in each month from June 1977 to May 1978, while cascade impactor samples were collected in each month from January to May 1978. At each location, the samplers were placed about 3.9 m above ground level.

The particulate filters of fiber glass, adjusted to pH 6.5 to prevent sulfate formation in the presence of airborne sulfur dioxide, were conditioned before and after each sampling period at a constant relative humidity of 50 ± 2% and temperatures of 22 ± 2 °C for 24 h and weighed to obtain the weight of collected particulate matter. During the above periods, a total of 350 samples were collected.

Extraction of Organic Matter. The collected high-volume samples and size-fractionated samples were grouped into bundles representing monthly sampling periods, each size range being grouped separately. Each sample bundle was installed in a glass extraction thimble, equipped with a sintered glass disk at one end, and inserted in a Soxhlet extraction apparatus. The filter bundles were extracted with 250 mL of redistilled, pure dichloromethane for 10 h in the dark.

The cooled, dichloromethane-soluble fraction (DSF) in the receiving flask together with the washings of the extractor with 25 mL of CH_2Cl_2 were filtered through a sintered glass funnel,

Table I. Seasonal Concentrations (Geometric Mean) of Suspended Particulates and Dichloromethane-Soluble Fractions (DSF) in Hamilton Air Samples

period	no. of samples	mass concn particulates, $\mu g/m^3$	DSF concn, $\mu g/m^3$	% DSF/ particulates	MMD, μm	σg
		Barton-Wentworth Site 29025, High-Volume Sampler				
June–Aug 1977	13	121.0	6.1	5.04		
Sept–Nov 1977	10	83.7	6.3	7.52		
Dec 1977–Feb 1978	9	58.6	4.3	7.34		
March–May 1978	10	89.8	5.3	5.90		
		West-Central Site 29008, Andersen Cascade Impactor				
June–Aug 1977	15	120.0	23.8	19.2	3.0	10.8
Sept–Nov 1977	12	93.6	21.7	23.2	3.3	19.8
Dec 1977–Feb 1978	11	94.2	14.9	15.8	2.4	16.2
March–May 1978	10	104.8	17.9	17.1	3.3	7.4

and the flask and funnel were rinsed several times with 5-mL portions of CH_2Cl_2. The filtrate and rinsings were reduced to a volume of about 3 mL in a pear-shaped flask by flash evaporation at 35 °C. This solution was transferred to a weighed vial, the pear-shaped flask was rinsed several times with 1-mL portions of CH_2Cl_2, and the washings were also transferred to the vial. After the solution was evaporated to dryness under a stream of dry nitrogen at room temperature, the organic residue was weighed, dissolved in 0.5 mL of pure toluene, and stored in a refrigerator at −15 °C in the dark until further analysis.

Chromatographic Isolation and Spectral Analysis. The following PAHs were isolated from the organic extracts of DSF using a two-step thin-layer chromatographic (TLC) separation process: benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), benzo[k]fluoranthene (BkF), perylene (Per), dibenzo[def,mno]chrysene (DBdef,mnoC), benzo[ghi]perylene (BghiPer), naphtho[1,2,3,4-def]chrysene (NdefC), and benzo[rst]pentaphene (BrstPenta). Toluene solutions of these purified, recrystallized PAHs were employed as internal standards in the following analysis.

Preliminary separation of PAHs was accomplished through the use of neutral aluminum oxide plates as the stationary phase and a mixture of pentane–ether (19:1, v/v) as a mobile phase. Aliquots of the toluene solution of each organic extract were spotted 1.5 cm from the bottom of the plates by a 2-μL disposable capillary pipet with the aid of a Desaga template. The area of the application was kept as small as possible by repeated application to achieve better resolution. The internal standards were applied at three equally spaced spots to facilitate identification of the polycyclic compounds. After the spots were air-dried, the plates were placed inside the developing tank under subdued light.

When the solvent had risen to a height of 15 cm on the plate, the chromatogram was removed from the tank, air-dried, and examined under a long-wavelength UV light in the dark. The fluorescence areas of the samples corresponding to the internal standards of interest were marked and removed from the plate. The PAHs were then eluted with 15 mL of redistilled dichloromethane, and the solvent was evaporated using a stream of dry nitrogen. This procedure resulted in the separation of the PAHs into three groups of compounds. Each residue was dissolved in 0.25 mL of pure toluene.

The same procedures for spotting, development, and elution were carried out for subsequent separation on 30% acetylated cellulose plates. The mobile phase employed was a mixture of 1-propanol–acetone–water (2:1:1, v/v/v). This accomplished the resolution of the above groups of compounds into the eight individual PAHs. Each individual PAH was removed and eluted with anhydrous diethyl ether because dichloromethane dissolves cellulose. The solvent was evaporated to dryness

Table II. Effect of Prevailing Wind Direction on Total Concentration of Suspended Particulate Matter at Hamilton Sites

date 1977	prevailing wind direction	particulate concn, $\mu g/m^3$	
		cascade impactor, site 29008	high-volume sampler, site 29025
June 6	N	84.4	149.1
June 29	SW	139.5	83.4
Oct 5	SW	188.3	89.0
Oct 18	SW	133.7	98.7
Nov 4	NE	50.5	125.1
Nov 17	NE	63.7	103.3

under a stream of nitrogen, the residues were dissolved in a small volume of spectrograde pentane and filtered to remove any suspended material, and the solutions were degassed by displacing any dissolved oxygen with dry nitrogen. The solutions were adjusted to a volume of 3.0 mL with pentane for fluorescence analysis. Pure PAH standards were chromatographed under identical conditions as the sample in this two-step TLC separation. The following percentage recoveries were obtained: BaP, 92.4; BeP, 93.5; BkF, 92.7; Per, 87.3; DBdef,mnoC, 93.6; BghiPer, 95.6; NdefC, 94.7; and BrstPenta, 92.3. Reproducibility of these recoveries ranged from about ±3 to ±5%.

Analysis of the above pentane solutions of samples and standards was conducted by recording the fluorescence excitation and emission spectra with a Farrand MK1 spectrophotometer, using spectral data published by Pierce and Katz (17). The method was calibrated by preparing curves of fluorescence emission at maximum excitation wavelength for each standard PAH in the concentration range of 0.05–0.50 mg/L. Beer's law is obeyed in this concentration range.

Results and Discussion

Particulate and DSF Concentrations. Seasonal mean concentrations of suspended particulates at the two Hamilton sites and the corresponding values of the DSF (dichloromethane-soluble fraction) are presented in Table I. The cascade impactor concentrations of particulates represent the totals of all five collection stages of this sampler, with the corresponding mass median diameters (MMD) and σg (the 84.3% value of the particle diameter divided by the 50% value, derived from a plot of percent of particles less than stated size vs. the log of stated size). It may be assumed that the particulate collection efficiencies of the two sampling instruments are substantially similar and any reported differences in particulate concentration are due to meteorological factors,

Table III. Comparative Seasonal Concentration Levels of PAHs in Airborne Particulates, West-Central Station 29008 (Cascade Impactor Samples)

PAH	June–Aug, 1977		Sept–Nov, 1977		Dec–Feb, 1978		March–May, 1978	
	ng/1000 m³	µg/g	ng/1000 m³	µg/g	ng/1000 m³	µg/g	ng/1000 m³	µg/g
BaP	3 224	26.9	4 699	50.2	4 199	44.6	2 496	23.8
BeP	2 624	21.9	3 002	32.1	2 655	28.2	1 896	18.1
BkF	945	7.9	1 836	19.6	1 775	18.9	1 281	12.2
Per	298	2.5	596	6.4	439	4.7	351	3.4
DBdef,mnoC	116	0.97	185	1.98	112	1.19	70	0.67
BghiPer	13 023	108.5	19 318	206.4	16 823	178.6	11 585	110.5
NdefC	2 218	18.5	2 221	23.7	2 437	25.9	1 154	11.0
BrstPenta	654	5.5	604	6.5	471	5.0	261	2.5
total PAH	23 102	192.7	32 461	346.9	28 911	307.1	19 094	182.2

particularly with regard to the influence of prevailing wind direction in transporting particulate pollution from heavy industrial emissions to each sampling site.

A striking difference in the data in Table I for the two types of sampling instruments is shown by the much higher DSF concentrations in samples collected by the cascade impactor. The lower values for percent DSF in total particulates collected by the high-volume sampler are in good agreement with published data for this method (16). Furthermore, it has been shown that solvent extraction for 10 h is more than sufficient to remove all of the soluble organic fraction (17). The factor of location of the sampling site can also be ruled out, since operation of an Andersen sampler at the Barton-Wentworth site (29025) and a high-volume sampler at the West Central site (29008) for 5 months, from January to May 1978, yielded similar higher values for percent DSF in cascade impactor samples. It is concluded that the differences in amount of organic fraction are due to the volatilities of the PAHs and lower molecular weight compounds, which result in losses by sublimation in the presence of the much higher airflow passing through the filter of the high-volume sampler.

As shown in Figure 1, the geographical locations of the two sampling stations are at opposite directions from the heavy industrial sources of particulate emissions, including iron and steel manufacturing facilities and coke ovens. Particulate loadings, therefore, are influenced strongly by the prevailing wind directions. Examples of this effect are shown in Table II, for particulate samples collected on similar days. In prevailing southwest winds, much higher particulate loadings are present at site 29008, whereas in north-northeast winds the higher concentrations appear at site 29025.

Seasonal Effects on PAH Concentrations. Comparative concentration levels of the eight PAH compounds for the four seasons of the year in the cascade impactor samples collected at station 29008 are presented in Table III. The highest concentrations were registered by BghiPer, followed in descending order by BaP, BeP, and NdefC or BkF. The remaining PAHs were present in much lower concentrations.

It has been shown generally that in urban areas where the principal sources of emission are from the combustion of fossil fuels and motor vehicle traffic, the gross concentration of PAHs is higher in the winter months than in the summer months (4, 18). Similar differences between warm and cold months of the year are illustrated by the data presented in Table III for site 29008.

Influence of Sampling Method on PAH Concentrations. A study was made of the PAH concentration levels in particulate samples collected by the cascade impactor vs. the high-volume sampler, over a 5-month period. The data for the two Hamilton sampling sites are shown in Table IV. In general, markedly higher concentration levels of PAHs were found in samples collected by the cascade impactor. It is reasonable to assume that the continued passage of air at the

Table IV. Comparison of Average Concentrations of PAH in Airborne Particulates Collected by Andersen Cascade Impactor vs. High-Volume Sampler, Sampling Period, January–May, 1978

PAH	West-Central site 29008, ng/1000 m³		Barton-Wentworth site 29025, ng/1000 m³	
	Andersen	high volume	Andersen	high volume
BaP	2 831	2862	6 607	3066
BeP	1 943	941	2 556	2653
Per	347	119	557	306
BghiP	13 033	5243	16 120	7117
BkF	1 431	871	2 384	1137
NdefC	1 333	1183	4 159	683
DBdef,mnoC	71	43	57	32
BrstPenta	389	229	640	184

high flow rate of about 1.5 m³/min through the fiber glass filter of the high-volume samplers, over a 24-h period, resulted in a loss of PAH by sublimation from the deposit of particulate matter. The most abundant PAH, BghiPer, showed a loss of about 56 to 60%. The loss of BkF varied between 40 and 52%. The results for the other PAHs were much more variable. In most cases, PAH losses in particulates collected by the high-volume sampler, in comparison with corresponding cascade impactor values, were greater at the Barton-Wentworth site than at the West Central site.

Particle Size Distribution of PAHs. The average concentrations of the eight PAHs in five size classifications from <1.1 to 7.0 µm and percentage distributions over the sampling period of 1 year are shown in Table V. In the particle size range of ≤1.1 to 3.3 µm, the percentages of PAHs varied from 72.1 to 88.8, while in the range of <1.1 to 7.0 µm, the percentages were as high as 87.5 to 95.1. These data emphasize the importance of size fractionation in the analysis of particulate samples for PAH and the deficiency of the high-volume sampling method in this respect. The latter method collects particles up to 30 µm or larger. Particles greater than 10 µm contribute significantly to the aerosol mass but add little to the concentration of PAHs.

Comparative annual average concentrations of PAHs in the air of Hamilton, Ontario, New York City (19), and Los Angeles (20) are presented in Table VI. With the exception of DBdef,mnoC (anthanthrene), the Hamilton PAH concentrations are considerably higher than corresponding PAH concentrations in the two much larger U.S. cities. Benzo[ghi]perylene occurs in much higher concentrations than the other PAHs in the air of both Hamilton and Los Angeles. It is also present in the air in much higher concentrations than other PAHs in Toronto (16). These facts make it likely that the most prolific source of BghiPer is the exhaust from motor

Table V. Average Concentrations (ng/1000 m³) of PAHs and Percentages in Particulate Size Ranges at West-Central Station 29008

PAH	<1.1 μm concn	%	1.1–2.0 μm concn	%	2.0–3.3 μm concn	%	2.2–7.0 μm concn	%	>7.0 μm concn	%
BghiP	4193	27.6	4184	27.5	3428	22.6	1761	11.6	1620	10.7
BaP	725	19.4	893	23.8	1259	33.6	458	12.2	410	10.9
BeP	981	41.6	462	19.6	552	23.4	176	7.5	183	7.8
NdefC	908	46.7	481	24.8	335	17.3	112	5.8	106	5.5
BkF	629	43.5	273	18.9	319	22.1	129	8.9	96	6.6
BrstPenta	117	29.3	102	25.6	68	17.0	62	15.5	50	12.5
Per	161	38.5	93	22.2	101	24.2	29	6.9	34	8.1
DBdef,mnoC	24	20.0	62	51.7	14	11.7	14	11.7	6	5.0

Table VI. Annual Average PAH Concentrations in Air of Hamilton, Ontario, New York City, and Los Angeles (ng/m³)

PAH	Hamilton site 29008, cascade impactor, 1977–1978	site 29025, high vol sampler 1977–1978	site 29025, high vol sampler 1975–1976 [a]	New York City, [b] 1975	Los Angeles, [c] 1974–1975
BaP	3.65	3.62	2.30	1.15–1.30	0.46
BeP	2.54	2.77	1.85	1.40	0.90
BkF	1.46	1.49	1.86	0.60	0.20
Per	0.42	0.30	0.29	0.10–0.20	0.10
DBdef,mnoC	0.12	0.02	0.18		0.23
BghiP	15.19	10.55	6.73	0.90	3.27
NdefC	2.00	0.89	1.03		
BrstPenta	0.50	0.20	0.26		

[a] Katz, Sakuma, and Ho (16). [b] Dong, Locke, and Ferrand (19). [c] Gordon (20).

vehicles, since the major sources of particulates in both Los Angeles and Toronto are due to this type of transportation.

PAH levels in Hamilton are much higher than those found in many cities of considerably greater population and may be characteristic of cities that contain large iron and steel manufacturing and coke oven facilities. The U.S. Environmental Protection Agency (6) conducted a comparative study of BaP concentrations in the air of coke oven cities vs. non-coke oven cities over the period 1966–1972. The coke oven cities were found to show consistently higher BaP levels in every year, the ratios of coke oven/non-coke oven ranging from 1.42 to 3.34 and generally about 2.

Conclusion

The PAH analysis of samples of suspended particulates collected by high-volume filtration through fiber glass filters at ambient temperature may be subject to errors due to losses by volatilization or sublimation of tricyclic, tetracyclic, and higher molecular weight compounds. In this study, it has been shown that the soluble organic fractions and the concentrations of pentacyclic and hexacyclic PAHs in samples collected by the cascade impactor are consistently higher than corresponding values in samples collected by high-volume filtration.

BaP has been used as an index of airborne PAH levels in many urban pollution studies. However, its usefulness is limited, and it is a poor index in cities where motor vehicle traffic is one of the major sources of air pollution. This is illustrated in the data for Los Angeles, where the dominant PAH is benzo[ghi]perylene. In the study of Hamilton, BghiPer was the most abundant PAH, and this was found also for Toronto and several other Ontario cities (16). However, BaP levels represent an important fraction of the PAH content in urban areas where the dominant source is coal combustion.

Information on the mutagenic activity of 30 PAH compounds and several quinones of BaP in airborne particulates has been presented recently by Salamone, Heddle, and Katz (21), using the Ames bacterial assay. PAH compounds are not direct-acting carcinogens or mutagens, but some members of this class may be converted to derivatives of varying potency by microsomal enzymes that are present in the liver and other mammalian tissues. Of the eight PAH compounds analyzed in this study, the following substances are known to possess a high carcinogenic potential: benzo[a]pyrene, benzo[rst]-pentaphene, and naphtho[1,2,3,4-def]chrysene. Moderate carcinogenic activity is manifested by benzo[k]fluoranthene and benzo[ghi]perylene. The remaining three PAHs, consisting of benzo[e]pyrene, perylene, and dibenzo[def,mno]-chrysene, are inactive (22).

Literature Cited

(1) Gelboin, H. V., Ts'o, P. O. P., Eds., "Environment, Chemistry and Metabolism", Vol. I, Academic Press, New York, 1978, p 408.
(2) U.S. National Academy of Sciences, "Particulate Polycyclic Organic Matter", Washington, D.C., 1972, pp 38, 61.
(3) U.S. Department of Health, Education and Welfare, Division of Air Pollution, "Motor Vehicles, Air Pollution and Health", Washington, D.C., 1962, p 184.
(4) Pierce, R. C., Katz, M., *Environ. Sci. Technol.*, 9, 347–53 (1975).
(5) De Maio, L., Corn, M., *J. Air Pollut. Control Assoc.*, 16, 67–71 (1966).
(6) U.S. Environmental Protection Agency, "Preferred Standards Path Report for Polycyclic Organic Matter", Office of Air Quality Planning and Standards, Durham, N.C., 1974.
(7) Rondia, D., *Int. J. Air Water Pollut.*, 9, 113–21 (1965).
(8) Pupp, C., Lao, R. C., Murray, J. J., Pottie, R. F., *Atmos. Environ.*, 8, 915–25 (1974).
(9) Brockhaus, A., *Atmos. Environ.*, 8, 521 (1974).
(10) Bertsch, W., Chang, R. C., Zlatkis, A., *J. Chromatogr. Sci.*, 12, 175 (1974).
(11) Pellizari, E. D., Carpenter, B. H., Bunch, J. E., Sawicki, E., *Environ. Sci. Technol.*, 9, 552–5 (1975).
(12) Thomas, J. F., Mukai, M., Tebbens, B. D., *Environ. Sci. Technol.*, 2, 33–9 (1968).
(13) Tebbens, B. D., Thomas, J. F., Mukai, M., *J. Am. Ind. Hyg. Assoc.*, 27, 415–22 (1966).
(14) Lane, D. A., Katz, M., in "Fate of Pollutants in the Air and Water Environments, Part 2", Suffet, I. A., Ed., Wiley-Interscience, New York, 1977.
(15) Burton, R. M., Howard, J. N., Penley, R. L., Ramsay, P. A., Clark,

T. A., *J. Air Pollut. Control Assoc.*, **23**, 277–81 (1973).
(16) Katz, M., Sakuma, T., Ho, A., *Environ. Sci. Technol.*, **12**, 909–15 (1978).
(17) Pierce, R. C., Katz, M., *Anal. Chem.*, **47**, 1743–8 (1975).
(18) Sawicki, E., Elbert, W. C., Hauser, T. R., Fox, F. T., Stanley, T. W., *J. Am. Ind. Hyg. Assoc.*, **21**, 443–51 (1960).
(19) Dong, M., Locke, D. C., Ferrand, E., *Anal. Chem.*, **48**, 368–72 (1976).
(20) Gordon, R. J., *Environ. Sci. Technol.*, **10**, 370–3 (1976).
(21) Salamone, M. F., Heddle, J. A., Katz, M., *Environ. Int.*, **2**, 37–43 (1979).
(22) Searle, C. E., Ed., *ACS Monogr.*, **No. 173** (1976).

Chemistry of Precipitation at Gainesville, Florida

Charles D. Hendry and Patrick L. Brezonik*

Department of Environmental Engineering Sciences, University of Florida, Gainesville, Fla. 32611

■ Chemical analyses of wet-only and bulk precipitation collected from June 1976 to July 1977 indicate that rain is the predominant deposition mechanism for SO_4^{2-}, NH_4^+, NO_3^-, Mg^{2+}, and K^+, but dry fallout is of comparable importance to rainfall for deposition of Na^+, Cl^-, and Ca^{2+}. Heavy metal levels (especially Zn) were highly variable in both types of samples. The (volume-weighted) average concentrations of total nitrogen, NH_4^+, and NO_3^- in bulk precipitation were 0.82, 0.12, and 0.23 mg of N/L, respectively. Averages for ortho- and total phosphate were 24 and 85 μg of P/L, respectively, in bulk precipitation and 19 and 34 μg/L in wet-only samples. Highest nutrient concentrations occurred in spring and early summer. Total loadings of N and P from bulk precipitation (1.15 g of N and 0.12 g of P/(m²·year)) are above permissible rates (relative to eutrophication) for shallow lakes. The volume-weighted mean pH of wet-only precipitation was 4.53; bulk precipitation had a slightly higher pH. Lowest pH values occurred in spring and summer. Acidity titrations and ionic balances indicate that rainfall acidity resulted mainly from sulfuric acid (69%) and nitric acid (23%).

Geochemical cycles of many elements have important atmospheric pathways. Various contaminants are emitted into the atmosphere by human activities and enter these natural cycles; wet precipitation and dry fallout return these contaminants to earth where they can affect biologic processes in aquatic and terrestial ecosystems valuable to man. Since precipitation is instrumental in cleansing the atmosphere of natural and artificial contaminants, the study of precipitation chemistry is a convenient method for monitoring atmospheric contamination.

The relative ease of sample collection has given rise to many precipitation studies. The chemistry and acidity of precipitation in Europe and the northeastern United States have been well studied (*1–4*). Nutrient levels of rainfall in temperate regions similarly have received considerable study, primarily as a result of efforts to compute nutrient budgets for lakes in eutrophication management studies (see reviews in ref *5–7*). In comparison, relatively little information is available on the general chemistry, acidity, and nutrient content of rainfall over the southeastern United States.

The results presented here are based on a year-long (June 1976–June 1977) study of bulk and wet-only precipitation in north-central Florida. This study had the following objectives: (1) to determine fluxes of nutrients (N and P forms) and major ions to aquatic and terrestrial systems from bulk and wet precipitation; (2) to determine the acidity of precipitation and the principal acids responsible for the observed acidity; (3) to examine the importance of dry fallout as a source of mineral input by comparing bulk and wet-only precipitation fluxes; (4) to evaluate the relative importance of rainout and washout

processes for removal of various substances from the atmosphere by rainfall; and (5) to determine ambient levels of heavy metals (Cd, Pb, Cu, and Zn) in Florida rainfall.

Previous Studies

Although several previous studies have reported on the chemical composition of precipitation in Florida, most studies had limited objectives and involved only a few parameters or short sampling periods. Comprehensive data on the chemical composition of rainfall in Florida thus are scarce. The most important previous studies on Florida rainfall chemistry are described below.

Junge (*8*) and Junge and Werby (*9*) reported on the major ions (including NH_4^+ and NO_3^-) in wet-only rainfall collected during 1955–1956 at four Florida locations as part of a nationwide study of precipitation. A second national sampling network (*10*) in operation from 1960 to 1966 included a station in Tampa and reported data on major ions, inorganic N, and heavy metals in wet-only precipitation.

The nutrient content (i.e., nitrogen and phosphorus forms) of Florida rainfall has been measured at several sites in north-central Florida (*11, 12*), near Lake Okeechobee (*13*), Fort Lauderdale (*14*), and Tallahassee (*15*). The latter authors also measured pH and major ions in rainfall at Tallahassee during 1974–1975. Their data and those of Bourne (*16*) for a site near Gainesville during 1974–1975 apparently are the earliest measurements on the pH of Florida precipitation.

Sampling Procedures and Analytical Methods

Wet-Only Precipitation Collection. Wet-only precipitation was collected manually from July 1976 to July 1977, on the University of Florida campus, using a collector constructed of polyethylene sheeting attached to a (1 m diameter) plastic ring 2 m above ground level. The sheet formed a funnel that channeled rainfall into tygon tubing leading to an 18-L polyethylene reservoir.

The collector was kept covered to exclude dry fallout until near the start of a rain event, when it was uncovered and rinsed with deionized, distilled water, and the reservoir was connected to the tubing. Immediately following the rain event, the sample was collected, and the collector was covered again. A 50-mL aliquot was acidified by adding 0.5 mL of redistilled HNO_3 for metal analyses. The remaining sample was stored at 4 °C until chemical analyses were run.

Bulk Precipitation Collection. Bulk precipitation was collected approximately 8 km northwest of Gainesville at a cypress swamp site located on a large pine plantation. The cypress swamps are currently under study as possible sites for disposal and natural treatment of secondary sewage effluent (*17*). Bulk precipitation was collected from June of 1976 to July of 1977, atop a 20-m steel tower at the center of one of the