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AIR QUALITY IN A NEWARK SUBWAY STATION

BY

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A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

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NEW JERSEY INSTITUTE OF TECHNOLOGY

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Newark, New Jersey

1977

ABSTRACT

During the period from June, 1974, to January, 1976, 103 24-hr samples of the air at the Broad Street station of the Newark City Subway were collected by cascade impactor. The size distributions (based on Stoke's equivalent diameters) of the total suspended particulate matter were determined gravimetrically. Samples were also analyzed by atomic absorption spectrometry to obtain information on the concentration of iron, manganese, lead, copper, zinc, and cadmium in each size fraction. The geometric mean particulate level was found to be more than twice the Federal Ambient Air Quality Standard and triple that of ambient Newark air sampled nearby. The metal concentrations (with the possible exception of lead) were found to be small fractions of their respective ambient standards. The iron, manganese, copper, and zinc aerosols had the relatively large diameters ($MMD \approx 3 \mu$) common to particles produced by grinding processes. Lead and cadmium were found to be sub-micron condensation aerosols.

During the last three months of the survey, weekly rush-hr samples were also collected. The geometric mean particulate concentration of these samples was almost double that of the 24-hr samples taken in the corresponding period, with similar ratios being noted for all metals except zinc (which had a very small increase). Therefore, results indicate that almost all of the particulate matter was generated by traffic, both inside and outside of the subway tunnel.

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AIR QUALITY IN A NEWARK SUBWAY STATION

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INTRODUCTION

Air quality in urban areas, and its effect on public health, is receiving increasing attention. One area which has received only limited study, air quality in subway systems, has an important bearing on public health, due to the large number of people exposed to the air in the tunnels. To assess the hazard posed by the particulates found in a subway environment, information is needed on their concentration, size, and chemical composition. Therefore, in May of 1974, an air quality survey of the Newark City Subway was initiated, and a 5-stage impaction sampling setup was installed in the system's Broad Street station.

To determine the composition of the particulates, x-ray fluorescence analysis was performed on the samples from the first sampling runs, the results of which indicated the presence of iron, manganese, copper, zinc, and lead. This information provided the guide for the subsequent atomic absorption (AA) analysis for quantitative data. During the preliminary AA analysis, minute amounts of cadmium were also detected, leading to this metal's inclusion in the survey.

Until the last three months of the 1½-year survey, all of the air samples were collected over 24-hr periods; however during these last three months, a weekly sample was taken for the six hours encompassing the rush hours of the day. At the same time, weekly 24-hr samples were also being collected (within one day of the rush-hr samples), with

the results being compared to the rush-hr results in order to determine the amount of particulate matter generated by traffic, both inside and outside of the subway station.

A DESCRIPTION OF THE NEWARK CITY SUBWAY AND THE BROAD STREET STATION

The Newark City Subway (NCS) is a small transit system consisting of electrically powered trolley buses, the electrical circuit being completed by means of an overhead copper rail and the steel tracks upon which the cars ride. The NCS system extends for 4.7 miles (one way), with only the downtown 1.5 miles of track being underground.¹ The downtown section has the greatest similarity to the average subway system, due to the fact that it is enclosed and is in an area with heavy automobile traffic. Therefore, the air-sampling equipment was installed (10 feet above the tracks) at the Broad Street station, which is directly below the heart of Newark's business district.

An overview of the Broad Street station is shown in Figure 1. Ventilation is provided primarily by vents located in the sidewalks above. Additional air is provided by a flow from a small, unenclosed area of track about $\frac{1}{2}$ mile west of the station, the amount being determined by the outside wind velocity. General air flow in the tunnel is from west to east; therefore the sampler was upwind of the waiting passengers, except when turbulence from passing outbound subway cars generated momentary east-to-west currents.

Since ventilation air for the station comes from the street outside, the tunnel air can be expected to contain street pollutants as

¹R.B. Trattner and others, "Respirable Dust Content of Subway Air," Environmental Letters, X (1975), 248.

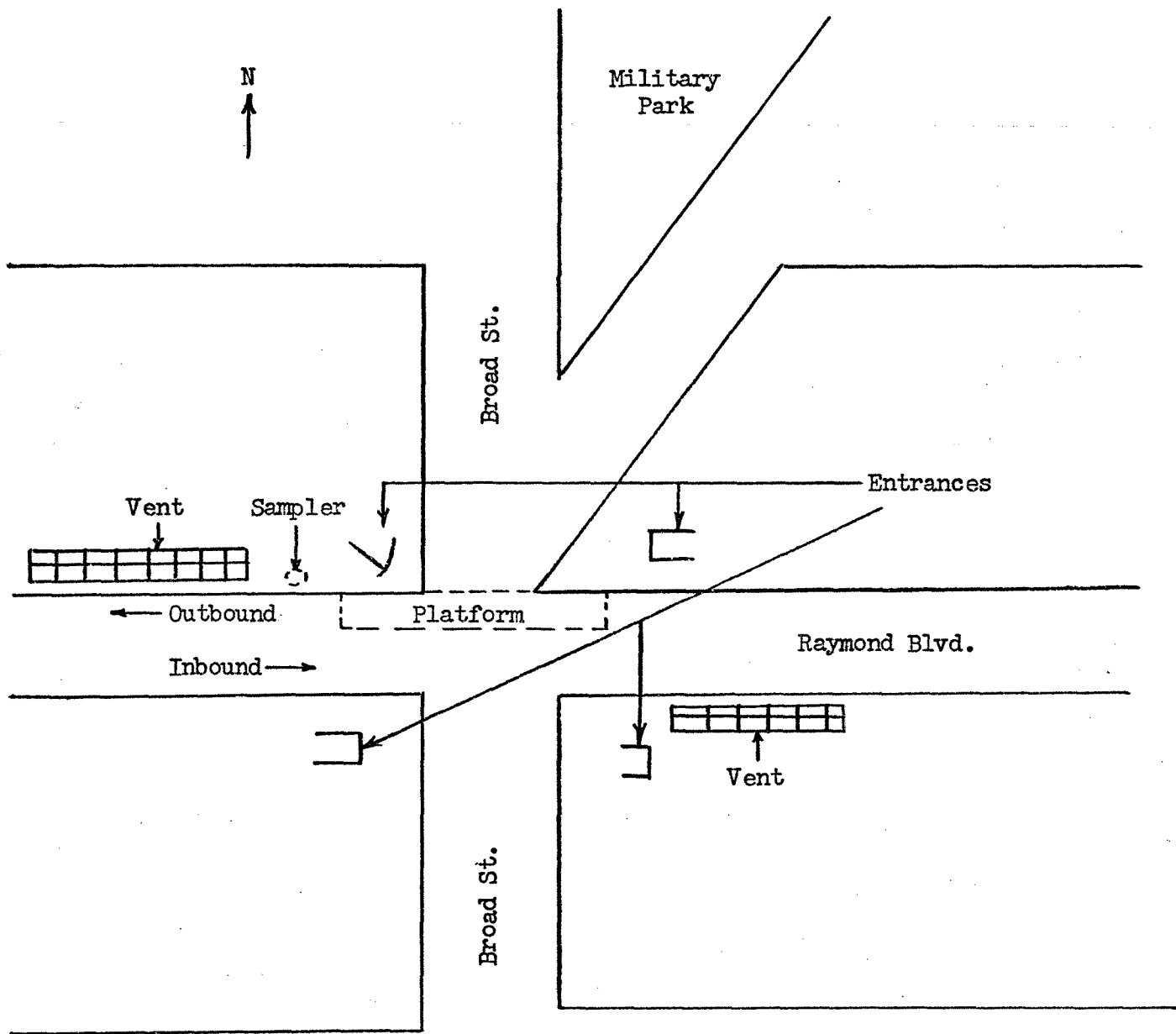


Figure 1. Diagram of the Broad Street Station.

well as those generated within the tunnel. The concentration of these contaminants should vary greatly during the course of a day because both automobile and subway traffic are heaviest during the rush hours and very light during the night hours.

The temperature in the tunnel is held relatively constant (midday averages of 25°C in summer and 8°C in winter were recorded), due to the moderating effects of the tunnel walls and the use of heaters in the winter months.

AIR SAMPLER THEORY

The inhalation threat posed by particulate matter is a direct function of aerodynamic particle size. Therefore, to fully assess the health effects associated with the various contaminants being studied in this survey, it is necessary to have not only total concentrations, but also the size distributions of the aerosols. Particle sizing was accomplished through the use of the modified Andersen sampler, a 5-stage cascade impactor with an in-line backup filter.

The complete sampling setup used is shown in Figure 2 (Research Appliance Co., Addison Park, Pa.). Air enters the sampler head and passes through a series of jets, 400 per stage, with each stage having progressively smaller diameter jets. Below each stage is a preweighed collection surface upon which the particles are impacted. At each jet the fraction of the particles impacted is a function of the jet velocity, the jet-to-collection-surface distance, and the collection efficiency of the previous stage. After passing the fifth surface, the remaining unimpacted particles are collected on a 4-inch-diameter backup filter of 3.0- μ pore size.

The effective cutoff diameter (ECD) in microns for each stage can be determined through the use of the dimensionless inertial impactor parameter, Ψ .

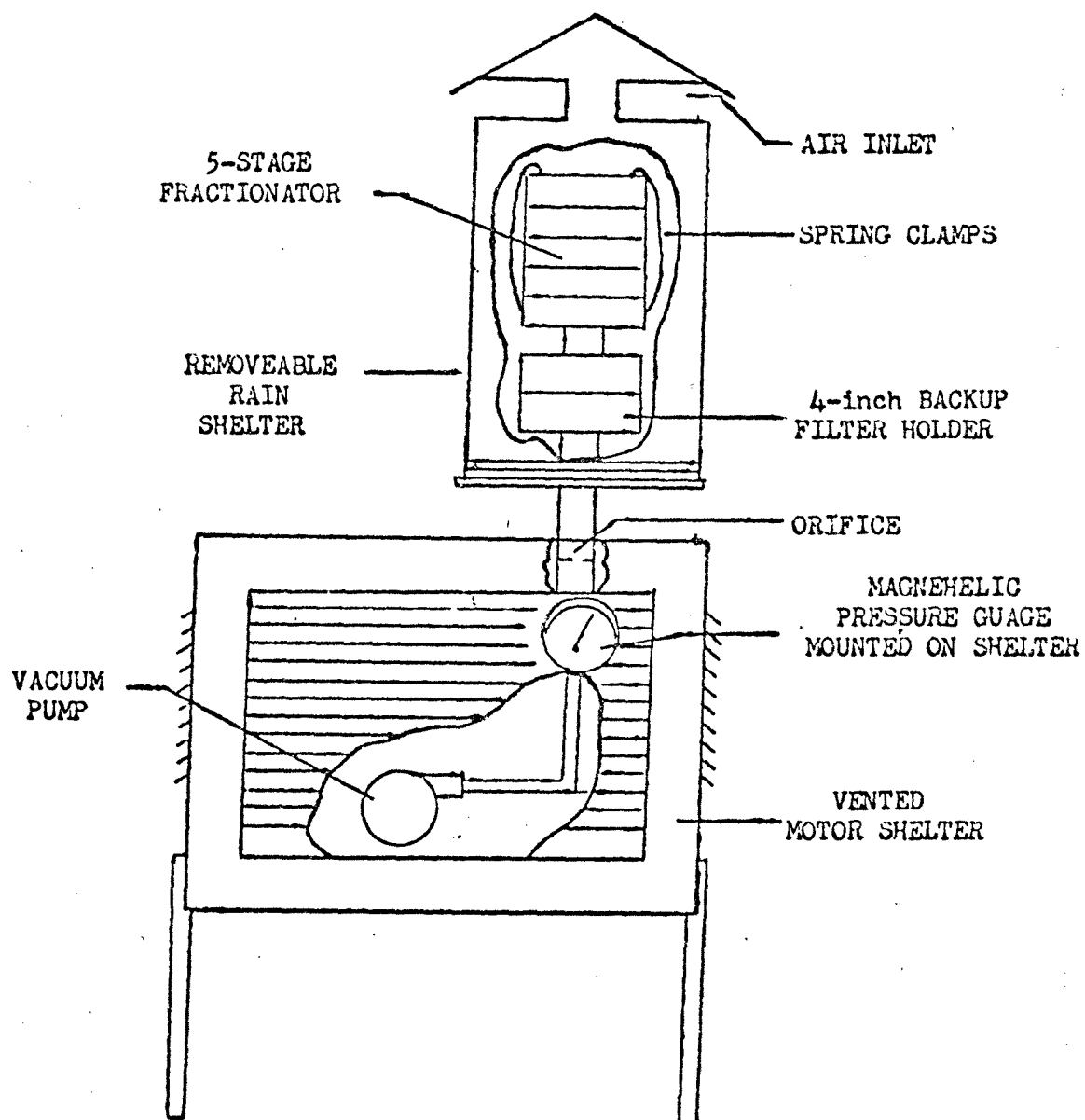


Figure 2. Diagram of the Fractionating Sampler and shelter.

$$\Psi = \frac{V_j^2 \rho_p^{CD}}{18n D_j}$$

where: Ψ = .144 for the Andersen sampler
 V_j = jet velocity
 ρ = particle density
 n = viscosity of the air
 D_j = diameter of the jet
 D_p = effective diameter of the aerosol particle
 C = Cunningham correction factor:

$$C = 1 + \frac{3.45 \times 10^{-4} T}{D_p}$$

where: T = absolute temperature, °R
 D_p = particle diameter in microns (μ)
 (C can be significantly greater than one for particles less than one micron in diameter.)

The ECD, which is the quantity $D_p (C\rho)^{1/2}$, can therefore be found for each stage once the flow rate is known. It is expressed in terms of an aerodynamic, or Stoke's equivalent diameter (i.e. $D_s = D_p (C\rho)^{1/2}$), instead of an effective diameter (D_p) because this is a more useful term for predicting particle behavior in the respiratory tract.¹ Particles with aerodynamic diameters of 1 μ or smaller have been found to have the highest rate of deposition in the lungs,² and thus pose the greatest health hazard.

¹It is also convenient because in many cases (i.e. condensation aerosols), the particle density is unknown (due to trapped air, etc.).

²U.S. Dept. of HEW, "Air Quality Criteria for Particulate Matter" (Washington, 1969), p. 115.

PROPERTIES OF ATMOSPHERIC PARTICULATE MATTER

Particulate matter is generally formed by two different methods. Particles of relatively large size ($D_p > 1 \mu$) tend to be generated from grinding processes as irregularly-shaped dusts, and are termed dispersion aerosols. Smaller-sized particles ($D_p \ll 1 \mu$), known as condensation aerosols, arise by vapor condensation and therefore, are usually spherical in shape.

"Dispersion aerosols are easily formed in sizes larger than 1μ , but with more difficulty in smaller sizes, where surface free energy becomes appreciable and may inhibit further disintegration."¹ Since these particulates are fairly large, they settle in still air at velocities approximated by Stoke's law:

$$V_s = \frac{gD_p^2(\rho - \rho_a)}{18\eta} \approx \frac{gD_s^2}{18\eta}$$

where: g = gravitational constant, 32.2 ft/sec^2
 ρ_a = density of air
 with the other terms being previously defined

The physical laws governing condensation aerosols are more complex. Particles with diameters less than 0.1μ undergo large Brownian motions, causing them to agglomerate. For particles between 0.1 and 1μ , Brownian motion is decreased and settling velocities in still air, though finite,²

¹Gordon D. Nifong, Edward A. Boettner, and John W. Winchester, "Particle Size Distributions of Trace Elements in Pollution Aerosols," Industrial Hygiene Association Journal, XXXIII (1972), 569.

are small compared with air motions.

The operation of these physical mechanisms causes the whole population of particulate matter³ to assume a certain size distribution, approximating a symmetrical, bell-shaped probability curve. This particulate data⁴ should result in a straight line when plotted on logarithmic-probability coordinates, with the diameter recorded at 50% (D_{50}) being the geometric mean median diameter (MMD). Standard deviation (σ_g), an indication of the range of particle sizes, is defined as:

$$\sigma_g = D_{84.13}/D_{50} = D_{50}/D_{15.87}$$

with these diameters being the respective limit values of 1, 0, and -1 in a log-normal distribution function.

In some cases, such as a large-diameter dust sample taken near its source, particulates do not have time to achieve a log-normal distribution. When this occurs, the resulting plot yields a line that bends toward the abscissa, and the data should be plotted on Cartesian-probability paper. The value D_{50} would then be an arithmetic mean, and

²At $D_p < 1 \mu$, particles tend to "slip" between air molecules, with their terminal settling velocities being determined by $V_s = V_s C$.

³The individual elements contained in these particulates should also have log-normal size distributions.

⁴The diameters being plotted can be either effective or Stoke's equivalent diameters. All the diameters being used in this report will be Stoke's equivalent diameters.

standard deviation would be defined as:

$$\sigma_a = D_{84.13} - D_{50} = D_{50} - D_{15.87}$$

ATOMIC ABSORPTIONTheory

Atomic absorption spectrometry is an excellent method for the measurement of a large number of elements in complex matrices, due to its sensitivity, relative lack of interferences, low cost, and simplicity of operation. Therefore, it readily lends itself to the analysis of metals in particulate matter. The basic principle of AA spectrometry is that when light of a particular element's characteristic wavelength is passed through a vapor containing the ground state atoms of that element, it will be absorbed in the process of exciting the atoms, with the degree of absorption being relative to the number of atoms present. The intensity of the transmitted light can be represented by Beer's law:

$$I_t = I_o e^{-(kcl)}$$

where: I_o = intensity of radiation at the source
 I_t = intensity of transmitted radiation
 k = absorption coefficient at the given wavelength
 c = concentration of absorbing atoms
 l = length of the absorption path

Therefore:

$$\log \frac{I_o}{I_t} = kcl = \text{absorbance}$$

and the concentration is proportional to the absorbance, since k and l are constants.

For most elements, a graph of absorbance vs. concentration will give a linear calibration up to an absorbance of about 0.5, followed

by a slight bend (for up to 1.0 absorbance) towards the concentration axis, due to reduced sensitivity.¹ By plotting the absorbances of known standards, one can find the concentration of the sample being analyzed, once its absorbance is known.

The atomic absorption spectrometry system being used is shown in Figure 3. The flame temperature is approximately 2450°K, a temperature at which ground state atoms comprise over 99% of the atoms in the vapor. Since AA spectrometry measures concentration through the use of ground state atoms, it is more accurate² than methods that measure the number of excited atoms.

Interference Effects

Although AA spectrometry, through its simplicity, is relatively free of interference effects, some are nevertheless encountered. Two forms of chemical interferences, incomplete dissociation of compounds and ionization effects, are related to those physical and chemical processes which inhibit the formation of ground state atoms in the flame.

When choosing a solvent for the digestion of a sample, one must take care that the solvent does not react with the element being measured, to form compounds which are not completely dissociated at the

¹A notable common exception is iron (at a wavelength of 248.3 nm), which shows a very large curvature.

²Accuracy of + 1% or better is obtainable. See, for example, W.J. Price, Analytical Atomic Absorption Spectrometry (London, 1972), chapter 4.

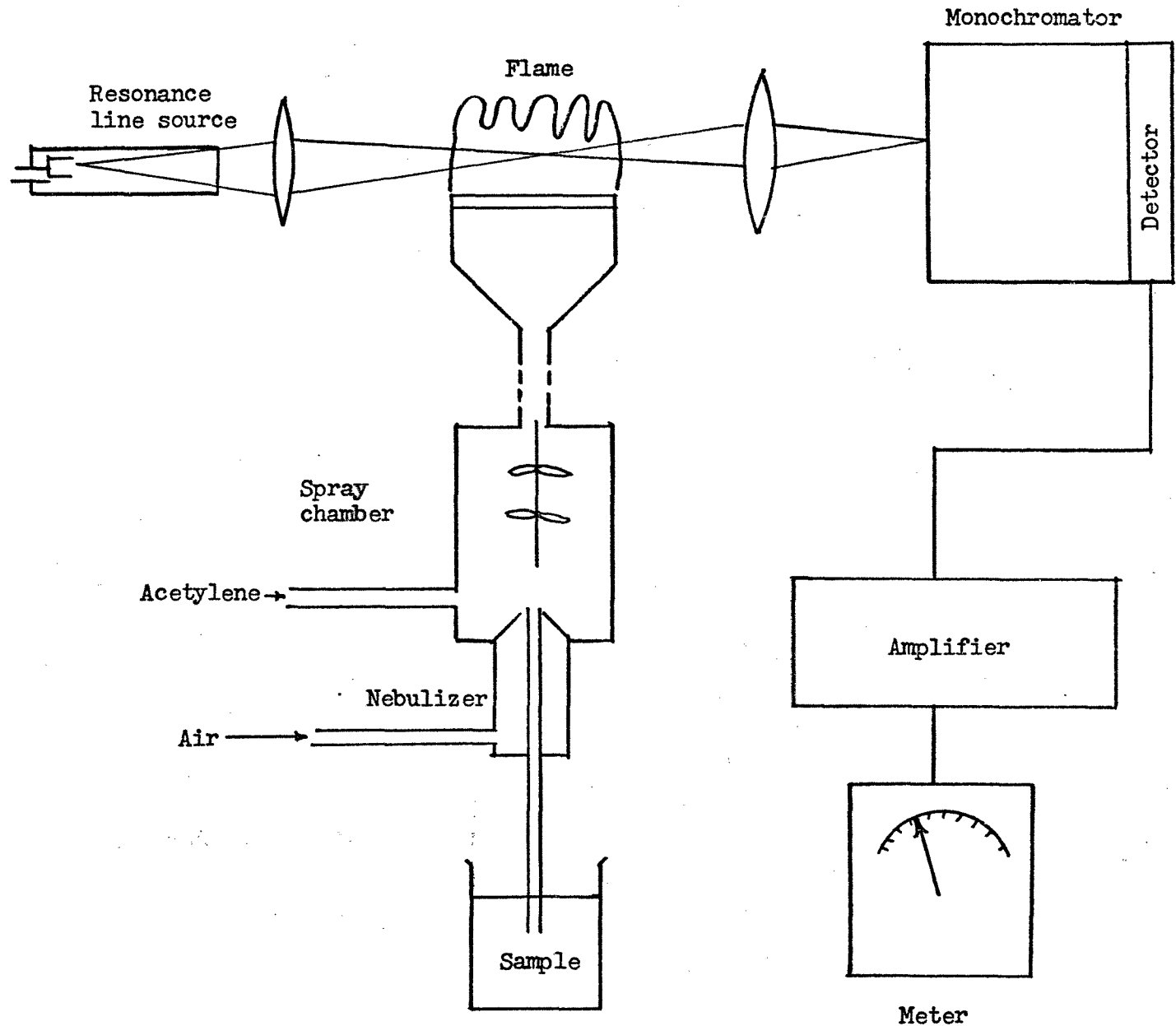


Figure 3. Schematic Diagram of the Atomic Absorption Spectrometry System Used.

temperature of the flame, thus preventing the formation of ground state atoms.

High-temperature flames, such as air-acetylene or nitrous oxide-acetylene, may cause appreciable ionization of the alkali metals. This can be overcome by the addition of a more easily ionized element to the analyte solution.

Another type of interference can take place through the presence of matrix effects. Since the flame method of AA spectrometry uses a nebulizer, any variation in the physical properties of the test and standard solutions can produce matrix errors.

Finally, if a sample contains a large amount of dissolved solids, light-scattering effects may give the appearance of greater absorbance (especially at low wavelengths). These errors can be corrected through the use of a hydrogen continuum lamp.

AIR QUALITY STANDARDSSuspended Particulate Matter

The term "particulate matter" takes in a wide variety of solid and liquid materials found in the air, including such toxic substances as lead and asbestos; therefore these poisonous materials must be considered separately in terms of ambient air standards. After ruling out toxic materials, there still remain a number of harmful and damaging effects which are characteristic of high levels of particulates. These include adverse health effects, such as lung irritation and an apparent association with emphysema and lung cancer;¹ reduced visibility; and damage to materials.

Thus, in April, 1971, the following Federal Air Quality Standards for suspended particulate matter were established:²

75 $\mu\text{g}/\text{m}^3$ annual geometric mean

260 $\mu\text{g}/\text{m}^3$ 24-hr maximum, not to be exceeded more than once a year

Metals

The particulate matter commonly found in city air consists of a large number of chemical substances, including many metallic pollutants.

¹ Community Air Quality Guides — Total Particulate Matter, American Industrial Hygiene Association (1969), p. 4.

² Howard E. Hesketh, Understanding & Controlling Air Pollution (Ann Arbor, Mich., 1972), p. 11.

Generally, metals constitute less than 3% of the weight of the particulate matter;³ however due to the nature of the subway environment, the percentage in this survey is expected to be much higher.

Of the six metals being studied in this survey, only two, lead and cadmium, are innately poisonous.⁴ The other four are essential to human health and present no danger except in extremely high doses. The air quality standards for the six metals will be presented in the following discussion.

Lead. Lead is the second largest (next to iron) metallic pollutant of the atmosphere. In cities, it is largely present as the lead salts, $PbClBr$ and $PbNH_2Cl$, which originate from auto exhaust;⁵ therefore the concentration of lead is a function of proximity to traffic. Because lead is a cumulative poison, its presence in the air represents an increasing potential health hazard for urban dwellers. The metal's deleterious effects include damage to the liver, brain, and central nervous system, and the production of anemia and bleeding.

No general agreement exists as to what atmospheric levels of lead are acceptable, and there is no federal ambient air quality standard

³Henry A. Schroeder, "Metals in the Air," Environment, XIII (August, 1971), 31.

⁴Ibid., p. 20.

at present. Geometric mean maximum standards ranging from 1 to 10 $\mu\text{g}/\text{m}^3$ have been suggested.^{5,6} It should be noted that for the lower standard to be achieved in urban areas, the amount of lead in gasoline would have to be greatly reduced or its use discontinued entirely.

Cadmium. Relatively little or no cadmium is found in community air. Most cadmium is found naturally as a mineral mixed with zinc, and therefore, the processing and subsequent usage of zinc will generally result in both zinc and cadmium emissions. Cadmium is also released into the atmosphere as a result of incineration of cadmium-containing products such as rubber tires and plastics; however it is almost always associated with zinc and can be roughly correlated as to concentration.

The presence of any cadmium in the air is of concern because the metal is very toxic at high concentrations and is injurious in a different way at low concentrations. The most serious consequence of occupational exposure to cadmium oxide fumes is severe lung injury, which can prove fatal after exposure to a high concentration of the fume (such as that produced by welding on cadmium-plated metal). Chronic exposure to low doses of cadmium has produced kidney⁷ and liver damage.⁸ From

⁵Hesketh, p. 118.

⁶Community Air Quality Guides -- Lead, American Industrial Hygiene Association (1969), p. 4.

⁷B.G. Liptak, Environmental Engineers' Handbook, vol. 2 (Radnor, Pa., 1974), p. 202.

⁸Schroeder, p. 21.

the standpoint of exposure to cadmium in the general environment, however, these effects are unlikely to occur, due to the very low concentrations encountered (reports from thirty-six cities with cadmium in the air gave concentrations ranging from 0.01 to $0.37 \mu\text{g}/\text{m}^3$),⁹ but a link to hypertension is suspected.¹⁰

There is no established ambient air quality standard for cadmium, but a maximum ambient concentration of $10 \mu\text{g}/\text{m}^3$ has been suggested.¹¹

Iron. Iron is the single largest metallic pollutant of the atmosphere and is generated by both man and nature. It is usually found as a dispersed dust of iron or iron oxide and is non-irritating to the mucous membranes even at its TLV of $10,000 \mu\text{g}/\text{m}^3$. This threshold limit has been suggested "to prevent the development of x-ray changes in the lungs on long term exposure,"¹² but it should be noted that these changes are not considered to be harmful to human health.¹³ Therefore, in considering human health, this TLV suggests¹⁴ a maximum ambient concentration of $1,000 \mu\text{g}/\text{m}^3$; however if the annoyance effects of visibility

⁹Ibid.

¹⁰Liptak, p. 202.

¹¹Hesketh, p. 117.

¹²Community Air Quality Guides — Iron Oxide, American Industrial Hygiene Association (1968), p. 3.

¹³Ibid.

¹⁴Using the method of Hesketh, pp. 116-19.

reduction and soiling are considered, an ambient concentration of 50% of the air quality standard for total suspended particulate matter (or $38 \mu\text{g}/\text{m}^3$) is suggested.¹⁵

Manganese, copper, and zinc. These three metals are essential for human health, and present no hazard at their usual concentrations in community air. In urban areas, they are usually generated in the industrial processing of the metals and by the burning of fossil fuels. The three metals can be toxic, but only at doses that miners or refiners are exposed to, when they can damage the nervous system. The dusts of manganese, copper, and zinc have TLV's of 2,000, 1,000, and 1,000 $\mu\text{g}/\text{m}^3$, respectively,¹⁶ suggesting¹⁴ maximum ambient concentrations of 200, 100, and 100 $\mu\text{g}/\text{m}^3$. However, a study¹⁷ has shown that even lower standards should be set when extremely fine dusts are involved.

¹⁵CAQG — Iron Oxide, p. 4.

¹⁶Threshold Limit Values for 1967, American Conference of Industrial Hygienists (1967).

¹⁷Robert P. Gleason, "Exposure to Copper Dust," American Industrial Hygiene Association Journal, XXIX (1968), 461-62.

EXPERIMENTALSampler Operation

For each run, five 3.25-inch-diameter glass fiber filters and a 4-inch-diameter backup filter were selected,^{1,2} placed in numbered glassine envelopes, and then dried in a dessicator³ for 24 hours, after which they were weighed to an accuracy of ± 0.00001 g on a Mettler balance. The preweighed filters were placed on their respective stages in the sampler head, and the sampler head was brought down to the subway station and inserted into the pump orifice.

After a sampling period of approximately 24 hours, the sampler was picked up and brought back to the lab, where the filters were folded in half, placed back into their respective envelopes, dried for 24 hours, and then reweighed. (The collection surfaces were handled with forceps throughout these operations.) The filters were then stored for subsequent AA analysis.

¹Aluminum foil collection surfaces were found to be unsatisfactory, due to large bounce-off errors. These errors lowered the effective MMD's and the measured particulate concentrations, due to high particle collection on the impactor walls. Bounce errors for glass fiber filters only became apparent when the particulate concentration exceeded $280 \mu\text{g}/\text{m}^3$. For further information, see T.G. Dzubay, L.E. Hines, and R.K. Stevens, "Particle Bounce Errors in Cascade Impactors," Atmospheric Environment, X (1976), 229-34.

²Filter pH had to be between 6.5 and 7.5.

³Due to breakdown in the constant-temperature-humidity room.

The average flow rate through the sampler was calculated from the beginning and ending airflow values, obtained from the use of a rotometer. This average (found to be a constant of $3.84 \text{ ft}^3/\text{min}$ through the course of the survey) was used to determine the ECD for each stage in the sampler; the calibration graph for the sampler yielded ECD's of 3.156, 2.344, 1.594, 0.969, 0.531, and 0.313μ for stages 1 through 6, respectively. (The ECD for the backup filter (stage 6) is an estimate.)

Once the ECD's and the particulate weights for the stages were known, a size distribution curve (see Figure 7) for each run was prepared, using calculations such as those in Table I. The best fitting line was determined by a least-squares fit.

During the last three months of the survey, peak levels of pollution were obtained through the use of a timing device attached to the pump. One day a week, the sampler was in operation for the hours of 6:30 to 9:30 A.M. and 3:00 to 6:00 P.M. For comparison purposes, 24-hr samples were also obtained for periods very close (within one day) to the rush-hr sampling days.

Digestion of the Collection Surfaces

The digestion method for the filters was that used by Ranweiler and Moyers,⁴ except that the samples were not ashed. Six 250-ml

⁴Lynn E. Ranweiler and Jarvis L. Moyers, "Atomic Absorption Procedure for Analysis of Metals in Atmospheric Particulate Matter," Environmental Science and Technology, VIII (1974), 153-54.

TABLE I. CALCULATION OF PARTICULATE SIZE DISTRIBUTION FOR 1/15/75

Atmospheric Conditions:

Tunnel temperature: (start) 5°C (end) 6.5°C

Barometric pressure: 30.14" 30.06"

Weather: cold w/thin cloud cover cold and cloudy

Sampling Time : 23 hrs. 42 minSampling Volume: 155 m³Particulate Weight Data:

Disk composition: glass fiber

Stage #	Disc Wt. (g)	Disc + Part. Wt.	Part. Wt.	ECD (μ)	Cum. % Undersize
1	0.36585	0.37438	0.00853	3.156	71.5
2	0.34210	0.34708	0.00498	2.344	54.9
3	0.36687	0.37024	0.00337	1.594	43.6
4	0.38723	0.39009	0.00286	0.969	34.0
5	0.36120	0.36432	0.00312	0.531	23.6
Backup	0.42851	0.43557	<u>0.00706</u>	0.313
			0.02992		

Particulate Conc.: 194 μg/m³

beakers were numbered 1 through 6 and thoroughly washed with deionized water. Each filter was placed in its corresponding beaker; soaked in 5 ml of a solution containing 2 ml of 65% HNO_3 , 0.5 ml of 30% HCl , and 2.5 ml deionized water; and warmed on a hot plate (60°C) for 5 minutes.⁵ The solution from each beaker was then poured into a correspondingly-numbered 50-ml (plastic) Nalgene flask, and each filter was washed with deionized water, with the washings being poured into the same flask.

Previous experience⁶ with similar filters has shown one digestion to be insufficient to dissolve all the metallic air pollutants. Therefore, the previous digestion procedure was repeated, with the filters finally being washed several times and enough deionized water added to the flasks to form 50 ml of solution. (Later analysis showed this double digestion to be sufficient to dissolve 99+% of the metals.)

The digestion procedure was repeated on blank 3.25 and 4-inch filters to determine the levels of contamination resulting from leaching of metals from the filters themselves (or from the dissolving solution). These values are reported in Table II.

⁵This turned the upper-stage filters bright yellow, and an oily solution was formed from the lower-stage filters.

⁶Delfim D. Dias, "Pistol and Rifle Range Air Quality" (Master's thesis, N.J. Institute of Technology, 1975) p. 31.

Atomic Absorption Analysis

The Atomic Absorption Spectrometer, Varian Techtron Model 1200 (see Figure 4), was used in conjunction with an oxidizing, air-acetylene flame, and in the concentration mode, to obtain concentrations of six metals in the solutions containing the dissolved particulates.

The concentration mode is a very convenient device for analyzing a large number of samples (as this survey required), since it eliminates the need for drawing a large number of calibration graphs. It gives a direct read-out in parts per million (ppm)⁷ for each metal as long as two standards (low and high) of known concentration⁸ are used. The low standard should have an absorbance between 0.1 and 0.2, and the high standard, an absorbance of from 0.5 to 0.8. The concentrations can then be dialed in, using the low standard for scale adjustment and the high standard for curve correction. The low and high standards used, and the other operating parameters for each metal studied in this survey are presented in Table II. The wavelengths chosen were those that would place the analyte concentrations in the optimum working ranges.

With the exception of high concentrations of dissolved solids in

⁷For liquids, ppm = $\mu\text{g/ml}$.

⁸Standards were formed from the dilution of 1000 ppm stock solutions.

TABLE II. OPERATING PARAMETERS FOR AA ANALYSIS

	Fe	Mn	Pb	Cd	Cu	Zn
Resonance Line, nm.	372.0	279.5	217.0	228.8	324.7	213.9
Slit Width, nm.	0.2	0.2	1.0	0.5	0.2	0.2
Lamp Current, mA.	10	10	6	3	10	5
Low Standard, ppm	10	0.625	2.5	0.313	0.625	0.313
High Standard, ppm	40	2.50	10	1.25	2.50	1.25
Conc. of Contaminants from Filters, ppm						
Stages 1-5	0.23	0.002	0.00	0.000	0.008	0.030
Backup	0.54	0.008	0.00	0.000	0.010	0.089

Flame Condition: Oxidizing for all metals

Fuel Flow Rate: Acetylene - 1.2 l/min

Oxidant Flow Rate: Air ----- 10 l/min

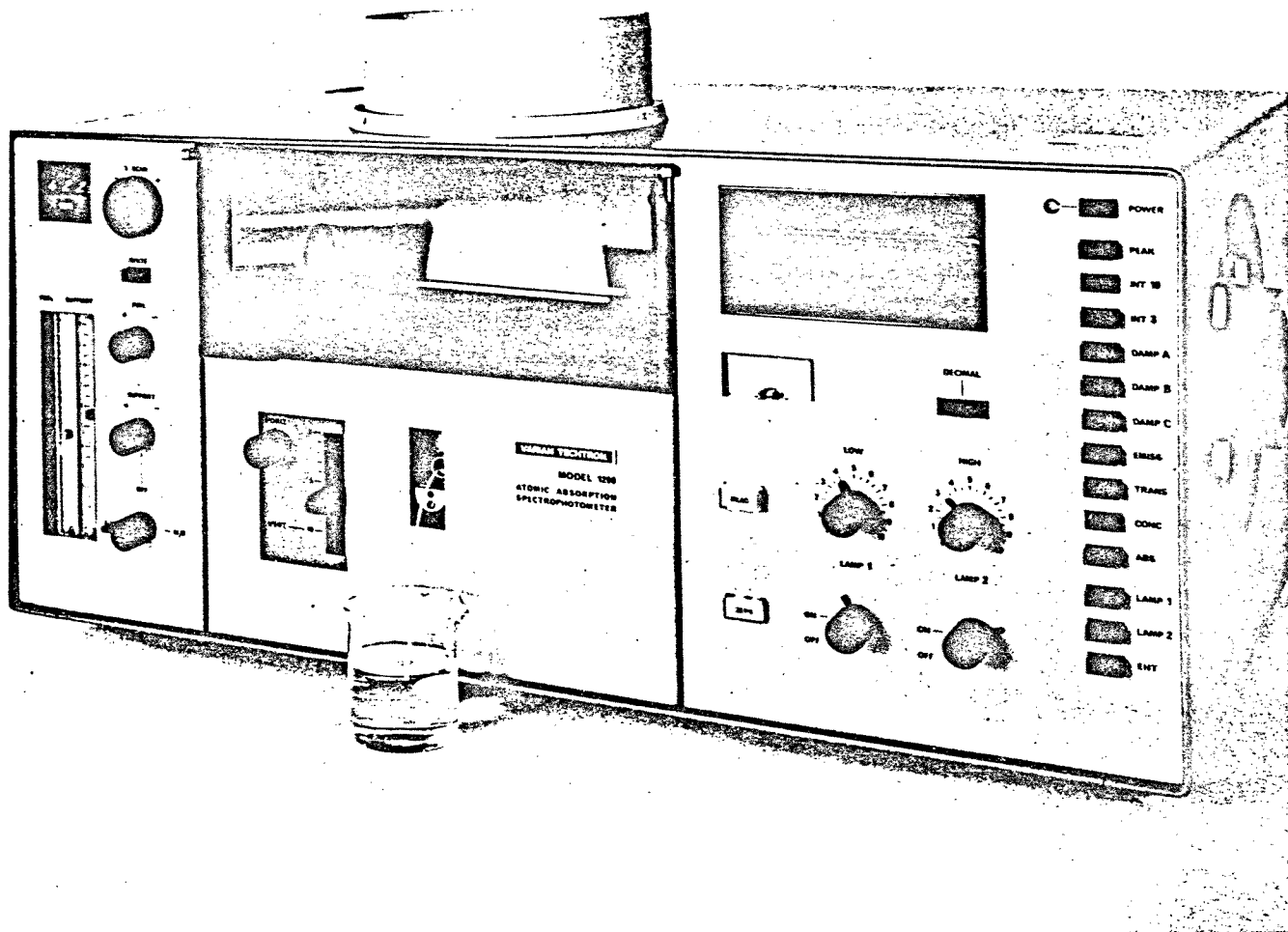


Figure 4. Varian Techtron Atomic Absorption Spectrometer — Model 1200.

the analyte solutions, conditions did not exist⁹ to cause interference effects. At the low wavelengths where elements such as lead (217 nm) were examined, the presence of dissolved bits of filter could have caused signal enhancement due to light-scattering effects. Therefore, the hydrogen continuum lamp was used to determine non-atomic absorption; at no time during the analysis was any found. (This result was expected, since the measured level of lead in the blank samples was zero.) Thus, the concentration of each metal in the atmosphere was found by:

$$\text{At. Conc. (}\mu\text{g/m}^3\text{)} = \sum_{st=1}^6 \left(\frac{\text{Soln. Conc. (ppm)} - \text{Filter Contam. (ppm)}}{\text{Air Sampling Volume (m}^3\text{)}} \times \right. \\ \left. 50 \text{ ml of soln.} \right)$$

Size distribution curves were then plotted by using the concentrations of metals at each stage and calculations similar to those in Table I (see Figure 7 for a typical plot).

⁹Depression of copper in the presence of zinc and manganese in the presence did not take place due to low concentrations involved, and the fact that an oxidizing flame, instead of a reducing flame was used.

DISCUSSION OF RESULTS

Concentration Levels

Total suspended particulate matter. Table IIIa summarizes on a seasonal and an overall basis, particulate concentrations and particle size parameters for 24-hr samples taken from the Broad Street subway station, and gives comparisons with concentration values obtained from the Newark EPA high-volume sampler. The overall geometric mean particulate level for the subway air ($187 \mu\text{g}/\text{m}^3$) was found to be more than twice the Federal Ambient Air Quality Standard ($75 \mu\text{g}/\text{m}^3$), with the 24-hr maximum permissible concentration being exceeded five times during the course of the survey.

A comparison with the EPA data from the more relevant Military Park site yields a striking result. Although the EPA sampler was located only a short distance from the subway station (see Figure 1), its concentration data is much lower.¹ Part of this discrepancy can be explained by the EPA sampler's being situated in a park and set back from traffic, while the subway station was fed by street-level vents. Another factor to take into account is the differences in the standard geometric deviations for the concentration levels. In this case, the σ_g 's denote the range of particulate levels and give estimates of the variability of the potential volume into which the pollutants were dispersed. The EPA σ_g 's are much higher than the σ_g recorded for the tunnel data,

¹Under the same conditions in an urban environment, the hi-vol sampler should give a higher concentration due to bounce-off errors incurred with a cascade impactor. For further information, see R. E. Lee and S. Goranson, "NASCIN. I. Size Distribution Measurements of Suspended Particulate Matter in Air," Environ. Sci. Technol., VI (1972), 1022.

TABLE IIIa. SEASONAL SIZE DISTRIBUTIONS FOR PARTICULATES, 1974-76

Data for Broad St. Subway Station:

Season	Sum.	1974			1975			Overall
		Fall	Win.	Spr.	Sum.	Fall	Win.	
No. of Samples	14	16	18	18	15	17	5	103
Av Midday Tunnel Temp, °C	25	15	9	14	26	18	6	17
Tunnel Particulates								
Av concn, $\mu\text{g}/\text{m}^3$	218	188	181	185	202	184	209	192
Av MMD, μ	2.08	1.95	1.97	1.99	2.32	2.12	2.01	2.07
Av st ar dev, μ	1.92	2.08	2.03	1.98	1.71	2.06	1.97	1.96
% part $\leq 1 \mu$	28	32	32	31	22	29	30	29

Max Concn - $422 \mu\text{g}/\text{m}^3$ Min Concn - $72 \mu\text{g}/\text{m}^3$ Samples Above $260 \mu\text{g}/\text{m}^3$ - 5

Geometric Mean Concn - $187 \mu\text{g}/\text{m}^3$ Standard Geo Dev For Concn Data - 1.29

Newark EPA Data for the Corresponding Period - High-Volume Samplers:

No. of Samples	9	6	12	8	10	15	...	60
Site A*								
Av Concn, $\mu\text{g}/\text{m}^3$	137	98	121
Site B								
Av Concn, $\mu\text{g}/\text{m}^3$	59	66	64	47	...	57

Site A: Geo Mean Concn - $107 \mu\text{g}/\text{m}^3$ Standard Geo Dev for Concn Data - 1.64

Site B: Geo Mean Concn - $52 \mu\text{g}/\text{m}^3$ Standard Geo Dev for Concn Data - 1.58

Site A: Parking Lot, Washington St. and Branford Place

Site B: Military Park (see Figure 1)

* Moved to site B in the Winter of 1974.

TABLE IIIb. COMPARISON OF PARTICULATE LEVELS FOR 11/75-1/76

	Rush-hr Samples	24-hr Samples	EPA Data
No. of Samples	12	12	10
Av Concn, $\mu\text{g}/\text{m}^3$	336	187	46
Av MMD, μ	2.25	2.02
Av St Ar Dev, μ	2.05	1.99
% Part $\leq 1 \mu$	27	30

and this is to be expected because outdoor sites are more vulnerable to the variable dispersion effects of the wind, while there is much less air circulation in the mostly enclosed subway station. Therefore, due to the sampler's proximity to a large aerosol source (the subway cars) and the station's having a lower degree of dispersion, the particulate levels in the tunnel are bound to be higher and more stable.

In general, it was observed that stagnant weather conditions brought about relatively high particulate concentrations in the subway station and that low concentrations were associated with windy days. A scan of the seasonal particulate data indicates that particulate levels are slightly higher in the summer periods, when the greatest number of hazy days are observed in downtown Newark.

Table IIIb presents a comparison between samples taken during

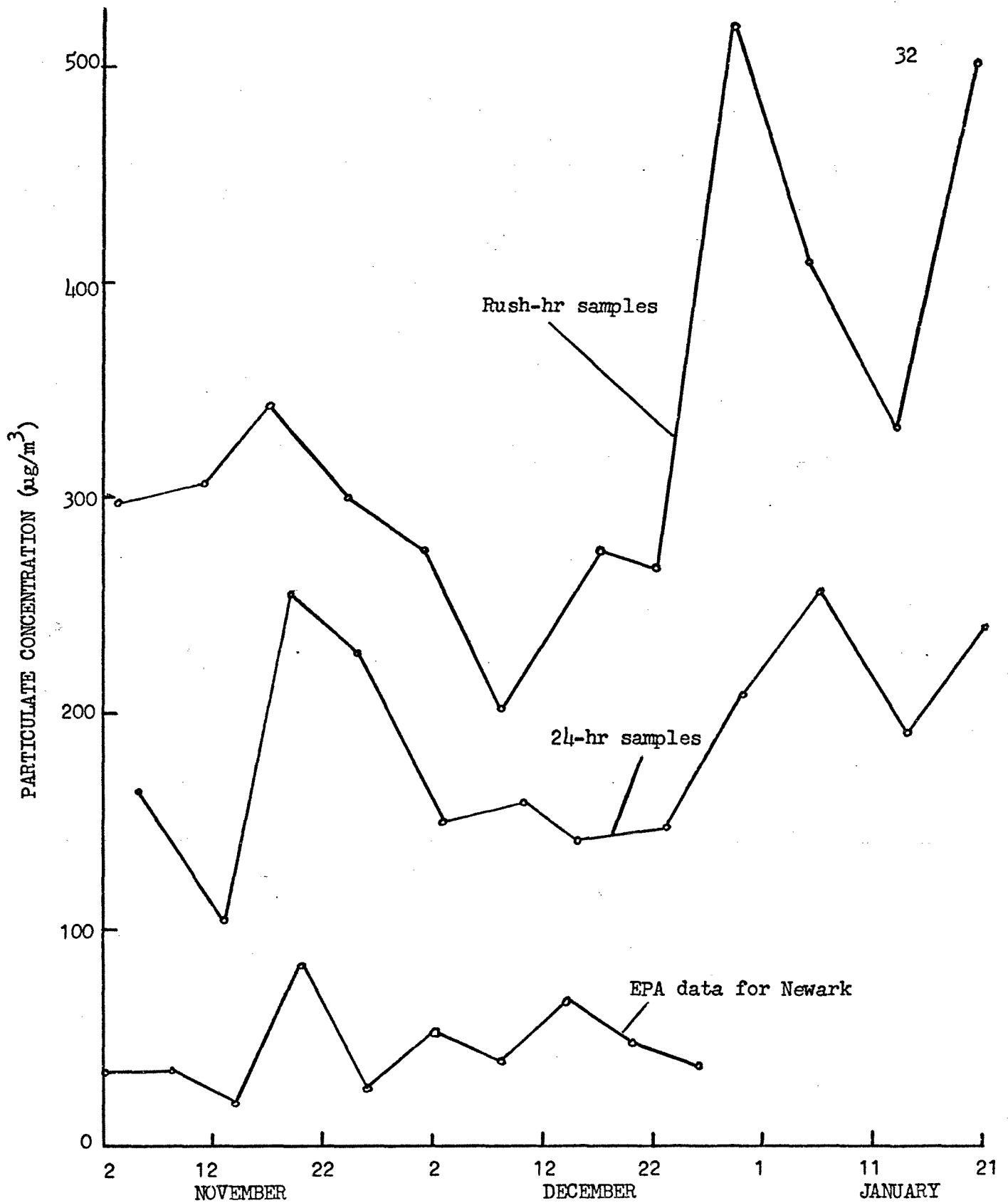


Figure 5. Comparison of Particulate Levels for the Last Three Months of the Survey, 11/75-1/76.

the rush hours and regular 24-hr samples taken within one day of the rush-hr samples. As can be seen from Figure 5, the EPA data is almost negligible, and there is a very good correlation between the concentration levels of the other two types of samples, with the rush-hr concentrations being nearly double those of the 24-hr samples. This demonstrates that the majority of the particulates was produced in the direct vicinity of the subway station. Since almost half the pollutants were generated during the six hours encompassing the rush hours when the subway and auto traffic was the heaviest, these modes of transportation are implicated as primary sources.

Metals. Table IVa summarizes, on a seasonal and overall basis, metal concentrations and particle size parameters for iron, manganese, lead, cadmium, copper, and zinc. Iron ($31.7 \mu\text{g}/\text{m}^3$) and lead ($3.85 \mu\text{g}/\text{m}^3$) exhibited the highest overall average concentrations. The lowest overall concentration was the $0.027 \mu\text{g}/\text{m}^3$ value recorded for cadmium. Intermediate overall concentration levels were observed for copper ($0.809 \mu\text{g}/\text{m}^3$), zinc ($0.749 \mu\text{g}/\text{m}^3$), and manganese ($0.384 \mu\text{g}/\text{m}^3$).

This table also shows very few clear trends in the seasonally composited metal concentration data. The uniformity of metal concentrations (with no discernable increases in winter) indicates that the contribution from space heating is negligible when compared to the contribution from transit sources. Since the subway station is surrounded

TABLE IVa. SEASONAL SIZE DISTRIBUTIONS FOR METALS, 1974-76

Season	Sum.	1974			1975			Overall
		Fall	Win.	Spr.	Sum.	Fall	Win.	
No. of Samples	14	16	18	18	15	17	5	103
Iron								
Av concn, $\mu\text{g}/\text{m}^3$	30.6	29.3	29.2	27.2	37.3	32.8	45.7	31.7
Av MMD, μ	3.09	2.89	3.08	3.12	3.19	3.11	3.12	3.08
Av st ar dev, μ	1.24	1.49	1.55	1.39	1.19	1.46	1.41	1.39
% part $\leq 1 \mu$	4.5	11.5	8.5	5.5	3.5	7.5	6.5	6.8
Manganese*								
Av concn, $\mu\text{g}/\text{m}^3$	0.380	0.366	0.363	0.338	0.437	0.390	0.517	0.384
Lead								
Av concn, $\mu\text{g}/\text{m}^3$	3.76	4.15	3.41	3.43	4.08	4.43	3.66	3.85
Av MMD, μ	0.68	0.72	0.79	0.80	0.84	0.70	0.69	0.75
Av st ar dev, μ	2.20	2.06	2.15	2.01	2.10	2.10	2.05	2.09
% part $\leq 1 \mu$	56	56	55	54	53	56	57	55
Cadmium**								
Av concn, $\mu\text{g}/\text{m}^3$	0.028	0.024	0.025	0.026	0.032	0.028	0.027
Av MMD, μ	0.62	0.61	0.87	0.75	0.51	0.52	0.67
Av st ar dev, μ	1.80	1.77	1.80	1.86	1.90	1.73	1.83
% part $\leq 1 \mu$	58	59	53	56	60	61	57
Copper								
Av concn, $\mu\text{g}/\text{m}^3$	0.861	0.894	0.828	0.562	0.879	0.790	1.08	0.809
Av MMD, μ	3.24	2.72	3.10	2.81	3.30	2.85	3.29	3.00
Av st ar dev, μ	1.88	1.99	2.02	1.87	1.84	2.08	2.06	1.96
% part $\leq 1 \mu$	12	20	15	17	11	13	14	15
Zinc								
Av concn, $\mu\text{g}/\text{m}^3$	0.762	0.895	0.709	0.818	0.600	0.781	0.482	0.749
Av MMD, μ	2.20	1.93	1.88	2.01	2.02	1.80	1.80	1.97
Av st ar dev, μ	1.48	1.53	1.47	1.23	1.41	1.34	1.56	1.41
% part $\leq 1 \mu$	21	27	28	21	23	28	31	25

* Manganese has the same size distribution as iron.

**The average concentrations of cadmium given are geometric averages.

by very tall buildings, this observation is not totally unexpected.

While the season-to-season averages registered little change, the day-to-day variations were considerable. In general, it was found that the atmospheric conditions that brought about a certain particulate concentration also brought about corresponding levels of the metals (see Figure 6). One notable exception is zinc, where concentration levels were discovered to be governed not only by atmospheric conditions, but also by wind direction, thereby indicating a fairly distant source for this metal.

Season-to-season lead levels were found to be relatively constant, with slight increases being recorded in the fall. Since the levels of particulates and the other metals did not register corresponding changes, the increase was probably associated with increased auto traffic. A slow drop in the lead concentration over the course of the survey was expected, due to the introduction of catalytic-converter-equipped cars in the Fall of 1974; however this did not take place. Apparently, not enough of these cars were on the road to make an impact discernable from normal seasonal changes.

The manganese/iron ratio was found to be very constant, both on a day-to-day and a stage-to-stage basis, thereby indicating that the steel from the tracks and subway car wheels is the overwhelming source of these metals.

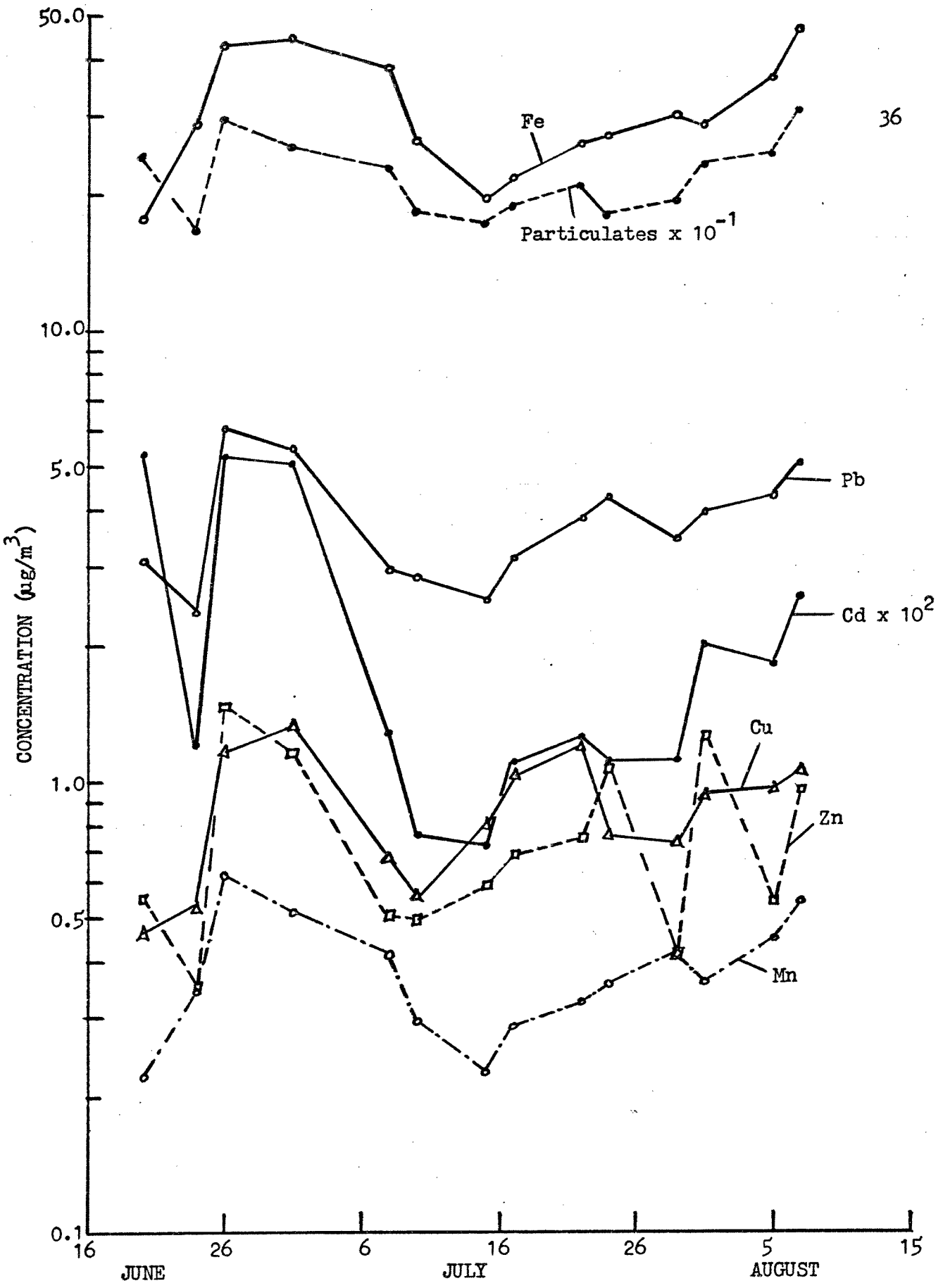


Figure 6. Particulate and Metal Levels for the Summer of 1974.

It was observed that particulate levels dropped on rainy days, thus suggesting a significant particle washout. However, this was ruled out because similar decreases in iron levels (iron is not exposed to rain) were noted. It is thus suggested that the wind associated with rainy days, rather than the rain itself, caused these drops.

Although both copper and steel particles are produced from scraping of rails by the subway cars, it can be seen from Table IVa that the amount of copper produced is very much smaller. This difference can be explained by the fact that the overhead copper rail has a much smaller surface area than the steel tracks and is subjected to much less pressure.

Cadmium concentration levels underwent larger swings than those of the other metals; therefore geometric average concentrations² are given. However, for the most part, there is still a correlation with the other metal levels, thus indicating a source in the vicinity of the subway station.

Table IVb presents a comparison between rush-hr and 24-hr samples. Dramatic differences in concentration levels are evident. Iron, manganese, and copper rush-hr concentrations were approximately twice their 24-hr concentrations. This is in line with the assumption that these

²Geometric averages are slightly smaller than arithmetic averages.

TABLE IVb. COMPARISON OF METAL LEVELS FOR 11/75-1/76

	<u>Rush-hr Samples</u>	<u>24-hr Samples</u>
No. of Samples	12	12
Iron		
Av concn, $\mu\text{g}/\text{m}^3$	84.3	36.3
Av MMD, μ	2.96	3.07
Av st ar dev, μ	1.43	1.46
% part $\leq 1 \mu$	8.5	8.0
Manganese*		
Av concn, $\mu\text{g}/\text{m}^3$	1.018	0.413
Lead		
Av concn, $\mu\text{g}/\text{m}^3$	6.12	3.98
Av MMD, μ	0.80	0.67
Av st ar dev, μ	2.01	2.07
% part $\leq 1 \mu$	54	56
Cadmium**		
Av concn, $\mu\text{g}/\text{m}^3$	0.058	0.030
Av MMD, μ	0.42	0.60
Av st ar dev, μ	2.03	1.77
% part $\leq 1 \mu$	62	59
Copper		
Av concn, $\mu\text{g}/\text{m}^3$	1.688	0.874
Av MMD, μ	2.99	3.05
Av st ar dev, μ	1.91	2.07
% part $\leq 1 \mu$	15	12
Zinc		
Av concn, $\mu\text{g}/\text{m}^3$	0.800	0.696
Av MMD, μ	1.84	1.79
Av st ar dev, μ	1.53	1.39
% part $\leq 1 \mu$	26	28

* & ** Same as Table IVa.

metals are primarily generated by the subway cars. Since about half of the routes are run during the six peak sampling hours, it is significant that about half of the daily total for each of these metals was collected during these hours.

Because iron and copper are both produced in the same process, it might be expected that their rush-hr/24-hr ratios would be exactly the same; however the iron ratio is somewhat higher. But if the average ambient Newark copper concentration of $0.2 \mu\text{g}/\text{m}^3$ is taken into account,³ the ratios are found to be very similar. (A sharp decrease in this background concentration would explain the drop in copper levels recorded in the Spring of 1975 (see Table IVa).)

Lead levels registered only a 50% increase for the rush hours. Since lead concentration can be correlated with auto traffic flow, this lesser increase indicates that auto traffic undergoes smaller peaks than subway traffic.

Cadmium rush-hr levels registered a 100% increase similar to the increases of the subway-produced metals; therefore a link with subway travel is suspected.

The relatively constant zinc levels shown in Table IVb tend to prove that zinc is a component of ambient Newark air, and that little

³EPA Office of Air Programs, "Air Quality Data for 1968" (Washington, 1972), p. 117. (Samples were taken a few blocks away from the Broad Street station.)

or none of it is produced near the subway station. In fact, the zinc concentrations measured at the station are in line with the EPA values for ambient Newark air.⁴

Particle Size Distributions

Particulate matter. Evaluation of the size distribution of the subway station aerosol finds it has two classes of formation (condensation and dispersion), which generate a probability curve with a saddle at approximately 1-2 μ . This bimodality implies that the sampler was located very near the aerosol sources, being that a log-normal distribution did not have time to be attained. In any case, a straight line can not be drawn on log-probability coordinates (the line bends sharply toward the abscissa); however it was found that a straight line could be drawn on Cartesian-probability coordinates (see Figure 7).

Results of the particulate size distribution curves are summarized in Table IIIa. The mass median diameter (MMD) data was derived by interpolation of the curves, with these diameters being arithmetic average Stoke's equivalent diameters. Since transit is the primary source of the particulates, it is not surprising that the MMD data is very uniform. Interestingly enough, due to the unique nature of the subway aerosol, very little of the particulate matter has a diameter close to the overall MMD of 2.07 μ .

⁴Ibid., p. 154.

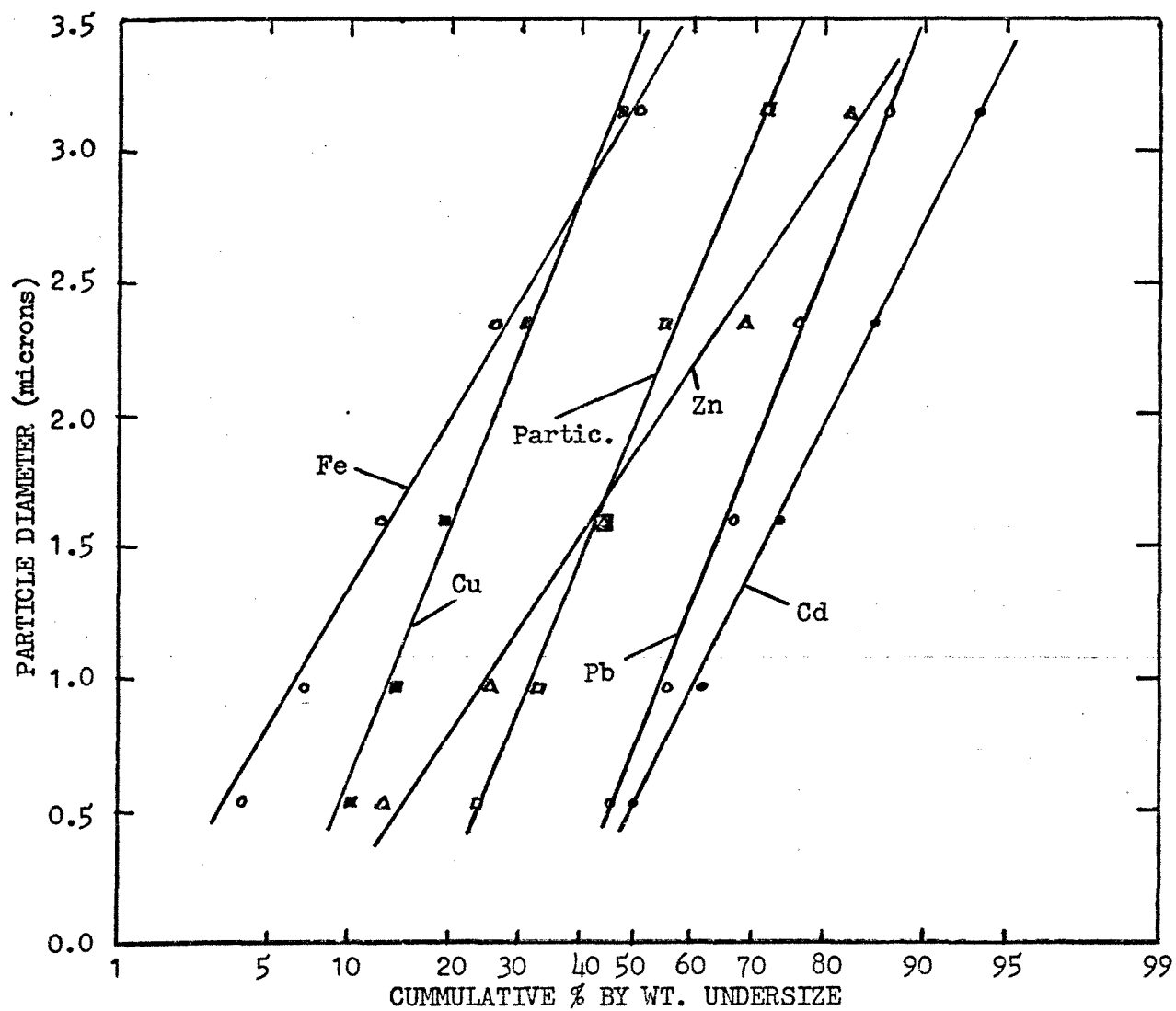


Figure 7. Size Distribution Curves of Particulates and Metals for 1/15/75.

Another useful representation of the particle size can be found in the percent particle mass less than or equal to 1μ , these values being interpolated directly from the size distribution curves. Since pulmonary deposition is appreciable for particles below 1μ , it is important to note that an average of 29% of the subway particulates fell into this category. However, it should be pointed out that average urban air, in comparable concentrations, would present more of a health hazard, due to the fact that its particulate matter has a submicron percentage twice as high and a MMD only a third as large as that of the subway station aerosol.⁵

Metals. A typical set of particle size distribution curves is shown in Figure 7. Log-normal fits could not be attained for the iron,⁶ copper, and cadmium data, due to each of these metals' having a greater amount of large particles than would be predicted by a log-normal function; however straight-line fits were obtained on Cartesian-probability coordinates. Lead and zinc have log-normal fits, but for comparison purposes, their data were plotted on the same coordinates used by the other metals.

⁵R. E. Lee and S. Goranson, "NASCIN. I. Size Distribution Measurements of Suspended Particulate Matter in Air," Environ. Sci. Technol., VI (1972), 1022-23.

⁶Since the unoxidized steel from the subway car wheels and tracks is the source of both the iron and manganese particulates, manganese has the same size distribution as iron.

The MMD data summarized in Tables IVa and IVb was derived by extrapolation or interpolation of the size distribution curves. Values less than 0.531μ or more than 3.156μ were obtained through extrapolation of the curves and should be regarded as estimates of the true values.

Examination of Table IVa reveals that iron (steel) and copper are associated with large particles (overall MMD's of 3.08μ for iron and 3.00μ for copper were recorded), demonstrating that they are dispersion aerosols produced by the grinding of rails. Since these large-diameter dusts were collected near their sources, their achieving arithmetic-normal (instead of log-normal) distributions is not out of line (see page 10). Furthermore, because the subway air contains a large concentration of iron, the large size of the iron particles helps produce the relatively large MMD found for the total particulate matter.

Zinc, too, is associated with large particles (an overall MMD of 1.97μ was recorded), but since it has a more distant source, it has time to achieve a log-normal distribution.

Lead and cadmium are associated with the more hazardous submicron-sized particles (the overall MMD was 0.75μ for lead and 0.67μ for cadmium); therefore they are condensation aerosols. The small size of the lead-associated particles is expected, since lead is produced through auto emissions. Interestingly enough, the lead aerosol, while produced almost as close to the sampler as the dispersion aerosols from the

44

subway cars, has a log-normal distribution. This can be explained by the fact that smaller particles more readily achieve this distribution.⁷

The small size of the cadmium aerosol indicates that it is generated from some high-temperature process, and since it does not achieve a log-normal distribution, it must have been produced even closer to the sampler than the lead was. Size and concentration comparisons rule out any link with zinc, although there is a link with the level of subway traffic (and, therefore, the number of people using the subway). After taking these observations into account, tobacco smoke emerges as the primary suspected source of cadmium, with auto emissions^{8a} contributing a small percentage.^{8b}

An indication of the absolute range^{8c} of particle sizes may be gained from the arithmetic standard deviation, which broadly represents the slope of the particle size distribution curve. In general, the condensation aerosols in this survey have larger absolute size ranges than the dispersion aerosols, and this means that their relative size ranges would be very much larger than those of the dispersion aerosols.

Due to their similarities in size and method of generation, copper and iron would be expected to have similar σ_a 's. However, copper has a much larger one and, in fact, demonstrates the greatest deviation from a log-normal deviation of all the metals. These discrepancies can be

⁷Nifong, Boettner, and Winchester, p. 574.

^{8a}U.S. Dept. of HEW, "Preliminary Air Pollution Survey of Cadmium and Its Components" (Raleigh, N.C., 1969), p. 27.

^{8b}A larger percentage would have been attributed to auto emissions if there were consistent stage-to-stage lead/cadmium ratios.

^{8c}An indication of the relative particle range may be gained from the geometric standard deviation.

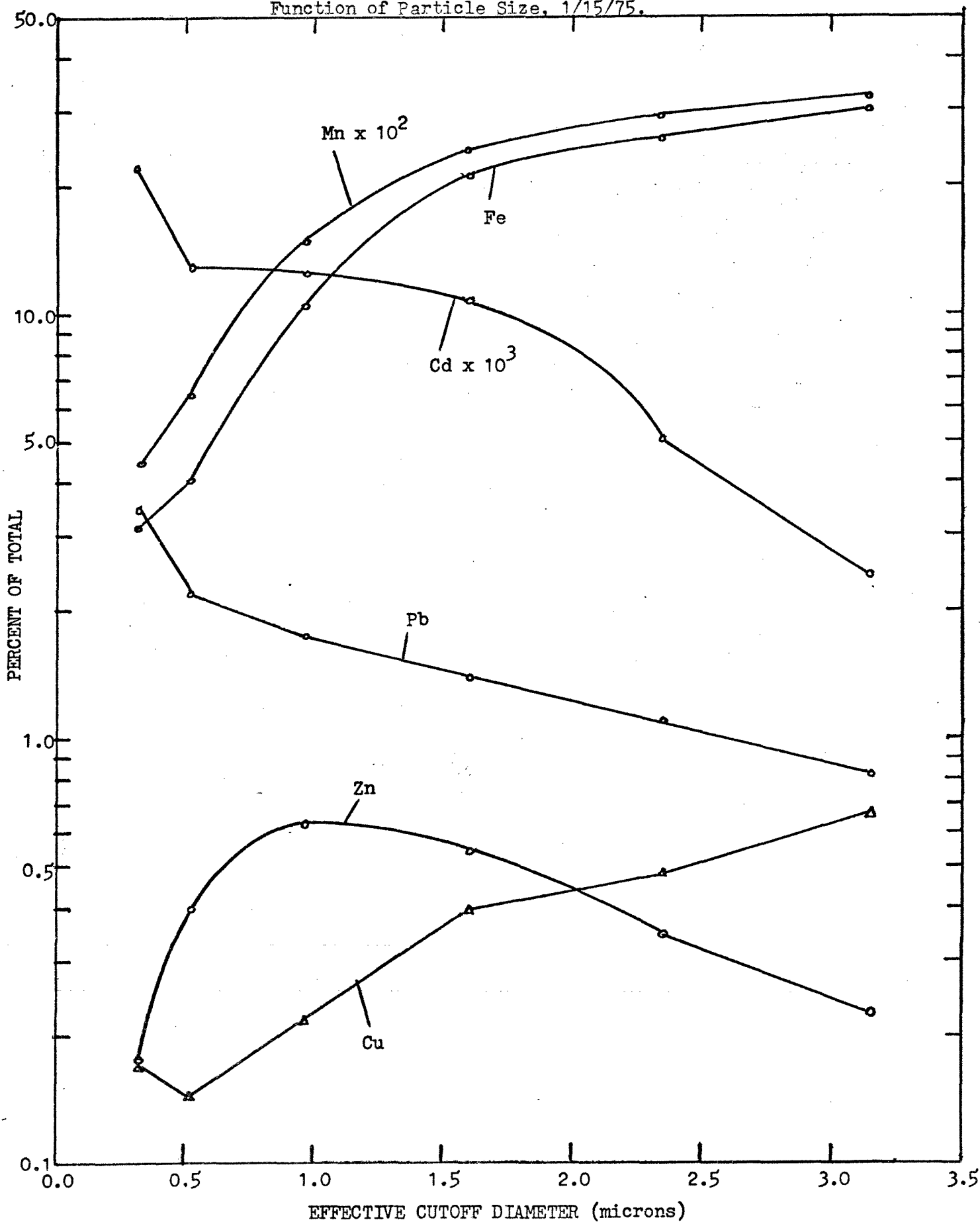
explained by the fact that the main source of copper was located directly above the sampler, and therefore, even the largest copper particles were collected before they settled out.

The size observations made with the MMD data are supported by the interpolated data of percent particle mass less than 1μ . For example, on an overall basis, 55% of the lead-associated aerosol is in the submicron range, while only 7% of the iron-associated aerosol is less than 1μ . This means that although the overall concentration of iron is much higher, both of these metals have similar rates of deposition in the lungs (since these metals have similar concentrations in their submicron fractions).

The constant nature of each metal's size data, as presented in Tables IVa and IVb, demonstrates that each of these metals has a single source (or a few similar-type sources). The regularity of the curves in Figure 8 proves this.

This figure presents the metal composition of the total particulate matter as a function of ECD for a typical run. The graphs give a good indication of the metal percentages usually encountered, since these metal percentages (with the exception of zinc and (occasionally) cadmium) were found to be strikingly uniform on a day-to-day basis; in fact, the percentages for the subway-produced metals in the upper stages, and lead in the lower stages of the air sampler were the same for the

Figure 8. Metal Composition of Total Particulate Matter as a Function of Particle Size, 1/15/75.



rush-hr samples as they were for the 24-hr samples. Since the large majority of the particulate matter remains unidentified⁹ (Figure 8 shows that while iron alone, contributes 30% of the large particles, metals contribute a very small percentage of the submicron particles), the uniformity of the percentages provides an identification of the sources. The constant percentage of lead in the submicron particles indicates that most of these particles are produced from auto traffic, while the large aerosols are shown to be produced mostly by processes involving the subway cars.

It has been shown that the subway-produced aerosols reach more extreme concentration peaks during the rush hours than aerosols produced outside the station. Since the subway particulates are larger in diameter, the shift in the particle size of the total particulate matter towards the larger particles during the rush hours (see Table IIIb) is logical.

Examination of the plots given in Figure 8 provides an indication of the extent to which these metal-associated particles can deposit in the lungs. While iron has a much greater overall concentration than lead, it can be seen from their plots that they have similar rates of pulmonary deposition. This is because iron's inhalation threat decreases with decreasing particle size, while lead's actually increases. Cadmium

⁹On an overall basis, metals constituted 19% of the total particulate matter.

has a plot similar to that of lead, but its concentrations are very much lower, meaning that much less of it would be deposited in the lungs. As with iron, the concentrations of the other metal components decrease sharply in submicron aerosols. (It should be noted that the anticipated size of the particles is taken into account when air quality standards are established.)

APPRAISAL

In considering the health hazard presented by the subway air, the exposure time is all-important. Since most of the air samples were collected over 24-hr periods, the concentrations of the studied pollutants were compared to ambient air quality standards; however no one is exposed to the tunnel air on a round-the-clock basis, and therefore, people can be exposed to contaminant levels higher than the ambient standards, without adverse effects. But even under ambient standards, only the particulate and lead levels could possibly be unacceptable in community air.

Because the subway passengers are exposed to the tunnel air for such a short time, there is no possibility that any of the studied pollutants—at the levels recorded—would present a health hazard for them. The only people who spend any considerable amount of time in the tunnels are the employees of the NCS: the two fare collectors, who work about four hours apiece during the rush hours at the Broad Street station (probably the worst station, as far as submicron particles are concerned); and the maintenance men and the subway conductors, who put in full working days in various places within the subway system.

While it appears, at first glance, that the particulate levels would present a problem for the subway workers (especially since most of them work when the levels are the highest), it should be noted that the ambient standard was established for air which generally has a percentage of submicron particles twice that observed in the subway

environment. Furthermore, a large amount of the particulate matter is in the form of innocuous steel dust. After taking these observations into account, the subway aerosol levels are found to be marginally acceptable for community air, but certainly acceptable for a work environment.

Lead should be treated as a pollutant encountered in the workplace. Therefore, the peak levels of lead should be compared to the TLV for this metal. Since the average rush-hr level of $6.12 \mu\text{g}/\text{m}^3$ does not even approach the TLV of $200 \mu\text{g}/\text{m}^3$ for lead fumes,¹ lead obviously does not pose a hazard for the subway workers.

It has thus been proved that none of the studied pollutants poses a health hazard to the people exposed; however the subway air can not categorically be declared safe. Further surveys of this type are needed in order to determine the concentration of carbon monoxide and ozone in the subway air. Also worthy of some further study are the components of the particulate matter that could not be identified.

¹CAQG—Lead, p. 3.

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APPENDIX

TABLE A. PARTICULATE CLASS INTERVAL DATA

<u>Conc. Range</u>	<u># in Interval</u>	<u>Cum. %</u>
0-70	0	0.0
71-100	1	1.0
101-125	5	5.9
126-150	15	20.4
151-170	12	32.1
171-180	7	38.9
181-190	17	55.4
191-200	8	63.2
201-210	6	69.0
211-220	4	72.9
221-230	9	81.6
231-240	3	84.5
241-250	7	91.3
251-260	4	95.2
261-280	0	95.2
281-300	2	97.1
301-325	2	99.0
326+	<u>1</u>	100.0
	103	

All concentrations (given in $\mu\text{g}/\text{m}^3$) are for 24-hr samples.

TABLE B. DAILY PARTICULATE CONCENTRATIONS (FIG. 5)

<u>Date</u>	<u>24-hr Sample Concentration</u>	<u>Rush-hr Conc.</u>	<u>EPA Conc.</u>	<u>Weather Conditions</u>
11/02/75	34
11/03	...	298	..	Ptly cldy & warm " " " " & hazy
11/05	164	Warm & windy Warm & clear
11/08	34
11/11	...	307	..	Raining & warm Cool, windy, & drizzling
11/13	103	Cool & raining Cold, windy, & snowing ltly
11/14	19
11/17	...	343	..	Sunny & cool Sunny & warm
11/19	254	Cool & cldy with low haze
11/20	85
11/24	...	301	..	Cold & cldy " " "
11/25	227	Cold & cldy " " "
11/26	27
12/01	...	276	..	Cold & raining Cold & ptly cldy
12/02	53

TABLE B. (Continued)

<u>Date</u>	<u>24-hr Sample Concentration</u>	<u>Rush-hr Conc.</u>	<u>EPA Conc.</u>	<u>Weather Conditions</u>
12/03	149	Cold, windy, & ptly cldy Cold, breezy, & ptly sunny
12/08	...	202	..	Cold & cldy Cold, brzy, & raining
12/08	40
12/10	159	Cool, ptly cldy, & windy V. cool, brzy, & cldy
12/14	67
12/15	141	Cool & cldy Cold, cldy, & brzy
12/17	...	275	..	V. cool, ptly sunny, & brzy Cold, clear, & windy
12/20	47
12/22	...	267	..	Cold, cldy, & windy " " " "
12/23	148	Cold, cldy, & windy Cold, clear, & windy
12/26	36
12/29	...	519	..	V. cool, clear, & brzy V. cool, snowing ltly, & brzy
12/30	209	V. cool, snowing ltly, & brzy Cool, cldy, & threat- ening

TABLE B. (Continued)

<u>Date</u>	<u>24-hr Sample Concentration</u>	<u>Rush-hr Conc.</u>	<u>EPA Conc.</u>	<u>Weather Conditions</u>
1/05/76	...	409	..	V. cold, clear, & windy Cold & clear
1/06	257	Cold & clear Cold, cldy, & threatening
1/13	...	333	..	Cold & cldy V. cool, windy, & clear
1/14	191	V. cool, windy, & clear Cold, windy, & cldy
1/20	...	501	..	Cold & snowing hard " " " ltly
1/21	239	Cold & snowing ltly V. cold, windy, & ptly sunny

All concentrations given in $\mu\text{g}/\text{m}^3$.

Starting and ending weather conditions are given.

TABLE C. DAILY CONCENTRATIONS (FIG. 6)

<u>Date</u>	<u>Total Part.</u>	<u>Fe</u>	<u>Mn</u>	<u>Pb</u>	<u>Cd</u>	<u>Cu</u>	<u>Zn</u>
6/20/74	243	17.7	0.220	3.06	0.053	0.467	0.552
6/24	165	28.5	0.340	2.35	0.012	0.518	0.346
6/26	290	42.7	0.617	6.00	0.053	1.163	1.446
7/01	253	44.4	0.508	5.44	0.051	1.315	1.152
7/08	226	37.7	0.409	2.93	0.013	0.672	0.499
7/10	181	26.1	0.293	2.78	0.008	0.551	0.490
7/15	170	19.3	0.225	2.50	0.007	0.787	0.581
7/17	185	21.5	0.284	3.08	0.011	1.022	0.675
7/22	204	25.6	0.322	3.78	0.012	1.192	0.744
7/24	174	26.7	0.352	4.20	0.011	0.750	1.054
7/29	190	29.5	0.409	3.39	0.011	0.725	0.405
7/31	228	28.2	0.355	3.91	0.020	0.916	1.241
8/05	243	35.6	0.446	4.22	0.018	0.947	0.544
8/07	301	45.7	0.542	4.98	0.025	1.035	0.939

All concentrations given in $\mu\text{g}/\text{m}^3$.

Cadmium concentrations are estimates.

TABLE D. SIZE DISTRIBUTION DATA (FIG. 7)

Stage #	ECD (μ)	Cum. % Undersize					
		Part.	Fe	Pb	Cd	Cu	Zn
1	3.156	71.5	50.4	86.8	93.5	51.5	80.3
2	2.344	54.9	25.9	76.6	85.6	30.7	62.6
3	1.594	43.6	12.4	67.8	74.1	19.5	44.0
4	0.969	34.0	6.7	58.5	62.7	14.1	25.5
5	0.531	23.6	4.3	45.6	49.8	10.3	12.7

TABLE E. METAL PERCENTAGE AT EACH STAGE (FIG. 8)

Stage #	% of Total Particulate Wt.					
	Fe	Mn	Pb	Cd	Cu	Zn
1	30.3	0.32	0.82	0.002	0.66	0.23
2	25.7	0.29	1.09	0.005	0.48	0.35
3	20.9	0.24	1.38	0.011	0.39	0.54
4	10.3	0.15	1.73	0.012	0.22	0.63
5	4.1	0.06	2.18	0.013	0.14	0.40
Backup	3.1	0.04	3.42	0.022	0.17	0.18