FINAL REPORT OF THE CONTROL OF SUSPENDED PARTICULATES STUDY in the NEW YORK METROPOLITAN AREA

by the
Interstate Sanitation Commission
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SUMMARY

Ambient air and source sampling methodologies were examined by five task forces to determine their applicability to projects associated with the control of suspended particulates. The chemical and physical analyses, conducted on various filter media, determined individual particle composition and size, organic tracer mass, and total suspended particulate (TSP) chemical fractions.

Using an electron microprobe the particle analysis task force compiled elemental spectra on individual source emission particles which included material collected from power plant, incinerator, automobile and industrial emissions. Fingerprints were obtained for each source type. Subsequently, individual particles found in samples collected at ambient air sampling sites in the New York Metropolitan Area could be identified as coming from the fingerprinted sources. Based on these comparisons it is projected that an elemental fingerprint spectra library for characteristic source particles can be constructed to assist in source characterization studies.

Two rapid and inexpensive techniques for the extraction of organics from Hi-Volume and other filter samples were developed. The first involved mechanical description of a filter for organic matter extraction; and the second involved dissolution of a filter for the extraction of polycyclic aromatic hydrocarbons. In addition, a technique for the determination of free carbon on glass fiber samples was developed and applied to ambient air samples. The organics task force also isolated a possible organic tracer for incinerators.

The near-street total suspended particulate task force examined four-hour Hi-Volume measurement of total suspended particulates taken on glass and nuclepore filters during 1974 at a site in Newark, N.J. and for nine months in 1975 at a site in Brooklyn, N.Y. Carbon monoxide (CO) and meteorological data supplemented the particulate dataset.

Monthly average concentration of TSP at the two sites were relatively constant; those months which had a high frequency of northwest winds averaged about 15% lower than the overall site average. The overall diurnal patterns at the two sites showed only morning peaks for TSP, while CO was marked by both a morning peak and a stronger afternoon peak.

A robust statistical analysis, known as "moving window statistics", was applied to the TSP, CO and elemental data. This graphical technique was useful in sorting out the directional trends of the data, and delineated the different behaviors of the pollutant levels as functions of the wind segments associated with the observations.

The directional and diurnal behaviors of the elements measured were similar to those of TSP. Pb and Br, which were assumed to be generated by automobiles, and the fuel-dominated S, did not exhibit afternoon peaks in their diurnal patterns. Enrichment factors were calculated for the elemental data. The largest factors were obtained for Pb and Br, indicating the magnitude of the impact of automobiles on the levels measured at the two urban sites. High enrichment factors were also found for S, probably caused by the ubiquitous burning of sulfur-bearing fossil fuel in the Northeast Quadrant of the United States.

Multi-variable regression models linear in the logarithms of the variables (wind speed, mixing height, temperature, time of day, wind direction sector and relative humidity) were developed for TSP and CO. The dependence of the pollutant on wind speed was consistently found to be on the order of -0.2, a much weaker dependence than the traditionally assumed inverse proportionality.

The regression models also were used to predict pollutant levels on days on which programmed street washing occurred. The street washings were limited to streets in the immediate vicinity of the sites. The conclusion of this analysis was that the street washings did not decrease the level of total suspended particulates.

Routine techniques for determination of particulate mass were employed by the material balance task force on twenty-four hour samples from New York City sites. The analyses accounted for approximately seventy percent of the mass, with sulfates, benzene extractable organics and free carbon comprising the major fractions. The remaining fractions are suspected to be silicates and polar organics. Eight trace metals which include V, Cr, Fe, Ni, Cu, Zn, Pb and Mn were found to account for approximately 5% of the particulates throughout the city.

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INTRODUCTION

The Control of Suspended Particulates Study, under the sponsorship of the Interstate Sanitation Commission, was initiated in 1974 in coordination with the States of New York and New Jersey, and the City of New York. The purpose of the study was to demonstrate analytical techniques which would provide data useful in devising specific strategies for the control of suspended particulate matter in the region. The Cooper Union for the Advancement of Science and Art, the Mt. Sinai School of Medicine and the Polytechnic Institute of New York were awarded subcontracts to participate with the government agencies in the project.

The Interstate Sanitation Commission was responsible for the administration and overall coordination of the program, while the New York City Department of Air Resources directed the technical program. The technical program was pursued by five task forces; the primary investigators are listed in the preceding section.

The project attempted to:

1) develop methodologies to determine the relationship between the chemical and physical nature of particle emissions and ambient concentrations;

2) design techniques for examination of the particle size and chemical nature of suspended particulates;

3) characterize the near-street total suspended particulate matter and to determine the contributions attributable to re-entrainment.

Toward these goals, particulate samples were collected from a number of emission source types in New York and New Jersey. Ambient particulate samples were collected at urban sites in New York and New Jersey.

Because of the nature of the tests to be performed it was necessary to collect the samples using a variety of procedures and sampling media. The following types of measurements were completed:

Total suspended particulate mass
Particle size distribution
Concentration of selected metals
Concentration of total organic matter
Concentration of selected ions
Concentration of free carbon

In addition, individual particles collected on special membrane filters from source emission and the ambient air were analyzed for their elemental composition using a scanning electron microscope.

In the section that follows, the results of the five Task Forces involved in this program are presented as individual chapters. In addition, there is a discussion and recommendation section which attempts to explain the significance of the Task Force results.

REPORTS OF THE CONTROL OF SUSPENDED PARTICULATES STUDY TASK FORCES

I SAMPLING

AMBIENT SAMPLING

Summary

Table 1 lists the ambient air monitoring sites utilized to obtain samples during the survey. The table also shows the projected and actual number of samples collected during the project.

Site Selection

The sites were selected to insure adequate geographical coverage and to measure the impact of different types of sources.

The ambient sampling in New York City was completed during all four seasons to insure that data on seasonal variation of particulate matter would be collected. The sites in New Jersey only sampled during the winter months; these were only used to determine the variation between New York City and New Jersey ambient particulate matter, and to compare the chemical and physical characteristics of the ambient samples to those collected at nearby sources.

Ambient Sampling Procedures

Four types of ambient samples were taken, namely:

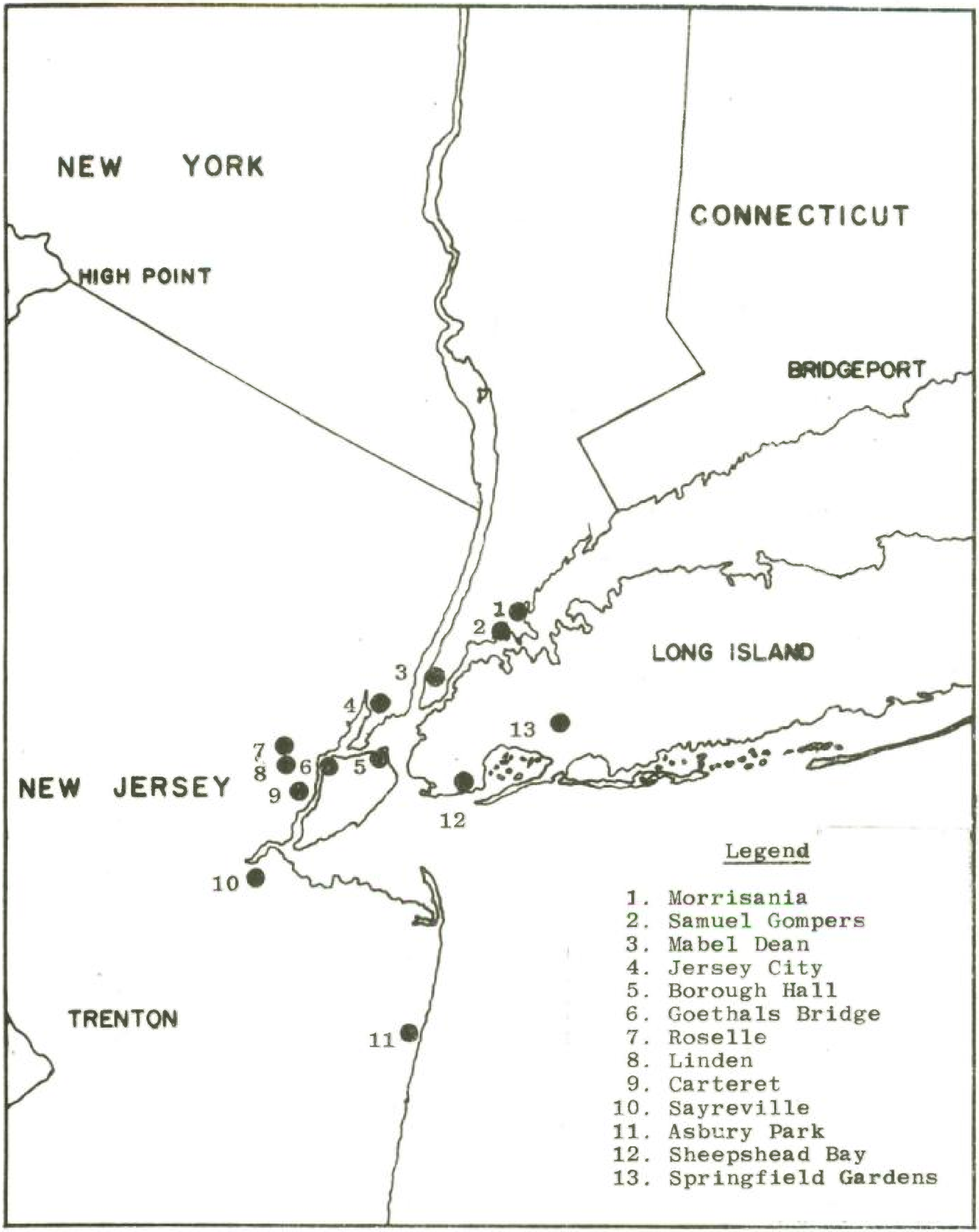
Glass fiber - for total weight, organic & inorganic constituents, anions and other mass balance constituents
Cellulose - for trace metals, inorganic and other mass balance constituents
Andersen (glass fiber) - for particle sizing
Nuclepore - for particle sizing and analysis

The glass fiber & cellulose filter samples were taken concurrently at a site that uses high volume air samplers, at a frequency of 20 samples per quarter. The method employed in securing samples is described in the Federal Register, Vol. 36, No. 84 page 8191-8194 (April 30, 1971).

The Andersen and nuclepore filter samples were taken concurrently at a site using modified high volume air samplers, at a frequency of one sample per month. The nuclepore filter was placed on the Hi-Vol head at the site. To prevent damage to the filter the change was done indoors.

The timer on the Hi-Vol with the nuclepore filter was set to operate for four minutes every 90 minutes for the normal 24-hour period. After the run the filter was placed in a folder and in turn into an envelope and delivered to the laboratory for analysis. The Andersen Head was delivered to the site intact, placed on another Hi-Vol and operated for the normal-24 hour period. After the run the Andersen Head assembly was delivered to the laboratory for analysis.

AMBIENT SAMPLING LOCATIONS



1. Morrisania
2. Samuel Gompers
3. Mabel Dean
4. Jersey City
5. Borough Hall
6. Goethals Bridge
7. Roselle
8. Linden
9. Carteret
10. Sayreville
11. Asbury Park
12. Sheepshead Bay
13. Springfield Gardens

TABLE 1. AMBIENT SAMPLING

SITE LOCATION & SAMPLE INFORMATION

SITE, LOCATION (STATION #)	Glass Fiber	Cellulose	Andersen	Nuclepore
Morrisania Health Station, Bronx, NY (3)	x	x	x	x
Samuel Gompers HS, Bronx, NY (6)	x	x	x	x
Mabel Dean Bacon Vocational HS Annex, Manhattan, NY (10)	x	x	x	x
Sheepshead Bay HS, Brooklyn, NY (26)	x	x	x	x
Springfield Gardens HS, Bronx, NY (30)	x	x	x	x
Goethals Bridge Toll Plaza, Staten Island, NY (31)	x	x	x	x
Staten Island Borough Hall, Staten Island, NY (32)	x	x	x	x
Asbury Park, JN (001) *	x	x		
Carteret, NJ (005) *	x	x		
Jersey City, NJ (014) *	x	x		
Linden, NJ (016) *	x	x		
Rosele, NJ (026) *	x	x		
Sayreville, NJ (028) *	x	x		
Number of Samples Projected	540	540	98	98
Number of Samples Collected	657	650	95	97

* Winter Samples Only

SOURCE SAMPLING

Results

Table 2 lists both the projected and the actual number of sources sampled during the project, as well as the approximate particulate emission rate for the general categories.

Table 3 lists all sources tested, and indicates what methods of sampling were used at each site.

Rationale & Considerations

At first glance Table 2 indicates that certain source categories were either over or under tested. Some of the reasons for the discrepencies are given below:

Space Heating & Power Generation - The gas fired boilers and gas turbines constitute a small fraction of particulate emissions from this source category, and so were tested less often than oil, the most prevalent fuel in the metropolitan area.

Incineration - The project failed to sample this category adequately; no samples were collected from onsite incinerators which constitute a substantial portion of the annual emission rate. Some municipal incinerators were sampled on different days and considered separate tests because of the differences in charging material.

Transportation - Gasoline vehicles constitute approximately 75% of particulate emissions from this category, and were tested adequately. However, other land vehicles were not. Testing ship and aircraft emissions was beyond the scope of this project.

Industrial - The variation among processes requires extensive testing to define emissions from each industry; this was also beyond the scope of the project. However a number of industrial sources were tested and catagorized.

Near Sources - Testing near sources or in their plumes was desirable since instack particulates, when emitted to the atmosphere, may change in their chemical and or physical nature. This testing was however beyond the resources and scope of this project.

Although seasonal variation in source emission was considered a possibility, manpower limitations, the cost of source testing, and the difficulty of choosing suitable sites, made it impossible to determine. A small number of sources outside the metropolitan area were sampled since a premise of the project was that similar sources, irrespective of location, would have similar emission characteristics.

Weaknesses of the source collection phase of the project were 1) the inability to define the number of source tests that constituted an adequate sample size to insure that the category was complete; and 2) important categories such as #2 and #4 boilers and on site incinerators were not tested.

Source Sampling Procedures

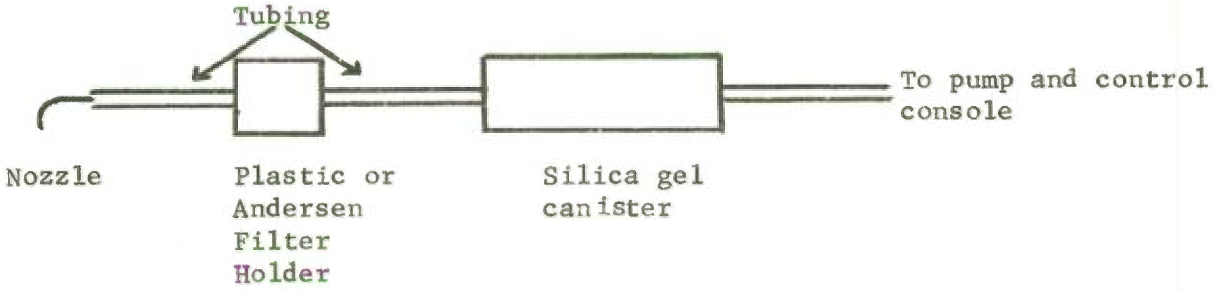
Five types of source samples were taken:

Glass fiber - for total weight, organic constituents and total particulate emission rate
Paper filter - for trace metals
Anderson III (glass fiber) - for particle size distribution by weight
Anderson IV (nuclepore) - for particle sizing and trace elements by particle
Nuclepore - for particle sizing and trace element by particle

Not all sample types were taken at each site.

The glass fiber filter samples were taken using the standard USEPA source sampling train described in the Federal Register, Vol. 36, No. 247, page 24888 - 24890 (December 23, 1971). At least two sample runs were conducted at each site when the standard USEPA source sampling train was used.

All other filter samples were secured using the assembley diagrammed below. All filter holders were loaded and unloaded in the laboratory.



If the stack temperatures were in excess of 250°degrees F the plastic filter holder of the glass fiber filters was placed outside the stack. A point near the center of the stack was selected as the sampling location and three paper filters were exposed for four, six and eight minutes each, to obtain sufficient particulate loading for analysis. Sampling approximated isokinetic conditions.

For the Anderson III (glass fiber) filter, the 250 degrees F criteria for placing the filter holder in stacks was not necessary. Stack gases from a centrally located point were drawn through the apparatus at a constant rate, approximating isokenetic conditions, until 15 cubic feet of air, under standard conditions, had been sampled.

For the Anderson IV (nuclepore) filter, the 250 degrees F criteria for placing the Anderson IV in the stack applied. Stack gases from a centrally located point were drawn through the apparatus for four minutes.

For the nuclepore filters the 250 degrees F criteria for placing the filter holders in the stack was necessary; a point toward the center of the stack was preselected as the sampling location and three nuclepore filters were exposed for 20, 40 and 60 seconds, to obtain sufficient particulate loading for analysis.

TABLE 2. SOURCE TEST DISTRIBUTION

Source Type	Number of Sources Initially Projected To Be Tested	 Actually Tested	Annual Particulate Emission Rate In Tons/Year *
Space Heating & Power Generation			
Utility			29,000
Coal	3	1	
Oil	3	3	
Gas	3		
Turbine	3	6(#zoil)	
Non Utility			93,000
Coal	3	2	
Oil	3	8	
Gas	3		
Incineration (Inc. Open Burning)			26,000
Municipal	3	7	
On Site	3		
Transportation (Inc. Shipping)			49,000
Gasoline	3	3	
Diesel	3		
Jet Fuel	3		
Industrial			17,000
Asbestos Plant Source (Unspecified)		1	
Anode Furnace		1	
Cupola		3	
Alum Plant		2	
Calciner (Unspecified)		1	
Coffee Roaster		1	
Asphalt Rotary Kiln		1	
Pathological Waste Incinerator		1	
Mineral Wool Plant Source (Unspecified)		1	
Aluminum Melt Furnace		1	
Pisment Manufacturing Plant Source		1	
Industrial Plant Source (Unspecified)		1	
Near Sources			Not Applicable
Congested Traffic	2		
Power Plant Pumes	2		
Incinerator Pumes	3		
On Burner Pumes	2		

* Annual emission rates based on USEPA AQCR printout dated September 25, 1975

TABLE 3. SOURCE SAMPLING

SITE LOCATION AND SAMPLE INFORMATION

Name & Location	Source Type	Standard EPA Train	Special Paper Filter	Andersen Mark III	Andersen Mark IV	Special Nuclepore Filter
Manville, N.J.	Asbestos Process	x	x	x	x	x
Cartaret, N.J.	Anode Furnace	x	x	x	x	x
Newark, N.J.	Cupola	x	x	x	x	x
Jersey City, N.J.	Boiler - #6 Oil	x	x	x	x	x
Linden, N.J.	Alum Plant	x	x	x	x	x
Irvington, N.J.	Cupola	x	x	x	x	x
North Bergen, N.J.	Calciner	x	x	x	x	x
Edgewater, N.J.	Coffee Roaster	x	x	x	x	x
Roseland, N.J.	Rotary Drier Aggregate	x	x	x	x	x
New York, N.Y.	Gas Turbine					x
New York, N.Y.	"					x

(continued)

TABLE 3 (continued)

Name & Location	Source Type	Standard EPA Train	Special Paper Filter	Andersen Mark III	Andersen Mark IV	Special Nuclepore Filter
New York, N.Y.	Gas Turbine					x
New York, N.Y.	"					x
New York, N.Y.	"					x
New York, N.Y.	"					x
New York, N.Y.	Pathological Waste Incinerator	x				
Manhattan, N.Y.	Boilers - #6 Oil	x				
Manhattan, N.Y.	"	x	x			x
Bronx, N.Y.	"	x	x			x
Brooklyn, N.Y.	"		x			x
Queens, N.Y.	Boilers - #6 Oil	x	x			x
Albany, N.Y.	Boiler - with water injection - #6 Oil	x	x			x

(continued)

TABLE 3 (continued)

Name & Location	Source Type	Standard EPA Train	Special Paper Filter	Andersen Mark III	Andersen Mark IV	Special Nuclepore Filter
Albany, N.Y.	Boiler - without water injection - #6 Oil	x	x			x
Brooklyn, N.Y.	Municipal Incinerator	x				
Brooklyn, N.Y.	Automotive Exhaust	x				
Plattsburg, N.Y.	Boiler - #6 Oil	x	x			x
New Jersey	Boiler Coal		x	x	x	x
Brooklyn, N.Y.	Incinerator - Stack #1 12/11/75	x	x			x
Brooklyn, N.Y.	Incinerator - Stack #1 12/16/75	x	x			x
Brooklyn, N.Y.	Incinerator - Stack #2 12/16/75	x	x			x
Brooklyn, N.Y.	Municipal Incinerator	x	x			x
Car Exhaust	Car Exhaust	x				
Car Exhaust	Car Exhaust	x				

(continued)

TABLE 3 (continued)

Name & Location	Source Type	Standard EPA Train	Special Paper Filter	Andersen Mark III	Andersen Mark IV	Special Nuclepore Filter
Brooklyn, N.Y.	Municipal Incinerator					
Brooklyn, N.Y.	Municipal Incinerator					
South Plainfield, N.J.	Mineral Wool		x			x
Bloomfield, N.J.	Aluminum Melting Furnace		x			x
Newark, N.J.	Cupola		x			x
South Kearny, N.J.	Unspecified		x			x
Newark, N.J.	Alum Scrubber		x			x
Kearny, N.J.	Boiler - #6 Oil		x			x
Hudson, N.J.	Boiler - #6 Oil		x			x
Newark, N.J.	Pisment Scrubber	x	x			x
New York, N.Y.	Boiler - Coal		x			x

(continued)

TABLE 3 (continued)

Name & Location	Source Type	Standard EPA Train	Special Paper Filter	Andersen Mark III	Andersen Mark IV	Special Nuclepore Filter
New York, N.Y.	Boiler - #6 Oil		x			x
Garden City, N.Y.	Municipal Incinerator		x			x
Garden City, N.Y.	Municipal Incinerator		x			x
Long Island, N.Y.	Boiler - Coal					

II PARTICLE ANALYSIS

ELECTRON MICROPROBE ANALYSIS OF SUSPENDED PARTICULATES

Introduction

There is now extensive data on the concentrations of respirable particulate matter and on the concentrations of various metals associated with particles in the ambient air. In most instances, the sample analysis procedure gives only the average metal concentration present in an air sample and little information is available on the chemical form, the mineral phase, or even the particle size associated with a given element. Most important is the lack of information on the contribution of various pollution sources to the ambient air particulate concentration at a given location. This makes it difficult to establish the most effective control strategies.

In order to obtain definitive information, individual respirable particles have been analyzed using electron microbeam techniques. Emissions from power plants, municipal incinerators, space heating units, various automotive exhausts, and selected industrial sources have been characterized, including the elemental analysis of various sized particulates and their grouping by elemental characteristics. Samples collected from the ambient air, both near to and distant from specific sources, have been analyzed similarly and grouped according to the elemental characteristics found in the various sources. Grouping of particles from sources and from the ambient air by their elemental spectra allows estimates to be made of the contribution of different sources to the particulate matter present in the ambient air at different locations, during the specific time that a given sample was collected.

Experimental Procedures

The analysis procedure entails the transfer of particles collected on appropriate filters to electron microscope grids. As nearly all air samples were collected on Nuclepore^{TM} polycarbonate membrane filters, a "direct transfer" procedure was utilized. Here, the collected material is stabilized on the filter by evaporating a carbon film which enmeshes all particles lying on the surface. A portion of the filter is then placed carbon film side down on a formvar-coated electron microscope grid. The membrane material is subsequently dissolved in chloroform vapors, leaving residue of the collected particles enmeshed in a carbon film. This procedure has the advantage of leaving undisturbed the form and distribution of the collected particles. In particular, agglomerates of particles that have been produced in the air prior to collection remain undisturbed. However, low air volumes must be sampled to prevent agglomeration of particles during collection.

For three samples of automobile exhaust, the air samples were collected on Millipore^{TM} cellulose acetate filters. Here, a portion of the filter and collected material is ashed in an electronically activated oxygen asher. The remaining residue of inorganic material is then dispersed on microscope slides in a nitrocellulose film, mounted on an electron microscope grid, and coated with carbon. This process has the disadvantage that agglomerates can be broken apart in the dispersal process. It should be pointed out here that direct transfer procedures cannot be used with Millipore^{TM} filters. Particles are often trapped deep within the interstices of the filamentary network. During the preparation of the sample for electron microscopy, the surface of the filter is coated with carbon film to immobilize the collected fibers. However, those trapped within the filter medium remain free, and can be lost during subsequent dissolution of the Millipore filter. We have found that the percentage of fibers lost by this procedure can be as high as 90%.

A grid from a sample of interest, prepared using one of the above procedures, is then mounted in the electron microprobe and the particles displayed in a transmitted electron image. Each particle present on the grid is analyzed by directing the electron beam of the microprobe onto it. These electrons, with an energy of 20 KEV, create vacancies in the inner electron shells of atoms of the particle of interest. As these refill, x-rays of an energy unique to each chemical element are emitted. The x-rays are detected in a lithium drifted silicon detector, and information on their number and frequency stored in the memory of a PDP 11/20 digital computer, which can display the energy distribution of x-rays from each particle and store such information on tape for further analysis. This energy distribution of x-rays will reflect the elemental composition of the particles from specific sources which are grouped according to characteristic elemental spectra. Grouping particles by elemental composition allows identification of unique particle spectra from specific sources which can serve as "fingerprints" for that source in the analysis of particles collected in the ambient air.

Results

Elemental Composition of Major Particulate Sources:

The procedure for the analysis of sources involved grouping together particles with having similar elemental spectra. Peak heights of the major elements were measured and tabulated for each group and ratios of important elements were calculated. When a consistent pattern was obtained, such data were used to characterize particles in the ambient air. As an example of this procedure, Table I lists the elemental peak heights of a variety of elements found in one class of particles from leaded auto fuel emissions, those with both chlorine and bromine present. While some elements, such as aluminum and silicon, vary considerably with respect to other elements, Pb/Cl and Br/Cl ratios were remarkably consistent, varying less than a factor of 2.

With such tabulations, the number of particles falling with a given description were enumerated and are listed in the source tables.

Automobile Emissions

Automobiles were sampled using the facilities of the Department of Air Resources at Frost Street, Brooklyn. Samples were collected from two vehicles using leaded gas, two using non-leaded gas, one using non-leaded gas with a converter and one using diesel fuel. These were sampled during portions of an eight and one-half minute EPA cycle. Of those cars sampled using leaded gasoline, 70% of the particles observed contained lead and of this group, half had chlorine or bromine present. Fig. 1 shows the characteristic elemental spectra of automobile emissions showing the presence of lead, chlorine and bromine. Other spectra with lead and chlorine, but no bromine were also characteristic. Sampling from an automobile using non-leaded gas with converter and from an automobile using diesel fuel also showed the presence of lead, but without the characteristic chlorine and bromine. The origin of lead in this case is not completely understood; however, during the sampling procedure, building air was mixed with the exhaust in order to obtain a diluted aerosol and although this added air was filtered, particles containing lead in the ambient air of the garage could readily pass through the filter. Table 2 provides a summary of information on the analysis of particles from the various vehicle sources.

Electrical Generating Plants

Three sets of samples from electrical generating plants were analyzed in some detail. These included the Hudson Generating Plant in Jersey City, N.J. using Number 2 crude oil, a turbine from the Ravenswood Generator of Consolidated Edison in Queens, N.Y., using Number 2 fuel oil, and a turbine from the same facility using kerosene. Of the predominant class of emissions from the Hudson plant, over 75% consisted of particles containing Al, Si, K, Ca, Ti, V and Fe. As V is not often found in emissions from other sources, it can serve as a marker for power plant emissions, particularly in association with K and Ca. The elements from the Ravenswood generator were similar although little Ti or V was found. The presence of Cr, Mn and other transition metals suggested that some erosion of turbine blades may be taking place.

Space Heating Emissions

The predominant elemental characteristic from space heating is particles containing Si, S and Fe but without Ti of V. This is consistent with the use of a higher quality of fuel oil compared with that of the oil fired electrical power plant. In some particles, transition metals such as Cr or Mn were also found along with K or Ca. Otherwise, the particles were similar to those found in the larger power plants. The elemental characteristics of particles emitted from power plants or space heaters is summarized in Table 3.

Municipal Incinerators

Pb and Zn are commonly found along with Cl although the ratios among these elements are highly variable. One noticeable feature of particles from municipal incinerators is the presence of Sn along with Pb and Zn, presumably from incineration of food cans with their lead-tin-zinc solder. These elemental characteristics are summarized in Table 4.

Analysis of Emissions from Specific Industrial Sources

As part of the source characterization of this project, emission samples from nine industrial sources were analyzed. There is great homogeneity in elemental characteristics. Although several of these sources show unique spectra, it might be expected that such particles would only be found in samples of suspended particulates collected near the source. Such samples and their analysis would allow a determination to be made about the dissemination of a particular source and under particular meteorological conditions. This would allow correlation to be made with various models of source dispersion.

Elemental Analysis of Samples of Ambient Air Particulate Matter :

Nine samples of ambient air in New York and New Jersey were analyzed and the possible origin of particles ascribed to area sources. The association of a particle with a given source is based on the similarity of the elemental spectra with that of particles emitted from those particular sources. In the case of power plants and space heating, vanadium was given particular weight under the circumstances. Lead with chlorine and particularly with bromine served to identify automobile exhaust particles, and the lead-tin-zinc or zinc-tin complex was a marker for incinerators. Silica, iron oxides and mica-like particles with aluminum silicon, potassium and calcium could be identified, however a definite association with an industrial site or with ground surface particles could not be made. In a few cases, particles probably originating in an industrial source typically consisted of a variety of heavy metals, and in two cases rare earth metals. Also listed are other particles identified according to elemental composition but to which no particular source could be ascribed.

Some particles match closely the elemental spectra of particular sources. The vast majority have characteristics of particular sources, but also contain elements not associated with the source in question. For example, one finds particles containing K, Ca, Pi, V and Fe in abundance analogous to those found in power plant emission. However, there may also be traces of zinc and lead. In other cases, a particle with high Pb, Cl and Si, similar to those found in automobile exhaust, may also have traces of Ti or V. The origin of this elemental mixture is probably agglomeration of the variety of microparticles in the ambient air each from different sources. Thus, we may be analyzing a particle made up of tens or even hundreds of individual microparticles having a size less than 0.1μ. Since constituent microparticles are not separately analyzed, the elemental emission spectra would average over the whole agglomerate. The extent to which this agglomeration takes place can be seen in Table 5 where the number and percentage of particles with lead or vanadium are listed according to source. Overall, approximately one-third of the particles are found to contain some vanadium and in one-third there is some lead. (Some particles may contain both elements and are included separately in each column). A limited number of particles were ascribed unambiguously to a given source such as automobile emissions, etc., whereas a much larger number have subunits associated with one or more of the sources under consideration. Table 6 summarizes the characterization of particles by possible origin for the different ambient air samples analyzed. Approximately 15% to 20% of the particles seem to come from power plants or space heaters, 5% from automobile emissions and 3% from incinerators. Approximately 3% of the particles are SiO_2, 6% iron oxides and 4% mica-like particles. Other industrial sources seem to contribute 2% of the ambient air particles studied in this project. Thus, overall an indentification or origin could be ascribed to approximately 40% of the particles analyzed. As has been mentioned, however, contributions of various sources could be recognized in many of the remaining particles to which no specific source was assigned.

Microscopic Size Analysis of Suspended Particulate Matter:

Photographs were taken of random grid squares of ambient air particles and a size distribution obtained by direct measurement of a photographic print. Figure 2 depicts this distribution according to both major and minor axes of this sized material. Figure 3 shows representative particles and agglomerates collected in ambient air samples. As can be seen from the photograph, the vast majority of particles greater than half a micron in size are agglomerates of micro-particles of less than two-tenths of a micron. While these agglomerates represented only 40% of the particles sized, they would have constituted a much larger faction of the particles analyzed with the electron microprobe. This is because of the difficulty in distinguishing particles under 2/10ths of a micron in size in the microprobe and the difficulty of greeting an adequate elemental spectra from extremely small particles.

Summary and Conclusions

Particles from a variety of emission sources have been analyzed and characterized according to their elemental composition. Sources included automobile emissions, electrical generating plants, space heating boilers, municipal incinerators and nine industrial sources. The emissions can be characterized by certain elements unique to the sources. For example, automobile emissions are commonly found to have lead with bromine and chlorine present. Space heating emissions and those from electrical power plants have a variety of transition metals including vanadium, titanium, chromium and manganese present. The unique characteristic of municipal incinerator emissions is the presence of lead, tin and zinc or zinc and tin. Industrial sources have emissions characteristic of the materials used therein. While smelters commonly have various metal emissions, others may contain silica, mica-like particles, gypsum, or specific elements.

Ambient air samples from nine ambient air stations in the New York metropolitan area were analyzed. Utilizing data on the elemental characteristics of various sources it was possible to indentify approximately 40% of the particles collected in the samples. Approximately 15% to 20% of the particles analyzed in the ambient air samples could be ascribed to emissions from electrical power plants or space heaters, approximately 5% to automobiles, and 2 or 3% to municipal incinerators. Additionally, percentages of silica, mica, iron oxide and other specific particles could be indentified. One notable feature of the analysis was the finding that many agglomerates of particles contained microparticles from a variety of sources. This was reflected by the large number of particles containing small amounts of lead from automobiles, and vanadium emitted from space heaters or power plants. Thus, while many particles had characteristics similar to a specific source, they did contain sub-units from a variety of sources. Overall, it was found that approximately one-third of the particles had detectable amounts of lead, and one-third detectable amounts of vandium.

The data in this study at this time are of limited extent. Data may be available for only one or two samples for a given source and the emissions at that time would be characteristic of the material undergoing combustion. Moreover, a limited number of particles were analyzed from each source. Similar qualifications exist in the analysis of particles collected in the ambient air. Samples taken at a given site reflect the conditions at that particular time and may not be an accurate average for that site. There is a need for more analysis.

While the data are limited in terms of samples and particles analyzed, they do demonstrate the feasibility of this method for characterizing ambient air particles according to source and composition. Further, they demonstrate the significance of automobile exhaust and power plant/space heating emissions to the ambient air samples studied in this project.

AUTOCORRELATION ANALYSIS OF SUSPENDED PARTICULATES

Introduction

Various methods exist for the measurement of particles in different size ranges. Some are limited in the size range of particles that can be analyzed; others require delays between the time of sample collection and the time results are obtained. Many are subject to the introduction of experimental artifacts. No one is wholly satisfactory.

A recent development in light-scattering is the use of intensity fluctuation spectroscopy to measure the rate of self-diffusion of suspended particles. From the measured diffusion constant, an effective aerodynamic size can be calculated independent of knowledge of particle mass. The self-diffusion is measured by observing the distribution in arrival times of single photons scattered by particles of interest from a laser light beam having coherence. In such a system, a monodispersed aerosol will produce a distribution in the intervals between photons that leads to a pure exponential autocorrelation function plus a constant, which may be considered as background. A correlation time is the interval required for the exponential portion of the autocorrelation function to decrease to 1/e of its initial value. The particle radius in nanometers may be estimated by the equation:

$$R= \frac{X\ 5.33\text{x}10^{+24}\ \pi K\ (273.15 + T)\ n^2\ \sin^2\ (0/2)}{\eta\ \lambda^2}$$

where X is the correlation time
K is Boltzman's constant, $1.38\text{x}10^{-16}$
n is the refractive index of the medium
θ is the scattering angle
η is the viscosity in centipoise
λ is the wavelength of light
T is the temperature in degrees Centigrade

If two or more particle sizes are present in the mixture, the autocorrelation function will consist of a sum of exponential components. The analysis of such multiple-component decay curves can be done graphically, but as the number of components increases, a computer analysis will facilitate the determination of autocorrelation times. In the limit of a continuous distribution of particles, the particle spectrum in question can be subdivided into regions of interest, each of which would be represented by a characteristic size and thus, a characteristic autocorrelation time. With these correlation times specified, the observed decay curves can be reconstructed using exponentials with the specified characteristics. The calculation is thus one of obtaining the weighting factor, or normalization constant, appropriate for each exponential. This weighting factor of a given exponential relates directly to the density of particles having a size characterized by the exponential's decay constant. To approximate a continuous spectrum using five exponential decay curves presents no analytical difficulty. While not previously used in size determination of airborne particles, intensity-fluctuation spectroscopy has proved of utility in the analysis of protein molecules and other suspended materials in liquids.

Instrument Development and Analytical Procedures

An intensity-fluctuation spectroscopy system required for this analysis was constructed using a two-watt argon laser purchased with funds otherwise available. Existing electronic equipment was modified to provide a detection system and a Saicor-Honeywell Analyser and PDP-11/20 Computer were purchased for use as an autocorrelation analyzer. Appropriate interfaces between the detection system and the analyzer were constructed. Necessary software was written and the apparatus tested utilizing sols of a given size suspended in various liquids. As constructed the apparatus was capable of determining size distributions from less than 0.001μ to 10μ or greater. For example, for a scattering angle of 10°, and $\lambda=514.5\mu$, $\eta=0.01$, $T=20°C$, $n=1.0$, the decay time would be 5 μsec. for a particle of 0.001μ size. As the instrument has a channel time resolution of 0.5 μsec., such a decay time could readily be observed.

The intensity-fluctuation spectrometer was tested first using these sols and dispersions of polystyrene spheres in water. Agreement between diameters measured using intensity-fluctuation spectroscopy and those determined by physical sizing was within 20%.

Scattering Tests with Monodispersed Aerosols

Several powders were obtained for use in calibrating the laser light scattering apparatus. These were blown by a 3-inch fan into a glass chamber in the scattering region of the lens. In a series of 16 runs using powders from a size of 0.02 μm to 30 μm, correlation times were measured and diameters of particles calculated according to the previously listed formula. It was found that there was very poor correspondence between the nominal size of the particles and diameters measured by light scattering. While the actual sizes of the particles ranged over three orders of magnitude, the sizes determined by this apparatus varied by less than a factor of 5. Moreover, the variation appeared to be random and not associated with physical particle size.

To pursue the origins of these discrepancies, successive determinations were made of dilute suspensions of polystyrene latex in a scattering cell. Five runs were made lifting the cell and replacing it in a laser beam between each run. Additionally, the liquid was removed and replaced in the cell. Overall, the standard deviation of data obtained from solution scattering varied less than 2.5% if no change in cell position was made. In those runs in which a cell movement occurred, variation was 11%. While some variation can be seen with these activities in scattering from solutions, the contribution to the major sources of error listed above is so small as to be inconsequential. It appears that the laser light beam itself alters the motion of the particles excessively. As an analysis of the size is based upon diffusional motion, alteration of the particles by the method of measurement cannot be tolerated. This is particularly applicable to the measurement of aerosols; in water or liquid solutions, the higher viscosity of the medium allows successful determinations to be obtained. The problem is greatest for particles of smaller size and appears at both large and small scattering angles. Some improvement may be expected by making measurements under pressurized conditions which would reduce the particle mean free pair. However, this would not circumvent the basic difficulty of the light pressure itself altering the basic diffusional motion of the particles. While the difficulties have not been clearly defined, it is unlikely that this method of measurement will prove to be feasible for particle sizing.

Table 1

Variations of Elemental Peak Heights in One Set of Characteristic Lead Auto Fuel Emissions

Elemental Peak Heights						Ratios of Elemental Peak Heights	
$Pb_{(L\alpha)}$	$Cl_{(K)}$	$Br_{(K\alpha)}$	$S + Pb_{(M\alpha,\beta)}$	$Al_{(K)}$	$Si_{(K)}$	Pb/Cl	Br/Cl
1.5	6.5	0.7	10.7	2.0	1.2	0.23	0.11
1.4	5.5	0.8	9.5	1.4	3.5	0.25	0.14
0.4	1.0	0.15	3.0	0.4	2.5	0.40	0.15
1.6	6.5	0.6	10.5	1.6	1.0	0.25	0.09
1.0	4.9	0.6	7.0	1.6	6.5	0.20	0.12
1.3	5.0	0.9	8.7	1.0	4.5	0.26	0.08
1.9	5.5	0.5	9.5	0.8	4.4	0.35	0.09
1.9	5.3	0.6	10.0	1.2	4.4	0.36	0.11
0.3	0.8	0.1	2.0	0.3	4.6	0.37	0.12
0.3	0.7	0.1	1.5	0.6	1.6	0.40	0.14
			Range of Elemental Ratios			0.20-0.40	0.08-0.15

Table 2

Elemental Characteristics of Particles Emitted from Automobile Sources

Source	Elements Present	% of total particles	Elements Never Present	Elements Rarely Present	% of total particles
Automobile using leaded gasoline	Pb, Cl, Br, S	22	Ti, V, Cr, Mn, Zn		
	Pb, Cl, S	18	Ti, V, Cr, Mn, Zn		
	Pb, S	31	Ti, V, Cr, Mn, Zn		
	Various, but no Pb	29	V, Cr, Mn, Zn, Pb	Ti	4
Automobile with converter using non-leaded gasoline	Pb	9	Ti, V, Cr, Mn	Zn	6
	Various, but no Pb	91	V, Mn, Pb	Ti Cr	1 1
Diesel automobile with converter	Pb, S, Ca (occ. Cr)	33	Zn	Ti, V, Mn	2
	Pb, S, P, Cl	31	Ti, V, Mn, Zn		
	Various, but no Pb	35	V, Mn, Zn, Pb	Ti	4

Table 3

Elemental Characteristics of Particles Emitted from Power Plants or Space Heating Boilers

Source	Elements Present	% of total particles	Elements Never Present	Elements Rarely Present	% of total particles
Electrical Generator using #2 Fuel Oil	Al, Si, K, Ca Ti, V, Fe	77	Pb, Zn		
	Ca, K, Cv, Fe	20	Ti, V, Pb, Zn		
	Various	3	Ti, V, Pb		
Turbine Generator using #2 Fuel Oil or Kerosene	S, K, Ca, Cv, Mn	66	Ti, V, Pb		
	Various	34	Cv, Mn, Ti, V, Pb		
Space Heating Boilers	Si, S, Fe	50	Ti, V, Pb		
	Si, S, Ti, V, Fe, Pb	27		Zn	13
	Various	23	Pb		

Table 4

Elemental Characteristics of Particles Emitted from Municipal Incinerator

Source	Elements Present	% of total particles	Elements Never Present
Hamilton Avenue Incinerator	S, Cl, K, Zn, Pb	61	Ti, V
	S, Cl, K, Zn	37	Pb, Ti, V
	S, Cl, K, Pb	2	Zn, Ti, V

Table 5

The Presence of Vanadium or Lead in Ambient Air Samples Analyzed from Various Sites

Sample Location	Particles Analyzed	Particles with Element Present					
		Vanadium			Lead		
		Significant	Trace	%	Significant	Trace	%
Springfield Gardens, Queens	68	8	15	34	3	12	22
Goethals Bridge, Staten Island	40	13	12	63	7	13	50
Staten Island Borough Hall, Staten Island	79	11	21	41	8	16	30
Sheepshead Bay, Brooklyn	78	8	18	33	6	13	24
Samuel Gompers High School, Bronx	80	4	5	11	9	29	48
51 Astor Place, Manhattan	18	0	0	0	1	0	6
Linden, N. J. 5/13/75	23	2	3	22	2	2	17
Linden, N. J. 5/12/75	19		2	11	4	2	33
Morrisania Health Center	79	10	17	35	10	13	29
Totals	484	56	93	31	50	100	31

Table 6

Possible Origin of Particles Collected at Various Ambient Air Sampling Locations

Sample Location	Particles Analyzed	Power Plants Space Heaters	Auto Emissions	Incinerators	SiO_2	Mica-like Particles	Iron Oxides	Industrial Sources	Source Unknown
Springfield Gardens, Queens	68	14	2	-	5	3	8	1	35
Goethals Bridge, Staten Island	40	19	2	-	2	-	-	1	16
Staten Island Borough Hall, Staten Island	79	17	3	1	2	5	1	5	45
Sheepshead Bay, Brooklyn	78	17	4	-	1	2	3	-	51
Samuel Gompers High School, Bronx	80	4	4	2	1	2	6	-	61
51 Astor Place, Manhattan	18	-	2	-	-	-	2	-	14
Morrisania Health Center	79	18	3	-	3	5	2	3	45
Linden, N.J. May 12, 1975	19	2	2	-	3	-	-	4	8
Linden, N.J. May 13, 1975	23	2	1	4	-	1	-	3	12
Totals	484	93	23	7	17	18	22	17	287
Percent of total particles associated with source		19	5	1	4	4	5	4	59

Figure 3. Typical agglomeration of microparticles found in the ambient air. (Magnification X 40,000)

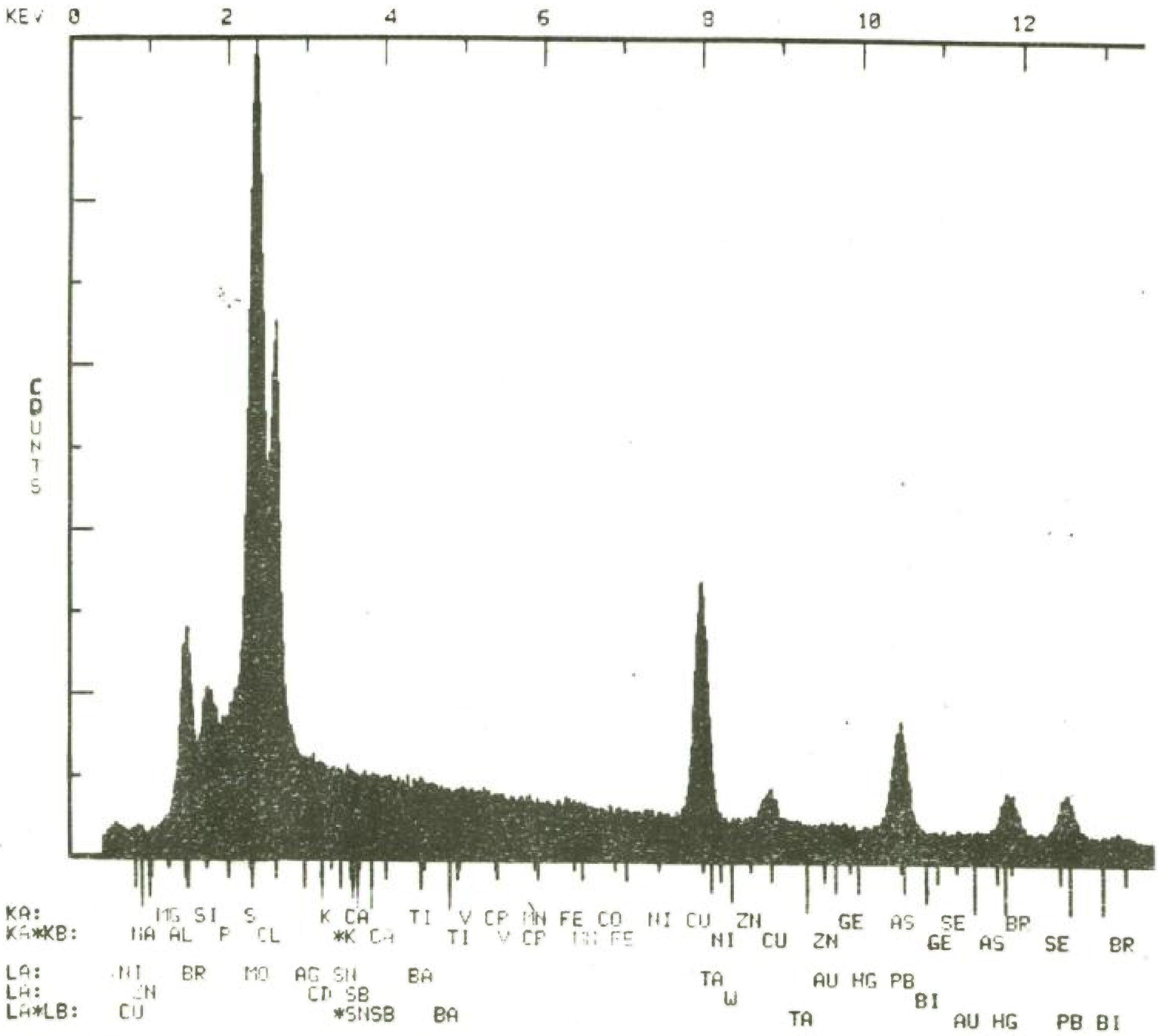
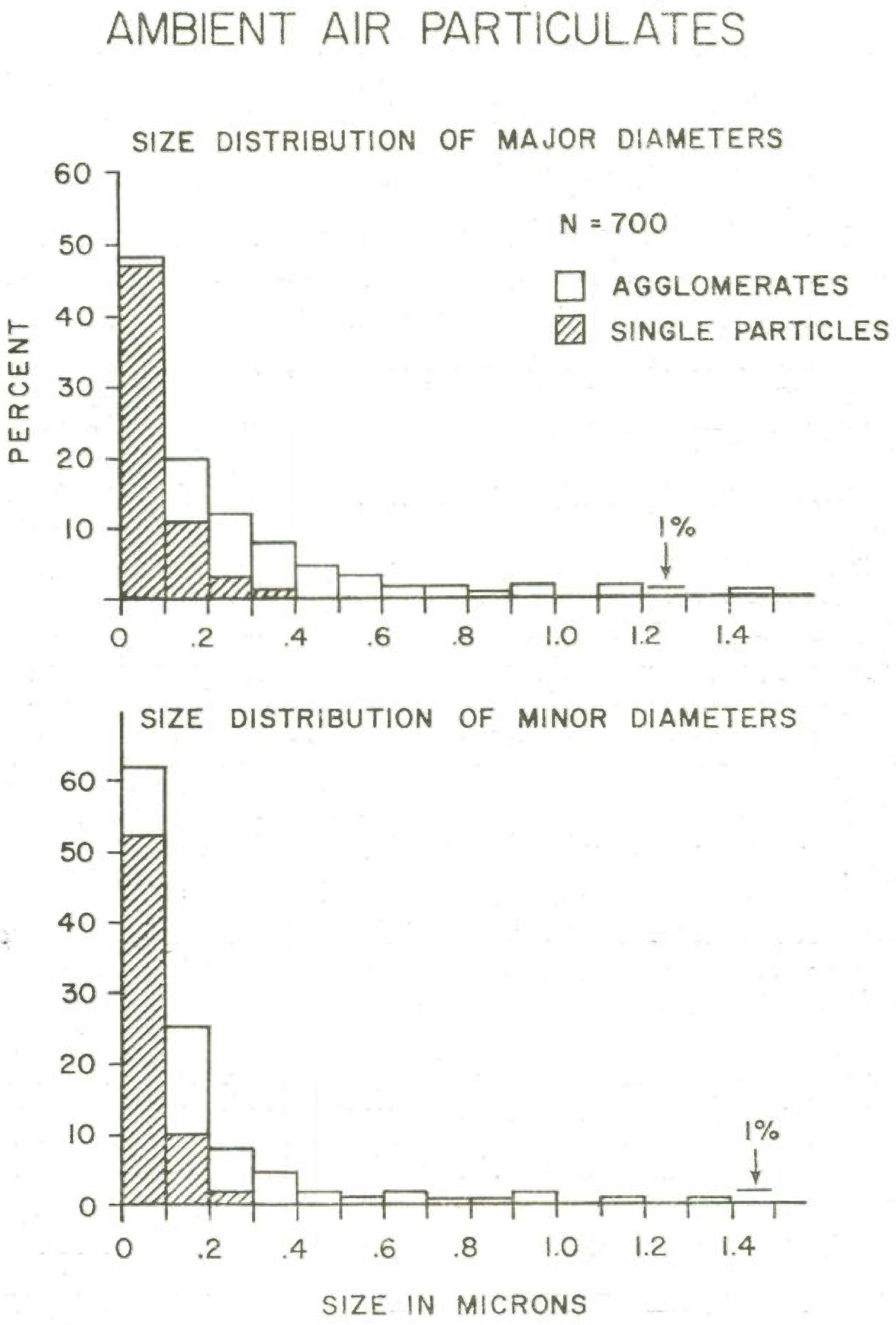


Figure 1. Elemental X-ray spectrum from a particle emitted from an automobile burning leaded gasoline.

Figure 2.



The size distribution of particles collected in the ambient air and observed by transmission electron microscope.

III ORGANIC TRACERS

Task Force Goals

A number of studies[1-6] have been published which describe the use of airborne inorganic compounds as chemical indicators of air pollution sources. For example, one study states that air pollution sources, whether natural or man-generated, produce a characteristic chemical fingerprint in approximately fixed proportions, and, if the pollution sources for a particular region are known, the contribution from each of these sources can be estimated from the measured elemental contributions. In this same study, 15% of the particulate matter was reported to be caused by natural sources, while 25% was man-made. An additional third of the resulting particulate matter collected was thought to be the result of atmospheric reactions (e.g. gas phase transformation reactions of hydrocarbons to particulate matter). This left approximately 30 per cent of the weight collected unlabelled (the authors suggest that part of the remaining 30 per cent could be water vapor). Although the methods discussed in these articles are elegant examples of human labor, the techniques are difficult to apply and to interpret.

It was the goal of this Task Force to search for airborne organic compounds that could be used as chemical tracers of pollutant sources, and, in addition, to develop those analytical methodologies deemed useful to make the search simpler.

Sample Collection Methodology

Most of the samples used for chemical analyses were provided by the "Sampling Task Force". Unless a specific reference is made otherwise, refer to the "Sampling Task Force" portion for the details of sampling techniques and methodology.

Methodology for Chemical Analysis

The following techniques were developed by the "Organic Task Force" during the course of the two-year study:.

A New Mechanical Disruption Technique for Organic Enrichment of Hi-Vol Samples[7].

While studying some airborne organic compounds, we developed a rapid, inexpensive and precise technique for the enrichment of the organic content of high volume samples collected on glass fiber mats. This method uses the mechanical disruption qualities of a blender, and the entire sample preparation takes approximately 30 minutes.

Each soiled mat (pretreated by flash-firing) is divided carefully (10-15 pieces) so that none of the sample is lost. These pieces are placed in the mechanical disrupter, and 150 ml of benzene (Burdick and Jackson) preheated to 60°C, is added to a heated (60°C) container. The temperature is maintained with a heating tape. The sample is disrupted for 10 minutes at approximately 2000 RPM. The process is interrupted long enough to wash down the container walls with an additional 50 ml portion of preheated (60°C) benzene, and the disruption of the sample is continued for an additional 10 minutes. The resulting slurry is filtered through a sintered glass funnel (medium) using approximately 100 ml of preheated (60°C) benzene to quantitatively transfer the sample. The filtrate is refiltered through a fine sintered glass funnel (ASTM 40-5.5F), washed with 10 ml of methanol and quantitively transferred to a 500 ml flask. The solution is evaporated to approximately 10 ml using a rotary evaporator and transferred to a tared 50 ml flask (small amounts of benzene insured quantitative transfer). The sample is evaporated to the desired concentration and is ready for the desired chemical analysis (e.g. GC/MS).

All parts of the disrupting apparatus that come in contact with the sample and solvent are made entirely of stainless steel. The cutting blades are mounted on a shaft that is powered by an air-driven E.H. Sargent and Co. motor. The container in which the sample disrupting takes place has a capacity of approximately one quart. Although the disrupter blades are capable of rotating at 3000 RPM, 2000 RPM was usually sufficient.

Reported results (cf. reference[7]) indicate that the mechanical disrupting technique compares favorably with a 6-hour Soxhlet extracting method.[8]

An Enrichment Method for Polycyclic Aromatic Hydrocarbons (PAH's) Collected on Glass Fiber Filters Using Hydrofluoric Acid[9]

This chemical method for sample enrichment employs hydrofluoric acid to destroy the glass fiber filters. The procedure is particularly useful for the rapid preparation of samples for GC/MS analysis.

20 ml of hydroflouric acid is placed in a 250 ml glass beaker since the use of polyethylene beakers or stirring rods leads to large losses of organics. The soiled glass fiber sample is added in small pieces to the hydroflouric acid; special care should be taken to avoid skin contact with the hydroflouric acid, and a well ventilated hood should also be used during the HF-treatment. When the entire sample has been introduced into the hydroflouric acid, the mixture is stirred carefully with a glass rod to insure complete dissolution of the glass fiber. 20 ml of distilled water is then added, the diluted mixture is transferred to a 250 ml separatory funnel, and the quantification of the transfer is insured by washing the beaker and the funnel with approximately 30 ml of water followed by a 50 ml rinse of cyclohexane (the water/cyclohexane washings are also added to the separatory funnel). The extraction is completed by carefully shaking the contents of the separatory funnel for 2-3 minutes. The bottom water layer is removed and saved for further cyclohexane treatment. The aqueous layer is further extracted with additional 50 ml portions of cyclohexane, and these extracts are added to the original cyclohexane layer. The resulting composite cyclohexane layer is washed with two 50 ml portions of distilled water, filtered through a sintered glass funnel, dried over anhydrous sodium sulfate, and the dried solution is refiltered through a fine, sintered glass funnel (ASTM 40-55F). The resulting cyclohexane solution is flash evaporated to near dryness, quantitatively transferred to a tared weighing bottle, and the final amounts of cyclohexane are removed by heating the sample in a 80°C oven with a nitrogen blanket. The sample is then ready for chemical analysis (e.g. GC/MS).

Phthalate Ester Analysis

A soiled glass fiber filtered (8" x 10") is cut in half with clean scissors, placed into loosely covered Soxhlet extractor and refluxed for 6 hours using 125-150 ml bezene (Burdick Jackson). The top of the condenser was loosely covered during the extraction. The extract was then filtered through a fritted-glass Buchner funnel (ASTM 10-20), and the benzene removed using an all glass rotary evaporator. The funnel was rinsed with two 10-ml portions of methanol (Burdick Jackson) and the washings combined. The residues were transferred to 10 ml vials using disposable pipettes with the aid of methylene chloride (Burdick Jackson). The solvent was removed from the vial by passing a steam of filtered, dry nitrogen over the warmed solution.

Analyses were accomplished by adding a measured quantity of an internal standard and monitoring the relative intensity of the base peaks of the unkown and the standard in a mass spectrometer. Data were recorded, stored and background automatically subtracted using a dedicated mini-computer data system.

Ring mono-deuterated isomers of di-n-butyl and dioctyl phthalates were selected for use as an internal standard, since their chemical identity to phthalates being analyzed precludes selective transmission or decomposition in the often unpredictable environment of a Watson-Biemann Separator. (In addition, since both unknown and standard elute together, it is not necessary to monitor the base peaks (m/e 149 and 150) continuously. One scan taken near the GC peak maximum is adequate for each compound of interest plus a scan for background level determination. Our analyses were made using continuous scanning.)

To each dry extract 100 microliters of a benzene solution containing 25 micrograms of 4-deutero-bis (2-ethyl hexyl) phthalate (DOP) and 5 micrograms of di-n-butyl phthalate (DBP) (78% isotopic purity) was added. Approximately 1 microliter was injected into the gas chromatograph - the effluent being split between a flame ionization detector and the mass spectrometer. The peak height ratios were recorded for m/e 149 and m/e 150 after automatic background subtraction. The base peak ratios were converted to micrograms of DOP using a calibration curve prepared by plotting the intensity ratios of $\frac{\text{m/e } 149}{\text{m/e } 150}$ against the corresponding micrograms of DOP and DBP.

The following scheme was selected for the preparation of the calibration curves:

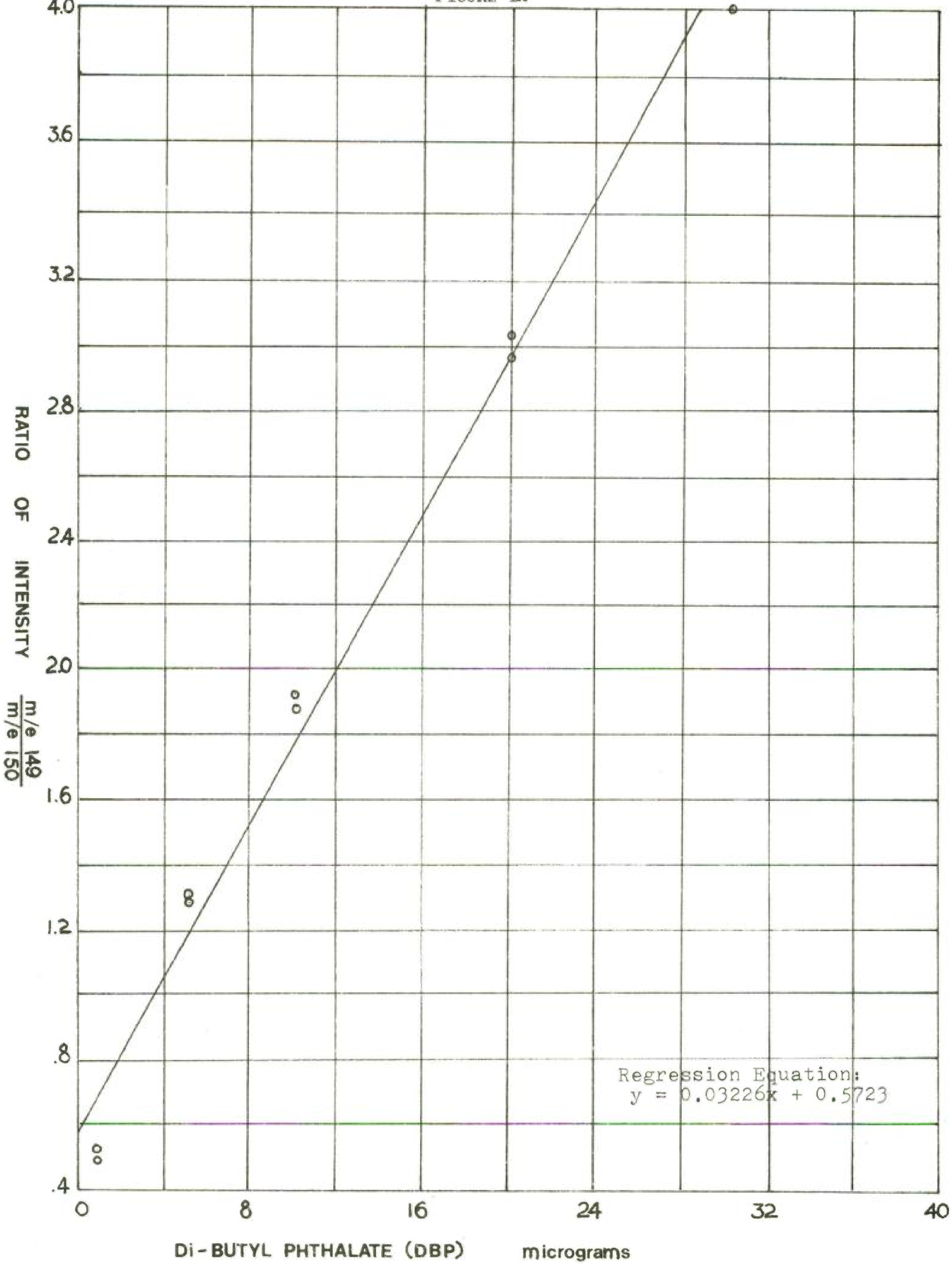
$$\frac{\text{Peak height m/e } 149}{\text{Peak height m/e } 150} = \frac{0.9095N = 5.62}{0.0836N = 19.38} = \frac{10.88N + 67.22}{N = 231.82}$$

(The fraction $\frac{10.88N = 67.22}{N = 231.82}$ is the result of dividing each value in the fraction $\frac{0.9095N + 5.62}{0.0836N + 19.38}$ by 0.0836, where N is the amount of the corresponding phthalate ester (in micrograms) used to prepare the calibration curve). The accompanying graph shows the fit using two separately prepared groups of knowns.

INSTRUMENT CONDITIONS

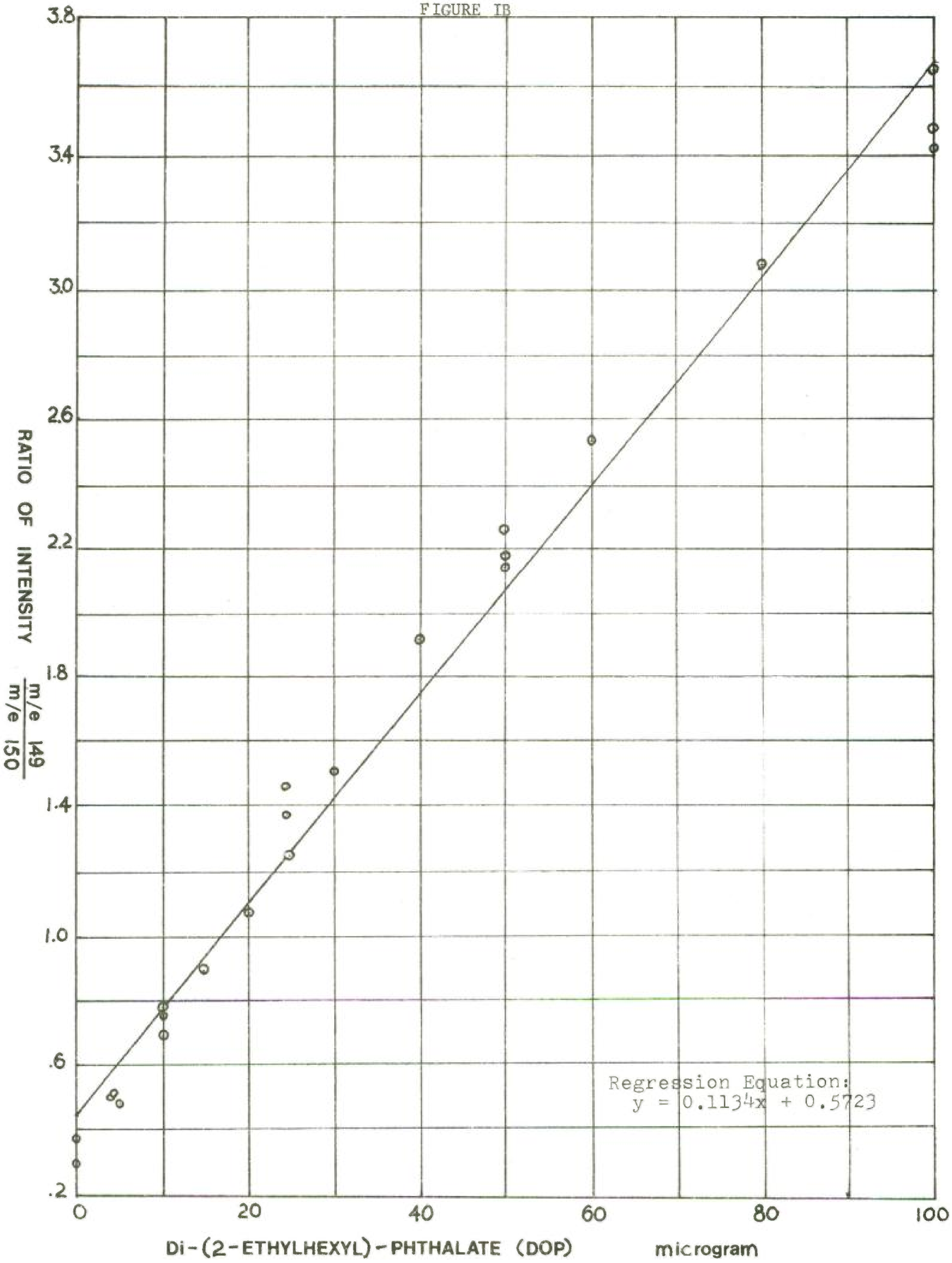
Gas Chromatograph	Mass Spectrometer	Data System
Inst: P.E. 800	Nuclide 1290 G	Incos 2100
Column: Dexil 300 6% on chromsorb W HP, 12'	Source: 225°C Ion. volt, 70_ev	Magnetic scanning, automatic background subtraction parameter set at near minimum
Carrier: H_e, 40cc/min.	Source Pressure: $2x10^{-6}$torr	
Oven 255°C Inj: 275°C Interface: Watson-Biemann type, 250° - 300°C		

FIGURE IA



RATIO OF INTENSITY $\frac{m/e\ 149}{m/e\ 150}$
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
.8
.4
0
8
16
24
32
40
Di-BUTYL PHTHALATE (DBP) micrograms
Regression Equation:
y = 0.03226x + 0.5723

FIGURE IB



Regression Equation:
$y = 0.1134x + 0.5723$

Determination Of Free Carbon Collected On High Volume Filters[12]

A soiled 8"x10" glass fiber filter collected over 24 hours is analyzed for free carbon. Hydrofluoric acid (15 ml) (care should be exercised when handling hydrofluoric acid to avoid skin contact) was placed in a 100-ml platinum dish, and half of the soiled glass fiber filter (4"x10") was cut into approximately 20 pieces, and carefully added (one by one) to the platinum dish containing the HF. (It should be noted that the dissociation of the glass fiber mat is rapid, and that the HF reaction should be carried out in an efficient hood). The mixture was stirred with a polyethylene rod, and 15 ml of distilled water was added. The diluted mixture was quantitatively transferred to a graduated 500 ml pyrex beaker, and 60 ml of concentrated ammonium hydroxide was carefully added with vigorous stirring. Now, exercising the same extreme care, 70 ml of concentrated nitric acid was added to the mixture, along with a few glass beads, and the mixture was evaporated to approximately 100 ml (a well ventilated hood is used). An additional 30 ml of concentrated nitric acid was added, and the mixture was reevaporated to a volume of about 100ml. The mixture was diluted with 250 ml of distilled water and 10 ml of concentrated hydrochloric acid was added. The resulting mixture was heated to boiling, and filtered hot through a tared, prefired (at 1000°C) asbestos Gooch crucible. The crucible and its contents were washed with 300 ml of a warm 1% nitric acid solution.

Finally, the crucible and its contents were dried at 150°C to constant weight (approximately 2 hours), cooled and weighed: the crucible was then heated to 700°C for 2 hrs, cooled, and reweighed. The difference in the two weights (150°C and 700°C) represents the weight of free carbon.

A more detailed discussion can be found in the literature (cf. reference 10).

Determination Of Free Carbon Collected On High Volume Paper Filters[11]

A soiled 8"x10" Schleicher and Schuell (S&S) No. 589 Green Ribbon filter paper sample collected over a 24-hour period was analyzed for free carbon. The filter was divided into equal halves (4"x10") so that the precision of the method and the validity of the analytical technique could be examined. To test the validy of the technique in question, one of the halves of each sample-pair was spiked with a weighed amount (25.0-65.0 mg) of lamp black.

Half of the spiked filter (4"x10") was cut into small pieces (15-20) and placed into a 500 ml glass beaker. Fuming nitric acid (25-30ml) was carefully added from a measuring cylinder (a well ventilated hood, playtex gloves, lab coat, and goggles should be used during this analysis). The contents of the beaker were gently heated over a hot plate and carefully swirled with the aid of a holder. The heating process was continued until the rate of brown fumes decreased, (care should be taken to avoid heating the mixture to dryness). Concentrated nitric acid (10 ml) was added to the resulting mixture, and it was boiled for 2-3 minutes; the contents were diluted to 300 ml with distilled water, and, after adding 5 ml of concentrated hydrochloric acid, the acidic solution was boiled for an additional five minutes to complete the solution. To this solution was added 200 ml of distilled water, the resulting mixture was cooled to room temperature and filtered through a tared asbestos Gooch Crucible. The crucible contents were washed with approximately 100 ml of warm 5% nitric acid, dried in a 110°C oven, cooled in a desiccator, and then weighed. Finally the crucible and its contents were heat-treated at 700°C for a half hour and re-weighed.

A more detailed discussion can be found in the literature (cf. reference 11).

PYROLYSIS PRODUCTS OF POLYVINYL CHLORIDE (PVC)

Pyrolysis Products of Di-(-2-Ethylhexyl) - Phthalate

Recently the thermal decomposition of polyvinyl chloride was reported indicating a range of organic compounds from methane to the xylenes[12]. Inasmuch as no compounds more complex than the xylenes were reported, it became of interest to this laboratory to examine pyrolysis derived compounds of PVC that might be formed at temperatures approaching that of operating incinerators (600 degrees C).

It was felt that perhaps an analysis of these compounds might reveal one or more unique compounds that could be used as tracers for incinerators. The following experimental procedure was followed: 0.25 gram of polyvinyl chloride (Conoco Chem. Co.) containing di-(-2-3thylhexyl)-phthalate (ratio 72:28) was placed in a stainless steel bomb (22 ml) and the bomb was positioned in a furnace while the temperature was raised from 250 degrees to 600 degrees C, (procedure took approximately 25 minutes). The 600 degrees C was maintained for an additional five minutes and the bomb was then removed and allowed to cool back to room temperature. The contents of the bomb were then extracted with 50 ml of boiling benzene (Baker Reagent Grade analyzed). The extract was then evaporated to near dryness and re-dissolved in approximately 5 ml of ether/benzene. The resulting solution was washed twice with 5 ml portions of 15% sodium carbonate, followed by distilled water (twice), and finally with saturated sodium chloride. The resulting benzene/ether solution was then dried with anhydrous sodium sulfate and this dried solution was evaporated to approximately 1 ml and analyzed.

The analysis was performed using Dupont 490 GC/MS equipped with a 12 ft. x 18 in. Dexsil 300 column (6% Dexsil 200 on 80/100 mesh Chromosorb W HP). The column temperature was initiated at 150 degrees C and terminated at 300 degrees C (at a rate of 4 degrees/min.). The chromatogram contained approximately 58 peaks. Some of these compounds have been tentatively identified, and the results are summarized in Table I.

TABLE I. GC/MS RESULTS OF PRODUCTS FROM PYROLYSIS OF PVC CONTAINING PLASTICIZER

Peak No.	Retention Time (minutes)	Tentative Identification	Comment
1.	3.8		
2.	4.0		
3.	4.2		
4.	4.8	Naphthalene	R.T.[*] plus M.S.[†]
5.	5.2		
6.	5.5		
7.	5.9		
8.	6.1		
9.	6.7	Methyl Naphthalene	Mol. ion[**]+loss of CH_3
10.	7.1	Methyl Naphthalene	Mol. ion+loss of CH_3
11.	8.0	Biphenyl	R.T. plus Mol. ion
12.	8.8	dimethyl Naphthalene	
13.	9.1		
14.	9.8		
15.	10.0	a dimethyl Naphthalene	Mol. + M-15[‡]
16.	10.4		
17.	11.2	Acenaphthene	R.T. + Mol. ion
18.	11.4		
19.	11.9		
20.	12.2		
21.	12.5		
22.	13.1		
23.	13.7	Fluorene	Mol. ion AW
24.	14.0		
25.	14.2	a Methyl Biphenyl	Mol. ion + M-15
26.	15.0		
27.	16.7	a Methyl Fluorene	Mol. ion + M-15
28.	17.1	a Methyl Fluorene	Mol. ion + M-15
29.	17.8		
30.	18.4		
31.	18.9		
32.	19.3	Phenanthrene or Anthracene	
33.	19.9		
34.	20.5		
35.	21.0		
36.	22.2	Methyl Phenanthrene (or) Methyl Anthracene	Mol. ion + M-15
37.	22.5	2-phenyl Naphthelene	R.T. + Mol. ion
38.	22.8	Methyl Anthracene (or) Methyl Phenanthrene	
39.	23.4		
40.	24.4		
41.	24.8		
42.	25.2		
43.	25.8		
44.	26.1		
45.	26.7		

(continued)

TABLE I . CONTINUED

Peak No.	Retention Time (minutes)	Tentative Identification	Comment
46.	28.0		
47.	29.1		
48.	29.9		
49.	30.3		
50.	31.1		
51.	33.1		
52.	33.8		
53.	34.6		
54.	35.6		
55.	38.1	Chrysene	
56.	38.4	Triphenylene	R.T. + Mol. ion
57.		Benz(α)Anthracene	
58. etc.	These higher temperature peaks will be studied at a later time		

*R.T. = Retention Time
†M.S. = Compound Fingerprint
**Mol. ion = Molecular ion
‡M-15 = Mol. wt. - 15

Organic Analysis of Municipal Incinerator

In an effort to check the notion that unburned phthalate plasticizer is entering the ambient air via the incinerator stacks, a sample of the Greenpoint Incinerator was provided to this laboratory by the Field Sampling Team. The sample was chemically processed and analyzed by GC/MS. Both di-n-butylphthalate and di(-2-ethylhexyl)-phthalate were found; however, no quantitive determination was made for either ester.

Airborne Di-Butyl- and Di-(-2- Ethylhexyl) - Phthalate at Three New York City Sampling Stations (13)

The 1975 yearly average concentrations of di-butylphthalate at three sampling stations in New York City (Queens, Brooklyn, and Staten Island) were 3.73, 5.69, and 3.28 nanograms per cubic meter respectively. The yearly average concentrations of di-(-2-ethylhexyl)-phthalate for the same period at the corresponding stations were 10.20 and 16.79 and 14.20 nanograms per cubic meter respectively. The experimental data are summarized in Table II and Figure II. For a more detailed discussion the reader should consult reference 13.

Organic Analysis of Oil-Fired Power Plant Stack Filter

A power plant (State Campus; boiler, number 2) stack filter containing a total of 132 milligrams of particulate matter was extracted with benzene in the usual way. A total of 1 miligram of benzene-extractable organics was recovered. A GC/MS analysis is summarized in Table III.

TABLE II

1975 Monthly Average Concentrations of Total Suspended Particulate Matter (TSPM), di-Butyl and di-(2-Ethylhexyl)-phthalate (DBP and DEHP), and Benzene Extractable Organics (BEO) at the Andrew Jackson High School Station (Sector 23[a]), the Tilden High School Station (Sector 27[b]), and the Seaview Hospital Station (Sector 34[c])

MONTH	TSPM(d)			DBP(e)			DEHP(e)			BEO		
	Micrograms/m^3			Nanograms/m^3						Micrograms/m^3		
	Sector			Sector			Sector			Sector		
	23	27	34	23	27	34	23	27	34	23	27	34
January	85.43	59.52	63.71	4.90	4.93	3.87	10.89	11.96	18.58	3.87	3.08	4.15
February	NDA	61.21	NDA	NDA	8.49	NDA	NDA	15.41	NDA	NDA	4.13	NDA
March	47.39	52.71	56.63	2.93	5.03	4.33	10.91	12.30	13.06	1.76	2.56	2.54
April	53.42	70.31	65.72	3.00	4.84	2.72	4.93	12.48	13.50	1.88	2.96	2.54
May	NDA	89.38	68.58	NDA	3.17	2.22	NDA	14.72	12.23	NDA	3.89	2.67
June	NDA	67.28	67.25	NDA	1.99	1.80	NDA	10.06	11.02	NDA	2.39	2.06
July	NDA	74.41	56.97	NDA	3.48	0.14	NDA	14.05	8.96	NDA	3.84	1.63
August	NDA	63.51	55.34	NDA	5.00	1.80	NDA	15.48	13.58	NDA	3.45	1.87
September	57.19	54.74	51.67	4.40	4.79	7.38	8.81	17.93	12.15	1.43	3.04	3.26
October	98.78	73.65	73.64	2.98	10.28	2.81	12.15	28.60	22.15	3.98	5.24	3.53
November	69.53	65.69	79.74	4.15	5.31	5.69	13.52	23.24	16.76	3.79	5.01	3.56
December	NDA	57.96	NDA	NDA	10.99	NDA	NDA	25.30	NDA	NDA	5.66	NDA

a) Analytical data based on 16 available samples

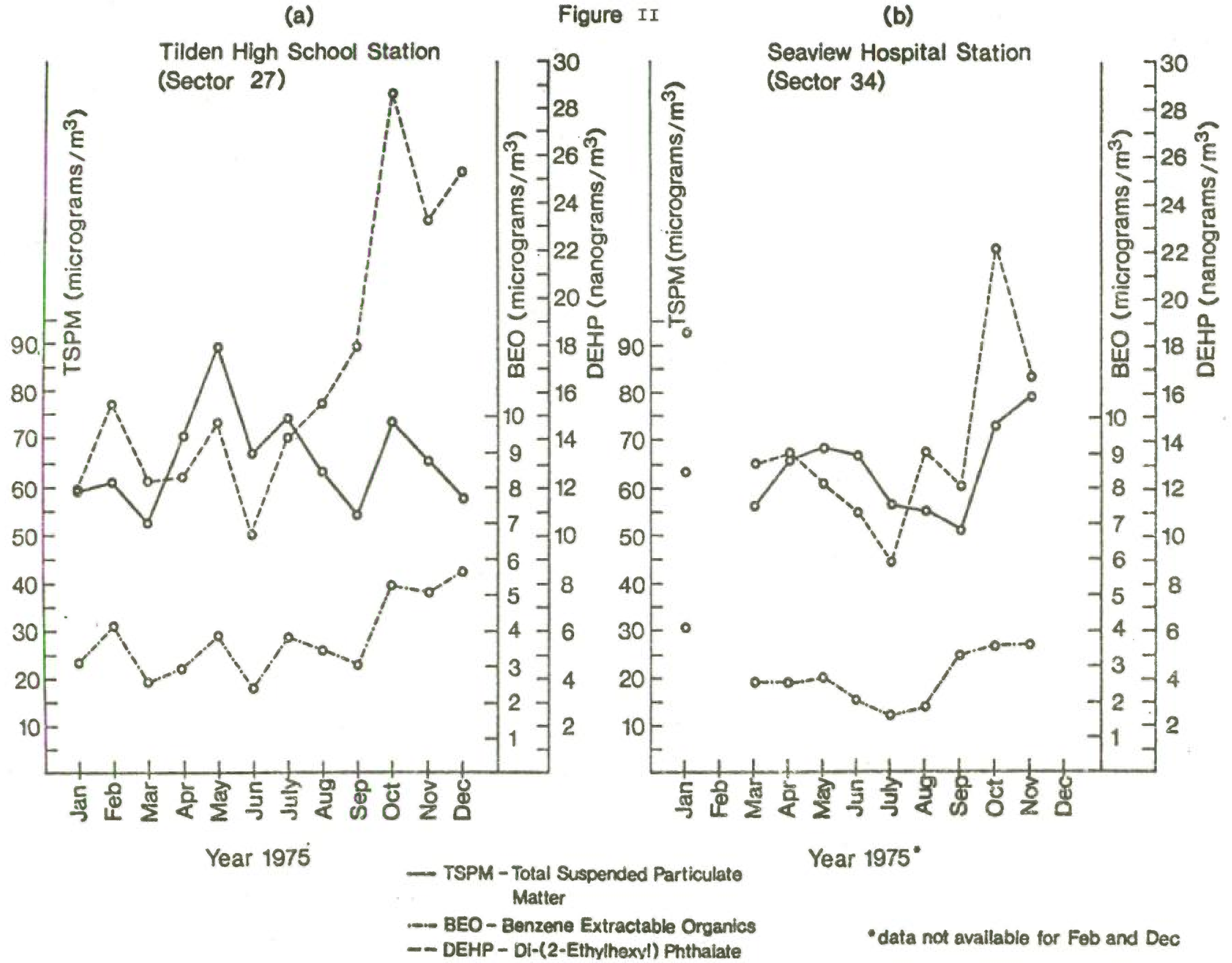
b) Analytical data based on 74 available samples

c) Analytical data based on 138 available samples

d) TSPM data were provided by the New York City Department of Air Resources

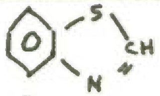
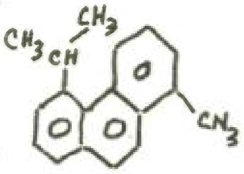
e) The analytical blanks were subtracted from the reported values

Figure II



*data not available for Feb and Dec

TABLE III GC/MS ANALYSIS OF POWER PLANT STACK FILTER

Peak No.	Peak Height*	Retention Time (Min.)	Comments
1	57 (15)	2.3	Benzthiazole 
2	9 (2)	3.1	a methyl naphthalene
3	66 (25)	4.5	probably 2,3-di-t-butyl-p-benzoquinone
4	70 (25)	5.7	not identified
5	45 (20)	8.7	possibly  (or an isomer)

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* The numbers in parenthesis are percents of the total sample injected into the F.I.D./G.L.P.C. and calculated with an electronic integrator (uncorrected for F.I.D. response).

Examination of Diesel-Powered Automobile Particulate Matter Filter

A sample filter (collected at the New York City Frost Street Laboratory) of a diesel automobile containing a catalytic converter was extracted with benzene and prepared for GC/MS in the usual way. A large portion of the sample analyzed contained saturated hydrocarbons (most likely unburned fuel). The largest GLPC peak found was indentified as benzthiazole (it should be noted that this compound was also found in the New York State Campus Power Plant sample). In addition, benzoic acid, hydroxybenzoic, and phenol were also found.

Examination of Gasoline-Powered Automobile Particulate Matter Filter

The total weight of particulate matter collected was 8 miligrams. An impinger sampler following the glass fiber sampler collected an additional 17 milligrams. When the impinger sample was extracted with 5% sodium carbonate and the extract prepared in the usual manner for GC/MS analysis, benzoic acid and a bromoderivative of benzoic acid were found.

CONCLUSIONS

Pyrolysis experiments of PVC with and without plasticizer revealed that the polycyclic aromatic hydrocarbons (PAH) listed in Table I are derived from the plasticizer (di-(-2 ethylhexyl)-phthalate). In addition, it was revealed in subsequent experiments that if the corresponding alcohol (2-ethyl-hexanol) is subjected to pyrolysis, a similiar list to Table II is produced. This suggests that the PAH's are probably derived from the alcohol portion of the ester.

Esters of phthalic acid (especially di-(-2ethylhexyl)-phthalate) show some potential as tracers for incinerators. This would be especially true for geographic areas that did not contain a large chemical industry. Further examination of this postulate is needed and necessary if its use as a tracer is to be seriously considered.

No unique compounds associated with power plant stacks were found when a limited number of stack sample filters were analyzed (cf. Table III). Perhaps further examination of other stack filters may reveal more unique compounds, but it appears from these limited data that effort would be better spent considering other techniques for the power plant case.

No unique tracer compounds were discovered for diesel powered vehicles; however, only one sample was examined.

In the case of gasoline-powered vehicle filter samples, a bromobenzoic acid derivate was found that might have some use as an organic tracer for gasoline automobiles. Further work would be necessary if this approach should be of interest.

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IV MATERIAL BALANCE

Two sets of 24-hour samples of suspended particulates were collected from Hi-Volume Samplers stationed on rooftops of seven stations dispersed throughout the City:

Station #3 - Morrisania Health Center - 1309 Fulton Ave, Bronx
65 feet above street level

Station #6 - Samuel Gompers High School, 455 Southern Blvd., Bronx
65 feet above street level

Station #10 - Mabel Dean Bacon High School Annex, 240 - 2nd Ave., Man.
100 feet above street level

Station #26 - Sheepshead Bay High School, 3000 Ave. X, Bklyn.
40 feet above street level

Station #30 - Springfield Gardens High School, Springfield Blvd. and 144th Ave., Queens
40 feet above street level

Station #31 - Goethal's Bridge Plaza, Staten Island
40 feet above street level

Station #32 - Borough Hall, St. George, Staten Island
50 feet above street level

The first set was collected on Schleicher & Schuell Grade #589 Green Ribbon cellulose paper during the years 1974 and 1975. These were used in the analysis of the following trace metals: V, Cr, Fe, Ni, Cu, Zn, Pb, Mn. Total weight was not determined for the paper filters because of the extreme hygroscopic nature of that media. A constant humidity chamber was not available for performing weighings. The second set was collected on Gelman's Type A Glass Fiber over the period January - July 1975. (No samples were collected during the month of May). These were used for the analyses of $SO_4^{=}$, NO_3^{-}, NH_4^{+}, Cl, Na, K, Mg, Ca, Al, benzene-extractable organics and elemental carbon as well as total weight collected.

Trace Metals Trapped on Cellulose Paper

The first set of 391 samples collected over the two year period was analyzed by X-ray fluorescence for the eight elements mentioned above. The Rigaku Simultix X-ray Fluorescence Spectrometer was calibrated with sections from Hi-Volume samples previously analyzed by atomic absorption. A summary of the results of those analyses for the seven stations is listed in the Table IA for the eight elements analyzed; these results include subtraction of an "average" blank.

The "average" blank was obtained from analyses of sections from several sheets from six different but representative lots of S and S 589 Green Ribbon paper. Unfortunately, paper blanks from the lots actually used in the study were not available. However, variation among the blanks would result in an appreciable margin of error only for those elements measured in very low concentrations such as Cr, Ni, and Mn. To check accuracy this study's two year averages for several trace metals can be compared with results from the literature[1] (See Table IB). For example,the data from station 10 show a close correlation for Cr, and Zinc, but only a fair correlation for Ni and Pb.

Correlation coefficients were calculated for all pairs of elements, and the significant ones (0.40 and above) are listed in Table II. The high correlation coefficient between V and Ni (0.82) probably stems from their common presence in fuel oil. The high correlation coefficient between Zn and Pb (0.60) supports Mt. Sinai's finding that particles emitted from municipal incinerators contain both Zn and Pb. Our findings of significant correlations of iron with vanadium and manganese with vanadium is further corroborated by Bernstein and Rahn's study at NYU Medical Center in 1976. [2] The results (Table II) also seem to indicate some seasonal effect; the correlation coefficient of several pairs of trace metals appears to be somewhat higher for one season as compared to the other. One pair (V-Fe) shows a correla-coefficient that is somewhat higher for both winter and for summer months than the respective correlation coefficient obtained for this pair for the entire study, implying a bimodal distribution. However, these results should be normalized for meteorological effects such as mixing depth in order to ascertain the actual changes in emissions.

The average concentration of total suspensed particulate matter over the two year period (1974-75) was determined for each of the seven stations in the study using NYCDAR data.
The percentage contribution of the sum of the eight metals analyzed in the first set data (V, Cr, Fe, Ni, Cu, Zn, Pb, Mn,) were determined and are listed in Table IIIA. Over the extended period of time, the average sum of the trace metals is a suprisingly constant percentage (4.1% - 5.2%) of the total material collected on the high volume filter, independent of location in New York City. Therefore, the total weight of suspended particulate matter should be a fair indicator of long term exposure to these elements.

Lee et al[3]examined TSPM data for 1970 from Chicago, Cincinnati, Denver, Philadelphia, St. Louis, and Washington, D.C. (see Table IIIB). The trace metal chromium, which is lowest in concentration of the eight metals analyzed (average of 0.008 $\mu g/M^3$ over the two year period in NYC) is omitted from Lee's study. The TSP fraction of the other seven elements is from 4.6 to 7.7%, a fairly close correlation to percentage contributions for the seven stations in New York City which ranged from 4.1 to 5.28%.

Analysis of Components Trapped on Fiber Glass Paper

The second set of samples of suspended particulate matter collected on fiberglass filters was analyzed for total weight, sulfate; nitrate, ammonium ions, chloride, sodium, potassium, magnesium, calcium, aluminum, total organic content (benzene-extractable), and elemental carbon. For the water soluble ions, a water extract was obtained by a 90-minute extraction of a section of each mat with boiling water. Sulfate, nitrate, ammonium, and chloride ions were then analyzed with a Technicon Autoanalyzer using established Technicon procedures:

Sulfate:	Technicon Industrial Method No. 118-71W (Methylthymol blue method)
Nitrate:	Technicon Industrial Method No. 43-69W (reduction-sulfanilamide-azodye method)
Ammonium:	Technicon Industrial Method No. 19-69W (sodium phenoxide-sodium hypochloride method)
Chloride:	Technicon Industrial Method No. 11-68W (thiocyanate method)

Sodium, potassium, magnesium, calcium, and aluminum were all analyzed by flame emission after adding lanthanium (0.05%). Operating conditions used were those described in Perkin Elmer's Analytical Methods for Atomic Absorption Spectrometry, March 1973. Total benzene-extractable organics and elemental carbon were analyzed on other portions of the glass fiber mat. Elemental carbon analysis required destroying a section of glass fiber mat with hydrofluoric acid and heating the insoluble residue at 700 degrees C for two hours.

Since blanks of the fiberglass lots used in the study were available, the blank values for each species were subtracted from all readings. Table IV gives the average values, maximum and minima of these variables for each station and for the whole data base.

Table IV shows that the averaged ratio of SO_4 to NH_4 for the 203 samples taken is much greater than would be expected if all SO_4 were tied up as $(NH_4)_2SO_4$ (3.4) and/or NH_4 HSO_4 (6.9). Therefore, considerable amounts of SO_4 could be present in other forms as well, possibly H_2SO_4. However, the magnitude of this ratio is inconsistent with previous studies. Based on the range and variation of SO_4, the NH_4 concentrations must be questioned. A histogram plot of the distribution of the individual ratios of all 203 samples which were analyzed for both SO_4 and NH_4 is shown in figure #1 (several points showing SO_4/NH_4 greater than 65 were omitted). the histogram shows that, even if a 50% estimated error was assigned to the experimental ratios obtained (this is analogous to setting SO_4/NH_4 equal to 5.3 + 50% for pure $(NH_4)_2SO_4$) only 13.5% of the 203 cases, or 27 cases fall in the proper range. Examination of these cases shows that they are nearly equally distributed among all of the stations, no station had more than 20% of its cases fulfilling the statistical requirement that the SO_4/NH_4 ratios fall in the range 0 - 9. If the estimated error is reduced to 20% (a more likely maximum), then the number of samples with SO_4/NH_4 ratios falling in this category (0 - 7.0) is reduced to less than 6% of the total number of 203 cases, or 12 cases. (See Figure #2)

Similarly, examinations of Table IV for Na/Cl ratios shows that there is much more sodium present than one would expect if all the sodium were tied up as NaCl. Thus the averaged ratio of Na/Cl for 61 samples is greater than would be expected for pure NaCl (Na/Cl=0.65). Figure #3 is a histogram plot of these 61 points and shows that, for an assigned 50% error in the ratio of 0.65 (involving the interval 0.32 - 0.98), 30% of the analyses, or 18 cases, fall in the proper range. If the assigned error is reduced to 20% (a more likely maximum), then the number of samples with Na/Cl ratio falling in this category (0.52 - 0.78) is equal to 10% of the 61 samples analyzed or 6 cases. Figure #4 presents a histogram pertaining to this interval.

Correlations between all pairs (66) of variables were calculated. A low correlation of 0.11 was obtained for the NaCl pair (based on 61 analyzed samples); this is consistent with the previous finding that average Na/average Cl is considerably off from the calculated theoretical NaCl value.

Significant correlation coefficients (0.40 and above), are listed in Table V with the number of analyzed samples on which each correlation is based. Of interest are the significiant correlation coefficients for SO_4-NH_4 (0.51) and of TSPM with (0.50), nitrate (0.49), sulfate (0.48)* and with total organics (0.40). The SO_4-NH_4 correlation coefficient, has some seasonality: the correlation coefficient for the summer months is considerably higher than for the winter months (0.74 for June-July, 27 data points and 0.65 for April, June and July, 72 data points as distinct from 0.40 for the winter months, 176 data points.)

Using SO_2 data obtained by sequental hourly samplers (peroxide method) at each of our stations, SO_2 - SO_4 correlations were calculated. Considerably higher correlation occurs if only non-raindays are considered; in fact, there is a further increase in the correlation coefficient if all those data points which had rain falling on the day preceding the measurement are eliminated. Thus the correlation coefficient for SO_2-SO_4 rises from 0.23 for all the data (168 data points) to 0.39 (93 data points excluding raindays) to 0.45 (68 data points) excluding data that had rain occuring in the previous day.) Examining this last group by season, correlation coefficients of 0.56 (35 data points) and 0.51 (33 data points) for the months of Jan.-March and April-July, respectively, are obtained.

The correlation coefficient for SO_4-TSPM is affected by the season and rain. The correlation coefficient increases from 0.48 (206 data points) to 0.69 (43 data points) if only the data points covering the results Jan. through March that did not have any rain on the day of the measurement nor any rain on the day preceding are considered. Similarly, the correlation coefficient for SO_4-carbon rises from 0.28 (145 data points) to 0.47 (29 data points) if only the data from January through March that were not rain days nor had rain on the day preceding the measurement are used. Significant correlation coefficients between SO_4 with both TSPM and with light scattering have been obtained in other studies: see Airborne Particles, EPA-600/1-77-053, Nov. 1977, Project Officer: Orin Stopinski, pp 75-82.

Using the TSPM weights collected on glass fiber filters, not only can the percentage that each variable contributes to the total weight be calculated, but the percentage of the total High -Volume sample is also accounted for. This is shown in Table VI.

Using the data in Table III for the trace metal contribution, Table VI shows that about 30% of the TSPM is still unaccounted for. Silicates would make up a major portion of this 30%; other contributors would be organics, Titanium, Bromine, Phosphorous and Carbonate. Using the Al contribution of Table VI and the data of Morrow and Brief[6] who found Si/Al = 2.37 for TSPM for metropolitan New York, Sept., 1970, the silicon contribution could be estimated as 14%. Oxygen tied up in the form of silicates would contribute more than 14%, probably closer to 20%.

This would bring the accounted total to over 100%. The error was probably because of too high an evaluation of the Al contribution since only 37 samples (out of a possible 206) were analyzed for Al. Thus, using the Morrow and Brief value for Al of 2.04 $\mu g/M^3$ (295 samples), which is half of the value found in this study, the Si contribution could be estimated at 7% and the oxygen content in the silicate at about 10%. This leaves 13% still unaccounted for. Lognormal plots show that, consistent with the literature (6, 7, and 8) pollutant concentrations are approximately lognormally distributed.

Stack Samples

Stack samples were collected on Schleicher and Schuell Green Ribbon paper from 25 sites in New York and New Jersey. These samples were analyzed by X-ray fluorescence for the elements V, Cr, Fe, Ni, Cu, Zn, Pb, Mn. (Since blanks were available of the same lots as used in the study, all X-ray fluorescence results had the blanks subtracted.) The results are listed under major and minor components in Tables VII and VIII. In addition Table VII lists the analyses of the effluent (collected on nuclepore) of 12 of these sites that were also performed by Mt. Sinai using an electron microprobe. The results were similar, the only exception was the second building boiler (Source Type #3) wherein Mt. Sinai specified that no vanadium was found in any of the 10 particles examined while DAR's X-ray fluorescence analyses found small amounts of vanadium present in the filter exposed for the eight minute collection time (the other two filters of 4 and 6 minute exposures showed only traces of vanadium).

Comparison with the literature[9] corroborates this study's findings (see Table VIII, Source Types #1,5) on the compositions of emissions from power plants and municipal incinerators. (While Zn, the element found in this study to be the greatest in concentration in effluent from municipal incinerators is not included in Lee and Duffield's compilation, they do mention other studies [10,11] which report Zn as part of the effluent from municipal incinerators, although no concentration are mentioned).

One result of the stack sampling analysis by X-ray fluorescence is the confirmation of Mt. Sinai's finding of Pb and Zn present in municipal incinerators (See Item #5, Table VII). Toward that end two plume rise equations (1. Briggs: 2. Holland) were used in the Air Pollution Concentration Segment of the Air Quality Implemention Planning Program, Federal EPA, to estimate the contributions of the six New York City municipal incinerators to each of the seven stations used in the study. Unfortunately, correlations between the results of the two modeling equations with that of the zinc concentrations obtained in the study were poor. (-0.14 for the Briggs and + 0.05 for the Holland).

TABLE IA
SUMMARY OF ANALYSIS OF PAPER FILTERS FOR 1974 AND 1975
$\mu g/M^3$

		V	Cr	Fe	Ni	Cu	Zn	Pb	Mn
Station 03	Average	.101	.007	1.933	.035	.173	.404	1.315	.055
(64 Samples)	Max.	.691	.303	4.745	.166	.660	1.615	3.032	.183
	Min.	.012	.000	.673	.005	.043	.088	.331	.000
Station 06	Average	.078	.009	2.015	.032	.156	.333	1.157	.030
(73 Samples)	Max.	.507	.062	4.321	.131	1.502	.980	3.133	.102
	Min.	.010	.000	.756	.006	.036	.065	.315	.000
Station 10	Average	.051	.008	1.567	.019	.182	.383	.865	.035
(55 Samples	Max.	.170	.044	2.882	.062	2.801	1.102	2.340	.179
	Min.	.012	.001	.603	.005	.034	.075	.348	.000
Station 26	Average	.059	.006	1.657	.027	.261	.525	1.030	.042
(50 Samples)	Max.	.316	.044	5.879	.095	4.153	2.911	2.748	.132
	Min.	.000	.000	.377	.000	.26	.073	.231	.000
Station 30	Average	.052	.005	1.143	.023	.110	.267	1.070	.023
(63 Samples)	Max.	.210	.012	2.268	.071	.405	1.075	3.179	.086
	Min.	.012	.001	.359	.001	.013	.033	.245	.000
Station 31	Average	.062	.011	2.015	.029	.181	.398	1.338	.035
(44 Samples)	Max.	.262	.049	4.726	.095	.463	1.500	3.767	.108
	Min.	.011	.002	.636	.003	.039	.080	.267	.00
Station 32	Average	.124	.012	1.924	.045	.152	.523	.986	.048
(42 Samples)	Max.	.355	.058	4.429	.124	.466	1.712	2.523	.136
	Min.	.024	.003	.596	.009	.024	.076	.238	.001
Combined	Average	.074	.008	1.736	.030	.171	.393	1.114	.038
(391 Samples)	Max.	.691	.062	5.879	.166	4.153	2.911	3.767	.183
	Min.	.000	.000	.359	.000	.013	.033	.231	.000

TABLE IB

Study at NYU-Medical Center, Lioy, Wolff, and Kneip, JAPCA 26 510 (1978)

µg/M^3

	Cr	Ni	Zn	Pb
Annual Average for 1974	.010	.045	.338	1.400
Annual Average for 1975	.004	.036	.293	1.070
2-Year Average	.007	.041	.316	1.235

TABLE II

Significant* Correlation Coefficients (Paper Filter Study, 1974 and 1975)

Element Pair	Winter **(192 Cases)	Summer ****(199 Cases)	Entire Study (391 Cases)
V - Ni	0.87	0.77	0.82
Fe - Mn	0.76	0.74	0.76
Zn - Pb	0.70	0.52	0.60
Ni - Mn	0.74	0.53	0.60
Ni - Zn	0.67	0.57	0.58
Zn - Mn	0.65	0.43	0.53
Ni - Pb	0.64	0.53	0.52
V - Mn	0.71	0.53	0.52
Fe - Zn	0.65	0.42	0.51
Fe - Ni	0.57	0.60	0.50
Fe - Pb	0.61	0.38	0.49
V - Zn	0.61	0.45	0.45
Pb - Mn	0.58	0.30	0.43
V - Fe	0.58	0.57	0.40
V - Pb	0.63	0.40	0.40
Cu - Zn	0.19	0.43	0.33
Cr - Zn	0.47	0.24	0.33

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* Significant correlation coefficients are taken to be all those of 0.40 and above.

** Winter months are taken to be November thru April inclusive.

*** Summer months are taken to be May thru October inclusive.

TABLE IIIA

COMPARISON OF TOTAL SUSPENDED PARTICULATE MATTER TO SUM OF EIGHT METALS FOR NYC 1974 - 1975

Station #	TSPM $\mu g/M^3$ 2 year aver.	Sum Of 8 Metals $\mu g/M^3$	Percent of Total
# 03	85.5	4.0	4.7
# 06	87	3.8	4.4
# 10	75	3.1	4.1
# 26	74	3.4	4.6
# 30	59	2.7	4.6
# 31	79.5	4.1	5.2
# 32	78.5	3.8	4.8

TABLE IIIB

COMPARISON OF TOTAL SUSPENDED PARTICULATE MATTER TO SUM OF SEVEN METALS (ANNUAL AVERAGES) FOR SIX CITIES - 1970

$\mu g/M^3$

Element	Chicago	Cincinnati	Denver	Philadelphia	St. Louis	Wash. D.C.
V	0.06	NR	NR	0.14	NR	0.09
Fe	1.1	1.8	0.8	0.7	1.1	0.6
Ni	0.06	0.06	0.06	0.06	0.06	0.06
Cu	0.1	0.2	0.4	0.1	0.1	0.2
Zn	0.5	1.7	0.1	0.4	0.3	0.3
Pb	3.2	1.8	1.8	1.6	1.8	1.3
Mn	0.03	0.17	0.02	0.05	0.03	0.03
Sum 7 Metals	5.05	5.73	3.18	3.05	3.39	2.57
TSPM	36.5	74.3	59.7	58.5	73.1	56.3
% Contribution of 7 metals to TSPM	5.8%	7.7%	5.3%	5.2%	4.6%	4.6%

NR = No Report

TABLE IV

ANALYSES OF SAMPLES COLLECTED ON FIBER GLASS FILTERS, JANUARY-JULY 1975

ug/M^3

STATION	TSPM	SO_4	NO_3	NH_4	Cl
3	87.44 a)	11.20	4.92	0.77	3.07
	173.00 b)	20.05	9.97	1.91	14.09
	44.00 c)	3.69	1.62	0.17	0.95
	18 d)	18	18	18	18
6	73.22	10.48	3.94	0.43	2.20
	89.00	15.52	6.14	1.38	5.78
	42.00	5.45	1.73	0.04	0.32
	9	9	9	9	9
10	70.52	11.53	4.86	0.65	2.50
	123.00	28.48	13.23	2.19	14.55
	40.00	3.92	0.96	0.01	0.18
	21	21	19	20	20
26	70.78	10.81	5.20	0.77	2.84
	163.00	22.81	14.65	2.90	16.91
	31.00	3.99	1.12	0.01	0.15
	32	32	32	32	31
30	53.65	9.84	4.49	0.75	2.79
	109.00	29.44	9.97	3.62	12.74
	19.00	3.64	0.29	0.03	0.22
	45	45	45	44	44
31	72.06	13.05	4.79	0.66	3.19
	120.00	25.78	11.21	2.62	17.62
	38.00	3.19	1.36	0.15	0.01
	35	35	35	34	34
32	73.85	14.03	4.70	1.07	2.76
	134.00	31.01	12.63	3.32	14.63
	30.00	4.32	0.26	0.06	0.01
	46	46	45	46	46
Combined	69.74	11.79	4.76	0.79	2.83
	173.00	31.01	14.65	3.62	17.62
	19.00	3.19	0.26	0.01	0.01
	206	206	203	203	202

a) Arithmetic Mean
b) Maximum
c) Minimum
d) Number of samples analyzed

TABLE IV (cont't)

ANALYSES OF SAMPLES COLLECTED ON FIBER GLASS FILTERS, JANUARY-JULY 1975

$\mu g/M^3$

STATION	Na	K	Mg	Ca	Al	Org	Carbon
3	-	-	-	-	-	5.72	12.43
	-	-	-	-	-	12.60	36.20
						2.60	3.90
	0	0	0	0	0	15	13
6	-	-	-	-	-	5.40	12.79
	-	-	-	-	-	7.10	17.40
	-	-	-	-	-	3.10	10.00
	0	0	0	0	0	8	8
10	2.09	0.45	0.78	2.44	7.91	4.35	7.70
	2.67	0.51	1.04		9.66	7.50	16.80
	0.88	0.41	0.65		6.16	1.50	1.50
	6	3	3	1	2	20	20
26	2.83	0.28	0.21	1.87	3.26	4.14	6.20
	5.42			2.16	3.63	8.70	14.10
	0.59			1.02	2.18	2.00	1.30
	8	1	1	5	5	30	29
30	2.71	0.46	0.56	2.49	4.29	4.41	4.36
	4.57	0.51	0.66	3.56	6.42	8.90	12.70
	2.02	0.43	0.38	1.82	1.01	2.00	0.90
	15	4	4	7	8	39	25
31	2.93	0.48	0.46	2.73	4.34	4.49	3.31
	4.36	0.61	0.78	5.97	6.64	6.10	4.80
	2.29	0.33	0.08	1.42	1.55	2.80	2.00
	16	10	10	13	15	23	16
32	4.41	0.45	0.72	2.24	3.03	9.40	7.16
	9.89	0.46	0.88	3.05	5.05	37.30	17.49
	1.49	0.44	0.56	1.50	1.50	1.60	0.70
	16	2	2	7	7	35	34
Combined	3.17	0.46	0.54	2.44	4.13	5.56	6.92
	9.89	0.61	1.04	5.97	9.66	37.30	26.20
	0.59	0.28	0.08	1.02	1.01	1.50	0.70
	61	20	20	33	37	170	145

TABLE V

Significant* Correlation Coefficients for Samples Collected on Fiber Glass

(Entire Study)

VARIABLE PAIR	CORRELATION COEFFICIENT	NUMBER OF DATA POINTS
Al - K	0.58	18
SO_4 -NH_4	0.51	203
Carbon - TSPM	0.50	145
NO_3 - TSPM	0.49	203
SO_4 - TSPM	0.48	206
Na - K	0.48	20
Ca - K	0.45	16
Al - Mg	0.44	18
Carbon - Mg	0.44	13
Organics - TSPM	0.40	170

* Significant correlations are taken to be all those of 0.40 and above

TABLE VI

SUMMATION OF ANALYSES COLLECTED ON FIBER GLASS FILTERS, JAN-JULY 1975

AVERAGE % (SPECIES WEIGHT/TSP WEIGHT PER SAMPLE)
OF SAMPLES ANALYZED

STATION	AVG. TSPM	SO_4	NO_3	NH_4	Cl	Na	K
3	87.4	12.90	5.79	1.00	3.64		
	18	18	18	18	18	0	0
6	73.2	14.85	5.57	0.57	3.20		
	9	9	9	9	9	0	0
10	70.5	16.62	6.64	0.94	3.83	3.34	0.71
	21	21	19	20	20	6	3
26	70.8	16.66	7.44	1.13	4.64	3.82	0.26
	32	32	32	32	31	8	1
30	53.7	18.94	8.26	1.48	5.48	5.04	0.92
	45	45	45	44	44	15	4
31	72.1	18.70	6.96	0.92	4.63	4.05	0.69
	35	35	35	34	34	16	10
32	73.9	19.26	6.36	1.47	3.94	6.31	0.73
	46	46	45	46	46	16	2
Combined	69.7	17.67	7.00	1.27	4.42	4.79	0.72
	206						

TABLE VI (cont'd)

SUMMATION OF ANALYSES COLLECTED ON FIBER GLASS FILTERS, JAN-JULY 1975

AVERAGE % (SPECIES WEIGHT/TSP WEIGHT PER SAMPLE)
OF SAMPLES ANALYZED

STATION	Mg	Ca	Al	Org.	Carbon	E_1*	E_2*
3	0	0	0	6.81 15	16.51 13	46.7	43.6
6	0	0	0	7.84 8	19.00 8	51.1	48.1
10	1.35 3	2.32 1	10.20 2	6.52 20	11.33 20	63.8	64.2
26	0.20 1	2.69 5	4.86 5	6.63 30	9.11 29	57.4	54.3
30	1.08 4	5.56 7	9.42 8	8.48 39	7.80 25	72.5	69.2
31	0.62 10	3.56 13	6.03 15	7.15 23	5.28 16	58.6	56.1
32	1.14 2	2.84 7	4.43 7	11.98 35	9.25 34	67.7	67.7
Combined	0.85	3.66	6.53	8.29	10.01	65.21	62.2

* E_1 Refers to sum of individual percentages in Table VI

E_2 Refers to sum of percentages formed by avg. value of species/avg. values of TSPM for that station

TABLE VI

SUMMATION OF ANALYSES COLLECTED ON FIBER GLASS FILTERS, JAN-JULY 1975

AVERAGE % (SPECIES WEIGHT/TSP WEIGHT PER SAMPLE)
OF SAMPLES ANALYZED

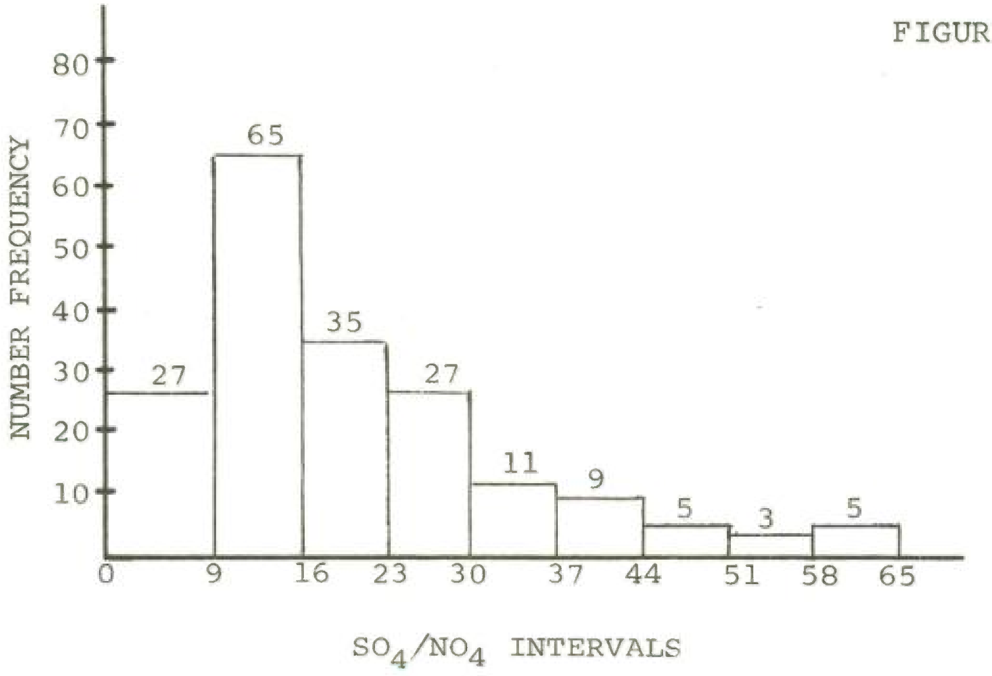
STATION	AVG. TSPM	SO_4	NO_3	NH_4	Cl	Na	K
3	87.4	12.90	5.79	1.00	3.64		
	18	18	18	18	18	0	0
6	73.2	14.85	5.57	0.57	3.20		
	9	9	9	9	9	0	0
10	70.5	16.62	6.64	0.94	3.83	3.34	0.71
	21	21	19	20	20	6	3
26	70.8	16.66	7.44	1.13	4.64	3.82	0.26
	32	32	32	32	31	8	1
30	53.7	18.94	8.26	1.48	5.48	5.04	0.92
	45	45	45	44	44	15	4
31	72.1	18.70	6.96	0.92	4.63	4.05	0.69
	35	35	35	34	34	16	10
32	73.9	19.26	6.36	1.47	3.94	6.31	0.73
	46	46	45	46	46	16	2
Combined	69.7	17.67	7.00	1.27	4.42	4.79	0.72
	206						

TABLE VIII STACK ANALYSES BY DAR (AVERAGE of 3 or 4 Filters)

Source Type	Y	Cr	Fe	Ni	Cu	Zn	Pb	Mn
							ug/m^3	
1. Asbestos Process							20	
2. Alum Plant			20				20	
3. Coffee Roaster		10	300	10	100	400	100	100
4. Building Boiler - #6 oil	10			5				
5. Multi Building Boiler - #6 oil								
a. boiler w/o water injection	1,400	50	1,000	700	100	300	100	30
b. boiler with water injection	1,300	60	700	500	100	200	100	20
6. Process Power Boiler - #6 oil	2,000	40		500			100	
7. Mineral Wool Process			2					
8. Aluminum Melting Furnace			40					
9. Public Utility Boiler - #6 oil								
a. boiler w/o water injection	100	10	300	100	100	90	70	30
b. boiler with water injectior	800	10	15,000	100	100	90	70	30
10. Pigment Process		100					1,000	
11. Cupola			30,000		1,000	20,000	20,000	10,000

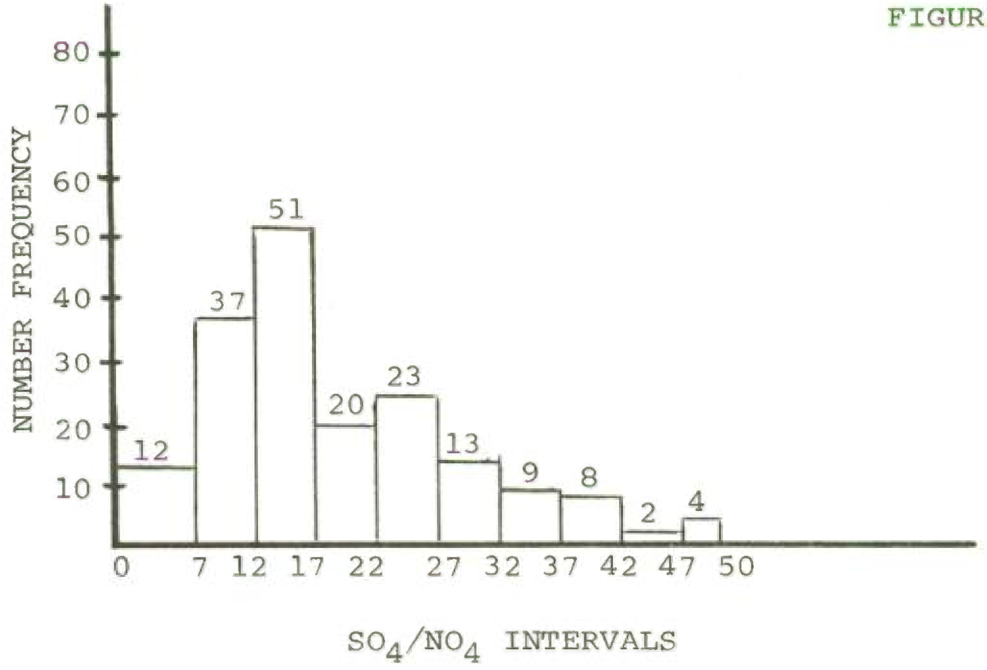
DISTRIBUTION OF RATIOS OF SULFATE TO AMMONIUM BY WEIGHT

FIGURE 1



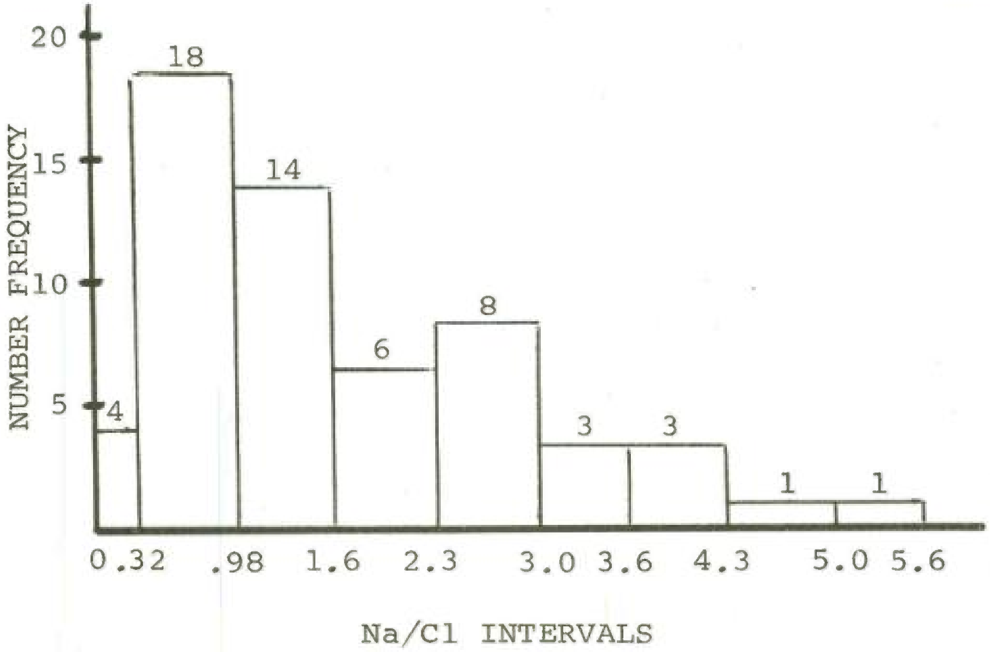
DISTRIBUTION OF RATIOS OF SULFATE TO AMMONIUM BY WEIGHT

FIGURE 2



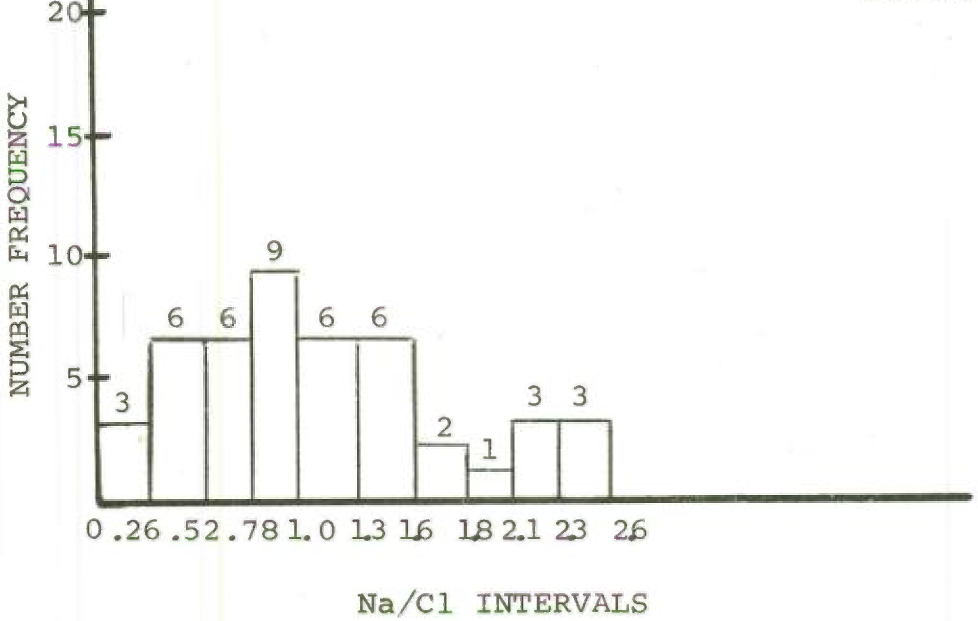
DISTRIBUTION OF RATIOS OF SODIUM TO CHLORINE BY WEIGHT

FIGURE 3



DISTRIBUTION OF RATIOS OF SODIUM TO CHLORINE BY WEIGHT

FIGURE 4



Material Balance References

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V. DESCRIPTION, CHARACTERIZATION AND ANALYSIS OF NEAR-STREET LEVEL TOTAL SUSPENDED PARTICULATES AT TWO URBAN SITES

Description of Dataset

Six four-hour samples were collected on a daily basis in Newark, NJ from September 1974 to January 1975 and in Brooklyn, NY from May 1975 to January 1976. The Newark total suspended particulate high-volume (TSPHV)* samplers were located at the site of the New Jersey Department of Environmental Protection (NJDEP) Air Monitoring Trailer, at the center city-commercial location of Washington Street and Branford Place. The Brooklyn monitors were located on the campus of the Polytechnic Institute of New York, on Jay Street between Myrtle Avenue and Johnson Street. TSPHV was monitored at the two sites using six high-volume samplers (General Metals Model 2000H) equipped with timers and was reported according to the start time of the sampling period, i.e., 0200, 0600, 1000, etc. Continuous CO data collected at both sites were averaged over the four-hour Hi-Vol sampling periods . The Newark CO data were obtained from the Newark Trailer of the NJDEP Continuous Air Monitoring Network, using a Beckman Model 866 non-dispersive infra-red absorption instrument. CO measurements at the Brooklyn site were made on-site using an Energetic (Model 2000) electro-chemical analyzer. The TSPHV and CO data were supplemented by other data as described in Table 1.1

Meteorological data from nearby airports were used for time interval overlapping the start of the sampling periods. Accordingly, the on-site observations were matched with the airport readings using the designation list as follows:

Correspondence Between Site and Airport Observations

Site Start Time	Airport Observations
0200	0400
0600	0700
1000	1300
1400	1600
1800	1900
2200	0100 (following day)

All of the analyses reported in the following sections, unless a specific notation is made to the contrary, were based on Monday-Friday sampling periods during which no precipitation was recorded. In the examination of the behavior of TSPHV and CO, holidays and days on which programmed street washing occurred were excluded, as were periods in which the hi-vols ran significantly over four hours.

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*Refer to Appendix A for a glossary of terms.

MONTHLY AVERAGE BEHAVIOR

Total Suspended Particulate, High Volume (TSPHV)

Composite monthly averages were calculated for the Newark and Brooklyn sites. These averages were not corrected for differences in the number of data points among each of the time-of-day samples. Figures 2.1 and 2.2 show the monthly variation at the sites in Newark and Brooklyn, respectively.

At the Newark site, it was found that the September and December 1974 monthly averages were both approximately 120 $\mu g/m^3$, while the Oct. 1974 average was approximately 20% lower and the November 1974 level approximately 10% lower. This trend is consistent with patterns observed at other high volume sites in the Newark area which are operated by NJDEP[1]. The NJDEP monitors were operated on an every-sixth day schedule in which every other operating day corresponded to the every-twelfth day NASN schedule 1974. The decrease seen in October can be attributed to cleaner air arriving from the northwest direction with elevated speeds and reduced temperatures.

In Brooklyn, the June, July, August, September, October 1975, and January 1976 monthly averages were within 5% of each other. The December average, on the other hand, was about 15% lower than the other months. Averages for May and November 1975 are not included because too few samples were taken during these months (11 in May, 16 in November) to constitute a representative average.

Carbon Monoxide (CO)

The monthly average behavior of CO in Newark was markedly different from the TSPHV. As seen in Fig. 2.3, the September average was 6.6 ppm, with the October average 10% lower, the November average 23% higher, and the December average 45% lower. The low December average in Newark was anomalous and similar behavior was not noted by other CO monitors operated by NJDEP.[2] The possibility of an instrument malfunction was ruled out by an examination of the monitoring log.

Valid CO data were available for only 25% of the TSPHV observations collected at Brooklyn. Approximately 70% of the CO data were collected during December, 1975 with the remaining 30% concentrated in July 1975. The average for July in Brooklyn was 2.5 ppm; the December composite was 55% higher.

Total Suspended Particulates, Nuclepore Filter (TSPNUC)

In Newark, a representative average of TSPNUC could be obtained for December only. The average was 120 $\mu g.m^3$, approximately equal to the corresponding TSPHV figure.

The highest monthly average TSPNUC in Brooklyn occured in June at 75 $\mu g/m^3$ in November, and dropped sharply to 37 $\mu g/m^3$ during December. The TSPHV readings were consistently higher than the TSPNUC measurements. The monthly averages were lower by 36% to 61% than the corresponding TSPHV measurements.

DIURNAL BEHAVIOR

In the sections that follow, descriptions of the diurnal behavior of various subsets of TSPHV, CO, TSPNUC, and elemental concentrations are given. A summary of the time-of-day averages for the different subsets are given in Table 3.1.

Overall Diurnal Behavior of TSPHV

The diurnal pattern of TSPHV in Newark, shown in Fig. 3.1, averaged over all months, showed a strong peak of 143 $\mu g.m^{3}$ at 0600 which dropped off to 127 $\mu g.m^3$ through the 1000-1400 sampling times. As expected, the TSPHV levels were much lower during the 0200 and 2200 periods. The lack of a pronounced afternoon (1400) peak belied the possible effect of the afternoon rush hour and contrasted the morning and afternoon peaks seen in the diurnal CO trace, as described in the next section.

The diurnal pattern of TSPHV at the Brooklyn site (Fig. 3.2) was similar to that in Newark. The composite average increased from an overall low of 83 $\mu g.m^3$ at 0200 to 135 $\mu g.m^3$ at 0600. The highest average of 140 $\mu g/m^3$ was seen at 1000 hours, and thereafter the TSPHV fell off throughout the rest of the day. There was less than a 4% difference between the 0600 and 1000 averages, so the pattern can be summarized as an early and midmorning plateau that was surrounded by lower levels in the evening and night hours. The expected afternoon peak was again prominent in its absence.

Overall Diurnal Behavior of Carbon Monoxide (CO)

The relative diurnal variation of CO at Newark proved to be similar to the Brooklyn variation (figs. 3.3 and 3.4). The diurnal traces showed local maximums at 0600 and 1400 hours. The 1400 average was the absolute maximum at both sites. The 1800 average was in both cases approximately only 10% lower than the 0600 peak.

Overall Diurnal Behavior of TSPNUC

TSPNUC data for Newark were available only for the month of December 1974 when the elemental observations were collected. The data will be discussed below in conjunction with the description of the elemental dataset. At the Brooklyn site, however, TSPNUC data were collected throughout the course of the sampling program. The averaged TSPNUC data from Brooklyn essentially echoed the behavior of the TSPHV data. As seen in Fig. 3.5, the absolute maximum of the TSPNUC trace occurred at 0600, but the 1000 average decreased by less than 3%. The pattern of the morning-early afternoon plateau, followed by a decrease for the rest of the day, was repeated.

Diurnal Variation of Elemental Concentrations and Corresponding Subsets of TSPHV, TSPNUC, and CO

Before discussing the diurnal behavior of the elements measured by X-ray fluorescence analysis of the nuclepore filters, a brief comparison of the sampling results with typical urban levels is in order. Average values for each element, along with a comparison with literature values, are listed in Table 3.2 for both the Newark and Brooklyn sites. As can be seen, the Ti and As levels in Newark and the As levels in Brooklyn were three orders of magnitude higher than levels that have been encountered at other urban sites. The calibration problem that was encountered rendered useless any further examination of this highly questionable data.

The diurnal behavior of the TSPHV, TSPNUC, and CO data collected during the elemental sampling was typical of that observed for the sampling program as a whole. At Newark, the TSPHV showed a sharp peak at 0600 and declined thereafter. The CO at the Newark site peaked at 0600 and 1400, and was at its highest at 1400. In Brooklyn, the daytime particulate "plateau" was demonstrated again.

In general, the diurnal patterns of the elemental concentrations reflected the TSPHV behavior. The diurnal patterns of Pb in Newark and Brooklyn, and of Br in Newark and Brooklyn, are shown, respectively, in Figs. 3.6, 3.7, 3.8 and 3.9. Inspection of Table 3.1 indicates that in Newark, all of the measured elements were characterized by a maximum value at 0600. At the Brooklyn site, the now familiar morning "plateau", i.e., the duration of elevated levels throughout the 0600 and 1000 sampling periods, was found for Br, Mn, Pb, Si and Fe. The diurnal patterns of the V and Zn, which have been linked in the literature,[9] were anomalous in that their times of highest concentrations occured during the 2200, 0200 and 0600 observations. The plateaus were sixteen hours out of phase with the other elements. It should be noted that, for no element was the difference between the minimum and maximum hourly averages greater than the observed standard deviation of the measurements of that particular element.

DIRECTIONAL BEHAVIOR

Moving Window Statistics: TSPHV, CO

Moving statistics of various datasets were calculated and graphed using the technique of Cleveland and Kleiner (10,11). The meteorological data used for the analysis of the Newark and Brooklyn data were measured at the Newark and LaGuardia airports, repectively. The distances and directions from monitors to airports were:

	Distance	Direction
Newark	3.5 km.	SSE (158°)
LaGuardia	13.7 km.	NE (47°)

Figures 4.1, 4.2, 4.3 and 4.4 are plots of the moving 50th precentile of, respectively, Newark TSPHV, Newark CO, Brooklyn TSPHV and Brooklyn CO, vs. the 50th percentile of wind direction. The plots encompass all valid data, subject to the limitations specified in Section 1. The number of data points used for the moving window statistics are indicated in each figure.

It can be seen that a directional pattern was more apparent in the Newark data as compared with the Brooklyn data. At Newark, high TSPHV was centered at 175°, with minimum levels at 350°. This directional trend was seen even more strongly in the CO data, where the maximum concentrations spiked sharply at 225°. The high level directions corresponded to the sector between 130° and 230°, approximately encompassing the intersection of Washington Avenue and Branford Place, where much stop and go traffic occurred. The spike at 225° corresponded, approximately, to the direction of the tailpipe of a vehicle stopped for a red light on Branford Place.

As will be seen later in Section 7.1, the directional trends noted here were incorporated into the regression models that were fit to the data. The inclusion of a wind direction variable served as both a surrogate for a source function and as a general indicator of background from incoming air masses.

The directional plots of the Brooklyn data were not as smooth as those for Newark. TSPHV showed a fairly constant value of the 50th percentile of 115 μg/m through the sector between 70° and 240°. Levels approximately 25% lower were seen in the 250-350 range, and a spike to 140 μg/m occurred at 50-60°. Four-hour average on-site wind measurements were found to be inadequate to define any variation in pollutant levels seen by the monitor. The use of the moving window analysis with meteorological data from LaGuardia Airport was justified by its application to the regression analysis, as seen in Section 7.1. A t-test on the directional variable was significant at the 1% level.

The CO data at Brooklyn exhibited a shape similar to the TSPHV data, albeit with a much smaller data base. The CO peak occurred at a broader band between 60°-110°. The distinction between the 120°-240° and 250°-350° sectors was less distinct than that seen in the 70°-240° and 250°-350° sectors, respectively, in the TSPHV data.

The monitoring location at Brooklyn was situated in a street canyon configuration, being surrounded, at least partially, on three sides by tall buildings. The CO directional plot showed evidence of the vertical wake and mixing effects observed in street canyons, whereby cleaner air, passing over a building, curls down into the street and returns upward, to the prevailing overhead air movement, along the face of the building it initially passed. Thus, emissions in the street are picked up and swept backwards, with respect to the overhead prevailing wind, then upwards into the air mass moving over the building tops. When this phenomenon occurs, monitors on the windward side of the canyon tend to record cleaner levels than those on the leeward side. Similarly, as appears to be the case for Brooklyn, the single monitor on one side of the street recorded higher levels when it was on the leeward side, with respect to the prevailing wind, than on the windward side.

Moving Window Statistics: Elemental Concentration

Because of the limited elemental dataset for Newark, gaps occurred at certain wind directions in the moving window plots. There was little data for the eastern sector. The general trend of the elemental data from the Newark site was a peak at 175°-200°, a decline from 200° to 250°, with constant lower values occurring from 250° to 350°. The peak was most pronounced in the Pb, Br and Si traces. The peak was less pronounced and shifted to the east in the S graph, while it almost disappeared with the V, Mn, Zn, and Fe traces. The Pb and Br curves (Figs. 4.5 and 4.6) are quite similar, but both show a deviation from the CO taken over a similar period.
The CO minimized at 300°, and increased thereafter, contrasting with the constant values of Pb and Br throughout the sector.

There was more data from the Brooklyn site in the easterly sector. Fe demonstrated little or no directionality. The pattern shown by S, V and Ti was characterized by low levels from 10°-180°, increasing thereafter to a maximum in the neighborhood of 240°, and a gentle decrease to moderate values. As seen in Figs. 4.7 and 4.8, the traces of Pb and Br were quite similar with relatively constant levels throughout, excepting a spike at 270° and a dip at 240°. Zn and Si were similar but more scatter was apparent. Mn showed highest levels in the 10°-50° sector; lowest levels occurred at 150°, increasing slowly to a higher level at 260° and decreasing thereafter. Little concurrent CO data were available for comparison; however, the peak at 50° was still evident, and levels in the sector 300°-350° were constant.

CORRELATIONS

Correlation coefficients were calculated for various parameters available for the length of the study and for the subsets corresponding to the elemental sampling. In the statistics shown below, correlation coefficients significant at the 5% level are denoted by an asterisk (*); those significant at the 1% level are marked by two asterisks.

Overall Correlation of TSPHV and CO

Correlation coefficients were calculated for TSPHV and CO for both the Newark and Brooklyn sites. The results are shown below on an overall as well as time-of-day basis. It should be noted here that the subset of valid Brooklyn TSPHV and CO was limited to observations made during the month of December, 1975.

TABLE 5.1

Correlation Between TSPHV and CO

Time	r, Newark TSPHV vs CO	r, Brooklyn TSPHV vs CO
All periods	0.704**	0.440**
0200	0.823**	0.512
0600	0.680**	0.536
1000	0.670**	0.339
1400	0.423**	0.237
1800	0.755**	0.449
2200	0.828**	0.435

The lack of an afternoon peak in TSPHV was reflected here in the afternoon period (1400) correlation coefficient, lowest of all of time-of-day statistics. Note that although the correlation coefficient for the 0200 and 0600 periods were larger than that for the overall dataset, fewer observations were involved, and therefore a correspondingly higher correlation was required to attest to the significance of the correlation.

Although the correlation coefficient between the overall Brooklyn CO and TSPHV (r=0.440) was significant at the 1% level, the correlation coefficient between Brooklyn CO and TSPNUC was even higher (r=0.720**). The correlation between Brooklyn CO and TSPNUC agreed with their respective diurnal patterns except for the absence of the 1400 peak. Like Pb and Br, TSPNUC maximized at 0600 and decreased thereafter. TSPHV, on the other hand, did not reach a maximum until 1000.

Elemental Concentrations and Corresponding Subsets of TSPHV, TSPNUC and CO

Correlation coefficients among the elemental concentrations, TSPHV, TSPNUC, CO and WSA are shown in Table 5.2 for Newark and Table 5.3 for Brooklyn. The Brooklyn CO correlations are shown separately in Table 5.4 because they were based on a set of only 18 observations. In the interests of readability, asterisks were not used in these tables to denote levels of a significance. The highest degree of correlation ($r \geq 0.900$) appeared between 1) Pb and Br (both sites); 2) Pb and Mn (both sites); 3) Pb and Zn (Newark only; for Brooklyn r=0.846); and Pb and Fe (Newark only). No significant correlations were found for: 1) CO and all other other observations (Brooklyn); 2) CO and S, Ti, Zn, Pb, Mn, or Br (Brooklyn). In addition, Br did not correlate with TSPHV and TSPNUC and Pb and Ti did not correlate with TSPNUC. One possible explanation is that the Brooklyn particulates may not be primarily associated with traffic sources, but rather multiple sources.

ENRICHMENT FACTORS

Enrichment factors were calculated for the Newark and Brooklyn fluorescence data. The enrichment factor (EF) is defined as[4] :

$$EF = \frac{(x/c)\ \text{atmos}}{(x/c)\ \text{soil}} \tag{6.1}$$

Where x refers to the concentration of the element of interest and C refers to the element used as a normalizing factor. The C element is chosen as one whose ambient concentration can be assumed to be of predominantly natural origin. The enrichment factor compares ambient elemental concentrations to those found in the continental crust and therefore is a measure of the degree to which the elemental content of the aerosol is produced by non-natural sources. Various investigators have used Al[4] , Fe[12] , Sc[4] , Na[12] , and Si[4] as C, the normalizing element. When the Newark data were analyzed, Si was used as the normalizing element. This analysis was reported for the Brooklyn data and was redone using Fe as the normalizing element. The results are shown below. The denominator in all cases was based on the crustal concentrations of the elements.[13]

Table 6.1

Enrichment Factors at Newark and Brooklyn

Mean Enrichment Factor (Standard Deviation)

Element	Newark (C=Si)	Brooklyn (C=Si)	Brooklyn (C=Fe)
SU	1200 (650)	670 (430)	310 (160)
VA	36 (21)	47 (33)	21 (6.9)
TI	*	15 (8.3)	6.6 (1.7)
FE	4.1 (2.0)	2.2 (0.77)	1.0 (0.0)**
ZN	450 (210)	402 (370)	180 (120)
PB	34000 (16000)	15000 (11000)	6800 (2500)
MN	105 (45)	69 (38)	31 (6.6)
BR	3200 (15000)	13000 (12000)	5200 (2600)
SI	1.0 (0.0)**	1.0 (0.0)**	0.52 (0.17)

*Data Invalid **By definition

The Fe-based EF's are about 50% of the Si EF's at Brooklyn, reflecting the relative levels of measured Fe and Si at the site. The higher relative Fe might be caused by enhanced Fe loading onto streets because of rust fallout from vehicles. The presence of Pb and Br in gasoline and of S from fossil fuel was marked by the magnitude of the enrichment factors of these elements.

It is of interest that the enrichment factors of Pb and Br are approximately equal; i.e., EF_{BR} is at least 75% of EF_{PB}. The average Br to Pb ratio was 0.18 (Std. Dev. = 0.02) for Newark and 0.21 (0.16) for Brooklyn, in good agreement with published values for aged automotive exhaust aerosol.[14]

REGRESSIONS

Power Law Models for TSPHV and CO

In order to assess the effect of street-washing on measured TSPHV, attempts were made to fit the Newark and Brooklyn TSPHV and CO to power law models of the form:

$$x = aWSA^{b}TEMP^{c}RELH^{d}MIXHT^{e}T_{200}{}^{f}T_{1000}{}^{g}T_{1400}{}^{h}T_{1800}{}^{i}T_{2200}{}^{j}ANG_{1}{}^{k}ANG_{2}{}^{l}DAY^{m} \quad (7.1)$$

Where x refers, as the case may be, to either TSPHV or CO. Separate regression models were determined for CO and TSPHV so the efficacy of street washing could be ascertained. The philosophy behind this approach was that any singular event occurring on a street washing day (other than the street washing itself) would show up in the modeled TSPHW and CO, but that the effect of street washing (if any) would be reflected only in the level of particulates. When logarithms of the variables are used, the models are linear and a simple regression formula can be used. Dummy variables were defined to denote the start time of the observations, the angular segments corresponding to them and, where appropriate, the day of the observation. The details of the variable assignment are shown in Appendix A.

The temperature was expressed as degrees Kelvin in the Newark regression and in degrees Fahrenheit for the Brooklyn analysis. The variable DAY was used only in modeling Newark CO, where levels on Thursdays and Fridays were on the average 20% higher than the other weekdays. The mixing height variable (MIXHT) was set as follows:

Start	Mixing Height
0200, 0600	Morning mixing height
1000, 1400, 1800	Afternoon mixing height
2200	Morning mixing height of next day

An attempt was made to interpolate a mixing height for the 1800 observations but this did not improve the regression. The leading coefficients, exponents, and regression statistics for the four models are shown in Table 7.1. The notation in Table 7.1 corresponds to that in equation 7.1.

In order to obtain a reasonable fit ($r \geq 0.50$), the regression of the Brooklyn TSPHV excluded data from June, July, and the latter half of December and January. This omission was made because the latter failed to demonstrate a discernable direction trend. The Brooklyn CO regression was based on December 1975 only, while the anomalous CO data of December 1974 were deliberately omitted from the Newark model.

The exponents of the wind speed variables in Table 7.1 are all (except Brooklyn CO) approximately -0.20. This is a much weaker dependence than the generally assumed inverse proportionality[17, 18]. The dependences on MIXHT were also weak, although the data available was probably not sensitive enough to reflect the true dependence. Overall, the greatest dependence was seen in the time variables. The matrix of dummy variables served as a surrogate for the pollutant source function and possibly for the diurnal variation of the mixing layer.

Tiao-Type Regression Analysis for Newark Data

A power law model of the average time-of-day TSPHV and CO at Newark was developed. The work followed that of Tiao[18], except that he dealt with twenty-four one hour averages and this study utilized six four-hour samples per day. The model was of the form:

$$x = a\,WSA^{b}\ MIXHT^{c}\ TC^{d} \tag{7.2}$$

TC represented the averaged traffic count data for Essex County, as determined by the N.J. Department of Transportation. Tiao's model was explicity linear in traffic; however, it was not possible to include this in the linear regression that was done. His model was of the form:

$$CO = \frac{a_o + aTC}{MIXHT^{c}WSA^{b}} \tag{7.3}$$

Model results are shown below.

	Tiao CO (18)	Newark CO	Newark TSPHV
a_o	28.91	--	--
a	0.49	12.06	83.6
b	-0.89	-1.68	0.20
c	-0.20	0.40	*
d	1 (by definition)	0.76	0.51

* not significant

The fit of the two Newark models was excellent ($r^2 = 0.98$), although the exponents of CO and TSPHV are quite different. The exponents for WSA and MIXHT as calculated for the Newark data, were in contrast to Tiao's results, but, as Tiao pointed out [19], the sums of the exponents of these two variables (-1.09 - Tiao vs -1.28 Newark) were similar.

Analysis of Street Washing Experiments

Concentrated programs of street washings were carried out on three days during the Newark study and on eleven days during the Brooklyn study. The first four washings were done manually with a 25 m. fire hose; all other washings were done by a municipal washer truck. Street washing commenced between 0500 and 0600 and continued for two to two and a half hours. The third street washing day at Newark was marked by the onset of demolition across the street from the monitor and for that reason, that day's data were excluded from the analysis shown below.

The regression models of Section 7 were used to predict concentrations of TSPHV and CO on the street washing days. The predicted levels were compared to the observed level by a straight line fit:

$$\mathrm{TSPHV}_{\mathrm{OSB}} = a\ \mathrm{TSPHV}_{\mathrm{PRED}} + b \qquad (8.2)$$

$$\mathrm{CO}_{\mathrm{OBS}} = c\ \mathrm{CO}_{\mathrm{PRED}} + d \qquad (8.2)$$

As previously stated, the philosophy behind this approach was that any meteorological or other phenomenon will be seen in both the TSPHV and CO; but the effect of street washing will be manifested only in the TSPHV levels. The regressions that were obtained are shown below. The regression of the Newark data included all observations with START = 0600; the Brooklyn regression included all street washing measurements that commenced at 1000 or later, reflecting the different times of commencement and duration of street washing at the two sites.

Table 8.1

Regression of Observed vs Predicted Levels on Street Washing Days

Subject of Regression	Regression Equation	No. of OBS	r^2	F_{calc}	F_{crit}
Newark TSPHV	OBS = 0.50 PRED + 18.3	11	0.603	13.66	10.56 (1%)
Newark CO	OBS = 1.00 PRED + 0.3	9	0.542	8.26	5.59 (5%)
Brooklyn TSPHV	OBS = 0.98 PRED + 7.6	42	0.595	58.74	7.31 (1%)
Brooklyn TSPHV (screened on basis of 0200 reading)	OBS = 1.01 PRED + 5.7	36	0.670	69.16	7.56 (1%)
Brooklyn CO	OBS = 0.34 PRED + 4.74	14	0.066	0.085	4.75 (5%)

The major conclusion that can be drawn from the above is that street washing has little or no effect on suspended particlates as measured at street level. If any effect was seen, it was an increase over what would have been otherwise predicted, although the uncertainty of the regression precluded such a conclusion.

As previously stated, the results of the site CO regression were to have been compared to the TSPHV model to sort out the effect of street washing. The Newark CO model showed that recorded levels were equal to what would have been otherwise expected and that no unforseen meteorological phenomenon was influencing the site at the time of the street washing. The result of the regression of the Newark TSPHV is somewhat ambiguous; in addition, it was based on only two days of sampling. Examining the ratios of observed to predicted TSPHV for the sampling periods was helpful in interpreting the data. As shown in Table 8.2, in all but one instance, the ratio stayed the same as, or increased from, the ratio of the 0200 observed to predicted TSPHV for the day in question. This result indicated that the street washings had no beneficial effect in decreasing the levels of TSPHV.

Table 8.2

Ratio of Observed to Predicted TSPHV
on Two Street Washing Days at Newark

	Sample Start Time					
Date	0200	0600	1000	1400	1800	2200
11/6/74	0.68	0.64	0.73	0.71	0.57	0.74
11/11/74	0.61	0.63	1.1	1.0	0.71	0.86

The CO-TSPHV comparison was not used in the analysis of the Brooklyn street washing experiment because the CO database was inadequate to found an adequate regression model. However, the Brooklyn street washing was consistently seen to have no effect on the levels of TSPHV throughout the various screenings that were done. The fourth entry in Table 8.1 above reflects this result. In this regression, two days were eliminated from the analysis of the Brooklyn TSPHV on the basis of their 0200 readings. Recall that the 0200 measurements were unaffected by the street washing and therefore were assumed to have been indicative of any day's unusual meteorological conditions. In the case shown above, one day was eliminated as atypical because of an unusually high 0200 reading, the other because of an unusually low 0200 observation.

CONCLUSIONS

Diurnal Pattern

The diurnal pattern of CO showed morning and afternoon peaks, corresponding to the times of rush hour traffic. Particulates, on the other hand, demonstrated elevated levels throughout the morning to the early afternoon. These trends were verified at Newark and Brooklyn. The diurnal patterns of the elements were similar to TSPHV, and in no case was an afternoon peak seen, even for the assumedly traffic-related Pb or Br.

Wind Speed Dependency

The power dependency of both CO and TSPHV on wind speed during the extended period of sampling was on the order of -0.2. An inverse proportionality was not seen. This was verified at both sites.

Only in the regression of Brooklyn CO, limited to December data only, and to the Tiao analysis, employing averaged pollutant levels, were the power dependencies approaching negative one.

Moving Window Analysis

Moving window analysis can indicate directional peaks and can be a powerful tool in modeling the variation of pollutants with meteorological parameters. The trends revealed by the moving window analysis can be incorporated into the regression analysis as an indicator of air mass movement. The latter may exert a greater effect on TSPHV levels than the hour-to-hour variations in wind speed. The directional trends, of course, are highly site-dependent.

Enrichment Factors

The largest enrichment factors were found for Pb, Br and S, reflecting the presence of the first two elements in gasoline and the presence of the latter in fossil fuel.

Street Washing

Street washing did not decrease the levels of TSPHV during the monitoring at Newark and Brooklyn and may actually have increased them.

RECOMMENDATIONS

In any further studies undertaken to characterize the urban particulate problem sampling should be done, as in this study, with a number of Hi-Vol samples less than 24-hrs in duration to determine the diurnal profile. A 24-hr sample masks the behavior of the aerosol. Sampling in this manner would also facilitate the application of a directional analysis, since no one wind direction measurement with any significance can be assigned to a twenty-four hour average.

In an investigative monitoring program, sampling should be done on a dichotomous basis. The determination of the coarse and fine fractions, as well as their diurnal patterns, would be useful in separating the component sources. In addition, a monitoring program conducted in this way would help to resolve the discrepancy noted in the diurnal pattern of TSPHV and CO.

Any further attempt to model levels of pollutants as linear or pseudo-linear functions of meteorological and other variables should be accompanied by simultaneous site mixing height measurements. The result of the morning sounding and afternoon forecast of mixing height was inadequate to describe the real influence of the mixing height on pollutant levels.

In any other program with similar aims, better traffic count data should be made available.

Some modification should be made in the model used to predict levels of particulates. The opposing effects of increasing wind speed on particulate levels (dilution vs generation of dust) were reflected in the weak dependence of particulates on wind speed ($\text{TSPHV WSA}^{-0.2}$). A more realistic approach may be a model form that incorporates the direct and inverse proportionalities.

An additional improvement in the modeling might be obtained if some provision was made for the inclusion of large scale meteorological movements. The model used relied on wind speed and direction to indicate the general meteorological conditions. Another approach would be to apply the power law model to each meteorological system encountered during the study. Analysis of this type might serve to explain the failure of the July Brooklyn data to correlate with anything. In the subject program, this approach was untenable because of the size of the database.

In any other experiment to assess the effect of street washing, more insight into the problem might be gained if vertical monitoring were conducted to assess "background" CO and particulates. Also, a program of street washing should provide for varying the area encompassed by the street washing route.

Samples of street dirt should be taken to assess the impact of resuspension.

Collectors could be mounted on a flat surface under cars to determine the amount of street dirt that originates from vehicle deterioration and rustout.

If a true measurement is to be made of the ambient concentration of Br, the samples should be cooled immediately after collection to prevent loss of the Br aerosol.

TABLE 1.1
Structure of Dataset

Variable Name	Variable Description	Source of Newark Data	Source of Brooklyn Data
TSPHV	Total Suspended Particulates collected on glass fiber filters (ug/m^3)	On-Site	On-Site
TSPNUC	Total Suspended Particulates collected on nucleopore filters (ug/m^3)	On-Site	On-Site
CO	Carbon Monoxide (ppm)	NJDEP, On-Site	On-Site
WSA WDA PRECIP TEMP RELH	Wind Speed (knots) Wind Direction (°) Precipitation (in. water) Ambient Temperature (C) Relative Humidity	NOAA Summary of Local Climatological Data (LCD) For Newark Airport	NOAA Summary of Local Climatological Data (LCD) for LaGuardia Airport
NEPH	Nephelometer readings (%)	On-Site	On-Site
Traffic Counts North & South	Number of Cars	On-Site	On-Site
As, Br, Fe, Mn, Pb, S, Si, Ti, V & Zn	Elemental concentrations from x-ray fluorescence analysis of nucleopore filters (ug/m^3)	On-Site	On-Site
MIXM	5 am sounding of mixing height	Fort Totten	Fort Totten
MIXA	Forecast of afternoon mixing height	Staten Island	Staten Island

TABLE 3.1
Time of Day Averages (Composite Diurnal Profile)

Subject of Averaging		0200	0600	1000	1400	1800	2200
All TSPHV	Newark	92	143	127	131	108	97
(ug/m^3)		(49) *	(57)	(41)	(43)	(58)	(45)
	Brooklyn	83	135	140	118	94	84
		(32)	(48)	(45)	(41)	(34)	(30)
All CO	Newark	3.4	6.7	5.0	7.6	6.1	5.1
(ppm)		(2.6)	(3.9)	(2.7)	(3.6)	(3.4)	(3.3)
	Brooklyn	1.7	4.9	4.4	5.6	4.6	2.6
		(1.7)	(3.0)	(3.0)	(3.6)	(2.9)	(1.8)
All TSPNUC	Newark	Data available only during times of elemental observations, see below					
(ug/m^3)	Brooklyn	48	71	69	62	55	49
		(18)	(24)	(26)	(21)	(24)	(21)
Elemental Concentrations (ug/m^3)							
S	Newark	3.9	4.7	4.0	3.2	3.3	3.5
		(1.9)	(2.0)	(2.0)	(1.2)	(1.1)	(1.9)
	Brooklyn	3.6	3.6	3.5	3.3	3.0	3.2
		(1.9)	(1.7)	(1.8)	(2.0)	(2.1)	(2.1)
V	Newark	0.058	0.073	0.072	0.050	0.050	0.045
		(0.018)	(0.018)	(0.031)	(0.011)	(0.011)	(0.012)
	Brooklyn	0.15	0.15	0.11	0.10	0.098	0.11
		(0.07)	(0.05	(0.03)	(0.02)	(0.025)	(0.04)
Ti	Newark	Data Invalid — See Section 3.3					
	Brooklyn	1.1	1.3	1.2	1.2	1.2	1.1
		(0.3)	(0.4)	(0.3)	(0.3)	(0.3)	(0.4)
Fe	Newark	2.4	3.3	2.4	2.4	2.2	1.9
		(0.8)	(0.9)	(0.8)	(1.0)	(0.7)	(0.8)
	Brooklyn	1.8	2.4	2.1	2.0	2.0	1.8
		(0.2)	(0.4)	(0.4)	(0.4)	(0.4)	(0.4)

TABLE 3.1 (Cont.)
Time of Day Averages (Composite Diurnal Profile)

Subject of Averaging		Composite Average for the Sampling Period 0200	0600	1000	1400	1800	2200
Zn	Newark	0.38 (0.07)	0.48 (0.06)	0.38 (0.12)	0.33 (0.05)	0.33 (0.05)	0.29 (0.04)
	Brooklyn	0.63 (0.35)	0.53 (0.28)	0.53 (0.27)	0.44 (0.21)	0.46 (0.26)	0.48 (0.29)
As	Newark Brooklyn	Data Invalid -- See Section 3.3					
Pb	Newark	4.9 (1.1)	6.6 (1.0)	4.7 (1.8)	5.0 (1.1)	5.0 (1.1)	4.1 (1.0)
	Brooklyn	3.5 (1.5)	3.9 (1.3)	3.9 (1.5)	3.6 (1.0)	3.4 (1.0)	3.4 (1.5)
Mn	Newark	1.2 (0.2)	1.6 (0.2)	1.2 (0.4)	1.1 (0.2)	1.1 (0.2)	0.93 (0.13)
	Brooklyn	1.2 (0.3)	1.3 (0.3)	1.3 (0.3)	1.2 (0.3)	1.2 (0.3)	1.2 (0.4)
Br	Newark	0.80 (0.29)	1.2 (0.3)	0.80 (0.36)	1.0 (0.3)	1.0 (0.3)	0.75 (0.27)
	Brooklyn	0.55 (0.35)	0.59 (0.28)	0.63 (0.36)	0.62 (0.42)	0.52 (0.24)	0.54 (0.33)
Si	Newark	3.7 (1.4)	5.7 (3.1)	5.5 (3.0)	3.8 (1.8)	3.8 (2.3)	2.8 (1.3)
	Brooklyn	5.1 (2.1)	6.0 (2.3)	6.4 (3.1)	5.9 (2.2)	5.7 (2.1)	5.0 (2.0)

TABLE 3.1 (Cont.)
Time of Day Averages (Composite Diurnal Profile)

Subject of Averaging	0200	0600	1000	1400	1800	2200
	Composite Average for the Sampling Period					
TSPHV (coincident with elemental observations; ug/m^3)						
Newark	92	144	130	116	89	92
	(30)	(23)	(44)	(41)	(34)	(20)
Brooklyn	102	141	130	110	93	86
	(35)	(42)	(27)	(22)	(28)	(31)
CO (coincident with elemental observations; ppm)						
Newark	2.0	4.1	3.0	6.5	3.5	2.5
	(1.6)	(3.0)	(2.0)	(4.1)	(2.7)	(1.2)
Brooklyn	1.2**	2.2***	4.0**	4.0**	2.7***	1.5***
	(0.8)	(2.0)	(0.0)	(1.6)	(0.8)	(0.7)
TSPNUC (Coincident with elemental observations; ug/m^3)						
Newark	107	162	102	101	92	94
	(71)	(59)	(55)	(59)	(54)	(44)
Brooklyn	59	69	68	64	53	50
	(19)	(21)	(17)	(17)	(15)	(14)

NOTE: *The number that appears in parentheses under each entry is the standard deviation of the arithmetic mean observation.

** Two observations only.
*** Four observations only.

TABLE 3.2

COMPARISON OF MEASURED ELEMENTAL LEVELS WITH PUBLISHED VALUES

SUMMARY OF NEWARK DATA

Element	Range of Values (ug/m^3)	Average (ug/m^3)	Std. Dev. (ug/m^3)	Relative Level Compared with that Reported in Reference ( )
S	1.2-9.7	4.0	1.9	Low (6)
V	0.03-0.11	0.057	0.019	Same (3)
Ti	19-110	42.3	21.0	High by 3 orders of magnitude (5)
Fe	1.3-7.0	2.6	1.1	Slightly High (3)
Zn	0.25-0.63	0.37	0.10	Same (3)
As	0.66-2.4	1.2	0.41	High by 2-3 orders of magnitude (4)
Pb	2.9-9.8	5.3	1.5	Slightly high (4)
Mn	0.77-2.1	1.2	0.32	High by factor of 4 (3)
Br	0.48-1.7	0.98	0.33	Same (7)
Si	1.4-11	4.0	2.3	Same (8)

SUMMARY OF BROOKLYN DATA

Element	Range of Values (ug/m^3)	Average (ug/m^3)	Std. Dev. (ug/m^3)	Relative Level Compared with that Reported in Reference ( )
S	0.74-8.1	3.4	1.8	Low (6)
V	0.061-0.33	0.12	0.049	Same (4)
Ti	0.73-2.0	1.2	0.33	Higher than (2) but Lower than (4)
Fe	1.4-3.8	2.1	0.51	Same order (6)
Zn	0.25-3.6	0.55	0.52	Same (3)
As	0.37-4.9	0.79	0.76	High by 3 orders of magnitude (4)
Pb	2.1-7.8	3.6	1.3	High by factor of 4 to 7 (4)
Mn	0.75-2.2	1.2	0.31	High by factor of 15 (4)
Br	0.27-1.5	0.52	0.25	High by factor of 3 (2,4)
Si	2.3-12	5.9	2.6	Same (6)

TABLE 5.2
Correlations Among TSPHV, TSPNUC, CO and Fluorescence Data at Newark

r	TSPHV	TSPNUC	S	V	Fe	Zn	Pb	Mn	Br	Si	CO
TSPHV	1.00										
TSPNUC	0.76	1.00									
S	0.62	0.75	1.00								
V	0.67	0.75	0.78	1.00							
Fe	0.78	0.86	0.85	0.86	1.00						
Zn	0.65	0.72	0.77	0.88	0.83	1.00					
Pb	0.76	0.81	0.81	0.84	0.94	0.93	1.00				
Mn	0.61	0.68	0.74	0.78	0.80	0.98	0.92	1.00			
Br	0.74	0.79	0.71	0.67	0.84	0.72	0.92	0.72	1.00		
Si	0.32	0.36	0.46	0.14	0.47	0.53	0.56	0.65	0.55	1.00	
CO	0.57	0.41	0.24	0.20	0.36	0.30	0.46	0.34	0.45	0.34	1.00

50 observations:

r_{crit} (5%) = 0.29
r_{crit} (1%) = 0.37

TABLE 5.3
Correlations Among TSPHV, TSPNUC, and Fluorescence Data Brooklyn

r	TSPHV	TSPNUC	S	V	Ti	Fe	Zn	Pb	Mn	Br	Si
TSPHV	1.00										
TSPNUC	0.83	1.00									
S	0.61	0.43	1.00								
V	0.45	0.32	0.55	1.00							
Ti	0.45	0.25	0.57	0.66	1.00						
Fe	0.70	0.69	0.20	0.40	0.47	1.00					
Zn	0.26	0.11	0.40	0.70	0.59	0.17	1.00				
Pb	0.34	0.20	0.37	0.76	0.79	0.41	0.85	1.00			
Mn	0.51	0.36	0.46	0.77	0.87	0.59	0.73	0.93	1.00		
Br	0.16	0.05	0.26	0.67	0.66	0.23	0.84	0.96	0.79	1.00	
Si	0.69	0.83	0.26	0.13	0.14	0.59	-0.15	-0.04	0.18	-0.22	1.00

79 observations:

r_{crit} (5%) = 0.22
r_{crit} (1%) = 0.28

TABLE 5.4
Correlations of CO with TSPHV, TSPNUC, and Fluorescence Data at Brooklyn

18 observations: r_{crit} (5%) = 0.47

CO	0.29	0.19	0.18	0.07	0.41	0.20	0.02	0.07	0.28	0.21	0.07

TABLE 7.1

Power Law Model Description

Variable	Exponent	Newark TSPHV Segment I	Newark TSPHV Segment II	Newark CO	Brooklyn TSPHV	Brooklyn CO (December only)
a		6.62×10^{-12}	442000	14.5	3.07	87.6
WSA	b	-0.391	-0.211	-0.233	-0.186	-0.892
TEMP	c	3.76	**		0.448	-0.268
RELH	d	*	*	*	0.569	**
MIXHT	e	**	-0.116	-0.111	**	**
T_{200}	f	-0.693	-0.742	-0.911	-0.535	-1.58
T_{1000}	g	0.545	0.000	-0.435	-0.151	**
T_{1400}	h	-0.431	0.000	0.000	0.000	**
T_{1800}	i	-0.562	-0.320	-0.153	-0.331	**
T_{2200}	j	-0.777	-0.383	-0.259	-0.528	-0.881
ANG_1	k	1.70	-1.26	-0.426	-0.315	0.590
ANG_2	l	*	*	-0.481	*	*
DAY	m	*	*	0.166	*	*
r^2		0.654	0.544	0.677	0.743	0.640
F_{calc}		10.18	33.67	29.75	58.85	26.75
$F_{crit}(1\%)$		2.99	2.96	2.47	2.66	3.34

* Variable not included in analysis
** Variable not significant

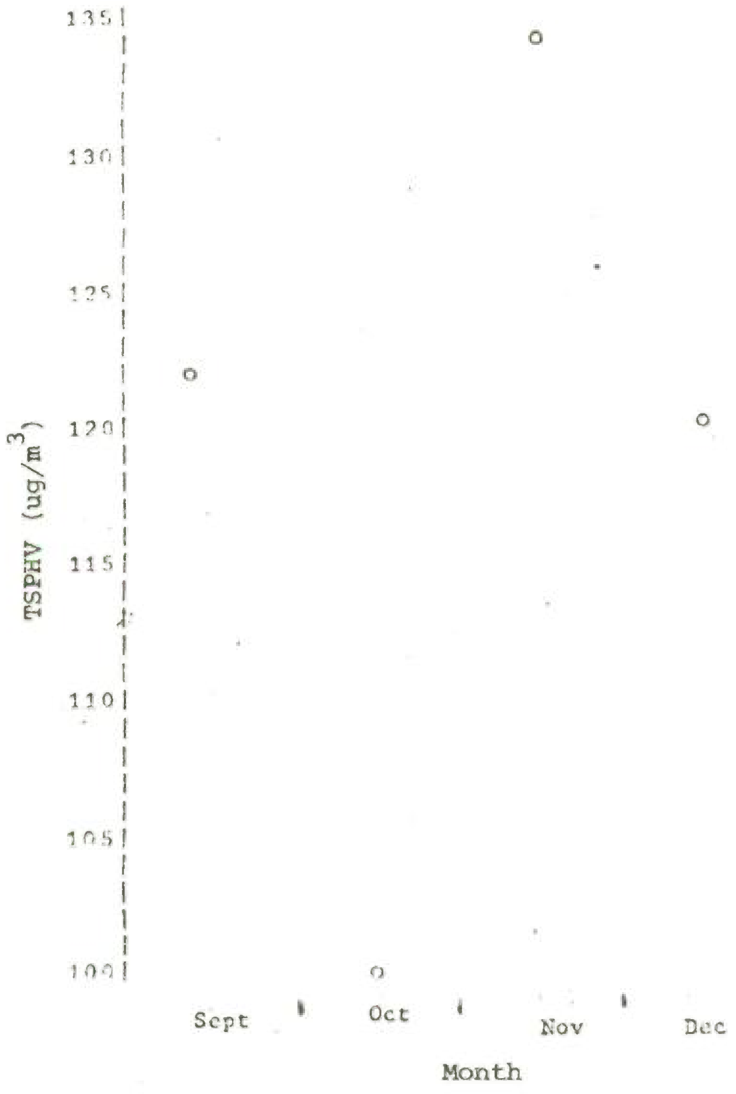

Fig. 2.1 Monthly Average Variation of TSPHV (ug/m^3) at Newark

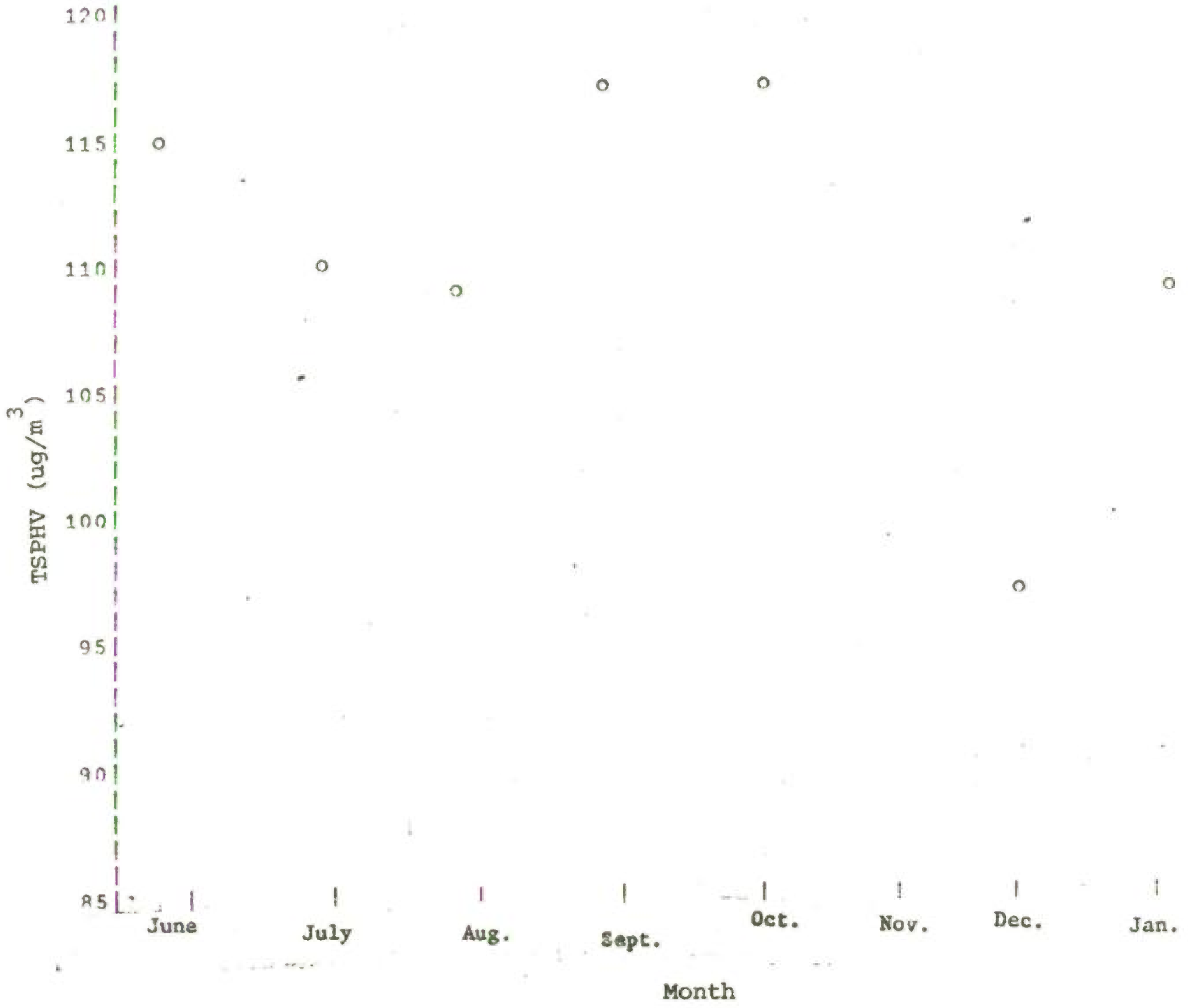

Fig. 2.2 Monthly Average Variation of TSPHV (ug/m^3) at Brooklyn

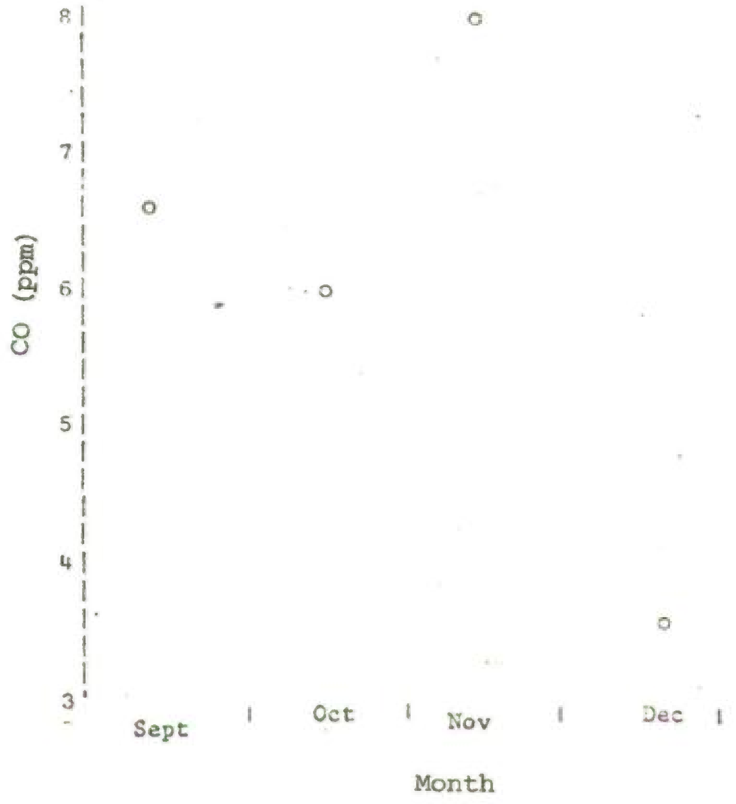

Fig. 2.3 Monthly Average Variation of CO (ppm) at Newark

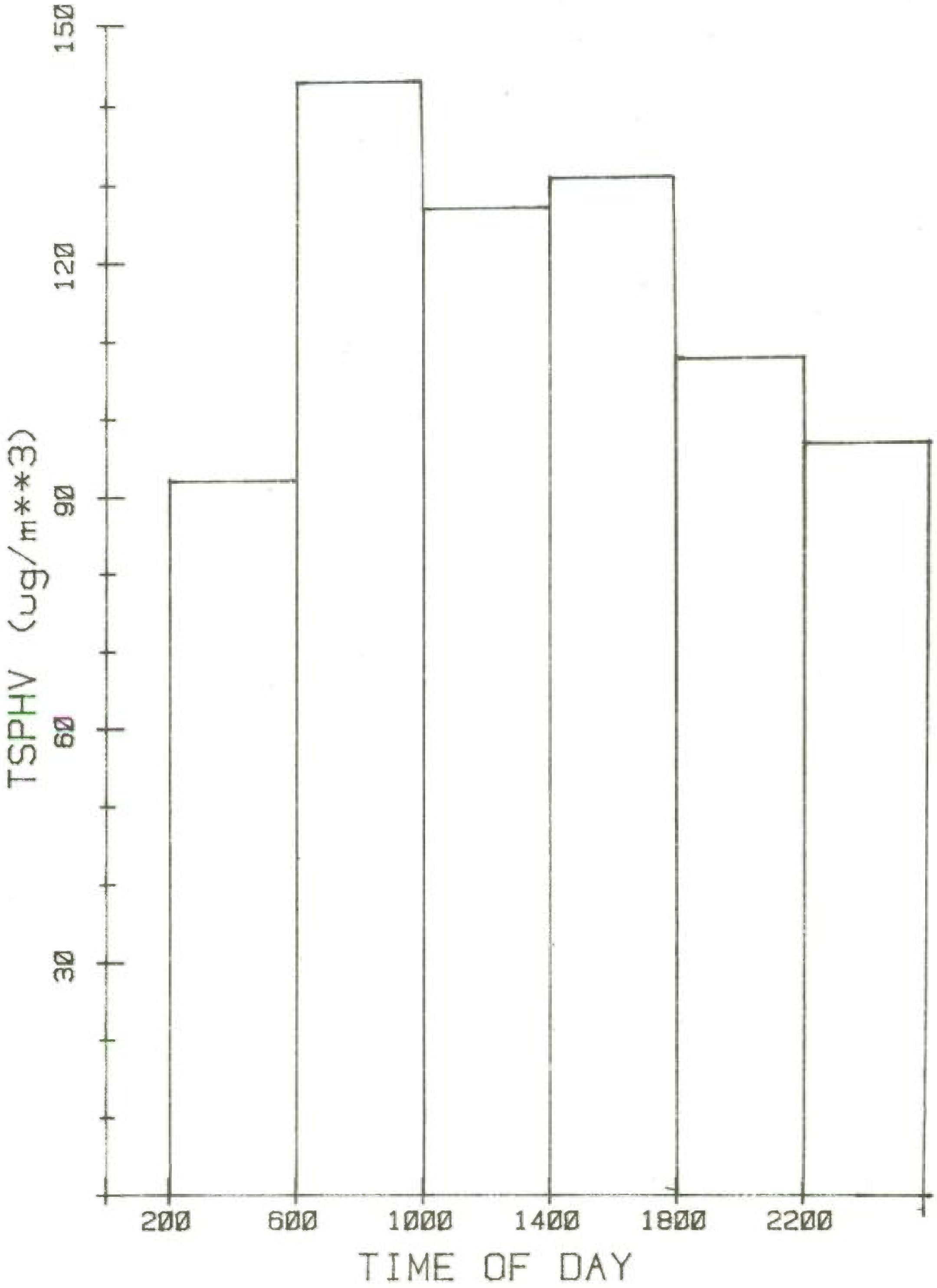

Fig. 3.1 Diurnal Variation of TSPHV at Newark

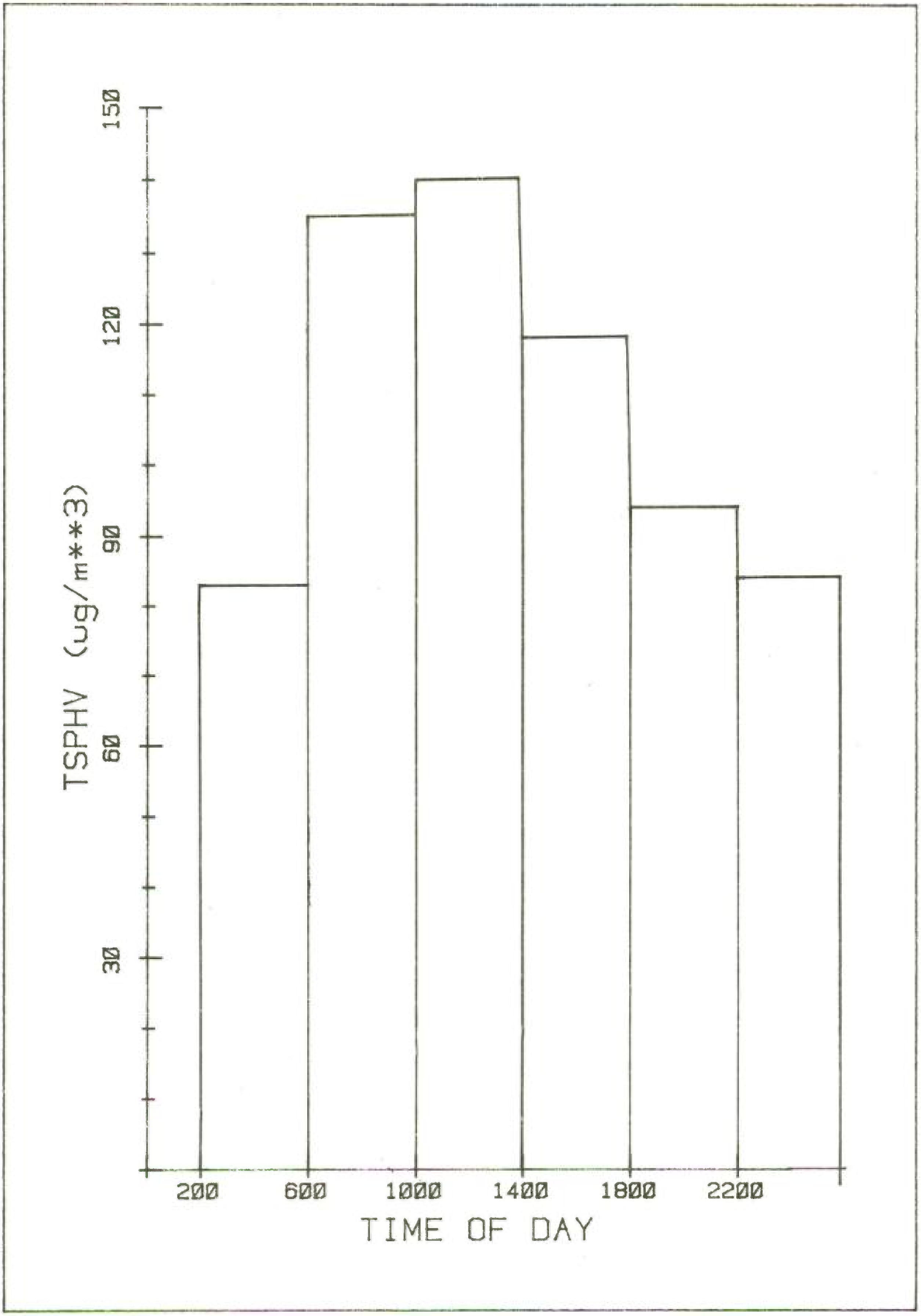

Fig 3.2 Diurnal Variation of TSPHV at Brooklyn

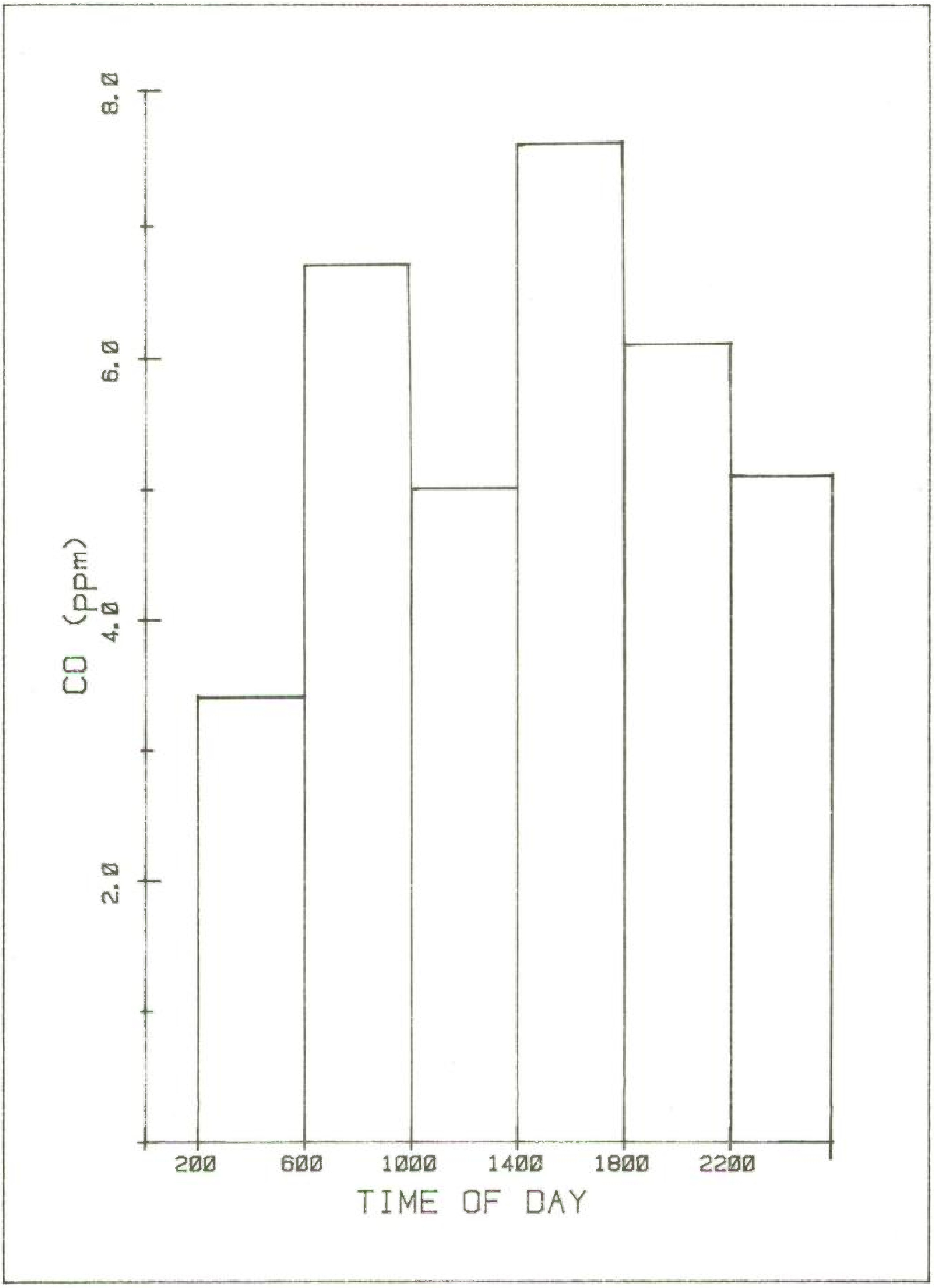

Fig. 3.3 Diurnal Variation of CO at Newark

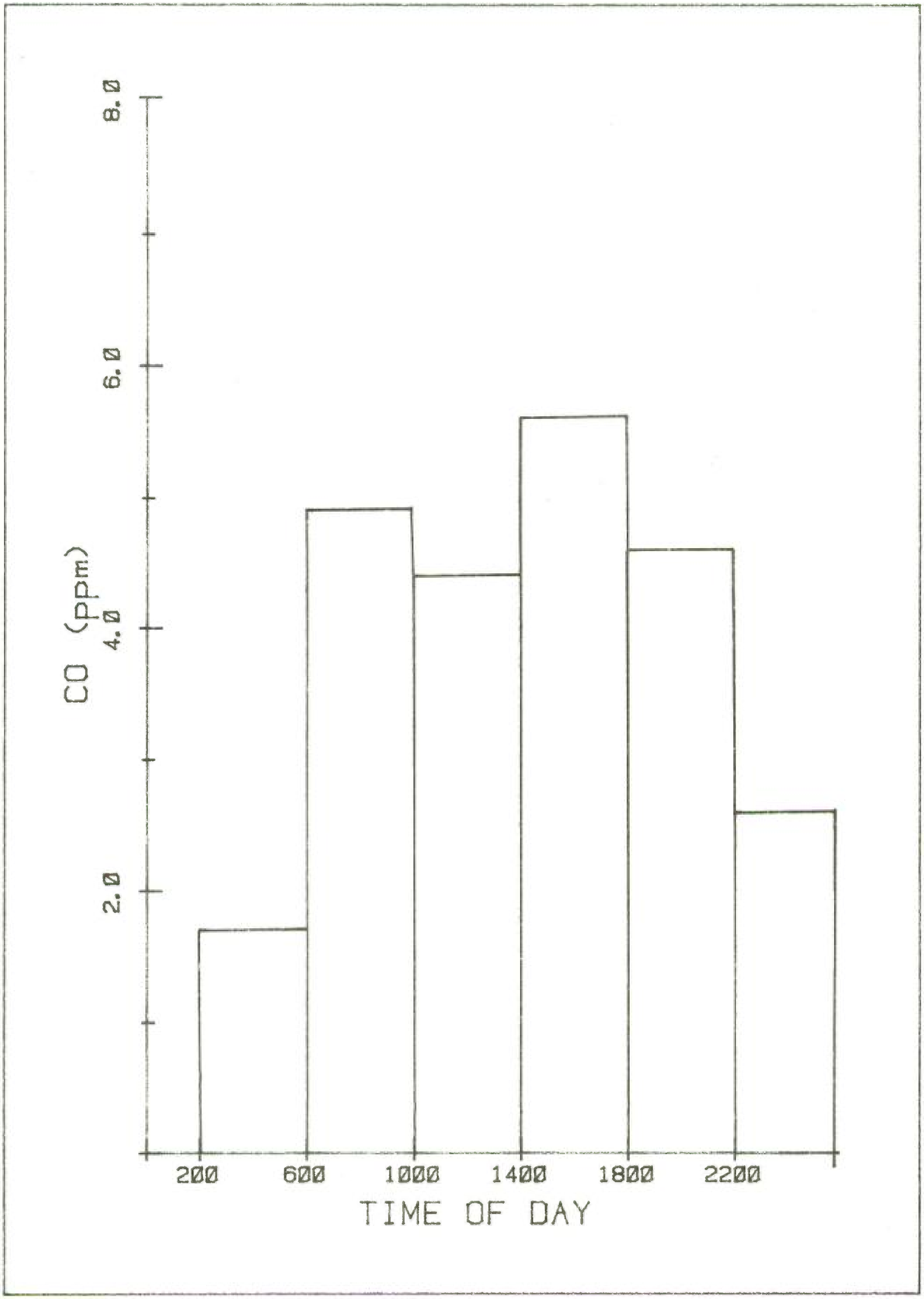

Fig. 3.4 Diurnal Variation of CO at Brooklyn

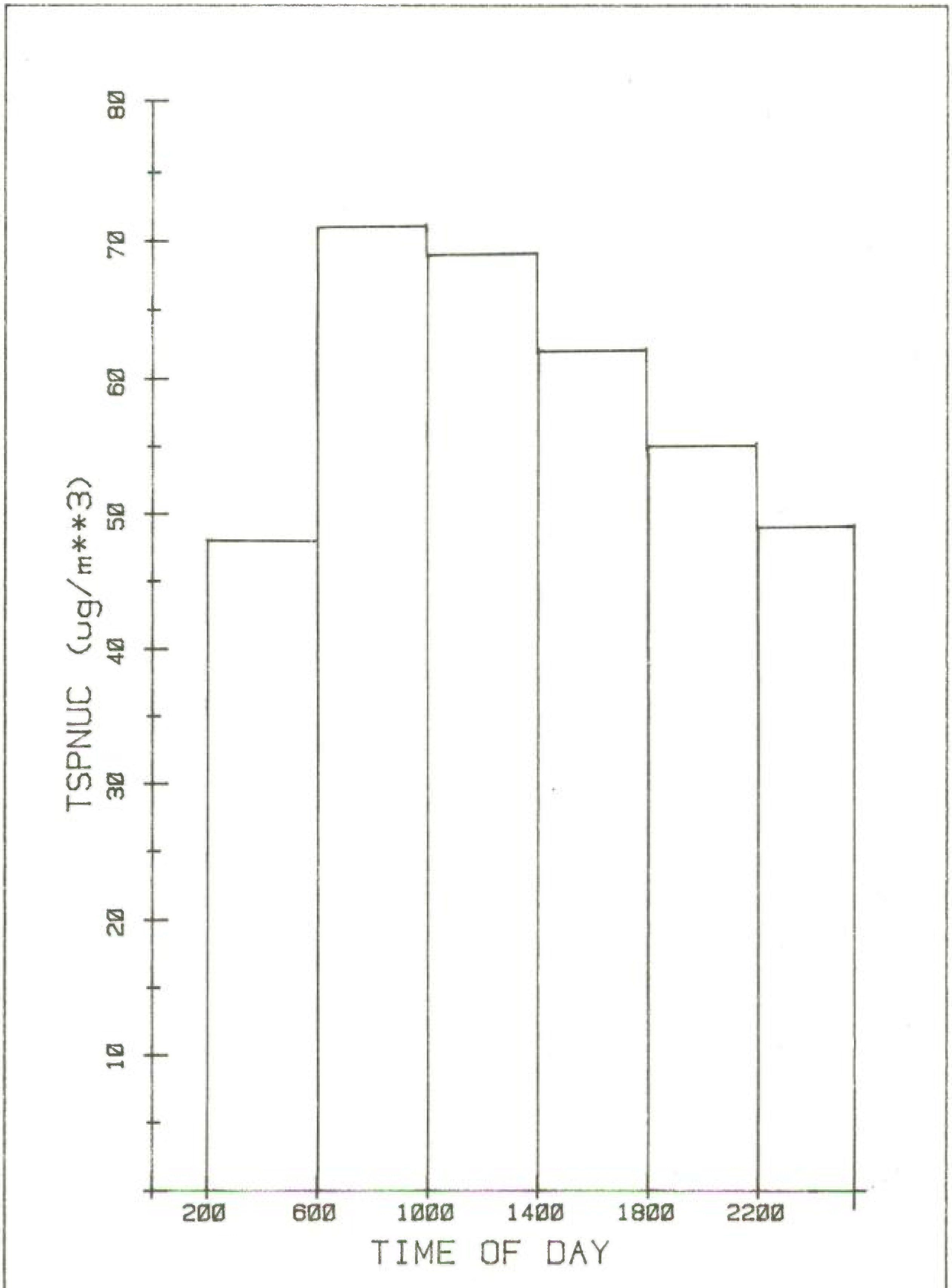

Fig. 3.5 Diurnal Variation TSPNUC at Brooklyn

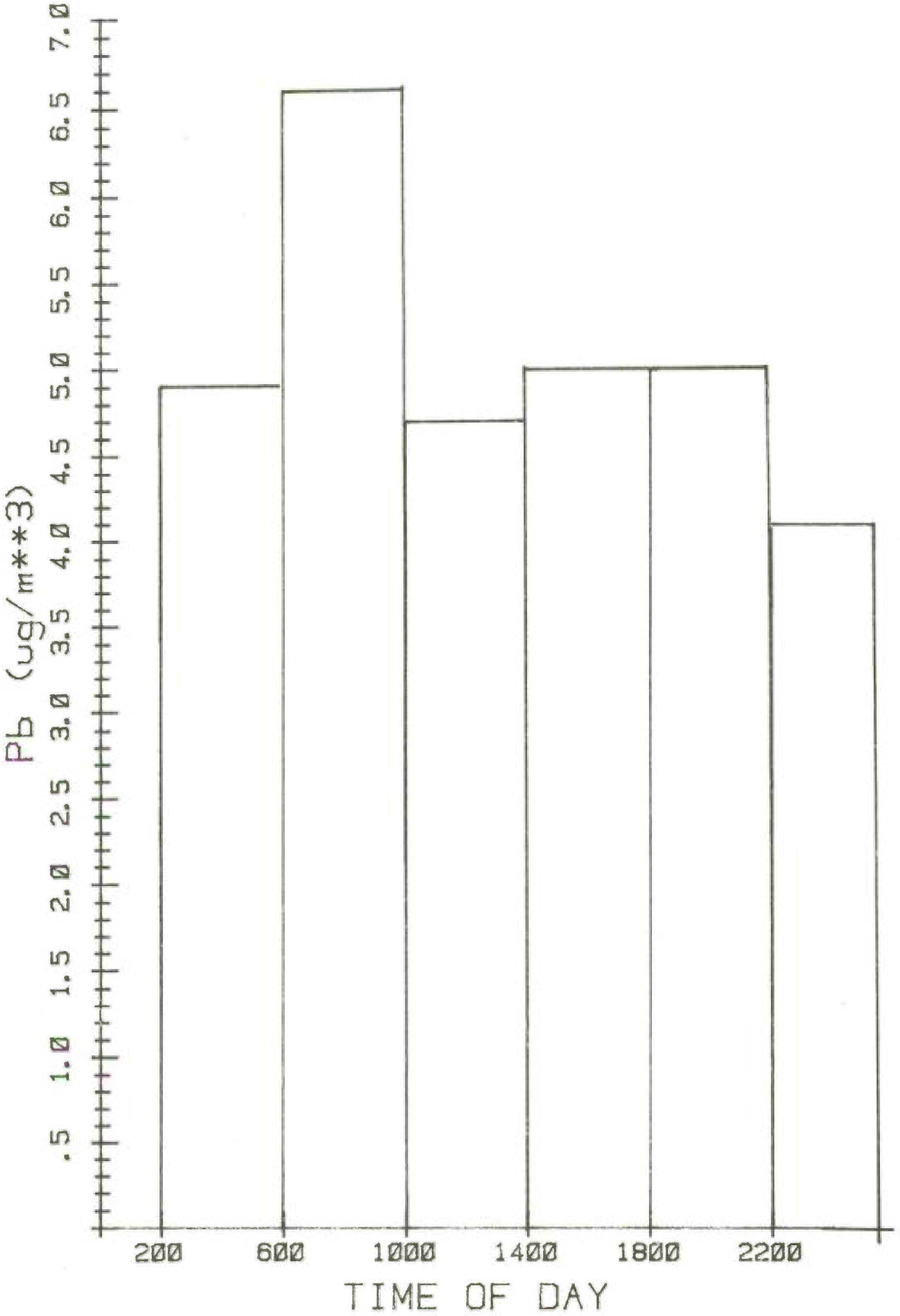

Fig. 3.6 Diurnal Variation of Pb at Newark

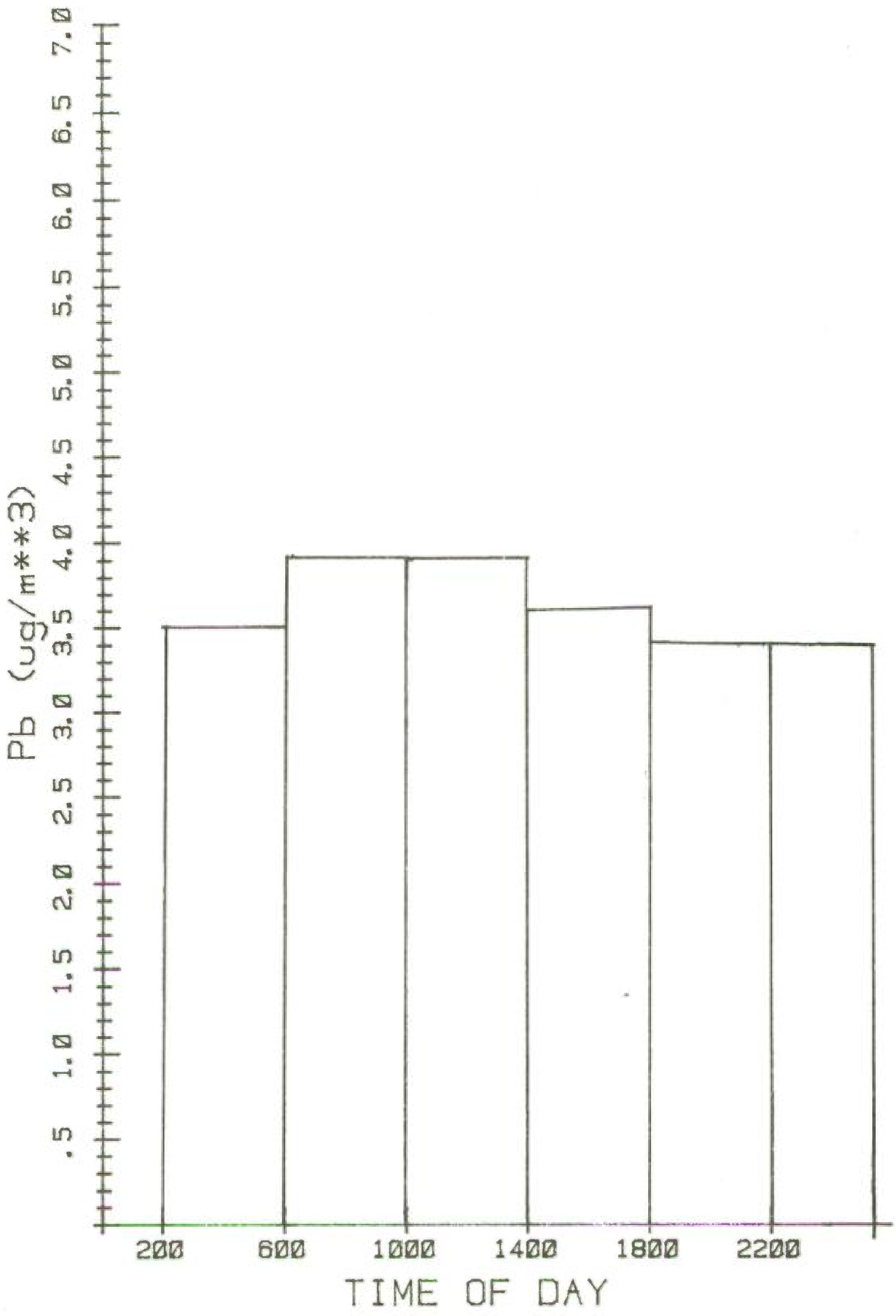

Fig. 3.7 Diurnal Variation of Pb at Brooklyn

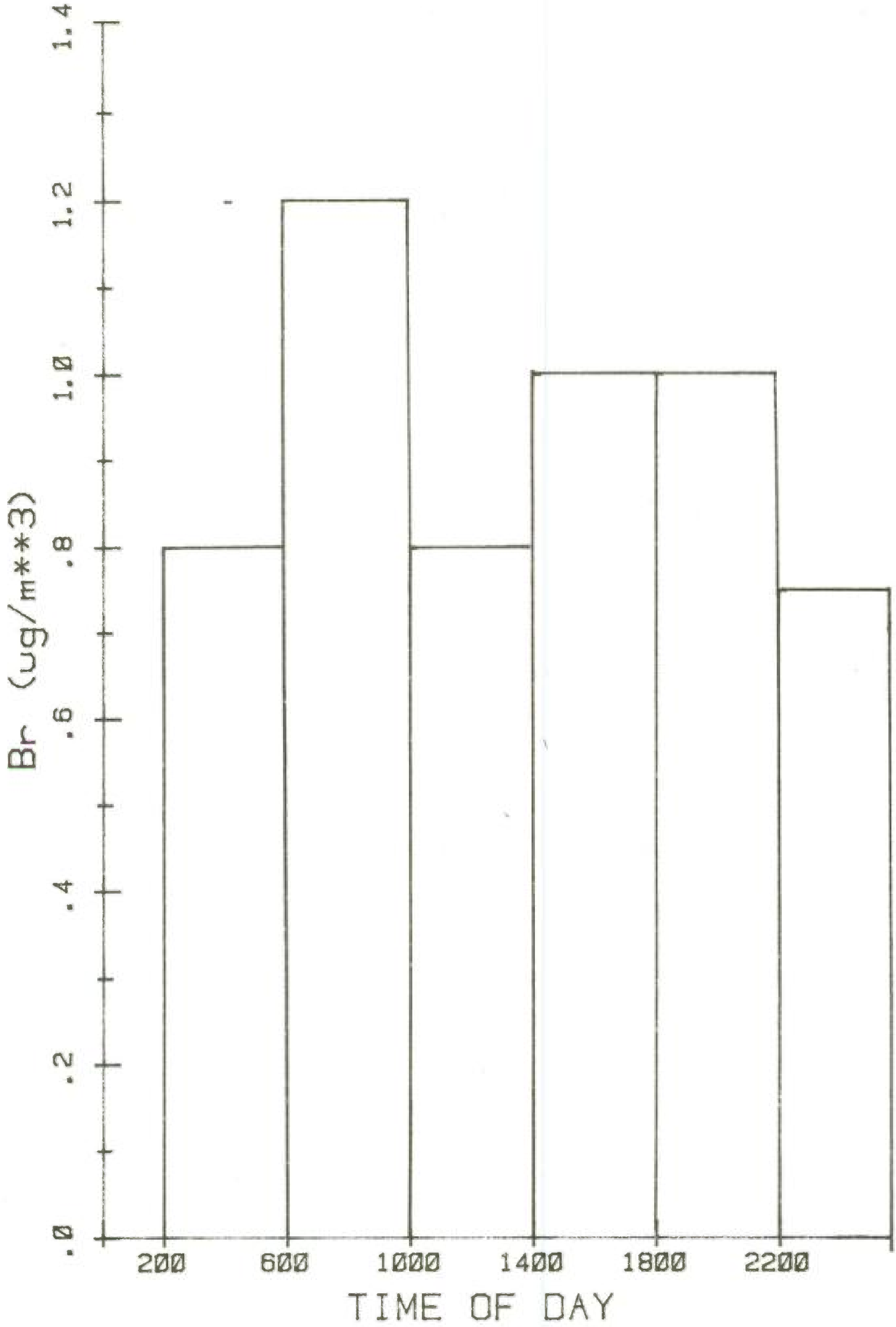

Fig. 3.8 Diurnal Variation of Br at Newark

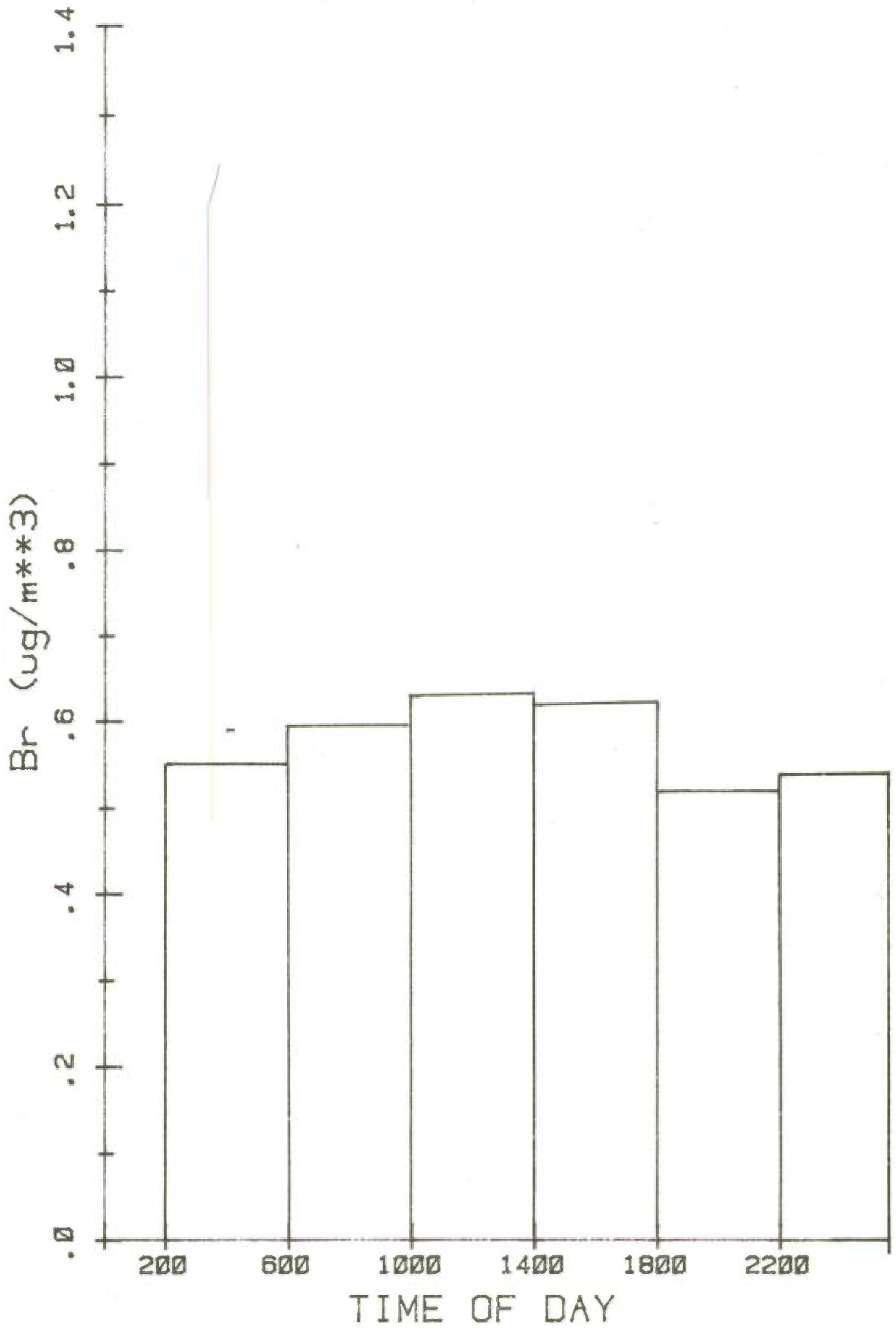

Fig. 3.9 Diurnal Variation of Br at Brooklyn

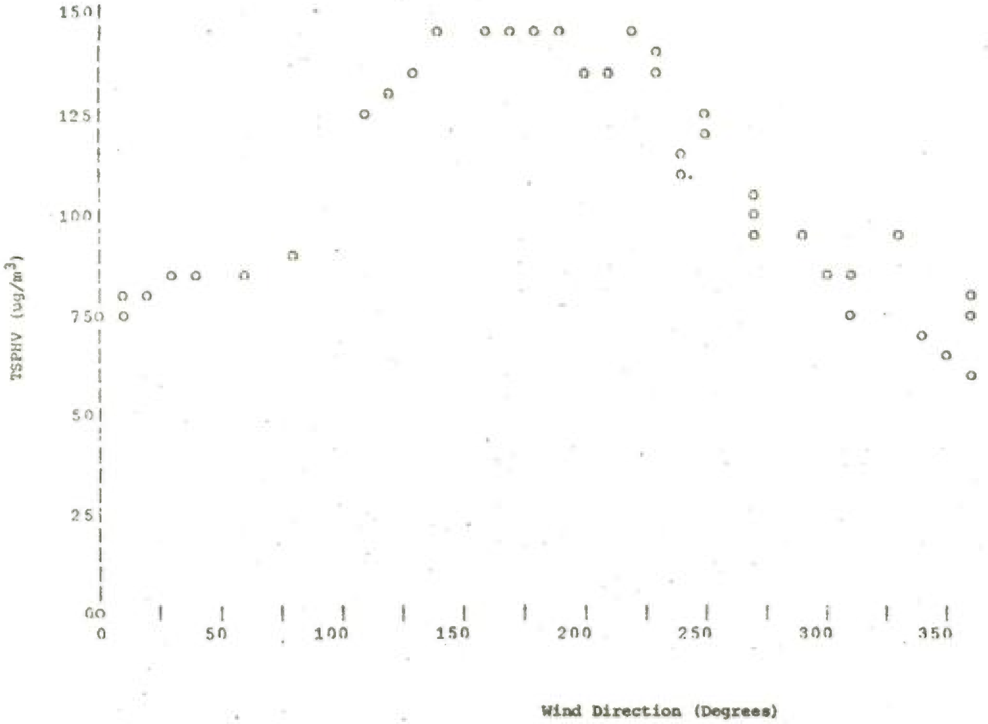

Figure 4.1 Moving 50th percentiles: Newark TSPHV (ug/m^3
vs. Wind Direction (window = 29)

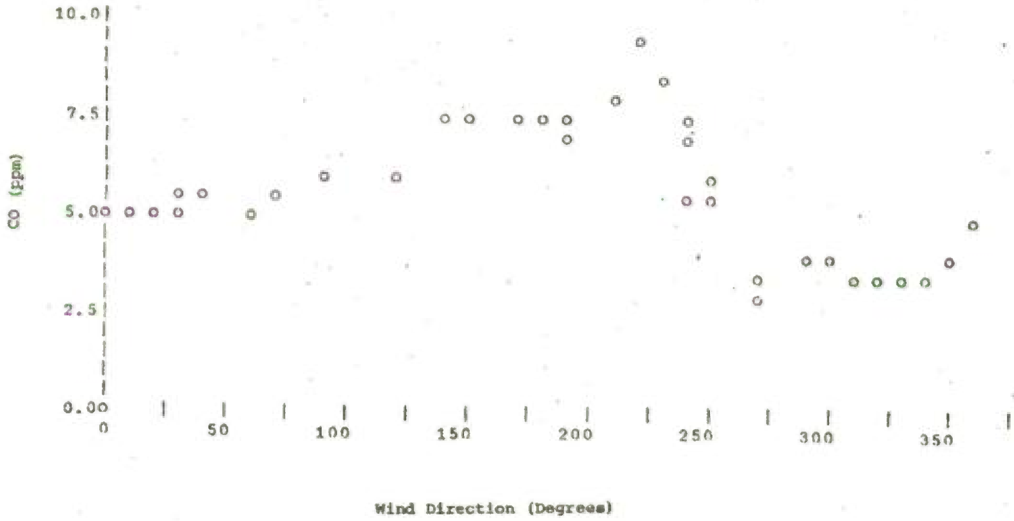

Figure 4.2 Moving 50th Percentiles: Newark CO (ppm)
vs. Wind Direction (window = 21)

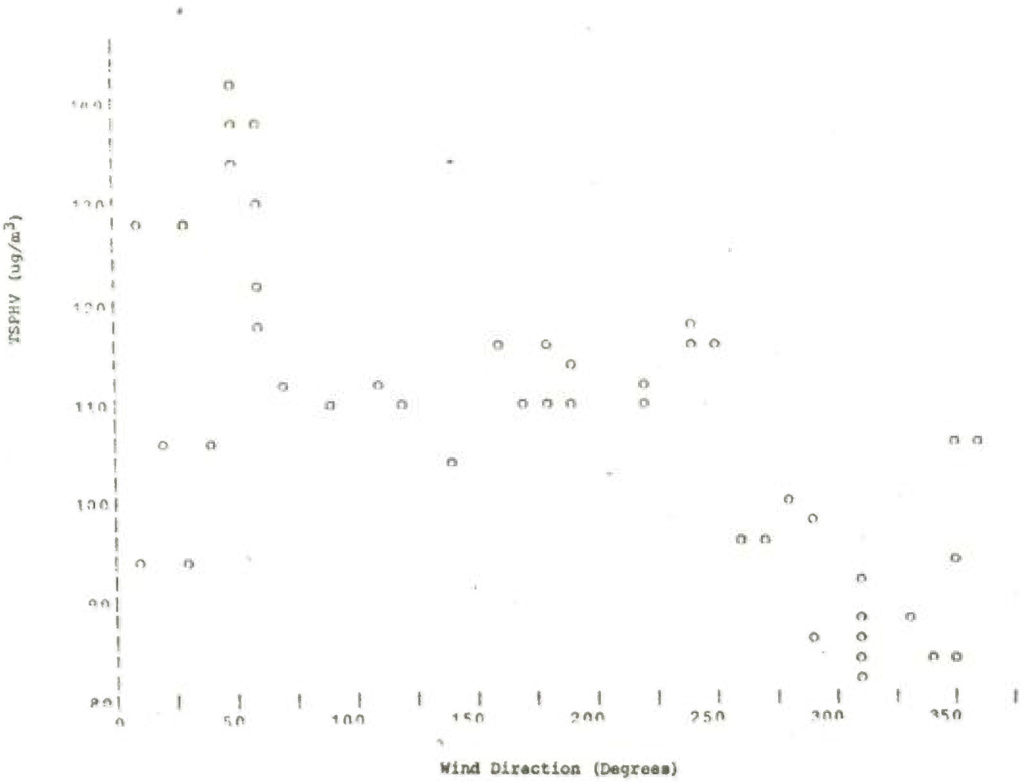

Figure 4.3 Moving 50th Percentiles: Brooklyn TSPHV (ug/m^3) vs. Wind Direction (window = 45)

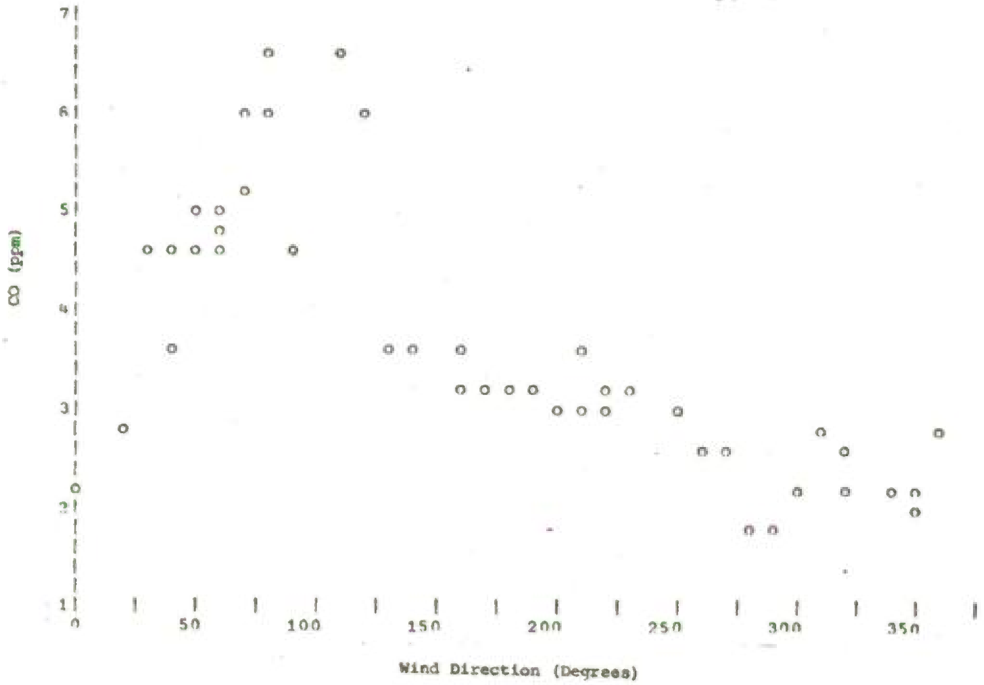

Figure 4.4 Moving 50th Percentiles: Brooklyn CO (ppm) vs. Wind Direction (window = 17)

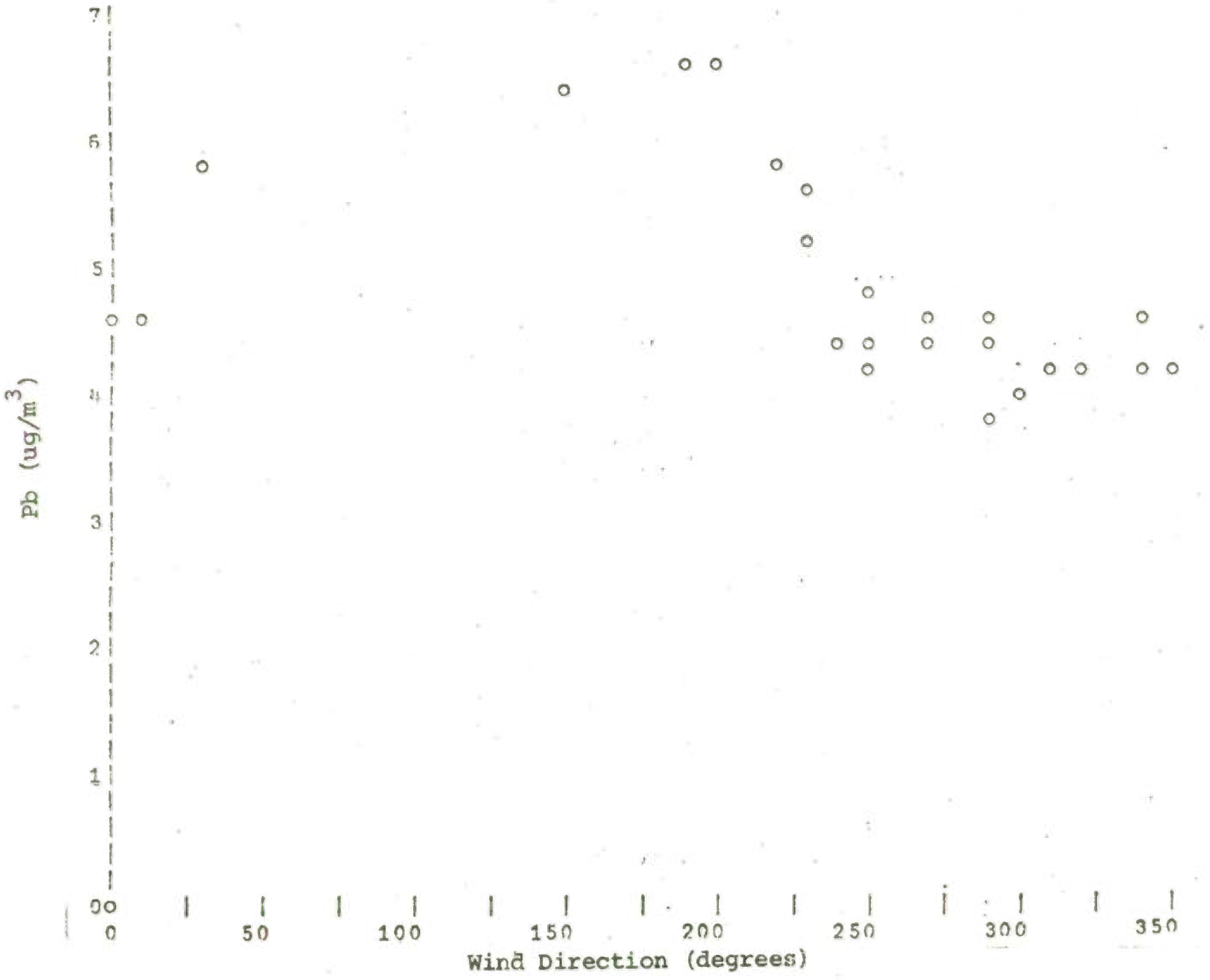

Fig. 4.5 Moving 50-th Percentiles: Newark Pb (ug/m^3) vs Wind Direction (Window = 12)

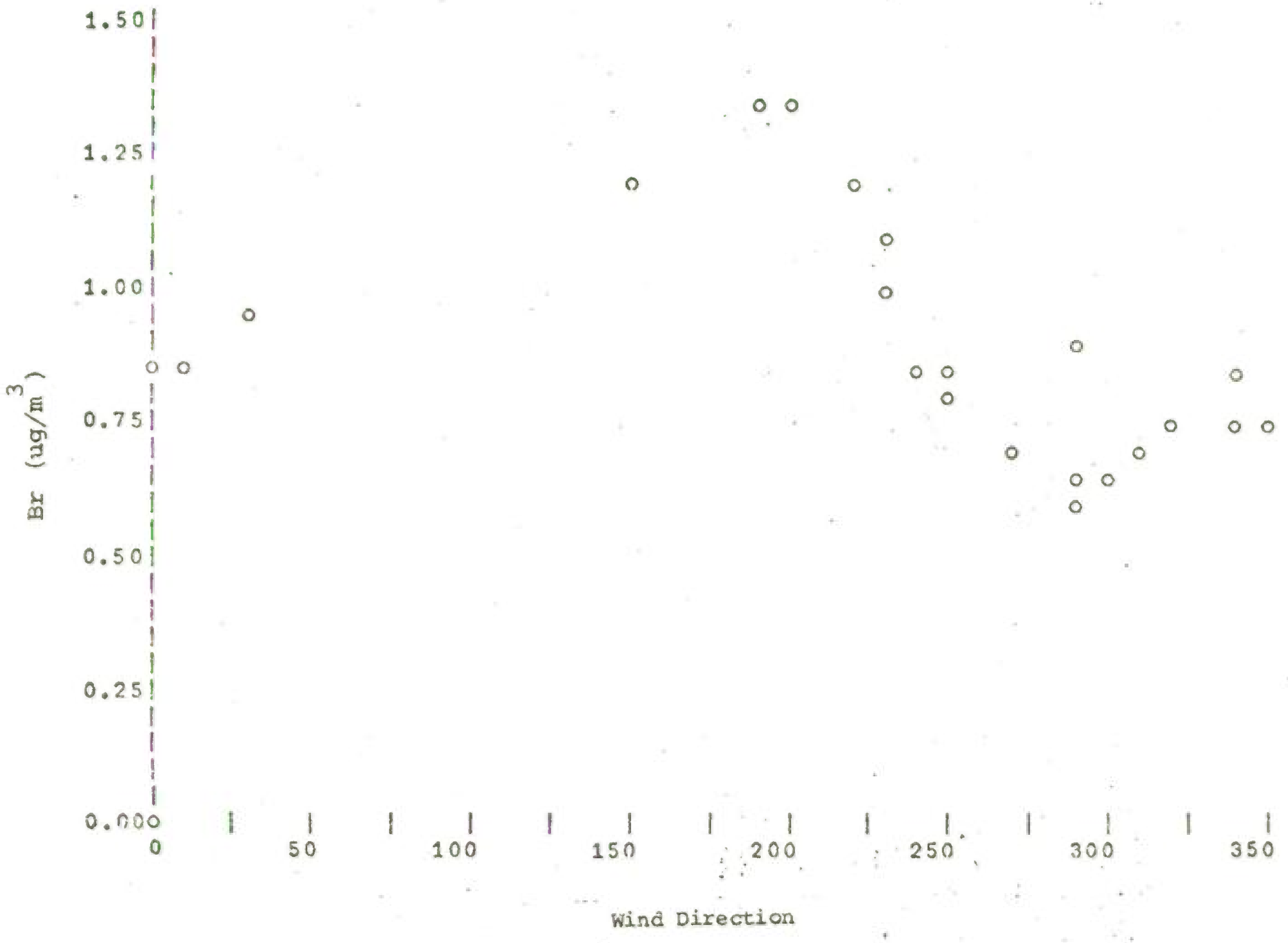

Fig. 4.6 Moving 50-th Percentiles: Newark Br (ug/m^3) vs Wind Direction (Window = 12)

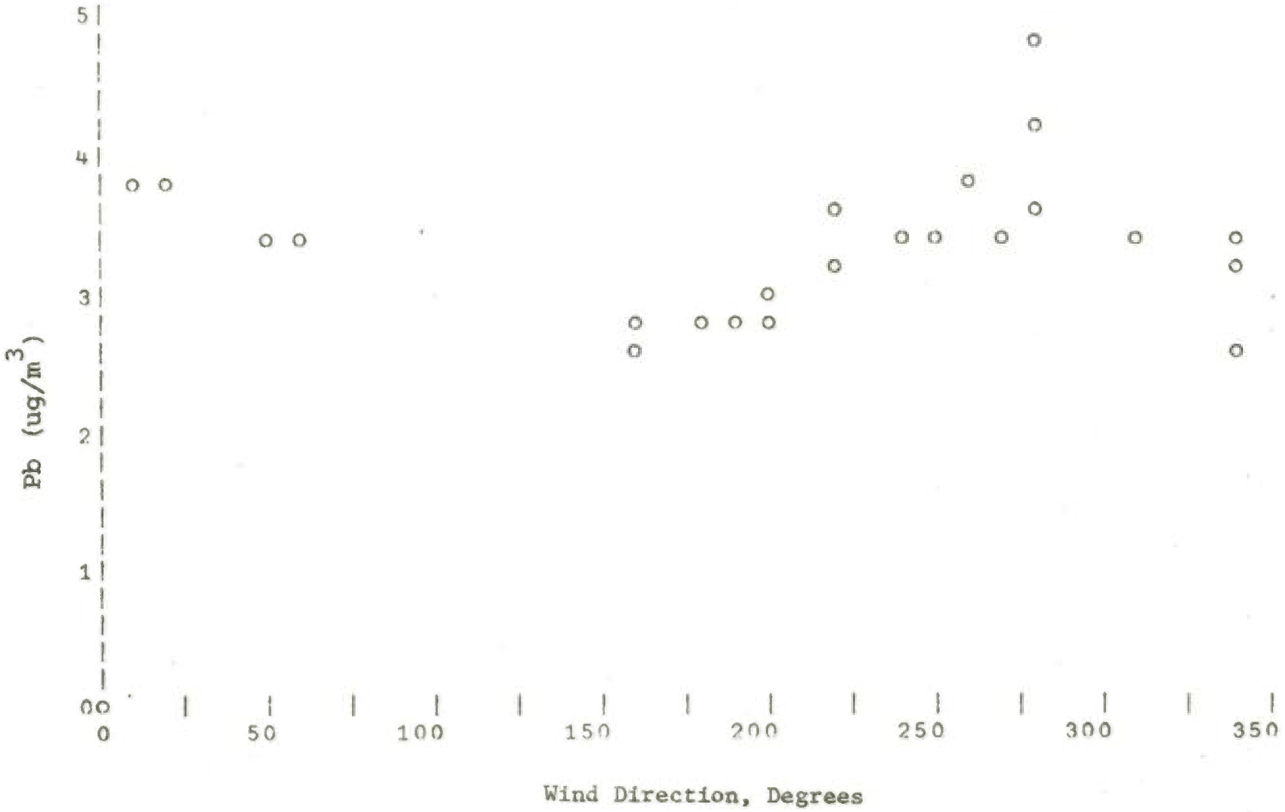

Fig. 4.7 Moving 50-th Percentiles: Brooklyn Pb (ug/m^3) vs Wind Direction (Window = 7)

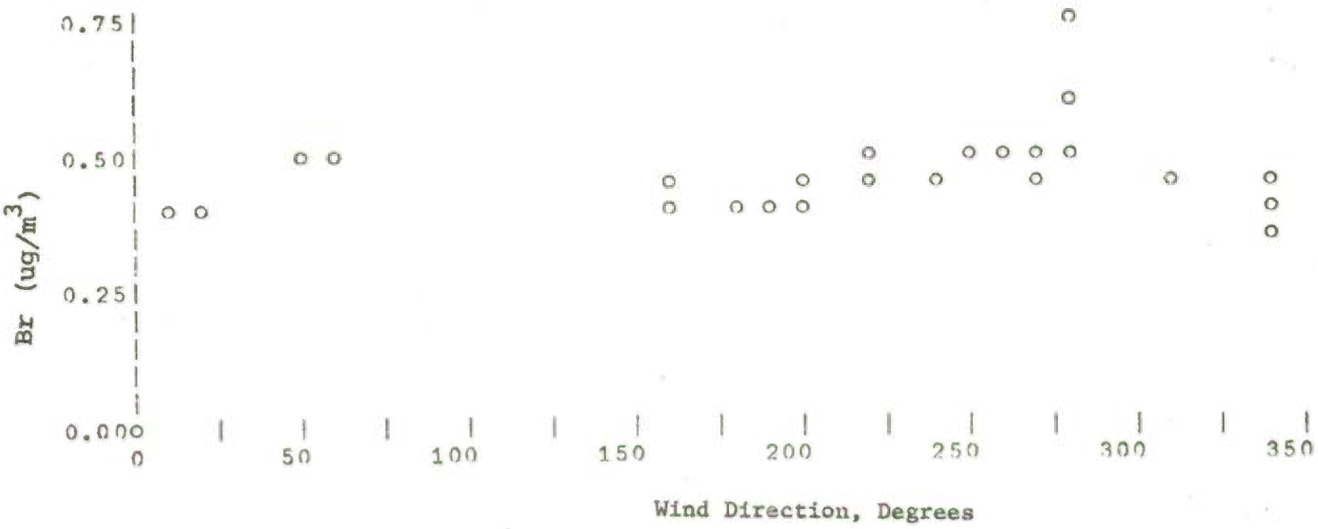

Fig. 4.8 Moving 50-th Percentiles: Brooklyn Br (ug/m^3) vs. Wind Direction (Window = 7)

APPENDIX A GLOSSARY OF TERMS

1.	ANG ANG1 ANG2	Dummy variables used in CO/TSPHV regressions to denote various wind direction measurements corresponding to pollutant observations.
2.	CO	Carbon monoxide, averaged over the four-hour high-volume sampling period.
3.	DAY	Dummy variable used in CO/TSPHV regressions to denote day of week of pollutant measurement.
4.	MIXA	Afternoon forecast of mixing height.
5.	MIXHT	Mixing height assigned to a pollutant observation, either MIXM or MIXA, depending on start time of measurement.
6.	MIXM	Morning sounding of mixing height.
7.	NEPH	Nephelometer reading.
8.	PRECIP	Precipitation recorded during four-hour high volume sampling period.
9.	RELH	Relative humidity during sampling period.
10.	START	Start time of four-hour high volume sampling period.
11.	T_{xxoo}	Dummy variable denoting start time of pollutant observation in TSPHV/CO regression
	T_{200}	= 1 if START = 0200, 0 otherwise
	T_{1000}	= 1 if START = 1000, 0 otherwise
	T_{1400}	= 1 if START = 1400, 0 otherwise
	T_{1800}	= 1 if START = 1800, 0 otherwise
	T_{2200}	= 1 if START = 2200, 0 otherwise
12.	TEMP	Temperature recorded at airport during four-hour sampling period.
13.	TRAFN	Number of cars passing monitor heading north during sampling period.
14.	TRAFS	Number of cars passing monitor heading south during sampling period.
15.	TSP	Total suspended particulate matter.

16.	TSPHV	Four-hour high volume sample of total suspended particulate matter, as measured on a glass filter.
17.	TSPNUC	Four-hour high volume sample of total suspended particulate matter, as measured on a nucleopore filter.
18.	WDA	Wind direction recorded at airport during four hour sampling period.
19.	WSA	Wind speed recorded at airport during four-hour sampling period.

APPENDIX B Definition of Time and Wind Direction Variables in Regression Models

I. Definition of Time Variables

In order to uniquely designate the START time of a CO or TSPHV observation, the following variable assignment matrix was used:

START	$\ln T_{0200}$	$\ln T_{1000}$	$\ln T_{1400}$	$\ln T_{1800}$	$\ln T_{2200}$
0200	1	0	0	0	0
0600	0	0	0	0	0
1000	0	1	0	0	0
1400	0	0	1	0	0
1800	0	0	0	1	0
2200	0	0	0	0	1

II. Definition of Wind Direction Variable

The wind direction variable or variables were defined differently in each regression according to the trends that were discovered by the moving window analysis of Section 4. The definition for each regression model follows:

A. Newark TSPHV: two separate regressions were developed for two wind direction sectors.

1. The first sector was defined for observations whose wind directions were 360° or less than or equal to 160°. When the wind direction equalled 360°, the wind direction variable was also set to 360°. For the rest of the sector, the wind direction variable was set equal to the wind direction plus 360°.
2. The second segment was defined for wind directions in the sector 170°-350°, inclusive. In this segment, the wind direction variable was simply set equal to the wind direction.

B. Newark CO: the data were divided into three angular segments, and a matrix of dummy variables defined thusly:

Angular Segment	Natural Logarithm of the first wind direction variable	Natural Logarithm of the second wind direction variable
1. A wind direction equal to 360° or in the sector greater than zero and less than or equal to 160°	0	0
2. Sector encompassing 170° to 260°, inclusive	1	0
3. Sector encompassing 270° to 350°, inclusive	0	1

C. Brooklyn TSPHV: the data were divided into two sectors; therefore, one dummy directional variable was defined as follows:

Segment	Natural logarithm of the wind direction variable
1. Wind direction less than 230°	1
2. Wind direction greater than or equal to 230°	0

D. Brooklyn CO: again, the data were divided into two sectors on the following basis:

Angular Segment	Natural logarithm of the wind direction variable
1. Wind direction greater than or equal to 30° and less than or equal to 120°	1
2. Wind direction less than 30° or greater than or equal to 130°	0

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VI. DISCUSSION & RECOMMENDATIONS

In the preceding chapters, the results obtained by the individual task forces were presented. The diversity of the analyses requires an evaluation of the methodologies and how they can be used in future particulate control activities. Also, the data obtained by some of the sections lends itself to comparisons and further understanding of particulate matter in the New York Metropolitan Area. These aspects of the Suspended Particulates Study are discussed below.

Methodologies for Control of Suspended Particulate Matter

For most of the analyses attempted by the organic and particulate task forces, stack test samples were required. Since the number of samples necessary to obtain a complete characterization of stationary and mobile source emissions is high, and the costs prohibitive, a venture similar to this study demands a thorough evaluation of the scope of the problem before source testing is initiated. Although, all source catagories and types were not tested, these stack tests included many major source types representative of this region, and extensive electron microprobe and selective organic analyses were conducted.

The results from the electron microprobe analysis indicate that it should be possible to construct a library of elemental fingerprint spectra for the kinds of particles unique to a particular source. With an extensive library of spectra, a source-ambient particle study could be handled more effectively, since a qualitative characterization of source contributions would be possible using ambient samples. The particle task force fingerprinted major source types, such as incinerators, power plants, and automobiles. In addition, various industrial sources were treated and individual elemental spectra were identified. With these data as a baseline, a library of fingerprint spectra should be established and expanded with data obtained from comparable tests. This should be a cooperative effort among air pollution agencies although just one organization should provide the facilities for cataloging the spectra. Because individual particles are analyzed, the mass apportionment must be verified by coincident mass analyses.

Examples of the applicability of this technique and these spectra were demonstrated at a number of ambient sites not dominated by a particular type of source in the immediate vicinity. The results for each ambient sample showed that particles associated with the major source types in the N.Y.C. Metropolitan Area were present and could be identified. In addition to such tests, near-source sampling should be conducted in future studies for kinetic and fine particle speciation. Tests on sources peculiar to a particular study area also should be included for more complete examination of the particle source relationship.

The organic task force attempted to define an incinerator tracer, and the results were encouraging. In fact, if the technique is further developed, it could be used to verify the particle spectra in the fingerprint library. Ambient samples were analyzed using this technique and the sensitivity allowed detection of phthalate tracers in the ng/m range.

A unique and significant product of the organic task force, which can be used to future ambient particulate matter studies, was the development of two rapid enrichment techniques for organic samples from high volume sample filters. The first technique, which can use benzene or other solvents for the extraction, employed mechanical disruption of the filter to obtain the extract. Extraction time when compared to that required for the Soxhlet method was reduced 12-fold. Mass concentrations extracted using standard and the new techniques for benzene extractable organics were compared and the results found consistent.[1] In addition, the results showed good reproducibility. This technique provides a rapid and inexpensive technique for organic analysis of hi-volume filter samples. The second technique for enrichment involved solution of the fiber glass filter media in hydrogen fluoride followed by extraction of polycyclic aromatic hydrocarbons. Standard techniques to obtain a representative sample of PAH require compositing of individual samples from a week of sampling.[2] Using the Soxhlet method this requires incorporation of seven separate apparatus setups. The newly developed technique. 1) speeds up the extraction process and 2) provides efficient compositing since all samples can be dissolved in a single apparatus, and quantitatively mixed together. Incorporation of these techniques in air pollution control studies hasten the availability of the extracted material for subsequent separation and analyses such as Gas Chromatograph - Mass Spectrometer Analysis.

In addition, the organic task force developed a technique for the determination of free carbon. With the recent discussions that have been presented[3] on the plausibility of carbon soot participating in the production of sulfate, this technique provides a tool for making qualitative and quantitative comparisons. A major advantage of the technique is that it can be used for particulate matter collected on a glass fiber filter.

The material balance task force primarily used routine analytical procedures, with the exception of the free carbon analysis, to determine the chemical composition of the ambient Total Suspended Particulates matter present in the New York Metropolitan Area. Coincident cellulose and glass fiber filter samples were obtained for the period January through July, 1975, and analyses completed. The analysis of the trace metals by x-ray fluorescence was done using the cellulose filter samples, and atomic absorption or wet chemical techniques were employed to determine sulfate, nitrate, ammonium, chloride, sodium, potassium, magnesium, calcium, aluminum, benzene extractable organics, and free carbon content. The results obtained from using these techniques could determine the content of 70% of the particulate mass in the N.Y.C. area. Other analyses are required to obtain a more complete characterization of the aerosol. and based on previous studies these would include silicates[4], oxidized hydrocarbons[5], and other trace elements. The variation in the percentage associated with each of these, however, would depend upon the location of the site (ie. urban centers on coastal versus continental locations, etc.)

Comparison of the collection efficiency of the cellulose filter with that of the glass filter, indicated only 75% of the mass was usually captured. This is in contrast to previous studies where 90% of the mass was collected. The reduction in particulate mass found in NYC atmosphere is probably the reason for this; a reduced mass loading takes longer to build up a mat of particles on the surface thereby increasing particle loss through the filter. It seems that high flow rates through the cellulose filter tends to increase the collection efficiency.

The near-street analysis task force used a number of techniques to examine particulate mass loading and the effect of automobile activity on the ambient concentrations. Total suspended particulate mass and its chemical composition is usually determined by the 24-hour integrated Hi Volume sample. To obtain information on the diurnal characteristics of the TSP, four-hour samples were taken. Simultaneous CO samples and trace metals samples were taken as indicators of source input. Subsequently, moving window statistical analysis was employed to evaluate wind influence. The results from this task force indicated there was a diurnal particulate matter concentration pattern at both the Brooklyn and Newark monitoring sites. However, these did not follow the carbon monoxide (CO) patterns, because the CO had two peaks during the day, while the TSP only had a morning peak. It appears that additional information on both local vertical mixing and traffic counts is required to analyze the causes of this difference. It is also the recommendation of the task force that, although the samples provided more information on the near-street situation, shorter term samples and size fractionation are needed to obtain better understanding of the major influences. The moving window analysis indicates that air mass versus local meteorological influences can be examined by choosing the appropriate meteorological data base. The wind direction analyses for both the Newark and the Brooklyn sites showed dissimilar results. At Newark, directional influence was observed, using wind direction data obtained from an airport 3.5 km away. If trajectory analysis could be employed, a better definition of the regional wind direction could be made. However, because the urban Brooklyn site was surrounded on three sides by buildings,canyon effects on the direction and speed of wind precluded this correlation. This difference has great importance in the understanding of urban pollution.

The possible contributions from re-entrainment of particles were studied at both the Brooklyn and Newark sites. The technique used involved street washing prior to sampling, with simultaneous sampling using Hi Volume samples on a 4-hour interval basis to examine the effects. The results showed that the street washing had little or no effect on particulate matter levels. In fact, for some sampling periods the particulate concentrations appeared to increase. This may have been caused by changes in wind direction and consequently the atmospheric concentrations or by availability, after street washing, of a more active street service for entrainment of particulates. From the near-street study and the results of the particle analysis task force, it would appear that a series of vertical profiles using sampling sites located adjacent to the street are required to examine the effects of re-entrainment. This would involve selection of a sampler similar to that used for the the electron microprobe analysis, and an attempt at determining the particle size and chemical composition of the aerosol. In this situation, a comparison of the fine and course particle characteristics is recommended. Street dirt sampling and analysis should also be done.

Results of the Physical and Chemical Analysis

Demonstrating the previous techniques, data was obtained on the composition of ambient particulate matter in the New York Metropolitan Area. The results are examined below.

The near-street task force investigated the diurnal TSP concentration patterns and some gas species, and, as expected, the morning and afternoon rush hours had a significant effect on the CO levels. However, the TSP did not follow the same trend. Maximum TSP occurred during the 0600-hour sampling period. Concentrations of TSP then decreased to a plateau during the midday period and continued to decrease through the night. The results also indicate that the trace elements follow a similar pattern, which suggests that increased vertical mixing during the day dilutes the TSP particles at the surface. The average 4-hour TSP levels ranged from 83 $\mu g/m^3$ to 140 $\mu g/m^3$, with a daily average of 119 $\mu g/m^3$, recorded at the Brooklyn site. Similarly, the average 4-hour TSP levels ranged from 92 to 143 $\mu g/m^3$, with a daily average of 116 $\mu g/m^3$, at the Newark site.

As mentioned, the moving window analysis revealed wind directional influence at the Newark site. The predominant direction for the occurrence of the highest TSP was the southwest. This is consistent with previous analyses that have shown there is an air mass component of the TSP which, in addition to local sources, will influence a particular site.[6,7] In contrast, at the Brooklyn site, no such relationship was observed, perhaps because of the dominance of the street canyon configurations. Therefore, as perviously stated, the urban canyon environment is a very special case.

A model of the dependency of TSP and CO on wind speed demonstrated a weak inverse correlation at both sites. It is the recommendation of the near-street task force that this or another model be developed to include both dilution and source terms to incorporate local versus air mass effects.

The concentration of Cr, Ni, Zn, and Pb detected at the material balance task force sites were consistent with those obtained at the New York University roof top site.[8] Subsequently, the material balance trace element particulate fractions were also correlated. The correlation coefficients between trace elements above 0.5 were compared with the mean elemental correlations for twenty nine cities throughout the world.[9] Table I lists these results; only V-Mn, Ni-Zn, and Zn-Pb showed signifant deviations.

The results of this study have demonstrated the applicability of certain techniques in the examination of particulate pollution. In addition, recommendations have been provided, which 1) should assist in the design of air pollution control studies, 2) describe the possibilities for a source fingerprint library, and 3) can expedite the analysis of particulate mass fractions.

Table I

A comparison of Elemental Correlations Determined for New York City with the Mean Elemental Correlations for Twenty-nine Cities Throughout the World.

Element Pair	Elemental Correlation NYC	Mean Elemental Correlations
V-Ni	0.82	0.90
Fe-Mn	0.76	0.65
Zn-Pb	0.60	0.40
Ni-Mn	0.60	0.47
Ni-Zn	0.58	0.38
Zn-Mn	0.53	0.62
Ni-Pb	0.52	0.58
V-Mn	0.52	0.16
Fe-Zn	0.51	0.51
Fe-Ni	0.50	0.49

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