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Suspended Particulate Matter in New York City: Element Concentrations as a Function of Particle Size and Elevation above Street

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Abstract

Aerosol samples were simultaneously collected at two street-level locations and the 16th floor, on two sides of a Manhattan city block. The results of PIXE analysis, together with CO and SO_2 data, show that the concentrations of substances emitted at street level (CO, Pb, etc) are significantly less at the 16th floor whereas particulate sulfur shows little variation. Other conclusions are presented.

I. INTRODUCTION

Measurement of air pollutants in large cities is essential to establish criteria for setting permissible levels and realistic air-quality goals. The enormous variety in parametric conditions in cities such as New York, make this task very difficult. Samples are collected at only a few locations and usually at rooftop levels (6th to 20th floors) to avoid practical problems encountered at street level. This study was undertaken to investigate the effect of the "canyon" settings typical of NYC, on both the horizontal and vertical circulation of street-level emissions. The distributions of Pb, Br, Fe, Ca, S, CO, and SO_2 as well as other elements were studied in 3 locations in a selected area of mid-town Manhattan. The results show that extrapolation of results from one location to another may be unreliable and that rooftop measurements do not indicate conditions at street level.

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II. EXPERIMENTAL PROCEDURE

A. Sampling

In this project, we decided that a three-point profile with respect to height and location would provide interesting information on the characteristics of the aerosol at Rockefeller Center, located in the center of Manhattan (Fig 1.) and typical of the midtown area. The sampling locations were chosen to explore both the effects of height and N-S vs. E-W streets (see Fig. 2.). The first sampler was located in a wooden shed approximately mid-block between 50th and 51st streets on 6th Ave. The impactor was about 1-2 feet from the curb and about 3 feet above street level. The surrounding area contains tall skyscrapers lining both sides of the street for many blocks in either direction. Traffic on 6th Ave. (3000-4000 vehicles/hr. during the day) rarely exceeds 20 mph and considerable time is spent idling at traffic lights. We estimated that 50% of all vehicular traffic in this area (and probably true of mid-town generally) is composed of taxi cabs, another 10% is due to busses except during rush-hour when the number of express busses entering and leaving the area increases. In addition, the 6th Ave. subway is located below street level with ventilating grids on both sides of the street. The traffic density increases from 7 a.m. to 8:30 a.m. and then levels off until around 4 p.m., when the commuter busses begin arriving. This rush-hour mode continues until around 6:30 p.m. after which traffic again becomes very light. The pattern is similar for 51st St., except that there are no busses.

The impactor on 51st St. was also housed in a shed as on 6th Ave. The "canyon" environment is also prevalent on 51st St. with many tall buildings lining each side of the street, traffic flow is about 1/4 that of 6th Ave. Also, there was less idling near the sampling shed because cross-town blocks are longer than avenue blocks and stopped traffic does not reach to the sampling site. The elevated sampling site was an open ledge on the 51st St. side of the top floor of 50 Rockefeller Plaza about 100 feet east and 16 floors above the ground-level site. Meteorological conditions on the 16th floor were somewhat different from ground level; temperatures were generally somewhat cooler (about 2 degrees on the average) than ground level and winds tended to be stronger. During the period July 19 to July 29, 1977, samples were collected on seven weekdays for 3 consecutive 2-hour intervals (pre, mid, and post-rush hour) either morning or afternoon, simultaneously at each location.

The above sampling configuration at Rockefeller Center enabled determination of the extent of atmospheric mixing from ground level to the 16th floor. The two ground-level stations allowed the extent of ground-level mixing to be determined. This information is, of course, important in answering the question of whether a sample at a particular elevated location is representative.

The collectors used were 6-stage cascade impactors (model DCI-6, Delron Inc.) operating at 13.0 l/min with stages 1 through 6 having 50% collection efficiencies for particles of 16, 8, 4, 2, 1, 0.5 µm, respectively. Samples were collected on 0.1 mil Mylar film, prewashed to reduce Zn, and coated with Vaseline to prevent bounce-off of particulates. The Mylar film, tightly stretched between two brass rings, was supported from behind by a piece of nylon to prevent distortion of the surface by the impinging jet stream during sampling.

The rings were removed after sampling and placed in a dust-proof sample holder for transport back to a clean area for slide mounting. The samples were mounted with a die-cut, self-adhesive, acetate backing which exactly fits the 2 x 2 mounts used in the sample changer. Once in place, the acetate backings were heat sealed inside the mounts and labeled for future analysis. The samples were stored until they were ready to be analysed.

B. PIXE System

A homogeneous proton beam (1 cm diameter) was obtained from the Brooklyn College Dynamitron (a 3.75 MeV Cockroft-Walton type accelerator) by scattering through a W foil and collimation. The beam enters the target chamber, which is under a slight positive He pressure, through a 1 mil Kapton window.

The target chamber contained the sample changer, a modified Carousel projector with lens, etc removed and so mounted that the emerging beam was 4 cm from the target. The Kapton window mounted on the end of the beam tube protrudes inside the chamber to a depth of about 6 in. The positive He pressure decreases the proton scatter, eliminates argon x-rays, eliminates charge build-up, and cools the samples during bombardment.

The Si(Li) detector was situated at 45 degrees from the front surface of the target about 6 cm away. The targets were dropped into the beam using the modified projector, remotely activated from the control room. A remote TV camera monitored which of the 80 slides in the storage tray was in the beam. Beam-current integration was achieved using a graphite-lined Faraday cup sealed at the open end with 0.1 mil Mylar and located directly behind the target. All spectra were collected for a predetermined accumulation of charge with system dead time taken into acount. With a proton current of 100 namps, each analysis took about 3 min.

C. Standards Preparation

Aliquots of carefully analysed solutions of a number of elements were evaporated on Mylar films and mounted in the same manner as the air samples. These standards were analysed by PIXE and the results were used to establish a calibration curve(counts vs. mass) for the range of elements determined. The precision of replicate samples and replicate analyses of the same standard samples was better than 5%. Standards were analysed before and after each set of samples.

III. RESULTS

A. Pollutants traceable to vehicular traffic:

CO, Pb, Br are three major tracers which can be used to monitor vehicular contributions to urban aerosols. CO was continuously measured (Ecolyzer) by the NYC Dept. of Environmental Protection at each location and 1-hour averages were determined (Fig. 3). These averages indicate a definite morning rush-hour pattern for all three locations, with the greatest change in CO levels occuring at 51st St. The effect of workday traffic can be seen as CO concentration levels at all these locations do not decrease to pre rush-hour levels until late evening. This indicates that the general air mass below rooftop levels has a "turn-over" period which is comparable with the rate of CO input sources. In addition, CO levels at the 16th floor only slightly reflect the large changes that can occur at street level. For example, from the 51st St. rush-hour peak of 13.6 ppm at 8-9 a.m. to 3.8 ppm at 8-9 p.m. there is a decrease by a factor of 3.6 whereas, for the same period the 16th floor changes by a factor of only 1.6. Thus, the very dramatic differences on 51st St. are greatly reduced as the air mass rises to the 16th Fl. A possible explanation for the "negative" afternoon rush-hour trend on 51st St. would be a smaller flow of westbound traffic in the afternoon compared to the morning.

We can see a striking difference in the daily trends on 6th Ave. compared to 51st St. Although the morning rush hour increase is not as pronounced as on 51st St., possibly due to the fact that the avenue is at least twice as wide as the side street, or that morning traffic may flow more in a cross-town direction towards the inner city than uptown, the afternoon rush-hour tells a very different story. Accumulation of CO at street level throughout the day culminating in a 4 p.m. rush-hour concentration 50% higher than the morning concentration also indicates very poor mixing of the local air mass. Finally, the significant differences that can occur between locations just around the corner from each other indicate that lateral mixing is also very slow compared to input source rates.

The fact that the 16th Fl. morning rush-hour peak in CO occurs at the same time as the peak on 51st St. indicates that the impact of increased emissions travels rapidly upwards but that the ensuing dilution reduces the concentration by a factor of 4. It may be that the mixing of the air mass on 51st St. and 6th Ave. occurs by the time it rises to the 16th Fl., although the trend on the 16th Fl. resembles the 51st St. results more closely. It is, on the other hand, quite possible that the CO concentration 16 floors above 6th Ave. will differ to the same extent as the two ground level sites but we have no such evidence.

These results emphasize the difficulty in obtaining truly representative samples. For example, the present federal standard for CO, (8 hr. averages to be less than this value 100% of the time), is 9 ppm. For July, 1977, the data at rooftop levels indicates New York is safely within the federal guidelines, the 51st St. data indicate federal standards are exceeded for the morning 8 hr. average (4 a.m.-12 noon) but not for the afternoon, and 6th Ave. data indicate federal standards are violated 100% of the time during the working day.

Pb and Br

On the basis of 377 analysed samples the ratio of Pb and Br was 4.11 ± 1.07 for the morning samples, 4.01 ± 1.10 for the afternoon, while for stage 6 the ratio was 5.20 ± 1.79 for the morning and 5.20 ± 1.19 for the afternoon. Fig. 4 shows the range of concentrations for morning and afternoon samples. It can be seen that levels of Pb and Br were higher on 6th Ave. than on 51st St., which in turn were higher than on the 16th Fl. The differences were not as great as they were for CO. The mass distributions for Pb and Br are shown in Fig. 5. They all seem to indicate a multi-modal nature to the Pb and

Br particles. Bromine and Pb correlate well with each other through all particle size ranges. The multi-modal nature might best be explained by Habibi's suggestion[1] that flush-out of the exhaust system under acceleration might be responsible for the release of large particles (related to exhaust-system erosion) upon which the lead salts have condensed.

To summarize, simultaneous sampling of CO, Pb, and Br at three different locations indicates;

a) poor vertical mixing of local aerosol
b) poor lateral mixing of local aerosol
c) pollutant levels vary with traffic patterns
(i.e., Aves. vs. Sts.)

B. Pollutants not traceable to vehicular traffic.

S,Cl,K,Ca,V,Ti,Mn,Fe,Cu,Zn, have been analysed at each of the locations. The nature and concentration levels of these elements of the aerosol are very similar in nature for all three locations and compare well with those found by Kneip and Eisenbud[2]. Two significant observations warrant discussion.

Iron

Previous studies of urban aerosols generally attribute Fe to automobiles in areas where steel or heavy industry are absent. In the former case where Fe is being produced almost exclusively from vehicle exhaust systems the Fe levels tend to be lower than the Pb levels. The 51st St. and 16th floor locations indicate this type of behavior. However, 6th Ave., with concentration levels an order of magnitude higher in some cases indicates a completely independent source of iron. The source of iron follows a definite rush-hour pattern unlike that of lead or any of the other species analysed. While vehicles are certainly recognized as a source of iron, such high concentrations varying independently from those of lead can only indicate another source on 6th Ave. at ground level. One possible answer is the 6th Ave. subway system. There are numerous entrances and ventilation gratings in the immediate vicinity of our sampling location. The levels of iron measured on 6th Ave. appear to correlate well with actual subway traffic. A verification of this source could be obtained by taking a sample below street level in the subway itself, but such a test has not yet been possible. Fig. 6 shows the dramatic rush-hour trends for iron on 6th Ave. as compared with Pb and Br and also to 51st St and 16th floor.

Sulfur:

Sulfur is present in New York air in both gaseous and particulate forms. The NYC Dept. of Environmental Protection measures SO_2 hourly at stations throughout the city. We have examined the readings for several of these stations (Fig 7.) and compared the trends with the level of S in particulate matter. The major sources of SO_2 during the summer are generally acknowledged to be the power generating plants located within the metropolitan area and hot-water heating. The levels of SO_2 generally ranged anywhere from 1 to 75 ppb during the sampling period. Fig. 7 shows the concentration of SO_2 on an hourly basis for the month of July at the representative stations chosen. In addition, the wind speed and direction for the corresponding hours of sampling is also plotted.

Particulate sulfur shows a different type of behavior from that of SO_2; the evidence (Fig. 7, Table 1) indicates that SO_2 and particulate S in NYC come from different sources. Our data (Table 1.) indicate that no local source of particulate sulfur was responsible for the high levels that were seen on some days. When particulate sulfur levels were high all three stations report analogous readings indicating no dilution effect (i.e. not emitted at ground level).

A preliminary analysis of these data indicates that, in general, SO_2 concentrations are relatively insensitive to wind direction compared to those of particulate sulfur. The latter decrease at a significantly greater rate as the wind shifts from west to east than do ambient SO_2 concentrations. This reinforces the idea that ambient SO_2 concentrations reflect local sources whereas the particulate S measured in the city is produced to a great extent during transport from sources to the west[3]. Experience in New York City has shown that severalfold reductions in ambient SO_2 concentrations have been accompanied by relatively minor reductions in particulate S concentrations.

The data also indicate that the particulate S contribution from street-level sources, i.e., motor vehicles, is much less than that from other sources. It can be seen from Table 1 that when particle S is low, the amount at ground level tends to be higher than at the 16th floor, possibly indicating a street-level source. A more conclusive investigation is needed to verify a local contribution.

Acknowlegement

We would like to thank John Sontowski, Ben Nathanson, Harold Nudelman and the staff of the N.Y.C. Department of Environmental Protection and Armand Gazes of the Brooklyn College Data Acquisition Center for their cooperation in this study. This work was partially supported by the Dept. of Energy, Division of Basic Energy Sciences, under Contract No. E(11-1)-3126.

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2. M.Eisenbud, T. Kneip, "Trace Metals in Urban Aerosols", prepared for Electric Power Research Instit.,EPRI 117, by New York University, Oct 1975.
3. J. W. Winchester, et. al., this volume.

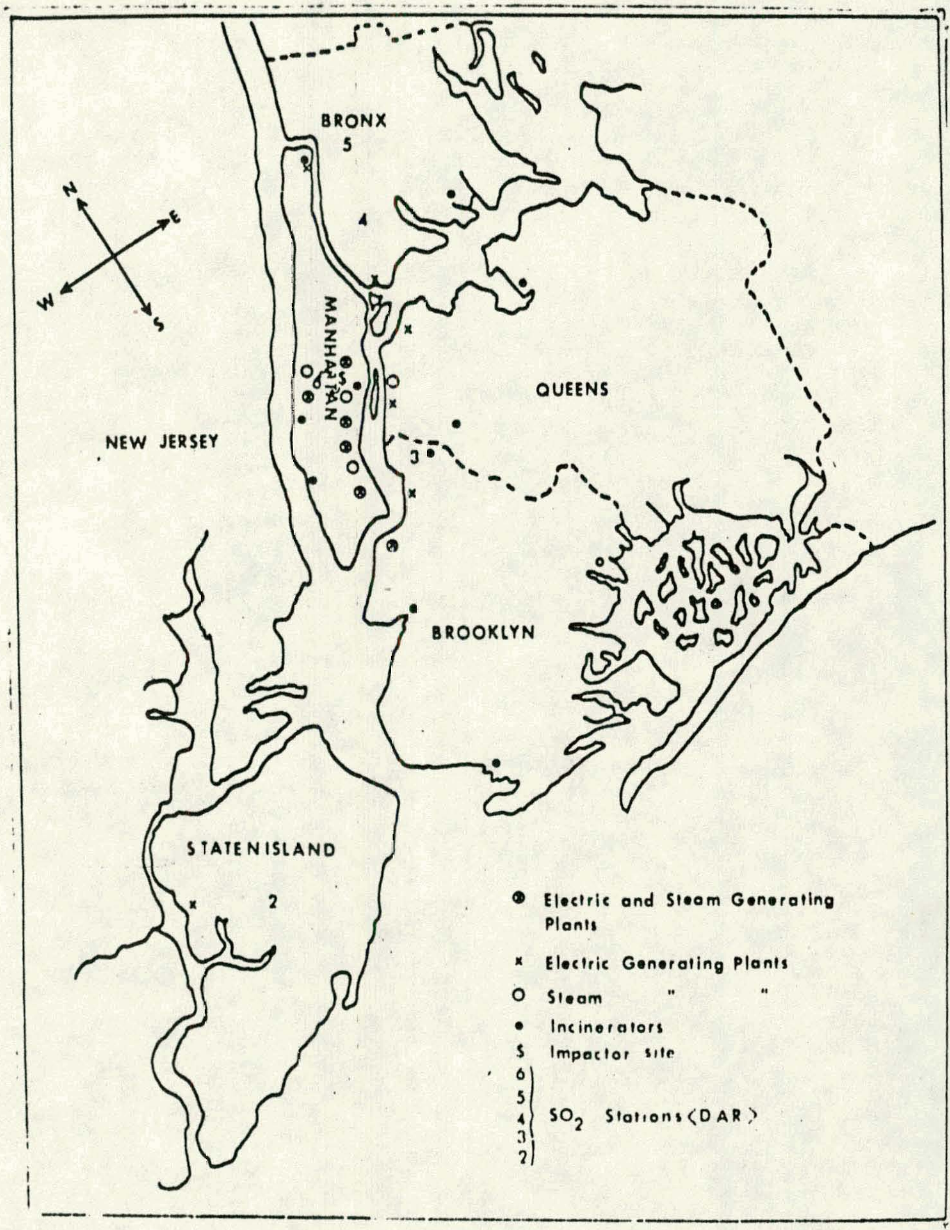
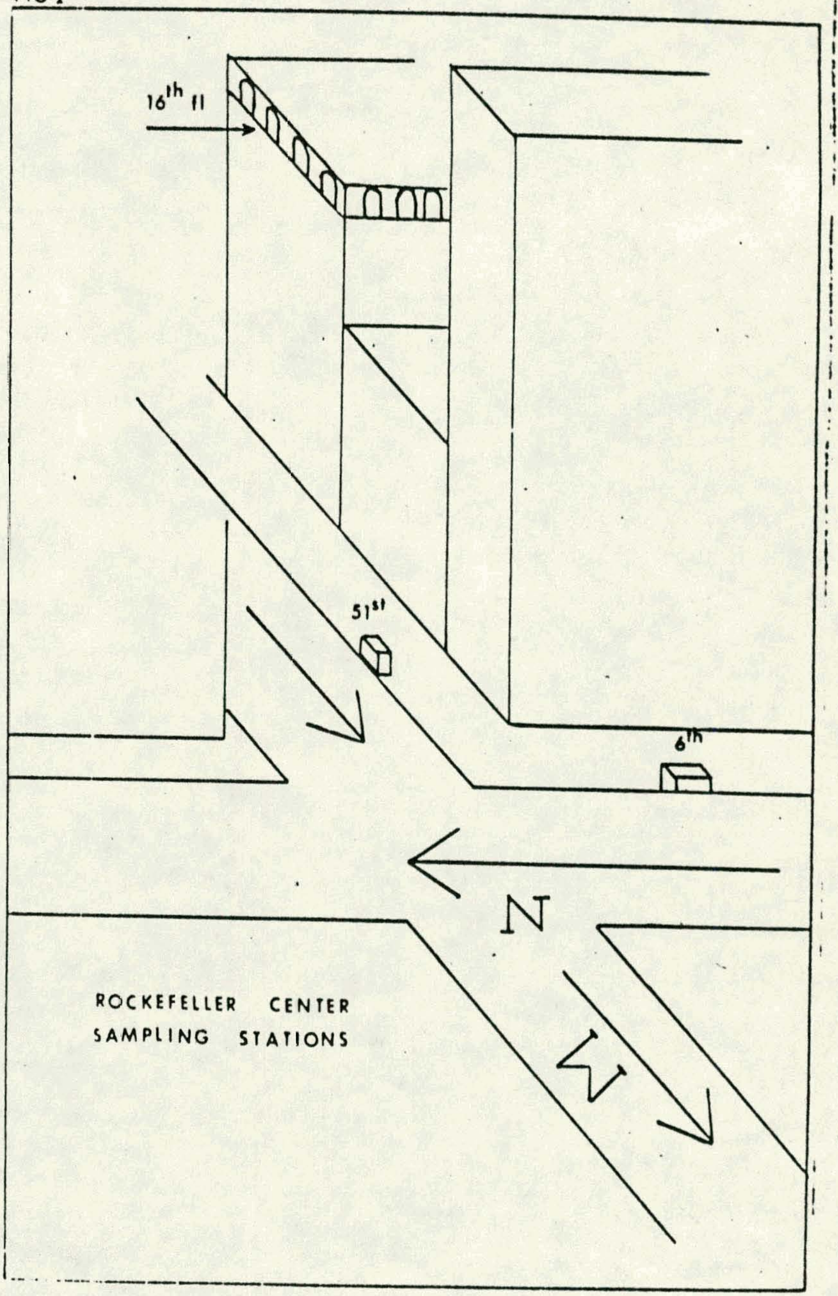


FIG 2



ROCKEFELLER CENTER
SAMPLING STATIONS

FIG. 3

Average Hourly CO Concentrations for Weekdays of July 1977

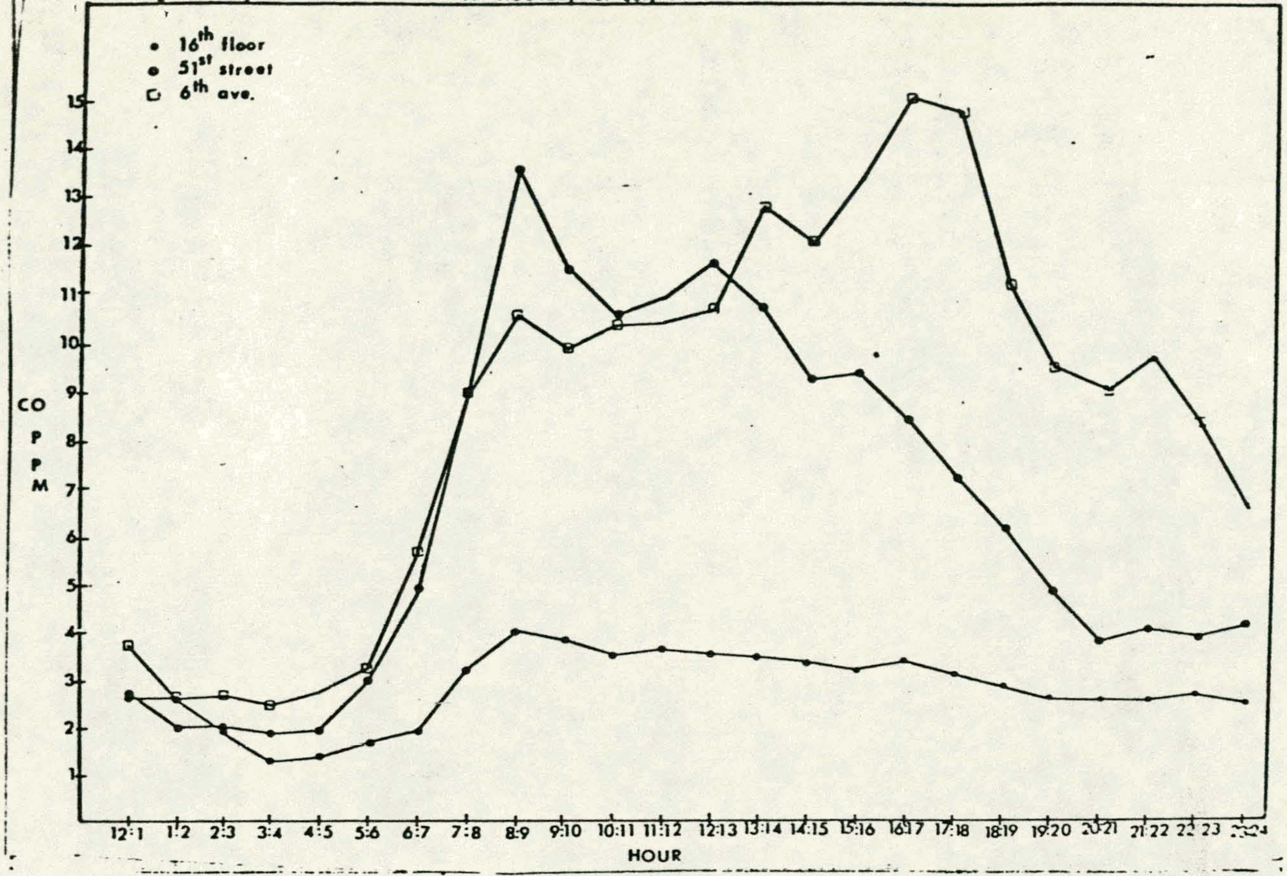
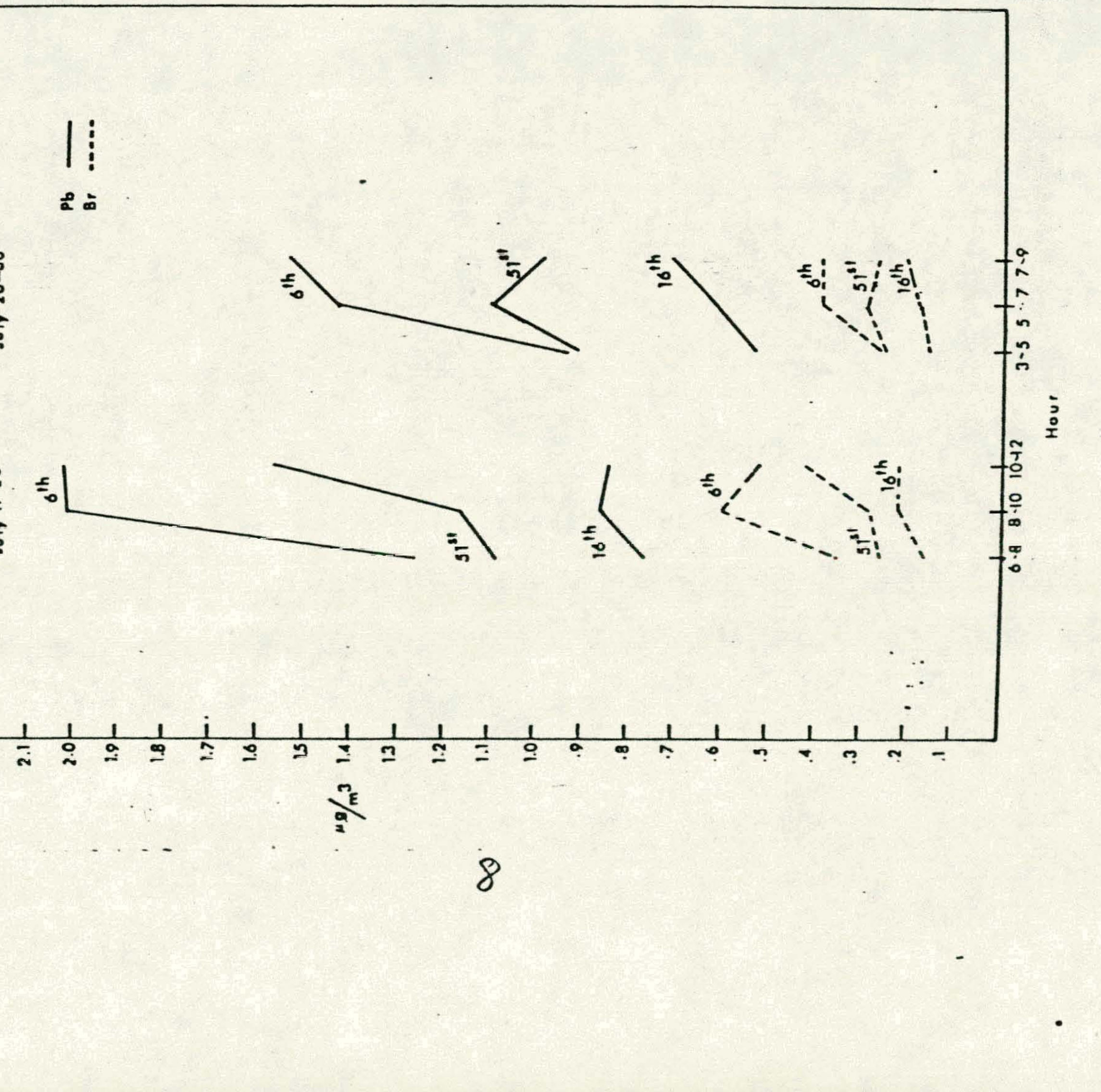


FIG. 4

Diurnal Variations in Average Conc. Pb & Br



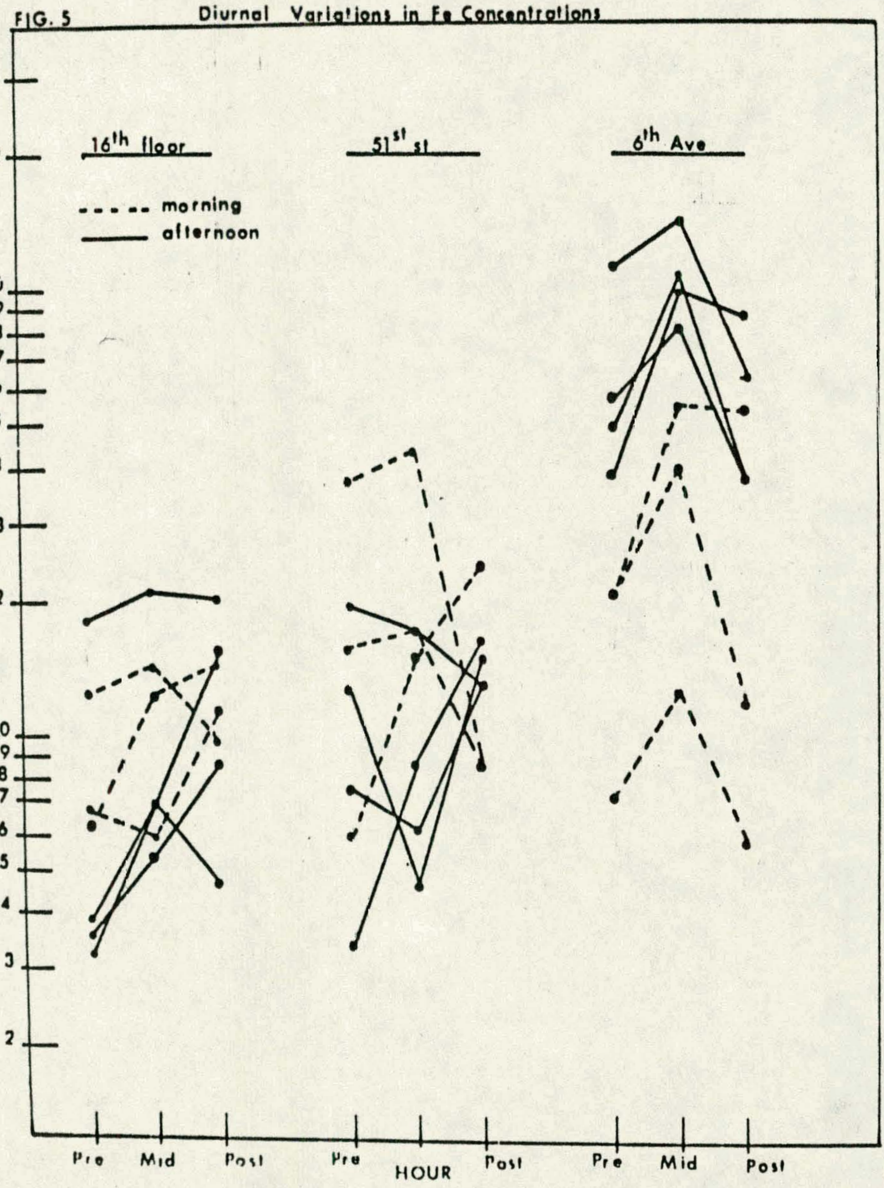


FIG. 5 Diurnal Variations in Fe Concentrations

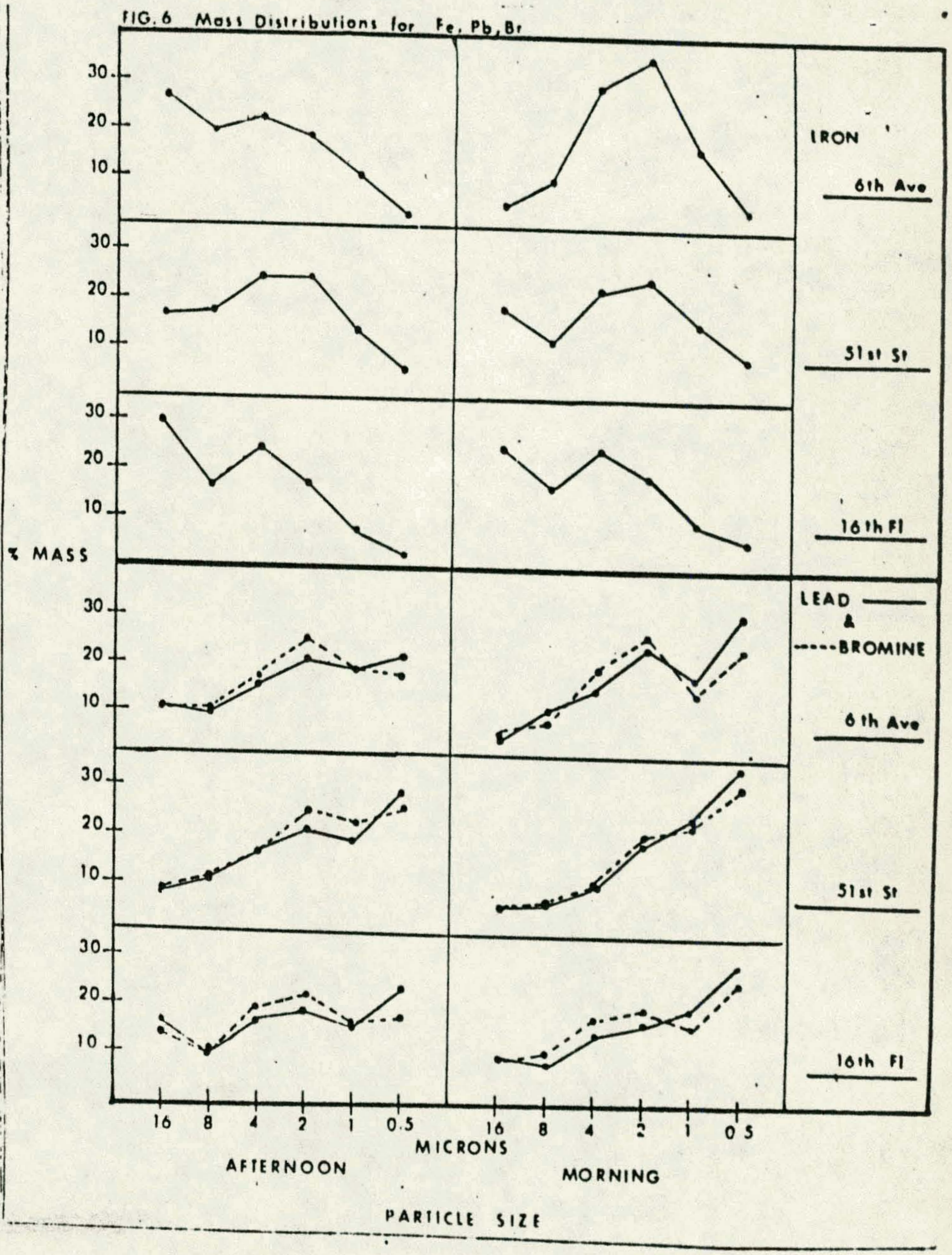


FIG. 6 Mass Distributions for Fe, Pb, Br

TABLE I

CORRELATION OF PARTICULATE SULFUR WITH WIND DIRECTION

(ng/m^3)

A) WINDS FROM S to SW

SITE	JULY 19th AFTERNOON			JULY 20th AFTERNOON			JULY 21st AFTERNOON			JULY 25th MORNING		
	PRE	MID	POST	PRE	MID	POST	PRE	MID	POST	PRE	MID	POST
16	2140	5249	6875	2567	6101	7605	5146	8520	5964	< 50	473	764
51	2217	3116	5987	1380	4704	6382	8540	10618	6120	1097	817	1440
6	1819	5771	9624	1626	6697	11632	6508	10145	4244	654	1395	2337

B) WINDS FROM NW to SE

	JULY 22nd AFTERNOON			JULY 27th MORNING			JULY 28th MORNING			JULY 29th MORNING		
	PRE	MID	POST	PRE	MID	POST	PRE	MID	POST	PRE	MID	POST
16	72	61	111	1127	638	722	1126	1401	1340	755	765	844
51	477	340	249	1106	939	1468	1356	1386	2040	924	925	921
6	350	252	98	1665	1707	1637	1468	....	1475	1095	1541	977

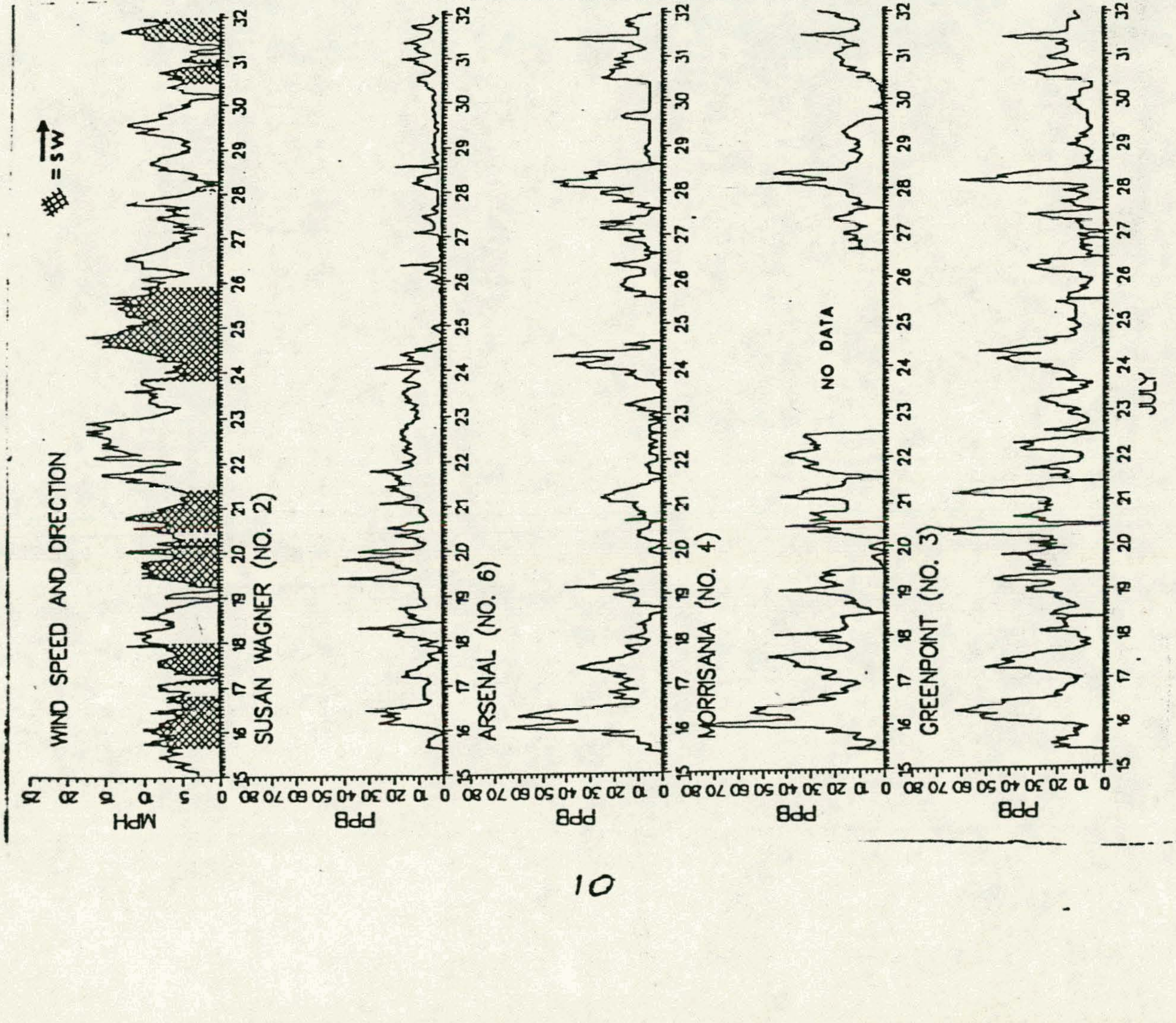


FIG. 7 Correlation of SO_2 with Wind Direction