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# **Potential Causes Of Elevated PM<sub>10</sub> And PM<sub>15</sub> Concentrations In The Inhalable Particulate Network**

EPA-450/4-84-016  
June 1984

# Potential Causes Of Elevated PM<sub>10</sub> And PM<sub>15</sub> Concentrations In The Inhalable Particulate Network

By  
C. Fred Rogers  
And  
John G. Watson

Desert Research Institute  
Reno, NV 89506

Project Officer: Thompson G. Pace  
Purchase Order 3E2117NAEX

U.S. ENVIRONMENTAL PROTECTION AGENCY  
Office Of Air And Radiation  
Office Of Air Quality Planning And Standards  
Research Triangle Park, NC 27711

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## ABSTRACT

This report discusses and characterizes 50 high  $PM_{15}$  site-days selected from the Inhalable Particulate (IP) Network over the years 1979 to 1982. The study is intended to characterize the potential causes of high  $PM_{10}$  concentrations in the U.S.; therefore, the correlation between  $PM_{10}$  and  $PM_{15}$  levels is shown and discussed. The available  $PM_{10}$  data are too sparse to support the study by themselves. The  $PM_{15}$  data from the IP Network were analyzed with respect to five hypothetical causes of elevated concentrations: 1) local industrial emissions; 2) local non-industrial emissions; 3) regional secondary particle events; 4) meteorological factors, such as stagnation and inversions; and 5) measurement anomalies.

Local industrial emissions were found to contribute to some degree in 48% of the valid cases and nearly all of them were at industrial site-types. Evidence of non-industrial source contributions was found in 56% of the cases at industrial, commercial, residential and agricultural site-types. This implies that industrial sources cannot be singled out as the sole contributors to elevated  $PM_{15}$ , even at industrial site-types. It was not possible, given the existing data, to support the concept of regional-scale events, but very high secondary aerosol contributions to  $PM_{15}$  were observed in 21% of the cases, mostly in the eastern U.S. Seventy-five percent of the valid high  $PM_{15}$  concentrations were associated with meteorological situations which limited the dispersion of pollutants. Twenty percent of the fifty  $PM_{15}$  values examined here were attributed to measurement anomalies.

#### ACKNOWLEDGEMENTS

The authors are grateful to Mr. Ed Barrows and Ms. Gail Prichard of Northrop Services in Research Triangle Park for their help in obtaining IP Network data. Mr. Harold Klieforth of Desert Research Institute provided meteorological data and valuable insight into its interpretation. Dr. Joe Walling, Mr. Warren Loseke, and Mr. Sam Cummings of EPA and Dr. Joseph Jaklevik of Lawrence Berkeley Laboratories supplied details of the analytical procedures which allowed consideration of the measurement processes in this data interpretation effort. Ms. Elaine Tanski and Ms. Nanette Ralph of Desert Research Institute typed, edited, and assembled this report.

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## SECTION 1

### INTRODUCTION

#### BACKGROUND

The Environmental Protection Agency had proposed a primary ambient air quality standard which would control particles smaller than 10 microns ( $PM_{10}$ ) rather than total suspended particulate (Federal Register, 1984). The proposed standard would allow  $PM_{10}$  concentrations in an air quality maintenance area to reach an annual arithmetic average between 50 and 65  $\mu g/m^3$  or a 24-hour average in excess of 150 to 250  $\mu g/m^3$  (Federal Register, 1984).

The current primary standard for Total Suspended Particulate (TSP) Matter, which nominally consists of particles in the 0 to 50 micron size range, is 75  $\mu g/m^3$  annual geometric average and 260  $\mu g/m^3$  over 24 hours not to be exceeded more than once per year. It has been hypothesized that the ten micron standard may be more lenient than the existing TSP standard with respect to the annual average (Environmental Reporter, 1983), and that the 24 hour standard for  $PM_{10}$  may be more difficult to meet than the annual standard in most urban areas. The goal of the work presented here is to examine elevated concentrations in EPA's Inhalable Particulate (IP) Network and to identify, to the extent possible, the causes of high 24-hour concentrations of particulate matter in various size fractions.

## OBJECTIVES

This study has three objectives:

1. Determine which data from the IP Network can be used to characterize days with high  $PM_{10}$  concentrations.
2. Devise a procedure for characterizing the high  $PM_{10}$  days by meteorological and chemical data such that emissions and meteorological causes may be identified.
3. Apply the characterization procedure to the high concentration days which have been identified.

## AVAILABLE DATA BASES

The IP Network was established in 1979 and is described by Rodes (1979) and Watson et al. (1981). The measurements contained in its data base have been examined by a number of researchers (e.g. Watson et al., 1981; Suggs and Burton 1983; Chow et al., 1981; Chow et al., 1982; Watson et al., 1983; and Trijonis, 1983). The data examined for this report were complete through 1982. The IP Network was established to 1) obtain statistical distributions of size-classified mass and chemical species, and 2) develop and test procedures for compliance monitoring. Its data were not specifically intended for determining the causes of elevated concentrations. It is fortuitous that such conclusions can be drawn from its measurements, though they must be considered speculative until specifically designed studies are carried out to confirm them.

At most sites particle mass concentrations are measured in the 0 to ~50  $\mu m$  size range (HIVOL) with standard hivol samplers, in the 0 to 15  $\mu m$  size range (SSI) with McFarland size-selective inlets and hivol blowers, and in the 0 to 2.5  $\mu m$  (FINE-15) and 2.5 to ~15  $\mu m$  (COARSE-15)

ranges with Sierra 244 and Beckman SAMPLAIR dichotomous samplers. The sum of FINE-15 and COARSE-15 is designated PM<sub>15</sub>. Beginning in 1982, samples at fifteen sites were taken in the 0 to 2.5  $\mu\text{m}$  (FINE-10) and 2.5 to 10  $\mu\text{m}$  (COARSE-10) size ranges with Sierra 244 dichotomous samplers equipped with the new Sierra 246 inlet, modified from the original 15  $\mu\text{m}$  design of Liu and Pui (1981). The sum of FINE-10 and COARSE-10 is designated PM<sub>10</sub>. HIVOL and SSI filter media consisted of Gelman micro-quartz in 1979, and Schleicher and Schuell HV-1 glass fiber for 1980 through 1982. All dichotomous samples were taken on 37 mm Ghia ringed Teflon filters.

Samples were taken at most sites on a schedule of once each 6 days and were analyzed gravimetrically for mass concentrations. Chemical analyses were performed on approximately one-quarter of all samples and were available through 1982. Reported chemical concentrations on the HIVOL and SSI samples, as measured by optical emission spectroscopy, are Ba, Be, Cd, Fe, Mn, Mo, Ni, Pb, V, and Zn.

Chemical concentrations on the dichotomous samples measured by x-ray fluorescence are Al, Si, S, Cl, K, Ca, Ni, V, Mn, Fe, Cu, Zn, Br, and Pb, and by automated colorimetry are sulfate and nitrate. The photon induced energy dispersive x-ray emission technique used for these analyses has not been standardized. Though within-laboratory replicate analyses for these species shows close agreement, very limited experience indicates that large inter-laboratory differences can exist. Only results for Br, Cu, Fe, Mn, Pb, V, and Zn have been found to be

relatively independent of the laboratory performing the work and are routinely included in the IP Network data base. Other elemental concentrations, specifically Al, Si, S, Cl, K, Ca, and Ni are measured by x-ray fluorescence at levels above detection limits. Such measurements are not normally reported owing to their lack of comparability. These data were obtained for this study to aid in the identification of aerosol sources. They will be used with full realization of their limitations.

Site surveys for those sites which are included in the National Air Monitoring System (NAMS) were also obtained in order to identify potential nearby sources of particulate matter, such as open fields, residential heating, motor vehicle exhaust, and vehicle resuspended dust.

Daily weather maps and vertical temperature soundings were obtained from the National Weather Service for the days and urban areas selected in this study.

This introductory description of the routine data acquired for this study does not adequately reflect the complexities of using it as part of a valid scientific methodology. In the following sections, the interpretation of these data will be integrated with an examination of the measurement processes through which they were derived in order to differentiate between high concentration values which are truly attributable to an environmental cause and those which, in all probability, result from the measurement process itself.

## CONTENTS OF THIS REPORT

This introduction states the objectives of the study, briefly describes the measurements on which the study is based, and previews its contents. In Section 2 a rationale is given for the use of  $PM_{15}$  measurements in place of  $PM_{10}$  measurements for selecting high concentration days. Only 235  $PM_{10}$  samples taken at 15 sites are available from the entire IP Network through 1982, and few of these are characteristic of high concentration days. Section 3 describes the IP Network data reports and the way in which they were used in this study. The high concentration days and locations selected from them are specified. Sections 2 and 3 accomplish the first objective.

In Section 4, the methodology for using the data is described. Several hypotheses concerning the causes of elevated concentrations are advanced. This results in the attainment of Objective 2.

The high concentration site-days specified in Section 3 are examined in Section 5 to determine which of the hypotheses advanced in Section 4 they support. Summary tables which unify data from the various data reports and descriptions of each case are presented in an appendix. The final objective of this study is then attained.

The final Section 6 summarizes the results of the study, presents its conclusions, and provides recommendations for further data analysis.

## SECTION 2

### IP NETWORK PM<sub>10</sub> CONCENTRATIONS

As noted in Section 1, only 235 PM<sub>10</sub> measurements have been made at 15 sites in the IP Network. None of these samples have undergone chemical speciation, and very few of them are associated with the sites or the days which appear to possess the highest pollution levels. Despite its limitations, this PM<sub>10</sub> data base needs to be examined in order to: 1) compare PM<sub>10</sub> mass concentrations with those which might comprise a national standard, and 2) determine whether or not conclusions drawn with respect to PM<sub>15</sub> might also apply to PM<sub>10</sub>.

### AVERAGES AND RANGES OF PM<sub>10</sub> CONCENTRATIONS

Table 2-1 lists the PM<sub>10</sub> sampling sites (with corresponding SAROAD codes), the number of PM<sub>10</sub> samples taken during 1982 at these sites, and, among other information, the arithmetic average, standard deviation, and range of PM<sub>10</sub> concentrations at each site for which there were greater than ten values. The PM<sub>10</sub> averages and ranges reported here were derived from the subset of individual PM<sub>10</sub> concentrations which corresponded to simultaneous PM<sub>15</sub> or SSI concentrations. These PM<sub>10</sub> averages ranged from 20  $\mu\text{g}/\text{m}^3$  at Research Triangle Park, NC, (which only had samples during the summer) to 75  $\mu\text{g}/\text{m}^3$  at Rubidoux, CA.

If a 65  $\mu\text{g}/\text{m}^3$  annual average were established as a national standard, these data show that Rubidoux might be in danger of exceeding it. Phoenix would also exceed an annual standard with a 50  $\mu\text{g}/\text{m}^3$  value. The

TABLE 2-1  
PM<sub>10</sub> SAMPLING SITES AND CONCENTRATIONS  
IN THE IP NETWORK

Site	SAROAD <sup>a</sup>	No. of PM <sub>10</sub> Samples	Simultaneous PM <sub>15</sub> Samples	Inclusive Dates	SSI <sup>a</sup> ( $\mu\text{g}/\text{m}^3$ )	PM <sub>15</sub> <sup>a</sup> ( $\mu\text{g}/\text{m}^3$ )	PM <sub>10</sub> <sup>a</sup> ( $\mu\text{g}/\text{m}^3$ )	PM <sub>10</sub> /SSI <sup>a</sup>	PM <sub>10</sub> /PM <sub>15</sub> <sup>a</sup>
M. Birmingham, AL	010380023	30	SSI - DICHOT	11/3/82 to 11/25/82	80 + 44 38 <sup>b</sup> to 233 <sup>c</sup>	70 + 44 30 <sup>b</sup> to 182	61 + 43 26 to 173	0.70 + 0.15 0.52 to 1.14	0.85 + 0.11 0.57 to 1.02
Phoenix, AZ Roosevelt St.	030600002	37	SSI - DICHOT	1/29/82 to 12/13/82	74 + 29 22 <sup>b</sup> to 132	52 + 21 12 <sup>b</sup> to 87	39 + 17 12 <sup>b</sup> to 79	0.52 + 0.10 0.19 to 0.68	0.76 + 0.13 0.48 to 1.08
Rubidoux, CA Mission St.	056535001	36	SSI - DICHOT	2/4/82 to 12/19/82	100 + 43 20 to 168	94 + 41 18 to 158	75 + 31 17 to 115	0.76 + 0.15 0.55 to 1.22	0.80 + .08 0.67 to 0.94
Pueblo, CO	061820001	1		12/19/82	d	d	d	d	d
Boise, ID File Sta. 6	130220003	2		12/1/82 & 12/13/82	d	d	d	d	d
Omaha, NB O St.	281880028	2		12/7/82 & 12/13/82	d	d	d	d	d
Reno, NV Kirman St.	290480001	2		12/7/82 & 12/13/82	d	d	d	d	d
Buffalo, NY PS 28	330660010	28	SSI - DICHOT	3/18/82 to 12/1/82	63 + 26 26 to 141	46 + 20 <sup>c</sup> 13 to 85	40 + 18 12 to 80	0.62 + 0.11 0.41 to 0.92	0.86 + 0.11 0.55 to 1.03
Durham, NC Magnum St.	341160006	2	SSI - DICHOT	10/2/82 & 11/19/82	d	d	d	d	d
RTP, NC	341160102	13	SSI	5/17/82 to 8/15/82	37 + 12 23 <sup>b</sup> to 53 <sup>c</sup>	d	20 + 9 11 to 33	0.55 + 0.22 0.33 to 0.83	d
Youngstown, OH	367760002	5		12/1/82 to 12/25/82	d	d	d	d	d
N. Braddock, PA Anderson St.	396620001	33	SSI - DICHOT	1/23/82 to 12/18/82	61 + 24 31 to 127	41 + 21 17 to 127	40 + 23 16 to 127	0.58 + 0.06 0.51 to 0.67	0.96 + 0.11 0.75 to 1.17
Philadelphia, PA 500 S. Broad	397140003	29	SSI - DICHOT	3/6/82 to 12/19/82	54 + 19 19 to 100	38 <sup>c</sup> + 17 12 to 79	34 + 14 11 to 66	0.60 + 0.09 0.39 to 0.86	0.86 + 0.10 0.63 to 1.04
El Paso, TX Tillman Health	451700002	3		12/1/82 to 12/19/82	d	d	d	d	d
Houston, TX	452560034	12	SSI - DICHOT	3/24/82 to 9/2/82	71 + 19 51 <sup>b</sup> to 108 <sup>c</sup>	45 + 16 32 to 72	39 + 13 29 to 61	0.58 + 0.11 0.31 to 0.67	0.86 + 0.09 0.74 to 0.97

<sup>a</sup>Average ± Standard Deviation and Range of Values

<sup>b</sup>Minimum on different day from PM<sub>10</sub> minimum

<sup>c</sup>Maximum on different day from PM<sub>10</sub> maximum

dInsufficient data

PM<sub>10</sub> concentrations at the remaining sites are well below the 50  $\mu\text{g}/\text{m}^3$  level. If a 150  $\mu\text{g}/\text{m}^3$  24-hour average standard were established, only N. Birmingham would exceed it. None of these sites would exceed a 250  $\mu\text{g}/\text{m}^3$  24-hour standard. As more PM<sub>10</sub> data are acquired from a wider variety of sampling sites, the relative stringency of the long-term and short-term standards will become better understood.

#### RELATIONSHIP OF PM<sub>10</sub> TO PM<sub>15</sub> AND SSI

Watson et al. (1983) calculated the probable ratios of PM<sub>10</sub> to PM<sub>15</sub> and SSI mass concentrations using hypothetical 10  $\mu\text{m}$  sampling effectiveness curves and measured sampling effectiveness curves for the Sierra 244 and McFarland 15  $\mu\text{m}$  size-selective inlets. The hypothetical 10  $\mu\text{m}$  curve is very close to the sampling effectiveness curve which was subsequently measured for the Sierra 246 10  $\mu\text{m}$  inlet to the dichotomous sampler (A. McFarland, personal communication, 1983). Therefore, the ratios calculated by Watson et al. for various particle size distributions should be close to those found in the IP Network if the size distributions and sampling conditions are similar to those which were assumed. Watson et al. (1983) report a range from 0.67 to 1.07 in the PM<sub>10</sub>/PM<sub>15</sub> ratio, depending on wind speed and particle size distribution. The PM<sub>10</sub>/SSI ratio ranges from 0.82 to 0.92.

The average ratios, their standard deviations, and ranges of PM<sub>10</sub>/PM<sub>15</sub> and PM<sub>10</sub>/SSI are reported in the last two columns of Table 2-1. The PM<sub>10</sub>/PM<sub>15</sub> average ratios range from 0.76 to 0.96, which



is within the range predicted by Watson et al. (1983). The  $PM_{10}$ /SSI average ratios range from 0.52 to 0.76, substantially lower than the range predicted by Watson et al. (1983). As noted in Table 2-1, the SSI averages and maxima are significantly higher than the  $PM_{15}$  averages and maxima measured simultaneously at the same sites. The largest discrepancy between averages among these cases occurred at Phoenix, AZ, where the SSI annual average was fully 42% higher than the  $PM_{15}$  annual average in 1982. The largest discrepancy between maximum concentrations among these examples occurred at Buffalo, NY, where the SSI measured  $141 \mu g/m^3$  on the same day that the  $PM_{15}$  concentration was only  $85 \mu g/m^3$ . Even the minimum concentrations measured with the SSI significantly exceed the corresponding  $PM_{15}$  values in every case. Watson et al. (1981) and Shaw et al. (1981) observed a similar discrepancy between these two samplers which are intended to measure the same concentrations. While both researchers raised the possibility of adsorption of atmospheric gases on the SSI filter medium, such an explanation cannot account for the large discrepancies between  $PM_{15}$  and SSI measurements.

Furthermore, Table 2-1 shows that in every case the maximum  $PM_{10}$  concentration occurred simultaneously with the maximum  $PM_{15}$  concentration. This was not the case for SSI measurements at N. Birmingham, AL, N. Braddock, PA, and Houston, TX, as indicated by the superscript "c" on the maximum value. (Though RTP bears such a superscript, it is not representative since it had no SSI measurement for the high  $PM_{10}$  day). The maximum  $PM_{15}$  concentration appears to identify days conducive

to maximum  $PM_{10}$  concentrations better than the SSI does. This may be because the  $PM_{15}$  and  $PM_{10}$  dichotomous sampler measurement techniques are more similar to each other than either one is with respect to the SSI. The question of which device best represents  $PM_{15}$  or  $PM_{10}$  concentrations has yet to be answered.

Finally, Figures 2-1 to 2-7 show the scatter plots and linear regression lines of  $PM_{10}$  vs. SSI and  $PM_{15}$  for seven of the sites having an adequate number of simultaneous measurements. Slopes, intercepts, and correlation coefficients are given on these graphs. These plots have been separated to show that there is no simple, universal relationship between one size fraction concentration and another. While all intercepts are near zero, as is to be expected, and correlations are generally in excess of 0.9, slopes vary among sites from 0.52 to 0.83 for the  $PM_{10}$ /SSI relationship and from 0.72 to 1.04 for the  $PM_{10}$ / $PM_{15}$  relationship among sites.

The conclusions of this analysis are:

- Maximum  $PM_{15}$  concentrations have a high probability of corresponding to maximum  $PM_{10}$  concentrations, and they can, therefore, be used to select sites and days which are conducive to high  $PM_{10}$  concentrations.
- While the  $PM_{15}$  concentration is a maximum which the corresponding  $PM_{10}$  concentration will not exceed,  $PM_{10}$  may be as low as 70% of corresponding  $PM_{15}$  concentrations.

#### DATA REJECTION

It is worth noting that several outliers were excluded from the statistical analyses appearing in Table 2-1 and Figures 2-1 to 2-7. For

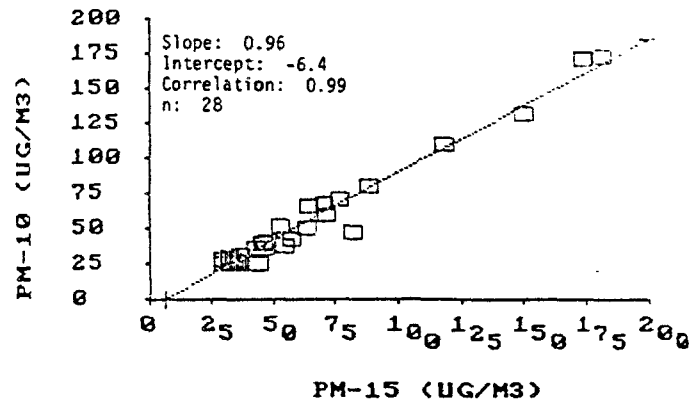
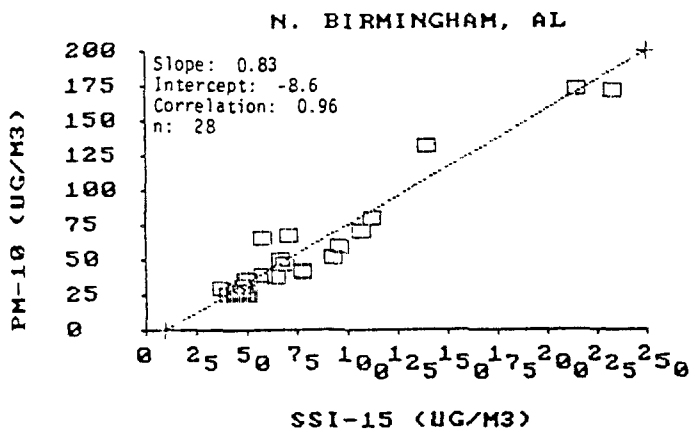


Figure 2-1.  $PM_{10}$  vs. SSI and  $PM_{15}$  Concentrations in N. Birmingham, AL.

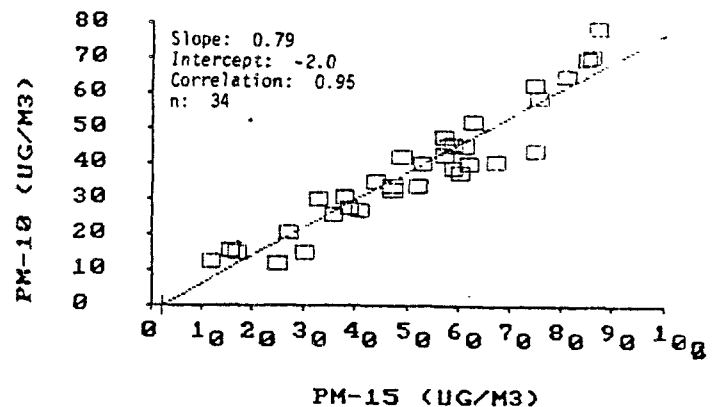
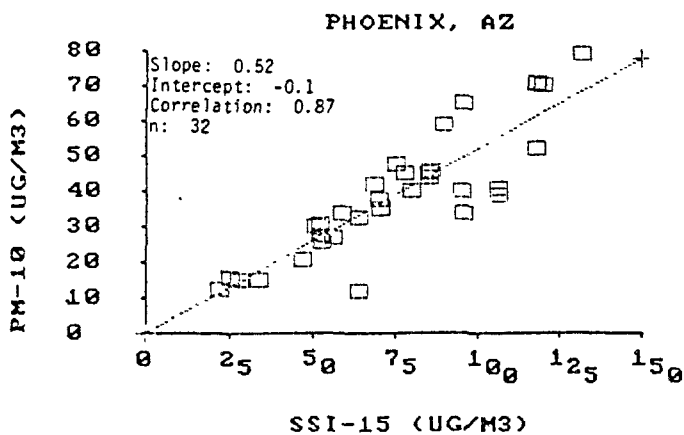


Figure 2-2.  $PM_{10}$  vs. SSI and  $PM_{15}$  Concentrations in Phoenix, AZ.

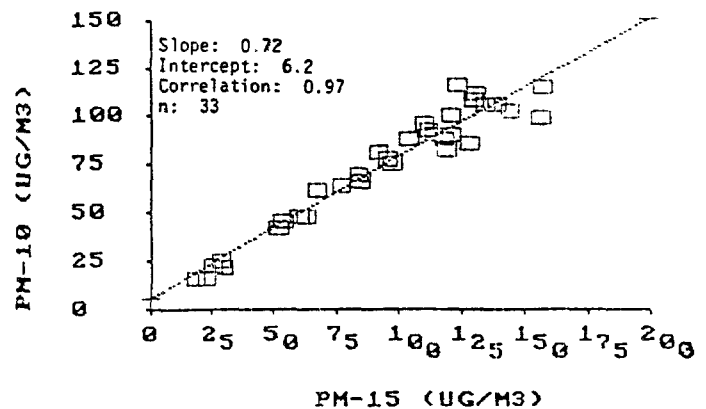
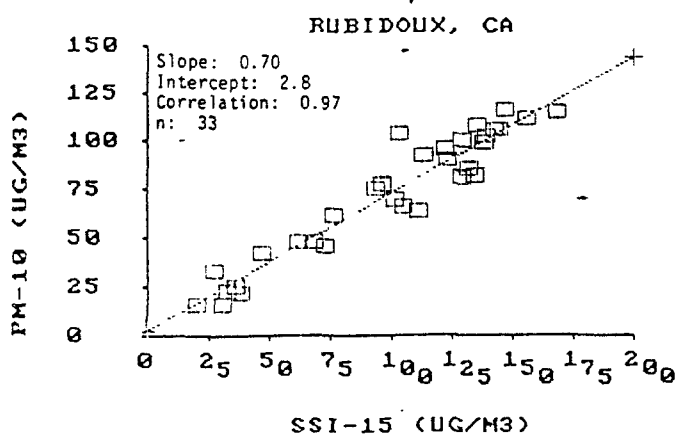


Figure 2-3.  $PM_{10}$  vs. SSI and  $PM_{15}$  Concentrations in Rubidoux, CA.

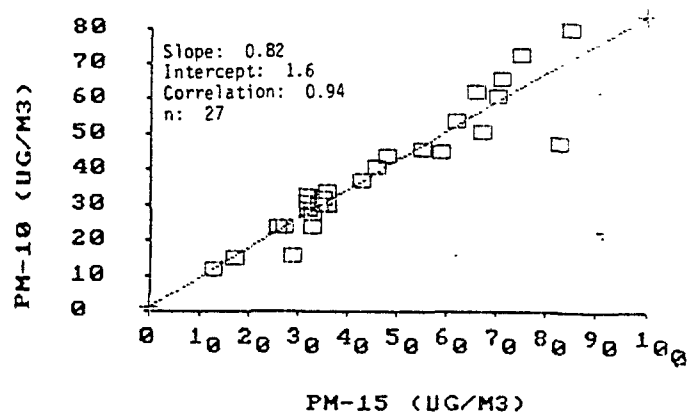
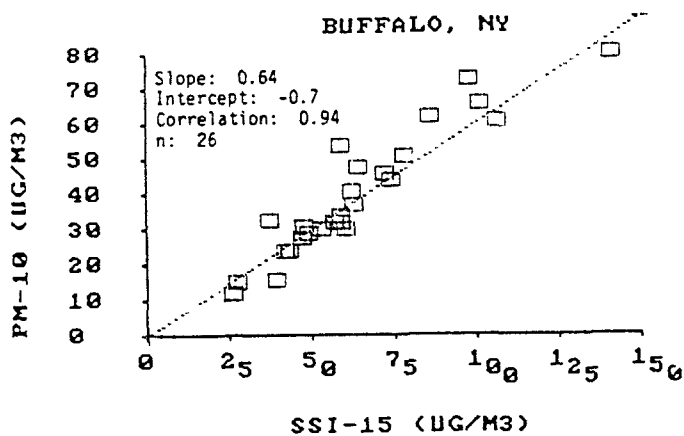


Figure 2-4.  $PM_{10}$  vs. SSI and  $PM_{15}$  Concentrations in Buffalo, NY

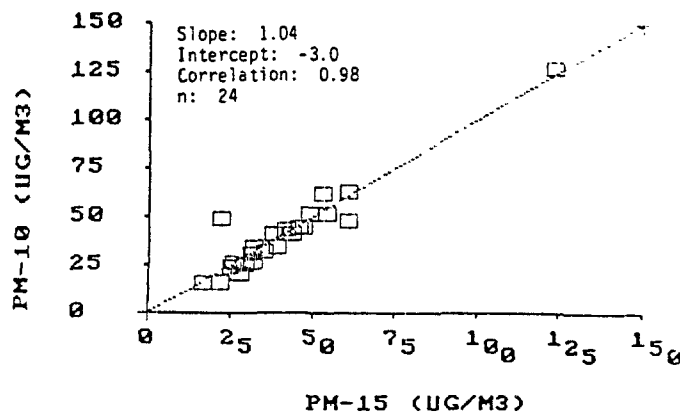
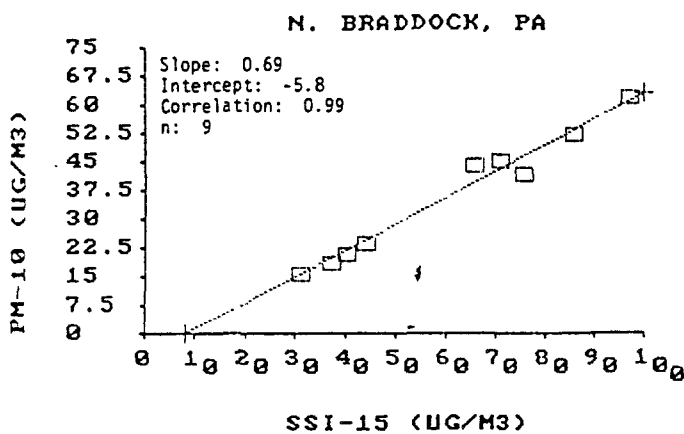


Figure 2-5.  $PM_{10}$  vs. SSI and  $PM_{15}$  Concentrations in N. Braddock, PA.

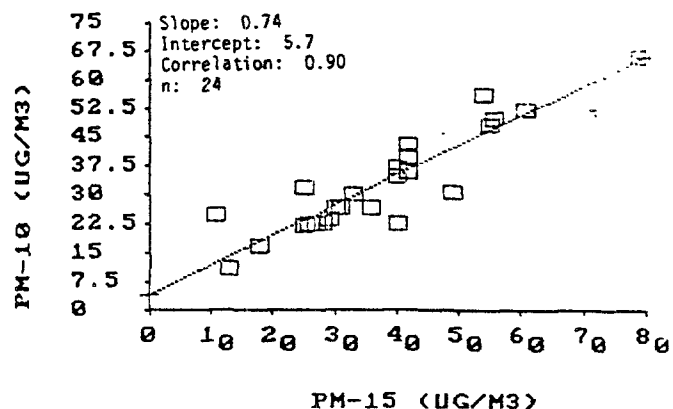
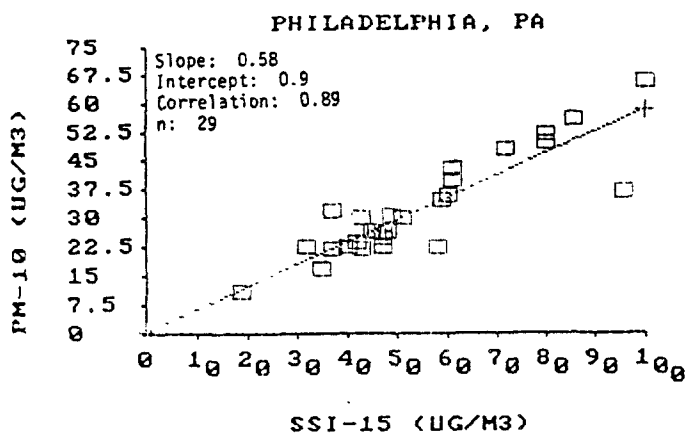


Figure 2-6.  $PM_{10}$  vs. SSI and  $PM_{15}$  Concentrations in Philadelphia, PA.

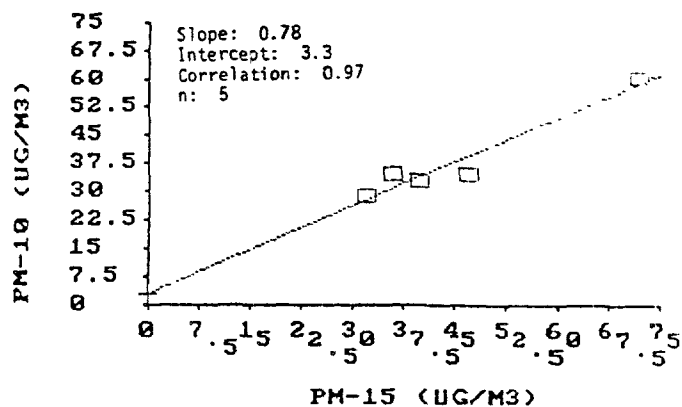
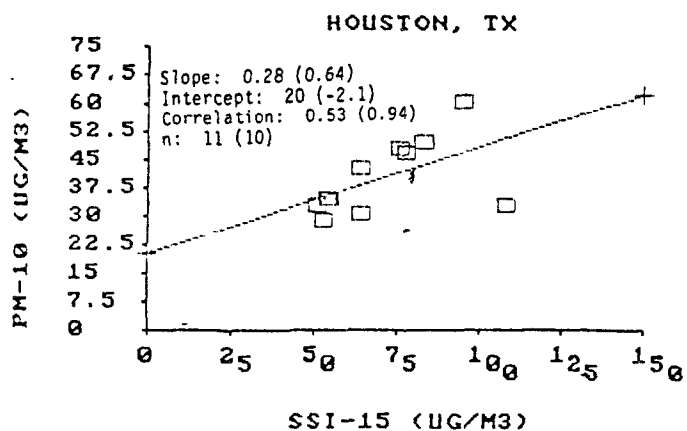


Figure 2-7.  $PM_{10}$  vs. SSI and  $PM_{15}$  Concentrations in Houston, TX.

The numbers in parentheses are those which are obtained when the (108,33) data point is removed.

example, at Rubidoux, a  $217 \mu\text{g}/\text{m}^3$   $\text{PM}_{15}$  corresponding to a  $20 \mu\text{g}/\text{m}^3$   $\text{PM}_{10}$  (no SSI or HIVOL) and a  $139 \mu\text{g}/\text{m}^3$   $\text{PM}_{10}$  corresponding to a  $110 \mu\text{g}/\text{m}^3$  HIVOL, a  $111 \mu\text{g}/\text{m}^3$  SSI and a  $97 \mu\text{g}/\text{m}^3$   $\text{PM}_{15}$  were eliminated. Similarly, at Philadelphia an  $11 \mu\text{g}/\text{m}^3$   $\text{PM}_{15}$  corresponding to a  $25 \mu\text{g}/\text{m}^3$   $\text{PM}_{10}$  was eliminated.

The effect of these outliers is illustrated in the  $\text{PM}_{10}$ /SSI plot for Houston, Figure 2-7, where a  $108 \mu\text{g}/\text{m}^3$  SSI corresponds to a  $33 \mu\text{g}/\text{m}^3$   $\text{PM}_{10}$ . Since the HIVOL value was  $144 \mu\text{g}/\text{m}^3$ , this pair was not removed for the linear regression or average ratio calculations. When it is removed, the correlation between  $\text{PM}_{10}$  and SSI increases from 0.53 to 0.9 and the slope increases from 0.28 to 0.64. Even a single pair of values can have a large effect on the conclusions drawn from IP Network data with the small number of samples presently available.

## SECTION 3

### METHODOLOGY

#### IP NETWORK REPORTS

Eight sets of data were received from the Environmental Protection Agency containing information relevant to the Inhalable Particulate Network. Their titles, the dates they were generated and a description of their contents is given below:

- Quarterly Statistical Summaries, generated 2/7/83: These contain geometric and arithmetic average, maximum, second maximum, and various percentile concentrations at each site over a three month period in each of the size fractions.
- IP-All Mass Data From Raw Master, generated 2/16/83: This report contains valid mass concentrations on individual days for all sites and all size ranges. It also contains validation flags which can be referenced against the Log Journal to determine the reason for the removal of a value from the data base.
- Log Journals, generated 2/7/83: These contain text descriptions of reasons for filter invalidation which are keyed to the All Mass Data from Raw Master report.
- All Data Filter Report, generated 2/7/83: This report contains reportable elemental, ion, and mass concentrations measured on both glass fiber and Teflon filters. In the report received, only mass and elemental data on HIVOL and SSI samples, and mass and ion data for dichotomous samples were included. To obtain elemental concentrations on dichotomous samples, other reports were requested.
- Non-Reportable Dichotomous Sampler Elemental Concentrations Sorted by Element, generated 4/12/82: This report contains the elemental concentrations, but it is difficult to use since it does not group elements by date and sampling site.
- Reportable Mass, Ion, and Elemental Data Report, generated 9/16/83: This contains reportable data sorted by site and date.
- Non-Reportable Elemental Data Report, generated 9/16/83: This report contains those elemental concentrations which are not reported in the IP data base, owing to the lack of comparability

between laboratories. They are grouped according to site and date.

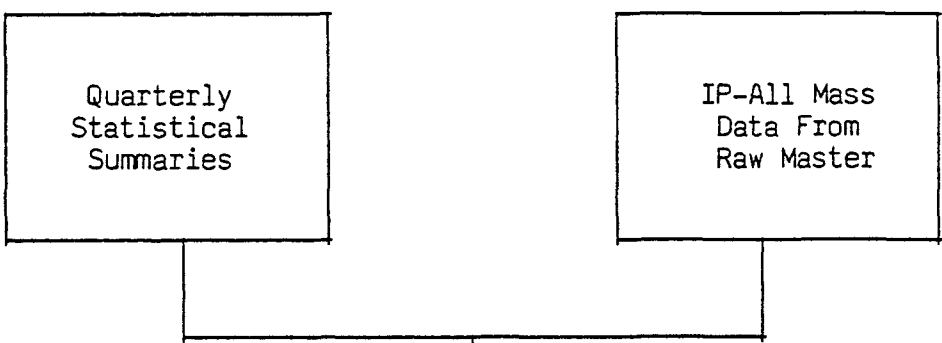
- Site Description Inventory, generated 9/7/83: This report contains the site name, address, SAROAD code, site classification, site elevation, probe height, and site coordinates.
- Mass Loading Multiplication Correction Factors, generated 2/18/83: These factors are calculated to correct volumetric flow rates to standard conditions for seasonal temperature variations and pressure variations with height. Only mass concentrations in the Reportable Mass, Ion, and Elemental Data Report have these corrections applied to them. No chemical data are corrected.
- NAMS Hardcopy Site Surveys, generated at various times: These were available for a subset of all the sites chosen.

In the course of this study, all of these documents were used. For example, when a measurement from a particular site-day could not be found in the Non-Reportable Elemental Data report, it often appeared in the Non-Reportable Dichotomous Sampler Elemental Concentrations Sorted by Element report, and vice versa.

Figure 3-1 schematically shows the way in which the IP Network reports were accessed to select high PM<sub>15</sub> days and to unify the information describing them.

An initial examination of the maximum concentrations reported in the Quarterly Statistical Summaries gave 111 site-days with PM<sub>15</sub> total mass readings above about 120  $\mu\text{g}/\text{m}^3$ . It was intended to also identify high PM<sub>10</sub> site-days but, as noted, these data proved to be sparse, with no supporting chemical and elemental data on the few candidate cases that were identified.





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Of the 111 PM<sub>15</sub> high site-days, 50 were indicated as having simultaneous elemental and chemical information in the IP-All Mass Data From Raw Master report by the presence of elemental and chemical information for the hivol and/or SSI at the given site. No elemental data for the dichotomous samplers were given in this report.

A detailed check of the 50 high site-days in the three chemical concentration reports revealed no information for several of the days which were thought to have chemical speciation. The original selection of 50 high site-days has been retained, however, and has been dealt with as effectively as possible. These 50 high site-days were found to concentrate largely around nine urban areas

The IP-All Mass Data From Raw Master report includes ten categories of flags arising from the IP Network's validation: 1) voided data/filter, 2) ratios out of range, 3) missed sampling schedule, 4) analysis pending, 5) high/low value, 6) questionable filter, 7) filter accepted after question, 8) questionable data, 9) data accepted after question, and 10) data validated to this point.

The Comprehensive Log Journal report supplies comments and notes difficulties entered by the field station operators, complementing the Validation Report. The Comprehensive Log Journal was consulted separately for each of the 50 high site-days. Again, the purpose was to flag suspect or invalid data.

National Weather Service reports contain meteorological data in the form of NOAA-National Weather Service daily weather maps. These maps

were examined for the high concentration days to identify high pressure periods, likely subsidence inversions, and frontal passages. Radiosonde soundings were also obtained for most cases. The daily weather maps (surface and 500 mb) for all cases, and the soundings (raobs) for the states of California, Oregon, and Arizona were available in the archives of the DRI Climatologist. The remaining raobs were requested from the National Climatic Data Center in Asheville, NC. Soundings geographically close to Chicago, IL, Cleveland, OH, and Youngstown, OH, are not taken and were not obtained. The vertical temperature sounding data were individually plotted on Skew T-Log P Adiabatic Diagrams. The height of the inversion, if present, was read from these diagrams. The atmospheric stability was also estimated by comparing the actual to the adiabatic lapse rate. General indications of prominent weekly weather features were sometimes obtained by consulting the NOAA publication Weekly Weather and Crop Bulletin. These weather data were used to identify subsidence inversions which result from persistent high pressure systems, radiation inversions which are often seen close to the ground on the morning sounding, stagnant conditions which are indicated by inversions and low wind speeds, or other meteorological factors such as high winds or precipitation that might be associated with elevated PM<sub>15</sub> readings.

The NAMS Hardcopy Site Surveys were supplemented with site descriptions and source type identifications from other studies to identify potential PM<sub>15</sub> sources, both in the neighborhood (within 1 mi) of the sampling site, and within the overall urban area. The site descriptions

provided other information with respect to the site location, classification and probe height. Table 3-1 summarizes this information and the PM<sub>15</sub> concentrations with their fine and coarse fractions. This table will be referred to in Section 5 to associate chemical concentrations with their potential neighborhood and urban scale sources.

TABLE 3-1 SAMPLING SITE DESCRIPTIONS

SITE	DESCRIPTION	SELECTED ELEVATED CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )				
		DATE	PM15	COARSE-15	FINE-15	
City: Birmingham, AL Name: North Birmingham SAROAD: 010380028 Elevation (ft): 600 Probe Ht (ft): 15 UTMX: 517.096 UTMV: 3708.367 UTM Zone: 16	Classification: Center City-Industrial  Neighborhood Scale: 3000 cars/day on paved street surrounding site. No visible road dust entrainment. Foundry 1/4 mi. E and vacant lot E of site.  Urban Scale: Smooth terrain. Coke ovens, line kiln, mineral handling, lead and aluminum smelting, iron and steel foundries, blast furnaces and cement.	7/14/80 12/5/80 8/26/81 5/5/82	135 165 113 182	80 91 52 118	55 74 61 64	
Descriptions: NAMS, Watson et al. (1981).						
City: Phoenix, AZ Name: Roosevelt St. SAROAD: 030600002 Elevation (ft): 1115 Probe Ht (ft): 15 UTMX: 403.039 UTMV: 3698.431 UTM Zone: 12	Classification: Center City-Commercial  Neighborhood Scale: 12,000 cars/day on paved street next to site. No visible re-entrainment. Vacant lots N and E of site  Urban Scale: Smooth terrain, mineral handling, feed and grain handling, blast furnace, cement.	6/21/81 11/6/81	146 107	39 77	107 30	
Descriptions: NAMS, Watson et al. (1981).						
City: Bakersfield, CA Name: Chester Avenue SAROAD: 050520003 Elevation (ft): 448 Probe Ht (ft): 56 UTMX: 316.661 UTMV: 3909.684 UTM Zone: 11	Classification: Center City-Commercial  Neighborhood Scale: 6000 cars/day on paved street. No visible road dust entrainment. Paved parking lot NE and vacant corner lot SW of site.  Neighborhood Scale: Smooth terrain. No source information.	11/17/80 12/23/80 1/10/81 2/3/81	183 197 176 128	110 54 52 33	73 143 124 95	
Descriptions: NAMS.						

TABLE 3-1 SAMPLING SITE DESCRIPTIONS

SITE	DESCRIPTION	SELECTED ELEVATED CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )			
		DATE	PM <sub>10</sub>	COARSE-15	FINE-15
City: Fresno, CA Name: Fresno County SAROAD: 052820002 Elevation (ft): 326 Probe Ht. (ft): 14 UTMX: 254.197 UTM Y: 4063.901 UTM Zone: 11	Classification: Suburban-Commercial  Neighborhood Scale: 15,000 cars/day on paved road 70 ft. from site. No visible dust entrainment.  Urban Scale: No information.  Descriptions: NAMS.	12/11/80	124	48	76
City: Rubidoux, CA Name: Rubidoux SAROAD: 056535001 Elevation (ft): 820 Probe Ht. (ft): 25 UTMX: 462.170 UTM Y: 3753.465 UTM Zone: 11	Classification: Rural-Commercial  Neighborhood Scale: 1800 cars/day on paved road 115 ft. from sampler. No visible dust entrainment. Vacant lot E and SE of site.  Urban Scale: No information.  Descriptions: NAMS.	10/12/79 10/24/79 6/20/80 8/7/80 5/22/81 5/22/82	124 157 156 164 126 217	48 53 87 105 81 53	76 104 69 59 45 164
City: San Jose, CA Name: No. 4th St. SAROAD: 056980004 Elevation (ft): ? Probe Ht. (ft): 15 UTMX: 598.399 UTM Y: 4127.505 UTM Zone: 10	Classification: Center City-Commercial  Neighborhood Scale: Three paved roads within 1/4 mile. Parking lot close by.  Urban Scale: No information.  Descriptions: NAMS.	10/30/80	120	47	73

TABLE 3-1 SAMPLING SITE DESCRIPTIONS

SITE	DESCRIPTION	SELECTED ELEVATED <sup>3</sup> CONCENTRATIONS (µg/m <sup>3</sup> )			
		DATE	PM <sub>10</sub>	COARSE-15	FINE-15
City: Hartford, CT Name: Public Library SAROAD: 070420003 Elevation (ft): 90 Probe Ht. (ft): 30 UTMX: 639.300 UTM Y: 4618.297 UTM Zone: 18	Classification: Center-City Commercial Neighborhood Scale: No information. Urban Scale: No information. Descriptions: None.	1/22/81	128	65	61
City: Chicago, IL Name: Washington High School SAROAD: 141220022 Elevation (ft): 616 Probe Ht. (ft): 31 UTMX: 455.036 UTM Y: 4607.597 UTM Zone: 16	Classification: Center City-Mobile Neighborhood Scale: No information. Urban Scale: None. Descriptions: None.	2/3/81	120	62	58
City: Buffalo, NY Name: PS 26 SAROAD: 330660003 Elevation (ft): 7 Probe Ht. (ft): 30 UTMX: 677.208 UTM Y: 4740.402 UTM Zone: 16	Classification: Center-City Industrial Neighborhood Scale: 30,000 cars/day on interstate 500 ft. from site. No visible dust entrainment. Steel mills 1 mi. E of site. Urban Scale: Smooth terrain. Feed and grain handling, coke ovens, mineral handling, iron and steel foundries, blast furnaces, incinerators. Descriptions: NAMS, Watson et al. (1981).	9/18/79 1/4/81 4/4/81 6/15/81	143 149 143 130	71 65 39 52	72 84 104 78

TABLE 3-1 SAMPLING SITE DESCRIPTIONS

SITE	DESCRIPTION	SELECTED ELEVATED CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )				
		DATE	PM15	COARSE-15	FINE-15	
		8/7/80	130	80	50	
City: Buffalo, NY Name: Big Sister SAROAD: 332000003 Elevation(ft): 7 Probe Ht. (ft): 30 UTMX: 667.208 UTM Y: 4740.208 UTM Zone: 16	Classification: Suburban-Residential Neighborhood Scale: Paved curbed roads and parking lots. Light traffic. Urban Scale: South of Buffalo near Erie. Up-wind sources may originate in Buffalo. Descriptions: Watson et al. (1981).					
City: Buffalo, NY Name: Lackawanna, Wilmuth Pump SAROAD: 333520001 Elevation (ft): 599 Probe Ht. (ft): 20 UTMX: 676.514 UTM Y: 473.731 UTM Zone: 17	Classification: Center City-Residential Neighborhood Scale: Light traffic on paved roads. Steel and iron works 1/8 mi W and NW. Urban Scale: Smooth terrain. Feed and grain handling, coke ovens, mineral handling, iron and steel foundries, blast furnaces, incinerators. Descriptions: Watson et al. (1981).	5/22/81 6/15/81 7/9/81	187 145 198	136 94 150	51 51 48	
City: Cleveland, OH Name: Bidouph and 54th SAROAD: 361300013 Elevation (ft): 812 Probe Ht. (ft): 40 UTMX: 439.701 UTM Y: 5497.278 UTM Zone: 17	Classification: Center City-Industrial Neighborhood Scale: No information. Urban Scale: No information. Descriptions: No information.	7/20/79 9/6/79 11/5/79 9/12/80 4/4/81 8/26/81 10/13/81	176 145 140 123 136 223 132	96 100 73 68 82 23 93	80 45 68 56 53 200 40	
City: Ironton, OH Name: Lawrence Hospital SAROAD: 363080010 Elevation (ft): 353 Probe Ht. (ft): 29 UTMX: 354.897 UTM Y: 4258.749 UTM Zone: 17	Classification: Suburban-Residential Neighborhood Scale: No information. Urban Scale: No information. Descriptions: None.	4/4/81	123	75	48	



TABLE 3-1 SAMPLING SITE DESCRIPTIONS

SITE	DESCRIPTION	SELECTED ELEVATED CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )			
		DATE	PM <sub>10</sub>	COARSE-15	FINE-15
City: Youngstown, OH Name: Commerce Street SAROAD: 367760002 Elevation (ft): 865 Probe Ht. (ft): 150 UTMX: 528.947 UTM Y: 5031.273 UTM Zone: 17	Classification: Center City-Industrial Neighborhood Scale: No information. Urban Scale: No information. Descriptions: None.	2/15/81	127	56	71
City: Portland, OR Name: Central Fire Station SAROAD: 381460015 Elevation (ft): 72 Probe Ht. (ft): 45 UTMX: 525.816 UTM Y: 5031.273 UTM Zone: 10	Classification: Center City-Commercial Neighborhood Scale: Heavy traffic on paved roads near site. Urban Scale: Hilly terrain. Paper mills, feed and grain handling, steel foundry, arc furnace, glass furnace, cement. Descriptions: Watson (1979).	10/12/79	207	116	91
City: Philadelphia, PA Name: Bridesburg Recreation SAROAD: 397140044 Elevation (ft): 75 Probe Ht. (ft): 25 UTMX: 494.664 UTM Y: 4420.858	Classification: Center City-Industrial Neighborhood Scale: Light traffic on paved uncurbed roads. Open playground with some exposed dirt E of site. Coke oven 1/8 mi. and chemical plant 1 mi. N of site. Urban Scale: Smooth terrain. Refineries, feed and grain handling, coke oven, mineral handling, cooper, lead, and aluminum smelting, iron and steel foundry, blast furnace, chemical plant, incinerators. Descriptions: Watson et al. (1981).	12/15/79 12/11/79	125 127	77 67	48 60

TABLE 3-1 SAMPLING SITE DESCRIPTIONS

SITE	DESCRIPTION	SELECTED ELEVATED <sup>3</sup> CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )				
		DATE	PM <sub>10</sub>	COARSE-15	FINE-15	
City: Philadelphia, PA Name: Allegheny SAROAD: 397140019 Elevation (ft): 1 Probe Ht. (ft): 10 UTMX: 491.225 UTMV: 4420.002 UTM Zone: 18	Classification: Center City-Industrial  Neighborhood Scale: Heavy traffic on dirty, paved road. Unpaved road 1/8 mi. W. Metal scrap yard 1/3 mi. NW, grain loading 1/8 mi. SW, and mineral handling 1/4 mi S.  Urban Scale: Same as Bridesburg Recreation site.  Descriptions: Watson et al. (1981).	11/20/79	134	52	82	
City: Philadelphia, PA Name: Presbyterian Home SAROAD: 397140036 Elevation (ft): 78 Probe Ht. (ft): 25 UTMX: 480.632 UTMV: 4413.513 UTM Zone: 18	Classification: Suburban-Industrial  Neighborhood Scale: No information  Urban Scale: Same as Bridesburg Recreation site.  Descriptions: Watson et al. (1981).	11/20/79 3/10/80	146 136	43 9	112 127	
City: Philadelphia, PA Name: T and A Pet Shop SAROAD: 397140042 Elevation (ft): 66 Probe Ht. (ft): 16 UTMX: 490.869 UTMV: 4419.388 UTM Zone: 18	Classification: Center City-Industrial  Neighborhood Scale: Moderate traffic on clean paved roads.  Urban Scale: Same as Bridesburg Recreation site.  Descriptions: Watson et al. (1981).	11/20/79	173	64	109	
City: Philadelphia, PA Name: NE Transfer SAROAD: 397140043 Elevation (ft): 80 Probe Ht. (ft): 30 UTMX: 493.240 UTMV: 4418.618 UTM Zone: 18	Classification: Center City-Industrial  Neighborhood Scale: Moderately heavy traffic on paved roads around site. A truck loading facility is at this site. A copper smelter is 1/3 mi. NW and an electric company is 1/8 mi. E of the site.  Urban Scale: Same as Bridesburg Recreation site.  Descriptions: Watson et al. (1981).	11/20/79	151	45	106	

TABLE 3-1 SAMPLING SITE DESCRIPTIONS

SITE	DESCRIPTION	SELECTED ELEVATED CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )				
		DATE	PM <sub>10</sub>	COARSE-15	FINE-15	
City: Pittsburgh, PA	Classification: Not classified.	10/30/80	184	60	124	
Name: Gladstone High School	Neighborhood Scale: 130,00 cars/day on paved	5/22/81	137	79	58	
SAROAD: 397260021	road 720 ft. from site. No visible dust en-					
Elevation (ft): 920	trainment. Steel mill 1/2 mi. NW of site.					
Probe Ht. (ft): 17	Urban Scale: No information.					
UTMX: 447.397 UTM Y: 5883.764	Descriptions: NAMS.					
UTM Zone: 17						
City: El Paso, TX	Classification: Center City-Commercial	11/29/79	126	81	45	
Name: Tillman Health Center	Neighborhood Scale: 20,000 cars/day on paved					
SAROAD: 451700002	road 350 ft. from site. No visible dust en-					
Elevation (ft): 3729	trainment. Ten-story building construction on					
Probe Ht. (ft): 40	block directly north of site in 1979.					
UTMX: 359.512 UTM Y: 3510.828	Urban Scale: Hilly terrain. Lime kiln, refinery,					
UTM Zone: 13	copper and lead smelting, iron and steel foundry.					
	Juarez, Mexico, contains many unknown sources just					
	across border.					
	Descriptions: NAMS, Watson et al. (1981).					
City: El Paso, TX	Classification: Rural-Agricultural	12/11/79	131	121	10	
Name: Clint High School	Neighborhood Scale: No information.	4/29/82	399	19	380	
SAROAD: 451710004	Urban Scale: No information.					
Elevation (ft): 3636	Descriptions: None.					
Probe Ht. (ft): 4						
UTMX: 383.429 UTM Y: 3491.921						
UTM Zone: 13						

## SECTION 4

### POTENTIAL CAUSES OF ELEVATED IP CONCENTRATIONS

In this section a list of reasonable hypotheses are presented concerning the causes of elevated  $PM_{15}$  in the case studies to be discussed in Section 5. The hypothesis list is not necessarily exhaustive, but covers major types of events. These hypotheses are not mutually exclusive, and more than one of them may be supported in each specific case. In particular, these hypotheses can be tested with the IP Network and weather service data available to this study. It is recognized that a given elevated  $PM_{15}$  concentration may derive from a combination of causes, or it may be caused by an entirely different kind of event from those advanced as hypotheses in the following list. These cases will suggest other possible causes which may be examined in future studies.

Hypothesis 1: High  $PM_{15}$  concentrations result from contributions from major local sources of industrial emissions.

This hypothesis is advanced partly because large industrial sources have "traditionally" (Yocom et al., 1981) been thought to be the major polluters. Furthermore, a large fraction of the high site-days in the present study derive from industrialized urban areas, such as Birmingham, Buffalo, Cleveland, and Philadelphia. Proximity of the sampling station to the industrial source is presumed to enhance the potential of a high reading, owing to reduced opportunities for time-dependent removal processes, such as gravitational deposition and scavenging by clouds and precipitation.

Support for this hypothesis involves use of the site surveys to identify nearby industrial sources and the aerosol chemical composition which is characteristic of the emissions from these sources. For example, if a given site is near a steel mill complex (as shown by the accompanying site description), and if the chemical data for the high site-day show high Fe and Mn concentrations, it might reasonably be concluded that the steel mill source contribution was significant. Similarly, Cu, Pb, or Al may be indicative of smelting operations, and Ca may be indicative of cement plant or construction activity. Care must be taken to avoid the high Al, Si, and Fe concentrations (particularly in the coarse mode), which indicate a crustal contribution. Table 4-1 was compiled from Watson et al. (1981) to provide some perspective on chemical concentrations. It contains the highest average values of each chemical species found in U.S. cities. When the values found on high site-days exceed these values by a factor of approaching 2 or more, concentrations of these species are noted as being elevated.

Hypothesis 2: High  $PM_{15}$  concentrations are caused by the presence of local non-industrial sources, including residential heating, wood or trash burning, vehicular traffic, and resuspension of the earth's crustal materials (e.g. dust storms, or traffic resuspension).

This hypothesis is advanced because its importance has been shown in several recent aerosol studies (e.g. Cooper et al., 1979; Chow et al., 1981; Chow et al., 1982). Furthermore, the present 50 site-day data set includes many cases where at least the crustal components, Al, Si, and

TABLE 4-1  
HIGHEST AVERAGE CHEMICAL CONCENTRATIONS  
IN U.S. CITIES<sup>a</sup>

<u>Species</u>	Concentration in $\mu\text{g}/\text{m}^3$	
	<u>FINE-15</u>	<u>COARSE-15</u>
Al	1.5	2.4
Si	2.5	6.2
Fe	0.9	2.8
SO <sub>4</sub>	10.4	7.0
NO <sub>3</sub>	6.9	3.6
V	<.020	<.020
Ni	<.005	<.005
Cl	1.6	1.8
Br	0.2	0.04
Pb	0.8	0.2
K	0.8	1.0
Mn	0.05	0.1
Zn	0.2	0.3
Cu	0.07	0.1
Ca	1.3	6.0
Mass	55	56

<sup>a</sup> From Table 9.2.2 of Watson et al. (1981).

Fe, are simultaneously elevated in the coarse mode. Other cases include elevated Cl (sea salt or road salting) and elevated Ca, which can also result from construction activity (cement) close to the sampling site. For example, In El Paso, TX, on 11/29/79, out of a total PM<sub>15</sub> mass of 126  $\mu\text{g}/\text{m}^3$ , 9.79  $\mu\text{g}/\text{m}^3$  were Si, 3.82  $\mu\text{g}/\text{m}^3$  were Al, and 1.74  $\mu\text{g}/\text{m}^3$  were Fe (in the coarse mode). Sulfate and nitrate levels were low, Cl totaled only 2.17  $\mu\text{g}/\text{m}^3$ , and the only other major contributing element was Ca, with 14.12  $\mu\text{g}/\text{m}^3$  in the coarse fraction, and 1.21  $\mu\text{g}/\text{m}^3$  in the fine fraction. The accompanying site survey showed construction in progress in October, 1979, in the adjacent city block to the north-northwest. These coarse fraction elements seem to indicate local crustal and possibly cement dust contributions.

It is not possible to distinguish between industrially generated road dust or motor vehicle exhaust and that which originates from the general population. In highly industrialized areas, the sources may indeed be of an industrial origin.

Hypothesis 3: High PM<sub>15</sub> concentrations are caused by regional scale secondary particulate matter, especially in the eastern USA.

This hypothesis is advanced because previous studies in the eastern USA have revealed significant aerosol sulfate contributions to the PM<sub>15</sub> concentrations (e.g. Mueller and Hidy et al., 1983). Those in the western USA have shown the same for nitrate (e.g. Hidy et al., 1975), and several of the following case studies have shown both very high particulate sulfate and nitrate readings.

This hypothesis is supported primarily by high sulfate or nitrate concentrations and a comparison of these values with those from other sites in the region. Because sulfur is measured by x-ray fluorescence, it is possible to verify the validity of most sulfate measurements through intermethod comparison. For example, some of the highest sulfate readings in the 50 high site-day list were found in Philadelphia, PA, where three cases of fine sulfate exceeded  $30 \mu\text{g}/\text{m}^3$ . This is much higher than the annual arithmetic average for fine particulate sulfate of  $7 \mu\text{g}/\text{m}^3$  for the period August 1977 to July 1978, as found in the SURE Program (see Table 6-22 of Mueller and Hidy et al., 1983). These authors discuss cases of 20 to  $30 \mu\text{g}/\text{m}^3$  TSP sulfate in terms of regional episodes.

Hypothesis 4: High  $\text{PM}_{15}$  concentrations are associated with the presence of atmospheric inversions and/or stagnation.

This hypothesis is advanced as one of the most traditional explanations for both the concentrating of primary particles and the generation of secondary particles. While daily wind speed, wind direction, temperature, and relative humidity may also affect  $\text{PM}_{15}$  concentrations, it was beyond the scope of this study to acquire and analyze these data.

Atmospheric temperature inversions do not cause high pollution levels by themselves. They do trap emissions close to the surface, however, and prevent their rise to higher levels where they can be dispersed by stronger winds. Conditions are usually very stable in the



layer under the inversion, with very low wind speeds which further inhibit the dispersal of pollutants.

Atmospheric soundings have been plotted for stations close to the IP Network site of relevance on high  $PM_{15}$  days. Twenty-seven of the fifty site-days were eventually provided with at least 0000Z sounding (which corresponds to 4 p.m. PST, 6 p.m. CST, and 7 p.m. EST) from a nearby radiosonde station. In some cases the 1200Z (which corresponds to 4 a.m. PST, 6 a.m. CST and 7 a.m. EST) sounding was also available. As the atmosphere is rarely dry- or pseudo-adiabatic, at least 75% of these soundings show inversions at one level or another (up to 500 mb, which was considered the maximum height of relevance). Therefore, important caveats must be applied to these data. For example, all five of the elevated Rubidoux concentrations occurred during inversions with inversion tops (here defined as the maximum temperature level) ranging from 900 mb to 750 mb on the San Diego, CA, and Vandenburg, CA, soundings (for example, see Figure 4-1). This is the frequently observed subsidence inversion resulting from the off-shore Pacific anticyclone, and its presence alone does not guarantee a high  $PM_{15}$  reading. Substantial on-shore winds during these inversions can dilute and remove the particle accumulation at coastal sites.

A different inversion example is found in the case of Hartford, CT, 1/22/81 (see Figure 4-2). The nearby Albany, NY, sounding at 0000Z shows a very cold surface temperature with an inversion top at 812 mb. The 1200Z surface maps show the slow eastward movement of an anticyclone

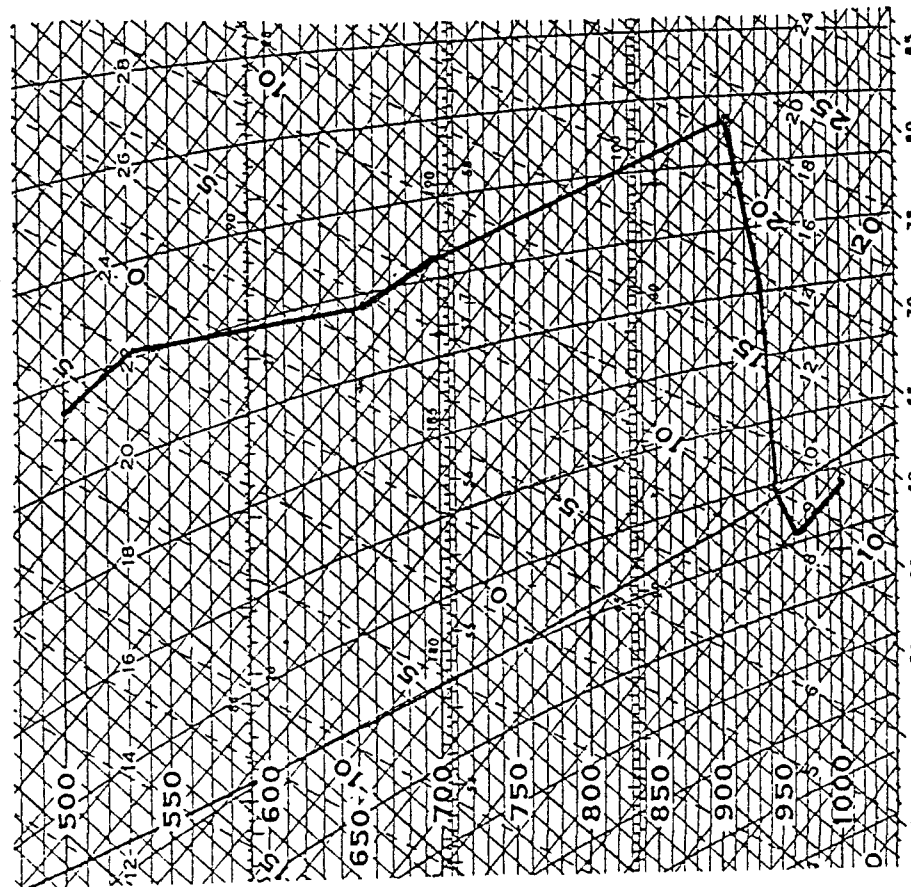


Figure 4-1. Example of a pronounced subsidence inversion based on the 0000Z Vandenberg, CA sounding relevant to Rubidoux on 6/20/80. The vertical scale is in mb. Celsius temperature is on solid lines slanting upwards from left to right.

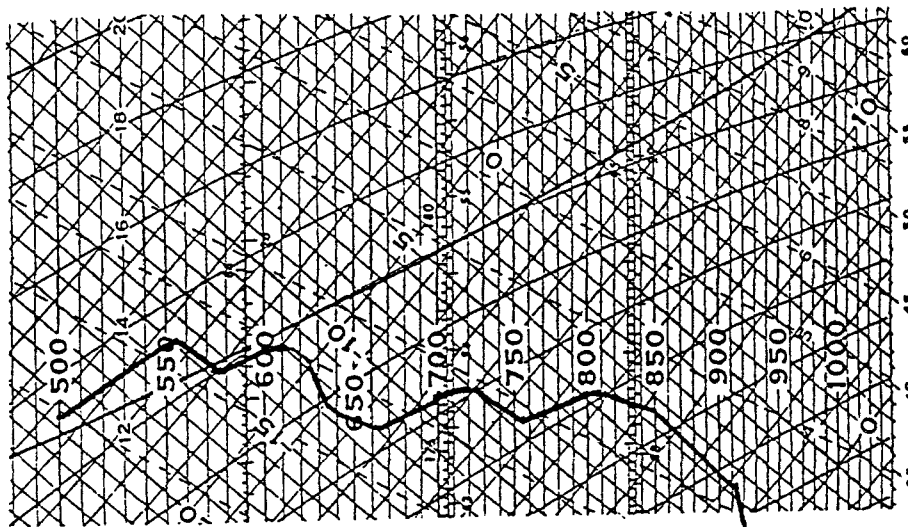


Figure 4-2. Example of a radiation inversion below 900 mb based on the 0000Z Albany sounding relevant to Hartford, CN on 1/22/81. Dry adiabats slant upward from right to left.

centered to the north of the New England states. The observed inversion is probably a result of both subsidence and radiation, with the 0000Z Albany, NY, surface wind at 4 knots. The approach of a cold front on 1/22/81 probably brought about the end of the high PM<sub>15</sub> episode, following very restricted movement of the aerosol beneath the inversion.

Atmospheric stagnation is the persistence of an inversion and low surface winds over a long time period. This stagnation is illustrated in the case of Portland, OR, 10/12/79 (see Figure 4-3). This day was preceded by four days of high pressure over the northwestern states. On 10/12/79, the Pacific Coast subsidence inversion appeared on both the Portland and the Vandenburg, CA, soundings at about 840 mb, and even the 500 mb wind over Portland was only about 10 knots out of the southeast. A record high temperature of 81°F, occurred on 10/9/79. These conditions are conducive to several days of sluggish circulation below 840 mb which prevents the dispersal of pollutants. They were followed by the approach of a weak cold front and precipitation on 10/13/79.

Hypothesis 5: High PM<sub>15</sub> concentrations are due to the presence of anomalies related to the measurement process.

This hypothesis is unlike the earlier four in that it did not present itself until after a preliminary scan of all the data relevant to the fifty high site-days. It was found, however, that a significant number (4) of the highest observed PM<sub>15</sub> site-day concentrations from

This is a detailed surface weather map of the North Atlantic and surrounding regions, showing pressure systems, isobars, and station data. The map includes latitude and longitude markings and a title "SURFACE WEATHER MAP AND STATION WEATHER AT 700 A.M. EST".

The map shows a high-pressure system (labeled "HIGH") centered over the North Atlantic, with isobars ranging from 1012 to 1024. A low-pressure system (labeled "LOW") is located over the Gulf of Mexico, with isobars ranging from 1008 to 1016. The map also shows various weather fronts, including cold fronts and warm fronts, and station data for numerous locations, including New York, Washington, and Miami.

The map includes latitude and longitude markings, with latitude ranging from 30°N to 45°N and longitude ranging from 70°W to 100°W. The title "SURFACE WEATHER MAP AND STATION WEATHER AT 700 A.M. EST" is located in the bottom right corner.

Figure 4-3. 1200Z Surface Weather Map. This example illustrates stagnant conditions relevant to Portland and Rubidoux on 10/12/79.

the eight major urban areas studied were suspect because the dichotomous sampler  $PM_{15}$  exceeded the hivol sampler TSP by more than the data flagging criteria adopted for the IP Network (U.S. EPA, 1980; Watson et al., 1981). These criteria, applied by EPA/EMSL, flag simultaneous measurement sets for which the ratio of  $PM_{15}$  to hivol mass concentrations exceeds 1.1. Such ratios do not invalidate the data points because it is impossible to determine which sample is in error with the available information. For this study, it is assumed that the hivol data derive from the older and more established measurement device, and that a  $PM_{15}$ /HIVOL ratio exceeding 1.1 probably indicates a faulty  $PM_{15}$  measurement.

Another type of measurement discrepancy involved out-of-bounds coarse/fine mass ratios. In this case, the IP Network flagging criteria identify coarse/fine ratios less than 0.3 or greater than 1.3. This criterion is not applied stringently here, but three cases are classified as anomalous: one with a coarse/fine ratio of 0.05 (El Paso, 4/29/82), one with a coarse/fine ratio of 0.07 (Philadelphia, 3/10/80), and finally a case with a coarse/fine ratio equal to 12.5 (El Paso, 12/11/79).

As noted earlier, additional hypotheses could be advanced. It will be seen in the next section, however, that these five simple hypotheses, individually and in combinations, are often supported by IP Network data.

## SECTION 5

### SUPPORT FOR HYPOTHESES

Detailed case studies for each site-day are presented in Appendix A. These case-studies include the ambient chemical data and a summary of the meteorological situation. Their results are summarized in this section for each of the hypotheses to determine whether or not it has general support. Unfortunately, all data were not available for all site-days, and the same set of samples is not drawn from to support every hypothesis.

#### INDUSTRIAL SOURCES (Hypothesis 1)

Thirty-six site-days had a full set of chemical concentrations, though three of these were suspect for one reason or another. Sixteen of the remaining 33 cases showed a marked influence of some industrial activity. All of these sites are located in cities where the indicated industrial activity is known to take place. All of the sites in Buffalo, NY, Cleveland, OH, Philadelphia, PA, Pittsburgh, PA, and Youngstown, OH, are classified as Center City-Industrial in Table 3-1. Only Bakersfield is Center City-Commercial.

Buffalo, Cleveland and Pittsburgh contain major steel mills within a mile of the sampling sites, and ambient concentrations of iron, manganese and zinc were often elevated above the values in Table 4-1 by a factor of two or more.

The coarse iron concentrations reached values as high as  $12.3 \mu\text{g}/\text{m}^3$  in Cleveland on 4/4/81. Fine iron concentrations reached  $8.1 \mu\text{g}/\text{m}^3$  at the same site on 7/20/79. Similar results were found for the high site-days in Buffalo and Pittsburgh.

In Philadelphia, the coarse and fine manganese concentrations reached 6.9 and  $0.9 \mu\text{g}/\text{m}^3$  respectively at the T and A Pet site on 11/20/79. A nearby minerals handling facility is a likely source. Copper and zinc were elevated at nearby sites and the site surveys note the presence of a copper smelter nearby.

Bakersfield attained one of the highest fine sulfate concentrations in the network on 1/10/81,  $45 \mu\text{g}/\text{m}^3$ . Even though this site is classified as Center City-Commercial it is known that oil fields surround the city of Bakersfield and that a substantial amount of sulfur-containing gases are emitted which could be the precursors to sulfate.

In none of the cases studied is the chemical species indicating the presence of a given source of a sufficient concentration to greatly influence the  $\text{PM}_{15}$  mass concentration. In fact, even if all of the chemical species measured at a IP Network site were summed, they would account for far less than half of the corresponding  $\text{PM}_{15}$  values. If steel mills, smelters, and mineral handling facilities contribute only the species which are measured, such as Fe, Cu, and Mn, then they are

not major causes of high  $PM_{15}$  concentrations. If these chemical concentrations are also associated with other, unmeasured species, then the contributions of industrial sources to  $PM_{15}$  could be much greater.

All of the Center City-Industrial sampling sites identified in Table 3-1 which had chemical concentrations were found to have some industrial influences. Only one which is not so classified, Bakersfield, shows a significant industrial influence, and this influence is apparently not due to industrial activities within the city.

#### NON-INDUSTRIAL SOURCES (Hypothesis 2)

The non-industrial sources include resuspended geological material and road dust (which may indeed be industrial in origin, but is considered separately here because it cannot be distinguished from its non-industrial counterpart), automobile exhaust, construction activities, heating and burning. Of the 33 valid site-days for which chemical species were measured, 18 showed significantly elevated chemical concentrations indicative of these non-industrial sources.

Geological material appears to be a contributor at P.S. #26 in Buffalo, Bakersfield, Rubidoux, and Fresno where very high Al and Si levels were measured. Coarse silicon and aluminum reached levels of 24 and  $9 \mu g/m^3$ , respectively, in Bakersfield on 11/17/80, which would make suspended dust a major contributor to the  $183 \mu g/m^3$   $PM_{15}$  concentration observed on that day. High speed Santa Ana winds are recorded for that period which probably raised the dust.



Elevated chloride levels sometimes accompany the higher aluminum and silicon concentrations, particularly during winter months. Hartford and Youngstown both exhibited higher than normal chloride levels on 1/22/81 and 2/15/81, respectively. The weather summaries for both cases show snow on the ground and it is known that roadways in these eastern cities are salted and sanded during snowfall. The chloride could result from traffic resuspension.

Motor vehicle exhaust is indicated by elevated Br and Pb concentrations with Br/Pb ratios in the range of 0.2 to 0.4. This situation is observed in Cleveland, at the T and A Pet and Presbyterian Home sites in Philadelphia, and in El Paso, but not to a great extent at other sites. One of the highest cases occurred at the T and A Pet site on 11/20/79 when  $PM_{15}$  lead reached  $2.4 \mu g/m^3$  and bromine reached  $0.6 \mu g/m^3$ . If one assumes that lead constitutes approximately 20% (e.g. Watson, 1979) or less of the mass of particulate motor vehicle exhaust, these levels imply a significant contribution to the  $173 \mu g/m^3$   $PM_{15}$  concentration observed on that date.

Calcium concentrations were elevated in the coarse fraction for a number of site-days, and the levels reached are rarely consistent with those expected from geological material. The case in El Paso was offered as an example in Section 4, and owing to a detailed site survey, it could be explained by nearby construction. The Ca source is not so obvious at Wilmuth Pump in Buffalo, NY, on 4/4/81, in Bakersfield on 11/17/80, and in Rubidoux on 8/7/80. For example, calcium contributes 27

$\mu\text{g}/\text{m}^3$  to the  $145 \mu\text{g}/\text{m}^3$   $\text{PM}_{15}$  concentration at Wilmuth Pump. Since calcium is a non-reportable species (as defined in Section 1), this may be a measurement anomaly, but its levels at other sites seem so consistent with normal geological material that it is difficult to believe the errors in its measurement can be so large. The El Paso case lends credence to the effects of nearby construction, and it may be that such activities periodically take place but are not adequately recorded.

Elevated vanadium and nickel levels are present at the T and A Pet, NE Transfer, and Presbyterian Home sites in Philadelphia, PA, indicating a potential source of residual oil combustion. All of these occurred on the same day, 11/20/79, a day on which the weather reports show higher than normal temperatures, but it was still cold enough to require heating. Stagnant conditions were also present, as will be discussed below.

One clear-cut case of vegetative burning contributions occurred in Bakersfield on 11/17/80. In this case, high speed Santa Ana winds fanned fires in southern California which destroyed much grassland and over 100 homes. Potassium in  $\text{PM}_{15}$  reached  $3.7 \mu\text{g}/\text{m}^3$  in Bakersfield and chloride was also elevated on this day. Both potassium and chloride are known to be products of vegetative burning (Watson, 1979). Though these species were elevated at other sites, notably Cleveland on 9/12/80 and 4/4/81 and Wilmuth Pump on 6/15/81 where the fine potassium concentrations reached  $2.3 \mu\text{g}/\text{m}^3$ , vegetative burning in these communities has not been reported in other studies.

The classifications of these sites where non-industrial sources contribute more than their typical share to the  $PM_{15}$  are industrial as well as non-industrial. P.S. #26, Cleveland, T and A Pet, NE Transfer and Youngstown, all classified as Center City-Industrial, show significant non-industrial contributions. Several of these non-industrial tracer concentrations are elevated on the same days for which industrial source tracers are elevated, demonstrating that the industrial sources cannot be singled out as the sole causes of high  $PM_{15}$  concentrations. Center City-Commercial sites with elevated non-industrial contributions are Bakersfield and Hartford. Presbyterian Home is Suburban-Industrial, Rubidoux is Rural-Commercial, El Paso is Center City-Commercial and Fresno is Suburban-Commercial.

The hypothesis that non-industrial sources are significant contributors to high  $PM_{15}$  concentrations is supported by the chemical concentrations and the site-types at which they occur for the majority of the 33 cases.

#### REGIONAL SCALE SECONDARY PARTICLES (Hypothesis 3)

The first identifier of a regional-scale secondary particle event is an elevated concentration of sulfate and/or nitrate at the sampling site. The second identifier is a simultaneous elevated value at a sampling site which is still within the region, but which may be several

hundred miles away. The final identifier is a synoptic weather system with warm moist air and high pressure which homogenously covers a large region.

Unfortunately, not all of this information was available for the high sulfate and nitrate concentrations contained in the 33 valid data sets with chemical species. Chemical concentrations in the IP Network were not uniformly measured on the same days at all sites. Complicating this was an inability to acquire weather data from every site which showed an elevated concentration. Thus, only seven out of 33 cases might support the notion of a regional-scale secondary particle event with sulfate or nitrate concentrations more than double the maximum averages listed in Table 4-1. Several other cases with lower concentrations showed high sulfate or nitrate values, but they were less than twice the maximum averages. The absence of sulfate and nitrate information from other sites on the same days precludes a complete evaluation of this hypothesis.

The most pronounced event occurred on 11/20/79 in Philadelphia, PA. Here, fine sulfate values exceeded  $30 \mu\text{g}/\text{m}^3$  at the T and A Pet, Presbyterian Home, and NE Transfer sites. Fine nitrate concentrations reached  $9 \mu\text{g}/\text{m}^3$  at NE Transfer. Sulfate and nitrate values from other eastern cities were not available on this date to confirm its regional nature. The weather maps show a large high pressure system which had persisted for three days with unseasonably warm weather. There is no question that these secondary species were major contributors to the

173, 152 and 146  $\mu\text{g}/\text{m}^3$   $\text{PM}_{15}$  concentrations at the T and A Pet, NE Transfer, and Presbyterian Home sites, respectively, especially when the unmeasured cations such as hydrogen ion and ammonium, associated with the sulfate and nitrate compounds are considered.

P.S. #26 in Buffalo experienced similar and high sulfate on 9/18/79 and 4/4/81. Some of the elevated sulfate may be of local or sub-regional origin in these cases, as nearby sites in Ironton, PA, and Cleveland, OH, show fine sulfate concentrations of 5  $\mu\text{g}/\text{m}^3$  and 8  $\mu\text{g}/\text{m}^3$  on 4/4/81. No sulfate and nitrate measurements were available from other sites on 4/4/79.

Western sites do not usually exhibit pronounced regional-scale phenomena owing to more complex topography (e.g. Flocchini et al., 1981). As already noted, a high sulfate concentration at Bakersfield was possibly due to the sub-regional conversion of emissions from nearby industrial sources. Corresponding readings at sites which are exposed to the same meteorological situations, such as Fresno, were not available.

Secondary aerosol products can be major contributors to high  $\text{PM}_{15}$  levels, but the information from the IP Network and other sources used in this study is insufficient to distinguish between regional-scale processes and local or sub-regional sources.

#### INVERSIONS (Hypothesis 4)

Vertical temperature soundings were available for 27 of the 36 site-days with chemical speciation. Of these, 24 corresponded with the 33 site-days for which no measurement anomalies were suspected. These inversions were nearly always accompanied by low wind speeds and often occurred at the end of a high pressure system which had persisted for two or three days.

Inversions and stagnant conditions do not cause high pollutant concentrations. They do provide situations which are conducive to an accumulation of pollutants. These conditions occur at all site types in both the eastern and western U.S.

Subsidence or radiation inversions were observed on the 0000Z soundings for eighteen of the 24 cases with complete and valid data, making this hypothesis the most completely supported of the five. Since these soundings were taken during the afternoon on or evening of the sampled day, they were probably more persistent than short-term radiation inversions which would have been present only during early morning hours.

#### MEASUREMENT ANOMALIES (Hypothesis 5)

The potential always exists for a specific measurement to be unrepresentative of reality, and the number of cases supporting this hypothesis provides a rough estimate of the proportion of high PM<sub>15</sub> concentrations which may result from an inadequate measurement process. The IP Network is particularly amenable to the identification of these

cases owing to the large number of simultaneous measurements taken at each site which require an internal consistency with each other. Ten out of the fifty high  $PM_{10}$  measurements were found to have combinations of 1) a  $PM_{10}$  concentration greater than the  $PM_{2.5}$  concentration, 2) a coarse to fine concentration ratio which is unlikely to be obtained from typical particle size distributions, and 3) chemical concentration levels which are an order of magnitude higher or lower than those typically found in ambient aerosol samples (see Table 4-1 for ambient chemical concentration levels).

TSP was less than  $PM_{10}$  in seven cases, the most obvious of which is the El Paso case, described in Section 4, in which the  $400 \mu g/m^3$   $PM_{10}$  exceeded the  $104 \mu g/m^3$  TSP by nearly a factor of four.

A high coarse/fine ratio is a reason by itself to explain a  $PM_{10}$  value. For example, this ratio was 12.5 in El Paso on 12/12/79, but the coarse aluminum, silicon and calcium values, while not exceptionally high, demonstrate a substantial coarse contribution from geological material. Fine concentrations for sulfate, nitrate, and the geological elements are generally low with respect to the values in Table 4-1. In this case, the data are considered valid. This is not the case for the Presbyterian Home site on 3/10/80 and a measurement anomaly is assumed.

The chemical species concentrations at the Wilmoth Pump site on 7/9/81 do not support the 3.1 coarse/fine ratio measured there. Most of the coarse concentrations are much too low to account for the coarse

mass. A better example is the case of Portland, OR, on 10/12/79 which exhibits a  $43 \mu\text{g}/\text{m}^3$  aluminum concentration. Though aluminum pot lines are located east of Portland, Watson (1979) never found them to be major contributors in downtown Portland. Similar high aluminum levels have been found at other Oregon sites in Portland, Deschutes County, and Eugene. The high aluminum concentrations may result from contamination of the samples.

The small 37 mm ringed Teflon filters used for  $\text{PM}_{15}$  sampling are much more susceptible to measurement anomalies than the large 8 x 10" Hiovol filters simply because a small gain in mass translates into a much larger gain in ambient concentration. Even minor contamination must be avoided and it is not always possible to do so.



## SECTION 6

### SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This report has attempted to identify the potential causes of elevated  $PM_{10}$  concentrations from measurements available in the IP Network Data Base and meteorological measurements from the National Weather Service. The number of  $PM_{10}$  measurements was found to be insufficient to meet the study objectives, but a high correlation was found between elevated  $PM_{15}$  and  $PM_{10}$  concentrations at sites where simultaneous measurements were taken. High  $PM_{15}$  concentrations were then used as surrogates for  $PM_{10}$ .

Five causes of elevated  $PM_{15}$  concentrations were advanced: 1) local industrial source emissions, 2) local non-industrial source emissions, 3) regional-scale secondary aerosol events, 4) subsidence and radiation inversions and air mass stagnation, and 5) measurement anomalies. Support for the first hypothesis was found in 16 of 33 cases (48%), nearly all of which occurred at industrial site types. The second hypothesis was supported in 18 out of 33 cases (55%) and included industrial, commercial, residential and agricultural site types. The regional-scale nature of the third hypothesis was difficult to support owing to inadequate data, though major secondary aerosol events were identified in 7 of 33 (21%) of the cases. Inversions and stagnation were observed in 18 of 24 (75%). Measurement anomalies occurred in ten of 50 (20%) cases. These anomalous measurements were not considered as support for the other four hypotheses even though the  $PM_{15}$  data were not necessarily invalid.

The conclusions drawn from this study are:

- Though industrial sites often exhibit elevated local industrial source contributions, these are often accompanied by elevated non-industrial and secondary aerosol contributions. Thus, local industrial sources are not the sole cause of elevated PM<sub>15</sub> concentrations.
- Most elevated PM<sub>15</sub> episodes are accompanied by adverse weather conditions, such as temperature inversions and persistent stagnation. Since these meteorological events are bound to occur from time to time in most urban areas, the only way to lower PM<sub>15</sub> levels is to reduce emissions.
- Secondary aerosol is a potentially major contributor to PM<sub>15</sub>, and its origin may or may not be within the region in which the samples are taken. Gaseous as well as particulate emissions reductions may be required to reduce elevated PM<sub>15</sub> concentrations.
- A significant potential for the erroneous measurements of high PM<sub>15</sub> exists, probably owing to the very small samples and flow rates of the dichotomous sampler. A small filter weight gain due to contamination can translate into a large increase in the computed ambient concentration.

The IP Network data base is a rich source of information on the size-classified concentrations of suspended particulate matter and its chemical composition. This qualitative examination of the potential cause of elevated PM<sub>15</sub> levels, and through them the PM<sub>10</sub> levels, found in the data base provokes several recommendations for improving its utility and analyzing it further. Three recommendations pertain to the enhancement of the data base itself:

- A comprehensive guide to the data base should be written. This guide would include a description of all the reports, their contents, the meanings of flags and symbols, and the criteria for quality control, sample analysis selection, and data validation. While this study adds new insights to those found earlier by Watson et al. (1981), these references do not adequately unify the necessary information.
- A sample selection strategy for chemical analysis needs to be formulated and applied. Evaluation of regional-scale events

was hampered by the lack of simultaneous chemical speciation from samples at nearby sites. Similarly, some of the highest PM<sub>15</sub> concentrations in the network were not submitted to chemical analyses, thereby hindering the interpretation of those high values. Presumably these samples are still archived and chemical analyses can still be performed. Several of these should be selected and analyzed in future studies.

- Site surveys and urban emissions summaries of all IP Network sites need to be compiled. The examination of elevated PM<sub>15</sub> concentrations with respect to Hypotheses 1 and 2 was hampered in many cases by the lack of site surveys and the source distribution maps similar to those presented in Watson et al. (1981). These would enhance the utility of the IP Network data base immeasurably.

Three recommendations pertain the further analysis of IP Network data:

- The non-reportable data listing classified by elements should be examined to identify days on which individual source-types are large contributors, and the PM<sub>15</sub> mass should be examined for these days to see if it is generally high. For example, PM<sub>15</sub> vanadium reached a near network high of 1.06  $\mu\text{g}/\text{m}^3$  in Hartford, CT, on 10/31/81, which may be indicative of a large contribution from residual oil combustion. PM<sub>15</sub> was only 41  $\mu\text{g}/\text{m}^3$  on this date, which by no means approaches a maximum. There may be many incidences when a source-type, as indicated by a trace element, reaches its maximum contribution, yet the overall PM<sub>15</sub> mass concentration is well within normal bounds.
- The occurrence of meteorological regimes needs to be identified. Days on which they occur need to be examined for elevated PM<sub>15</sub> concentrations. Several patterns of temperature soundings and synoptic weather maps have been found to correspond with elevated concentrations. If the meteorological conditions they represent are truly causal factors, then for each such case the PM<sub>15</sub> concentration should be above average. 1980 to 1982 weather maps need to be examined and classified for these cases and the concentrations for days on which they occur can be drawn from the data base.
- Source contributions need to be quantified by receptor modeling methods. Some local source samples might be taken for chemical mass balance analyses. Factor analysis and linear regression models might also be tested for creating site-specific source composition matrices.

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APPENDIX A  
CASE STUDIES OF ELEVATED PM<sub>15</sub> CONCENTRATIONS

Each of the 50 cases specified in Table 3-1 is examined in detail in this Appendix. The size-specific mass and chemical data have been grouped by urban area in Tables A-2 to A-11. Detection limits for the chemical species as a function of year are presented in Table A-1 for comparison against the values in the subsequent tables. The caveat that Al, Si, Cl, K, Ca, and Ni are not normally reported by EPA, owing to lack of interlaboratory comparability, is repeated here.

Also reported in Tables A-2 to A-11 are the coarse to fine mass ratios and the temperature/pressure correction factors. After examination of the various data reports, it was found that these factors were applied to fine mass concentrations in all cases, but they did not appear to have been applied to all coarse mass concentrations. The factors were applied to sulfate and nitrate values, but to none of the elemental concentrations. To maintain a consistent picture, the values reported in Tables A-2 to A-11 have not been corrected by these factors. In all cases, these factors do not differ from unity by more than a few percent and the adjustments are well within the routine data uncertainties of 5 to 10%. They have been listed to establish comparability of the values listed here with those presently in the IP Network data base.

TABLE A-1  
DETECTION LIMITS FOR SELECTED  
ELEMENTS QUANTIFIED BY X-RAY FLUORESCENCE

Element	<u>Detection Limit, <math>\mu\text{g}/\text{m}^3</math></u>			
	1979	1980	1981	1982
Al <sup>a</sup>	0.210	0.250	0.140	0.140
Si <sup>a</sup>	0.060	0.070	0.040	0.040
P <sup>a</sup>	0.035	0.040	0.020	0.020
S <sup>a</sup>	0.025	0.030	0.020	0.020
Cl <sup>a</sup>	0.055	0.065	0.040	0.040
K <sup>a</sup>	0.025	0.030	0.020	0.020
Ca <sup>a</sup>	0.030	0.030	0.020	0.050
V	0.015	0.015	0.010	0.020
Mn	0.010	0.010	0.010	0.020
Fe	0.010	0.010	0.010	0.020
Ni	0.005	0.005	0.005	0.005
Cu	0.005	0.005	0.005	0.005
Zn	0.005	0.005	0.005	0.005
Br	0.001	0.002	0.005	0.005
Pb	0.010	0.010	0.005	0.010

<sup>a</sup> These elemental concentrations are not normally reported by EPA because interlaboratory comparisons for their values have demonstrated ambiguous results.

TABLE A-2  
SITE-DAY DESCRIPTIONS FOR  
BIRMINGHAM, AL: NORTH BIRMINGHAM

SITE	-----N. Birmingham-----			
DAY	7/14/80	12/5/80	8/26/81	5/5/82
<u>Observable</u>				
HIVOL mass	236.9	277.3	178.2	305.4
SSI mass	157.4	214.0	141.4	214.7
PM <sub>15</sub> mass	134.4	164.5	112.9	182.3
COARSE-15 mass	79.9	90.7	51.8	118.6
FINE-15 mass	54.5	73.8	61.1	63.7
Al <sup>b</sup> C	No data	No data	No data	No data
F	" "	" "	" "	" "
Si <sup>b</sup> C	" "	" "	" "	" "
F	" "	" "	" "	" "
Fe C	" "	" "	" "	" "
F	" "	" "	" "	" "
SO <sub>4</sub> C	" "	" "	1.3	" "
F	" "	" "	25.0	" "
NO <sub>3</sub> C	" "	" "	0.78	" "
F	" "	" "	0.29	" "
V C	" "	" "	" "	" "
F	" "	" "	" "	" "
Ni C	" "	" "	" "	" "
F	" "	" "	" "	" "
Cl <sup>b</sup> C	" "	" "	" "	" "
F	" "	" "	" "	" "
Br C	" "	" "	" "	" "
F	" "	" "	" "	" "
Pb C	" "	" "	" "	" "
F	" "	" "	" "	" "
K <sup>b</sup> C	" "	" "	" "	" "
F	" "	" "	" "	" "
Mn C	" "	" "	" "	" "
F	" "	" "	" "	" "
Zn C	" "	" "	" "	" "
F	" "	" "	" "	" "
Cu C	" "	" "	" "	" "
F	" "	" "	" "	" "
Ca <sup>b</sup> C	" "	" "	" "	" "
F	" "	" "	" "	" "
COARSE/FINE	1.47	1.23	0.85	1.86
HIVOL Correction	1.010	0.978	1.020	1.020
SSI Correction	1.010	0.990	1.020	1.020
COARSE and FINE Correction	1.013	0.984	1.013	1.013

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories



TABLE A-3  
SITE-DAY DESCRIPTIONS FOR  
BUFFALO, NY: P.S. 26

SITE	-----P.S. 26-----			
DAY	9/18/79	1/4/81	4/4/81	6/15/81
<u>Observable</u>				
HIVOL mass	153.2	28.2	No data	No data
SSI mass	No data	No data	No data	123.6
PM <sub>15</sub> mass	143.1	148.9	142.0	130.2
COARSE-15 mass	71.3	64.9	38.6	52.2
FINE-15 mass	71.8	84.0	103.4	78.0
Al <sup>b</sup> C	2.14	No data	3.30	14.24
F	0.30	" "	4.91	6.24
Si <sup>b</sup> C	5.07	" "	2.03	2.16
F	0.55	" "	2.57	2.16
Fe C	6.17	" "	2.30	1.93
F	1.11	" "	5.14	2.19
SO <sub>4</sub> C	2.77	" "	2.13	2.35
F	30.30	" "	18.7	15.7
NO <sub>3</sub> C	2.70	" "	0.56	0.55
F	1.91	" "	0.81	2.60
V C	0.015	" "	0.010	0.010
F	0.015	" "	0.010	0.010
Ni C	0.017	" "	0.008	0.005
F	0.009	" "	0.020	0.010
Cl <sup>b</sup> C	0.54	" "	0.33	0.31
F	0.13	" "	1.10	0.70
Br C	0.024	" "	0.008	0.009
F	0.077	" "	0.084	0.081
Pb C	0.15	" "	0.045	0.067
F	0.41	" "	0.86	0.51
K <sup>b</sup> C	0.48	" "	0.22	0.21
F	0.64	" "	1.45	0.72
Mn C	0.32	" "	0.11	0.032
F	0.081	" "	0.18	0.073
Zn C	0.21	" "	0.031	0.044
F	0.25	" "	0.21	0.21
Cu C	0.41	" "	0.010	0.024
F	0.020	" "	0.048	0.032
Ca <sup>b</sup> C	6.70	" "	2.70	1.11
F	0.37	" "	3.60	1.02
COARSE/FINE	0.99	" "	0.37	0.67
HIVOL Correction	1.002	0.944	0.980	0.980
SSI Correction	1.02	0.964	1.002	1.002
COARSE and FINE Correction	1.005	0.970	1.005	1.005

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-3 (continued)  
SITE-DAY DESCRIPTIONS FOR  
BUFFALO, NY: BIG SISTER AND WILMUTH PUMP

SITE	Big Sister	-----Wilmuth-Pump-----		
DAY	8/7/80	5/22/81	6/15/81	7/9/81
<u>Observable</u>				
HIVOL mass	60.0	177.0	No data	No data
SSI mass	No data	168.1	163.5	209.0
PM <sub>15</sub> mass	129.5	187.2	144.9	198.2
COARSE-15 mass	80.0	136.5	94.2	149.6
FINE-15 mass	49.5	50.7	50.7	48.6
Al <sup>b</sup> C	No data	3.22	2.42	0.14
F	" "	0.44	0.65	No data
Si <sup>b</sup> C	" "	9.92	4.51	0.040
F	" "	1.10	1.48	No data
Fe C	" "	10.84	5.55	0.010
F	" "	5.55	7.05	No Data
SO <sub>4</sub> C	" "	2.25	3.9	4.7
F	" "	9.31	16.0	13.5
NO <sub>3</sub> C	" "	3.69	2.94	1.88
F	" "	2.13	0.93	1.10
V C	" "	0.014	0.010	0.22
F	" "	0.010	0.010	No data
Ni <sup>b</sup> C	" "	0.020	0.016	5.10
F	" "	0.013	0.015	No data
Cl <sup>b</sup> C	" "	1.41	1.2	0.040
F	" "	0.79	0.39	No data
Br C	" "	0.019	0.015	0.050
F	" "	0.089	0.035	No data
Pb C	" "	0.18	0.23	0.007
F	" "	0.94	0.63	No data
K <sup>b</sup> C	" "	0.90	0.58	0.020
F	" "	3.29	2.29	No data
Mn C	" "	0.39	0.10	0.62
F	" "	0.14	0.17	No data
Zn C	" "	0.12	0.29	3.25
F	" "	0.83	2.00	No data
Cu C	" "	0.018	0.012	0.26
F	" "	0.043	0.047	No data
Ca <sup>b</sup> C	" "	26.5	25.1	0.047
F	" "	2.46	1.75	No data
COARSE/FINE	1.61	2.69	1.85	3.12
HIVOL Correction	1.002	0.980	0.980	0.980
SSI Correction	No data	1.002	1.002	1.002
COARSE and FINE Correction	1.005	1.005	1.005	1.005

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-4  
SITE-DAY DESCRIPTIONS FOR  
CLEVELAND, OH: BIDOULPH & 54th

SITE	-----Bidoulph & 54th-----						
DAY	7/20/79	9/6/79	11/5/79	9/12/80	4/4/81	8/26/81	10/13/81
<u>Observable</u>							
HIVOL mass	No data	223.6	227.3	191.2	186.2	196.1	299.6
SSI mass	No data	No data	No data	134.0	No data	143.5	170.1
PM <sub>15</sub> mass	175.7	144.9	140.2	123.2	135.8	223.4	131.9
COARSE-15	96.0	100.3	72.5	67.7	82.5	23.1	92.5
FINE-15 mass	79.7	44.6	67.7	55.5	53.3	200.3	39.4
Al <sup>b</sup> C	4.12	3.19	2.79	3.45	2.74	No data	2.45
F	0.21	0.22	0.33	0.37	0.48	" "	0.26
Si <sup>b</sup> C	9.68	18.73	8.04	6.98	7.43	" "	8.10
F	8.74	1.16	0.76	1.21	1.18	" "	0.49
Fe C	8.13	4.51	5.36	4.29	12.30	" "	5.53
F	1.15	0.42	1.25	0.57	5.14	" "	1.47
SO <sub>4</sub> C	2.90	1.34	1.92	1.28	3.01	" "	2.31
F	18.52	17.82	15.90	12.84	8.06	" "	6.79
NO <sub>3</sub> C	2.88	3.80	1.22	2.67	0.79	" "	1.31
F	0.16	0.55	1.20	0.42	0.90	" "	0.78
V C	0.17	0.15	0.15	0.02	0.01	" "	0.01
F	0.15	0.15	0.15	0.02	0.01	" "	0.01
Ni <sup>b</sup> C	0.21	0.010	0.019	0.02	0.03	" "	0.01
F	0.19	0.006	0.018	0.01	0.02	" "	0.01
Cl <sup>b</sup> C	2.17	0.70	1.30	2.00	0.93	" "	1.84
F	0.30	0.090	5.26	1.79	1.19	" "	2.47
Br C	0.043	0.031	0.055	0.03	0.01	" "	0.01
F	0.11	0.038	0.33	0.10	0.04	" "	0.07
Pb C	0.52	0.16	0.42	0.17	0.80	" "	0.11
F	2.00	0.42	1.34	0.62	0.64	" "	0.55
K <sup>b</sup> C	1.01	1.09	0.72	0.82	0.74	" "	0.68
F	1.08	0.22	1.32	2.25	2.07	" "	1.33
Mn C	0.26	0.12	0.19	0.17	0.43	" "	0.19
F	0.063	0.024	0.092	0.05	0.33	" "	0.11
Zn C	0.49	0.14	1.05	0.35	1.30	" "	0.36
F	1.13	0.10	1.10	0.39	2.51	" "	0.71
Cu C	0.076	0.032	0.050	0.07	0.03	" "	0.04
F	0.093	0.018	0.065	0.07	0.06	" "	0.05
Ca <sup>b</sup> C	8.87	7.51	6.37	6.24	7.37	" "	9.35
F	0.58	0.40	0.54	0.58	.89	" "	0.53
COARSE/FINE	1.20	2.25	1.07	1.22	1.55	" "	2.35
HIVOL Correction	1.001	1.001	0.955	0.991	0.991		0.955
SSI Correction	No data	No data	No data	1.001	1.001		0.955
COARSE and FINE Correction	No data	No data	No data	1.008	1.008		0.974

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-5  
SITE-DAY DESCRIPTIONS FOR  
PHILADELPHIA, PA: T & A PET SHOP, NE TRANSFER,  
AND BRIDESBURG RECREATION CENTER

SITE DAY	T & A Pet 11/20/79	Bridesburg Recreation 12/5/79	NE Transfer 12/11/79	NE Transfer 11/20/79
<u>Observable</u>				
HIVOL mass	192.4	176.5	173.7	180.2
SSI mass	No data	No data	No data	No data
PM <sub>15</sub> mass	173.0	124.8	126.9	151.8
COARSE-15 mass	64.2	77.3	67.0	45.2
FINE-15 mass	108.8	47.5	59.9	106.3
Al <sup>b</sup> C	2.90	3.04	2.92	3.15
F	0.81	0.49	0.45	0.63
Si <sup>b</sup> C	6.39	4.73	5.67	6.46
F	0.99	0.45	0.59	0.79
Fe C	4.38	1.80	2.16	2.90
F	0.90	0.33	0.33	0.78
SO <sub>4</sub> C	4.2	0.8	2.0	4.6
F	35.0	7.2	10.9	31.3
NO <sub>3</sub> C	1.94	1.13	1.09	0.52
F	6.22	3.75	4.81	9.22
V C	0.14	0.02	0.02	0.05
F	0.15	0.02	0.06	0.10
Ni C	0.05	0.01	0.02	0.04
F	0.11	0.02	0.04	0.10
Cl <sup>b</sup> C	0.83	0.49	0.72	0.55
F	0.48	2.38	1.44	0.40
Br C	0.11	0.02	0.04	0.07
F	0.45	0.17	0.22	0.27
Pb C	0.59	0.15	0.22	0.34
F	1.82	0.56	0.76	1.26
K <sup>b</sup> C	0.62	0.47	0.50	0.59
F	0.44	0.28	0.27	0.31
Mn C	6.9	0.04	0.04	0.06
F	0.90	0.02	0.01	0.05
Zn C	No data	0.22	0.79	0.30
F	" "	0.26	0.93	0.50
Cu C	0.10	0.04	0.14	0.07
F	0.06	0.21	0.61	0.05
Ca <sup>b</sup> C	2.6	1.66	2.15	2.87
F	0.49	0.34	0.35	0.49
COARSE/FINE	0.59	1.64	1.12	0.42
HIVOL Correction	No data	No data	No data	No data
SSI Correction	No data	No data	No data	No data
COARSE and FINE Correction	0.965	0.965	0.965	0.965

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-5 (continued)  
SITE-DAY DESCRIPTIONS FOR  
PHILADELPHIA, PA: ALLEGHENY AND PRESBYTERIAN HOME

SITE	Allegheny-----Presbyterian Home-----		
DAY	11/20/79	11/20/79	3/10/80
<u>Observable</u>			
HI/OL mass	195.2	161.5	No data
SS mass	167.2	No data	No data
PM <sub>10</sub> mass	134.0	146.3	136.4
COARSE-15 mass	51.9	43.1	8.9
FINE-15 mass	82.1	112.2	127.5
As <sup>b</sup> C	No data	2.88	0.89
As <sup>b</sup> F	" "	0.68	0.27
S <sup>b</sup> C	" "	5.36	1.91
S <sup>b</sup> F	" "	0.98	0.21
Fa C	" "	2.45	0.67
Fa F	" "	0.82	0.18
Se C	" "	3.4	1.03
Se F	" "	35.0	4.06
Mo C	" "	0.47	0.79
Mo F	" "	2.61	1.29
V C	" "	0.16	0.02
V F	" "	0.13	0.02
Ni C	" "	0.05	0.01
Ni F	" "	0.10	0.02
Cr <sup>b</sup> C	" "	0.28	0.14
Cr <sup>b</sup> F	" "	0.40	0.35
B <sup>b</sup> C	" "	0.10	0.02
B <sup>b</sup> F	" "	0.32	0.11
Pb C	" "	0.42	0.13
Pb F	" "	1.70	0.60
K <sup>b</sup> C	" "	0.45	0.17
K <sup>b</sup> F	" "	0.55	0.19
Mn C	" "	0.04	0.01
Mn F	" "	0.05	0.01
Zn C	" "	0.16	0.05
Zn F	" "	0.38	0.11
Cu C	" "	0.03	0.01
Cu F	" "	0.06	0.02
Ce <sup>b</sup> C	" "	1.54	1.58
Ce <sup>b</sup> F	" "	0.34	0.28
COARSE/FINE	0.63	0.30	0.07
HI/OL Correction	0.947	0.947	0.947
SS1 Correction	0.947	No data	No data
COARSE and FINE	0.965	0.965	0.965
Correction			

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-6  
SITE-DAY DESCRIPTIONS FOR  
PITTSBURGH, PA, HARTFORD, CT, CHICAGO, IL  
IRONTON, OH, AND YOUNGSTOWN, OH

SITE	-----Pittsburgh-----		Hartford---		Chicago---	Ironton---	Youngstown
DAY	10/30/80	5/22/81	1/22/81	2/3/81	4/4/81	2/15/81	
Observables							
HIVOL mass	364.1	228.7	212.6	209.4	175.9	210.7	
SSI mass	No data	No data	154.0	No data	121.4	173.9	
PM <sub>15</sub> mass	183.6	137.5	126.4	120.1	123.7	127.3	
COARSE-15 mass	59.5	79.4	65.4	61.9	75.3	56.3	
FINE-15 mass	124.1	58.1	61.0	58.2	48.4	71.0	
Al <sup>b</sup> C	No data	No data	3.26	No data	2.65	2.74	
F	" "	0.67	0.54	" "	0.14	0.44	
Si <sup>b</sup> C	" "	No data	9.53	" "	8.00	5.95	
F	" "	0.89	0.52	" "	0.073	0.53	
Fe C	" "	7.24	2.26	" "	5.65	3.51	
F	" "	4.83	0.21	" "	0.053	0.80	
SO <sub>4</sub> C	" "	2.9	0.6	" "	0.89	1.6	
F	" "	16.3	11.1	" "	4.7	13.2	
NO <sub>3</sub> C	" "	1.008	1.22	" "	1.87	0.88	
F	" "	0.29	1.32	" "	1.96	1.72	
V C	" "	0.018	0.035	" "	0.010	0.010	
F	" "	0.010	0.067	" "	0.010	0.010	
Ni C	" "	0.042	0.042	" "	0.008	0.011	
F	" "	0.024	0.034	" "	0.005	0.012	
Cl <sup>b</sup> C	" "	No data	9.81	" "	0.30	7.43	
F	" "	0.66	0.300	" "	0.040	3.66	
Br C	" "	0.030	0.060	" "	0.008	0.047	
F	" "	0.17	0.35	" "	1.03	0.31	
Pb C	" "	0.24	0.29	" "	0.038	0.22	
F	" "	1.008	1.10	" "	0.050	0.79	
K <sup>b</sup> C	" "	0.76	0.76	" "	0.71	0.40	
F	" "	0.87	0.44	" "	0.22	0.50	
Mn C	" "	0.45	0.049	" "	0.23	0.081	
F	" "	0.37	0.024	" "	0.010	0.051	
Zn C	" "	0.35	0.094	" "	0.093	0.121	
F	" "	1.300	0.23	" "	0.005	0.43	
Cu C	" "	0.066	0.039	" "	0.013	0.019	
F	" "	0.10	0.071	" "	0.005	0.025	
Ca <sup>b</sup> C	" "	7.09	1.61	" "	6.27	4.82	
F	" "	0.80	0.37	" "	0.02	0.33	
COARSE/FINE	0.48	1.37	1.08	1.06	1.56	0.79	
HIVOL Correction	0.974	0.992	0.938	0.962	1.004	0.997	
SSI Correction	No data	No data	0.938	0.952	1.004	0.944	
COARSE and FINE Correction	0.980	1.016	0.962	0.970	1.012	0.978	

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-7  
SITE-DAY DESCRIPTIONS FOR  
PHOENIX, AZ: ROOSEVELT ST.

SITE	-----Roosevelt St.-----	
DAY	6/21/81	11/6/81
<u>Observable</u>		
HIVOL mass	92.1	157.9
SSI mass	54.3	115.7
PM <sub>15</sub> mass	145.8	107.6
COARSE-15 mass	39.0	77.2
FINE-15 mass	106.8	30.4
Al <sup>b</sup> C	No data	0.140
F	" "	0.140
Si <sup>b</sup> C	" "	0.054
F	" "	0.040
Fe C	" "	0.083
F	" "	0.037
SO <sub>4</sub> C	" "	0.5
F	" "	0.06
NO <sub>3</sub> C	" "	0.91
F	" "	0.42
V C	" "	0.010
F	" "	0.010
Ni C	" "	0.005
F	" "	0.005
Cl <sup>b</sup> C	" "	0.046
F	" "	0.040
Br C	" "	0.56
F	" "	0.58
Pb C	" "	0.005
F	" "	0.005
K <sup>b</sup> C	" "	0.066
F	" "	0.10
Mn C	" "	0.010
F	" "	0.010
Zn C	" "	0.005
F	" "	0.005
Cu C	" "	0.005
F	" "	0.005
Pb C	" "	2.39
F	" "	0.39
COARSE/FINE	0.37	2.56
HIVOL Correction	1.054	1.028
SSI Correction	1.054	1.028
COARSE and FINE Correction	1.032	1.003

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-8  
SITE-DAY DESCRIPTIONS FOR  
BAKERSFIELD, CA: CHESTER AVE.

SITE	-----Chester Ave.-----			
DAY	11/17/80	12/23/80	1/10/81	2/3/81
<u>Observable</u>				
HIVOL mass	234.0	230.3	202.3	132.6
SSI mass	213.1	217.7	183.9	143.3
PM <sub>15</sub> mass	183.1	196.8	176.3	128.3
COARSE-15 mass	110.3	54.2	52.6	33.5
FINE-15 mass	72.8	142.6	123.7	94.8
Al <sup>b</sup> C	8.83	4.18	0.14	0.14
F	0.73	0.42	0.14	0.14
Si <sup>b</sup> C	23.88	11.59	0.04	0.14
F	1.028	0.43	0.04	0.14
Fe C	5.41	2.43	0.064	0.057
F	0.44	0.17	0.064	0.064
SO <sub>4</sub> C	0.81	2.20	12.05	1.52
F	9.0	21.10	44.65	13.45
NO <sub>3</sub> C	2.62	1.28	1.01	1.16
F	6.76	46.0	13.78	25.70
V C	0.010	0.010	0.01	0.01
F	0.065	0.044	0.01	0.01
Ni C	0.025	0.016	0.005	0.005
F	0.17	0.013	0.005	0.005
Cl <sup>b</sup> C	0.52	0.081	0.04	0.04
F	0.25	0.48	0.04	0.04
Br C	0.11	0.064	0.31	0.37
F	0.63	0.51	2.28	2.87
Pb C	0.46	0.32	0.12	0.028
F	0.25	0.15	0.005	0.005
K <sup>b</sup> C	2.61	1.22	0.028	0.042
F	1.07	0.19	0.046	0.038
Mn C	0.11	0.046	0.01	0.01
F	0.016	0.010	0.01	0.01
Zn C	0.076	0.049	0.005	0.005
F	0.047	0.050	0.005	0.005
Cu C	0.022	0.016	0.005	0.005
F	0.023	0.013	0.005	0.005
Ca <sup>b</sup> C	4.52	1.91	0.02	0.02
F	0.48	0.18	0.02	0.02
COARSE/FINE	1.52	0.38	0.42	0.35
HIVOL Correction	0.968	0.968	0.968	0.968
SSI Correction	0.968	0.968	0.968	0.968
COARSE and FINE	0.986	0.986	0.986	0.986
Correction				

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories



TABLE A-9  
SITE-DAY DESCRIPTIONS FOR  
RUBIDOUX, CA: RUBIDOUX

SITE DAY	-----Rubidoux-----					
	10/12/79	10/24/79	6/20/80	8/7/80	5/22/81	2/22/82
Observables						
HIVOL mass	195.7	221.8	210.0	263.6	No data	No data
SSI mass	No data	No data	182.3	214.4	128.7	No data
PM <sub>15</sub> mass	157.3	171.0	156.0	162.3	125.6	217.0
COARSE-15 mass	53.3	67.6	87.0	103.7	81.1	53.2
FINE-15 mass	104.9	103.4	69.0	58.6	44.5	163.8
Al <sup>b</sup> C	3.83	0.31	3.92	4.91	3.88	No data
F	0.35	0.35	0.32	0.35	0.23	" "
Si <sup>b</sup> C	10.68	0.33	10.34	13.07	10.44	" "
F	0.57	0.55	0.49	0.53	0.29	" "
Fe C	2.90	0.036	2.90	3.73	2.60	" "
F	0.21	0.27	0.21	0.28	0.13	" "
SO <sub>4</sub> C	2.42	0.70	1.87	1.54	1.18	" "
F	9.25	6.68	9.58	9.72	4.92	" "
NO <sub>3</sub> C	8.39	3.58	8.58	0.42	6.84	" "
F	20.01	37.05	15.41	2.79	9.21	" "
V C	0.015	0.015	0.015	0.015	0.010	" "
F	0.015	0.015	0.015	0.015	0.010	" "
Ni C	0.015	0.005	0.008	0.013	0.007	" "
F	0.019	0.017	0.016	0.019	0.005	" "
Cl <sup>b</sup> C	1.24	0.055	0.65	0.58	1.42	" "
F	0.24	0.24	0.14	0.13	0.098	" "
Br C	0.092	0.001	0.032	0.048	0.033	" "
F	0.24	0.30	0.077	0.13	0.080	" "
Pb C	0.29	0.010	0.16	0.20	0.10	" "
F	1.16	1.57	0.51	0.78	0.32	" "
K <sup>b</sup> C	1.59	0.16	1.64	1.93	1.46	" "
F	0.18	0.10	0.14	0.18	0.088	" "
Mn C	0.066	0.010	0.059	0.081	0.053	" "
F	0.010	0.019	0.010	0.011	0.010	" "
Zn C	0.075	0.005	0.051	0.069	0.044	" "
F	0.057	0.068	0.039	0.057	0.023	" "
Cu C	0.079	0.005	0.025	0.035	0.019	" "
F	0.018	0.025	0.023	0.046	10.010	" "
Ca <sup>b</sup> C	7.47	0.14	5.94	10.16	4.15	" "
F	0.33	0.39	0.26	0.56	0.39	" "
COARSE/FINE	0.51	0.65	1.27	1.75	1.82	" "
HIVOL Correction	0.985	0.985	0.992	0.992	No data	" "
SSI Correction	0.985	0.985	0.992	0.992	No data	" "
COARSE and FINE	0.988	0.988	0.995	0.995	0.995	" "
Correction						

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-10  
SITE-DAY DESCRIPTIONS FOR  
EL PASO, TX: TILLMAN HEALTH  
AND EL PASO COUNTY

SITE	Tillman Health	El Paso County	
DAY	11/29/79	12/11/79	4/29/82

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Observable

HIVOL mass	206.3	217.6	104.2
SSI mass	147.3	No data	No data
PM <sub>15</sub> mass	126.0	130.9	399.6
COARSE-15 mass	81.4	120.7	19.1
FINE-15 mass	44.6	10.2	380.5
Al <sup>b</sup> C	3.82	3.40	No data
F	0.60	0.45	" "
Si <sup>b</sup> C	9.79	8.59	" "
F	0.68	0.61	" "
Fe C	1.74	1.15	" "
F	0.17	0.14	" "
SO <sub>4</sub> C	1.46	0.87	" "
F	3.21	1.30	" "
NO <sub>3</sub> C	1.24	0.30	" "
F	0.77	1.36	" "
V C	0.015	0.015	" "
F	0.015	0.015	" "
Ni C	0.008	0.006	" "
F	0.005	0.005	" "
Cl <sup>b</sup> C	0.54	0.32	" "
F	1.63	0.11	" "
Br C	0.11	0.010	" "
F	0.43	0.044	" "
Pb C	0.54	0.039	" "
F	1.59	0.15	" "
K <sup>b</sup> C	0.92	0.98	" "
F	0.50	0.45	" "
Mn C	0.074	0.029	" "
F	0.011	0.010	" "
Zn C	0.11	0.029	" "
F	0.10	0.015	" "
Cu C	0.064	0.11	" "
F	0.039	0.014	" "
Ca <sup>b</sup> C	14.13	5.59	" "
F	1.21	0.76	" "
COARSE/FINE	1.82	12.5	0.05
HIVOL Correction	1.043	1.043	1.145
SSI Correction	1.043	1.043	No data
COARSE and FINE Correction	1.042	1.042	0.076

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

TABLE A-11  
SITE-DAY DESCRIPTIONS FOR  
FRESNO, CA, SAN JOSE, CA, AND PORTLAND, OR

SITE	Fresno-----	San Jose-----	Portland
DAY	12/11/80	10/30/80	10/12/79

Observable

HIVOL mass	166.2	109.9	No data
SSI mass	138.9	No data	No data
PM <sub>15</sub> mass	123.5	120.1	207.0
COARSE-15 mass	47.9	47.0	115.6
FINE-15 mass	75.6	73.1	91.2
Al <sup>b</sup> C	3.87	2.75	42.87
F	0.25	0.54	7.79
Si <sup>b</sup> C	12.27	9.22	4.09
F	0.35	0.61	0.74
Fe C	2.21	2.23	1.72
F	0.10	0.30	0.67
SO <sub>4</sub> C	1.15	0.63	0.58
F	6.44	4.02	12.19
NO <sub>3</sub> C	0.42	1.53	0.72
F	28.61	13.75	4.47
V C	0.010	0.015	0.015
F	0.010	0.015	0.023
Ni C	0.013	0.011	0.017
F	0.025	0.013	0.042
Cl <sup>b</sup> C	0.092	0.17	0.32
F	0.10	0.25	0.67
Br C	0.005	0.087	0.065
F	0.030	0.47	0.47
Pb C	0.024	0.35	0.22
F	0.12	1.59	1.48
K <sup>b</sup> C	1.053	0.66	0.25
F	0.22	0.62	0.53
Mn C	0.030	0.042	0.066
F	0.010	0.011	0.12
Zn C	0.025	0.066	0.061
F	0.016	0.12	0.13
Cu C	0.19	0.031	0.088
F	0.028	0.065	0.087
Ca <sup>b</sup> C	1.87~	1.92	1.42
F	0.34	0.39	0.30
COARSE/FINE	0.63	0.64	1.27
HIVOL Correction	0.974	0.975	No data
SSI Correction	0.974	No data	No data
COARSE and FINE	0.982	0.979	0.969
Correction			

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

b. These concentrations are not normally reported by EPA owing to lack of comparability between analysis laboratories

The site-days have been arbitrarily divided into eastern and western sites because consistent differences were observed in both the meteorology and in the chemical character of samples taken in these sections of the country. Urban-scale subsets have been formed within these two geographical regions.

Each case study contains a general description of the aggregate information acquired for the specific urban-scale subset. These descriptions provide the basis for the support of the five hypotheses as described in Sections 4 and 5. In the several cases where data are inconclusive or inadequate to support or refute the hypotheses, the specific limitations are delineated so that future measurements may make up for present shortcomings.

## EASTERN SITES

### Birmingham, AL (4 Site-Days)

The Birmingham data set in Table A-2 contains no dichotomous sampler chemical or elemental information.

Since TSP is larger than  $PM_{15}$ , the ambient particle size distribution extended well beyond 15  $\mu m$  to larger sizes. The HIVOL/ $PM_{15}$  ratio, for example, ranges from 1.6 to about 1.8, being at its lowest value on 8/16/81 when the  $PM_{15}$  coarse/fine ratio reaches its minimum of 0.85. In all cases, the coarse mode appears to be a major, if not the dominant, component of the  $PM_{15}$ . This is consistent with local or neighborhood-scale sources. Industrial sources such as coke ovens, lime kilns, lead

and aluminum smelters, iron and steel foundries, blast furnaces and cement plants, are located in Birmingham, and a foundry is located 1/4 mile east of the site. The effects of these industrial sources cannot be ascertained in the absence of chemical species, particularly Fe, as an indicator of the foundry.

A vacant lot of unspecified nature is situated in the block southeast of the sampling site and the preponderance of coarse particles could result from some activity and an appropriate surface which would allow suspension of coarse particles on all four occasions.

Wind speed measurements from Centerville, AL, about 40 miles southwest of Birmingham, do not appear adequate for dust resuspension however. Surface winds on all of the Birmingham days were 6 knots, 2'0", and 4 knots, 30' and 10' respectively. The daily weather map for all four cases shows broad pressure regions that generally have been on the surface map for at least one or two days preceding each case, although a stationary front is drawn over central AL on 7/14/80. In all cases, the 500 mb winds are very light, for example, 2 knots, 35° on 8/26/81.

Chemical data are insufficient to identify secondary particle episodes. The weather maps generally indicate sluggish circulations in the vicinity of Birmingham, with southeasterly and southwesterly winds, not conducive to sulfate transport from the major sulfate producing regions to the north and east of Alabama for these days.

Though the circulation is sluggish, the available 0000Z soundings on 7/14/80 and 8/26/81 show only weak inversions at about 800 mb, and it is not clear that these were either subsidence inversions or major barriers to vertical mixing.

Data validation checks give no cause for rejection of the data for these days. Owing to lack of chemical and meteorological data these cases neither support nor refute any of the hypotheses.

#### Buffalo, NY (8 Site-Days)

Fe is the most likely contribution from steel mills close to P.S. #26 and Wilmuth Pump. Fe can also result from resuspension of earth's crustal material, but Watson (1979) summarizes a large selection of literature which indicates that the Fe/Si ratio for the total tropospheric background aerosol composition is usually considerably less than 1.0. These ratios are nearly equal to or greater than 1.0, and in several cases greater than 2.0, in both the fine and coarse samples, with the exception of 7/9/81 at Wilmuth Pump. For the Buffalo cases, the Fe concentration ranges from  $.01 \mu\text{g}/\text{m}^3$  to  $10.8 \mu\text{g}/\text{m}^3$ . The intermediate values for Fe range from about 2 to about  $6 \mu\text{g}/\text{m}^3$  in the coarse fraction and usually exceed the coarse Si concentration by 10% to 20%. Fine Fe concentrations range from  $1.11 \mu\text{g}/\text{m}^3$  to  $7.05 \mu\text{g}/\text{m}^3$ . Fe is enriched in Buffalo, especially in the fine fraction, and the nearby steel industry is a likely source. Local soils may have become enriched in Fe due to the long-term operation of iron and steel mills in

Buffalo. Resuspension of these soils may contribute to the high, coarse Fe concentrations. This doesn't explain the elevated Fe concentrations in the fine fraction where resuspended dust is less of a contributor.

Mn is a product of iron and steel processing. Watson et al. (1981) found EPA Network average coarse and fine Mn concentrations to be in the .01 to .03  $\mu\text{g}/\text{m}^3$  range. For these site days Mn ranges from .03, to 0.52  $\mu\text{g}/\text{m}^3$ . Intermediate values are in the 0.1 to 0.3  $\mu\text{g}/\text{m}^3$  range for both coarse and fine fractions showing substantial enrichment. The Mn coarse/fine ratio is greater than 1.0 when the Fe coarse/fine ratio is also greater than one. It is less than 1.0 when the same is true for Fe, although the absolute magnitudes of Fe and Mn do not show a clear correlation. Though Mn is a minor component of the particles generated by many types of iron and steel processes, the Mn values further support the hypothesis that iron and steel plants contribute to Buffalo's high readings.

High coarse Ca concentrations were found at the Wilmuth Pump site on 6/15/81 (26.1  $\mu\text{g}/\text{m}^3$ ), on 5/22/81 (26.5  $\mu\text{g}/\text{m}^3$ ), and at P.S. #26 on 9/18/79 (6.7  $\mu\text{g}/\text{m}^3$ ). Since Ca is a non-reportable chemical species, its high values may be caused by a measurement anomaly.

The P.S. #26 site is close to both a freeway and a railroad, but it is not clear that these have contributed in an important way. Pb concentrations, for example, are not excessive at P.S. #26.

Sulfate values exceed nitrate, with the maximum value being 3  $\mu\text{g}/\text{m}^3$  in the fine fraction at P.S. #26 on 9/18/79. Most fine

sulfate concentrations are in the range of 10 to 15  $\mu\text{g}/\text{m}^3$ , however, with coarse values considerably less. Watson et al. (1981) cite an average fine sulfate concentration of about 8  $\mu\text{g}/\text{m}^3$  for urban-industrial IP Network sites, and these values are not appreciably greater than Watson et al. values.

High  $\text{PM}_{15}$  levels were observed at both the P.S. #26 and Wilmuth Pump sites on 6/15/81, implying that one or more contributions were especially significant on that day or a subregional phenomenon resulted in high particulate matter loadings over the greater Buffalo area. The regional-scale contributions are not well supported because 6/15/81 did not emerge as a high site-day at any other eastern urban site.

Upper air soundings were available for all cases except 5/22/81. In the case of 6/15/81, high pressure at the surface was retreating as a warm front slowly advanced from the southwest. The sounding is very nearly wet-adiabatic from 850 mb up to 500 mb, suggesting the presence of an extensive cloud layer. The 0000Z surface wind was 12 knots at 240°. The 9/18/79 sounding (0000Z) shows more evidence of an inversion, with its top at about 780 mb. The 9/18/79 surface map shows high pressure retreating as a cold front approaches from the northwest.

The 4/4/81 sounding at 0000Z shows a pronounced inversion very close to the surface (about 970 mb or 355 m). Surface winds were 6 knots at 220°, but were much stronger and from the same direction aloft. Conditions had been dry for several days, and on 4/4/81 the surface map shows a low pressure system over the Great Lakes, approaching Buffalo



from the west and causing rain by 4/5/81. 4/4/81 was also a high site-day at Cleveland and Ironton, OH, and will be discussed shortly.

The 7/9 soundings show a weak inversion at 945 m (656 m) and a much more pronounced one in the 700-800 m region. At the surface wind is significant, 14 knots from 260° at 0000Z. The preceding days show surface high pressure retreating as a cold front approaches from the northwest bringing moderate amounts of precipitation by 7/10/81.

No soundings were available for 5/22/81, but the surface map indicates that there had been no precipitation for several days. On 5/22/81, surface high pressure was centered over southern Ohio, and a stationary front is shown to the north of the Great Lakes.

With the possible exception of Wilmut Pump's highest site-day, 5/22/81, all of these cases seem to follow several days of dry weather and surface high pressure leading up to a frontal approach on the high concentration day, often with precipitation by the next day. Particulate matter over Buffalo could be trapped during stagnant conditions prior to frontal passages. The mechanism seems particularly difficult to clarify when one considers that surface winds were often significant, and some sort of dictating transport mechanism, such as that observed in SURE (Mueller and Hidy et al., 1983), must be ruled out.

At the Big Sister site on 8/7/80, the  $PM_{15}/HIVOL$  ratio was 2.16, at P.S. #26 on 1/4/81, the highest day for this site, the  $PM_{15}/HIVOL$  ratio was 5.28. At the Wilmut Pump site on 5/22/81, the  $PM_{15}/HIVOL$  ratio was 1.36 and these cases support Hypothesis A. At the P.S. #26 site on

6/15/81, no HIVOL values are given, but the  $PM_{15}$  exceeds the SSI value by 5%. Though this is within EPA/EMSL criteria for acceptance, it is not a common finding in the IP Network.

#### Cleveland, OH (7 Site-Days)

No site survey and no nearby radiosonde soundings were available for Cleveland.

Graf and Draftz (1979) examined microscopic TSP compositions at nine sites in the greater Cleveland area during 1977. One of the sites was the same as the Cleveland site identified for the present study. Graf and Draftz present a list of 24 Cleveland emissions sources, estimates of their 1977 emissions, and a map showing their location with respect to the sampling sites. Two Republic Steel facilities, a DuPont plant, and the Lorain Cuyahoga Works of U.S. Steel are within one mile of the sampling site. Graf and Draftz note, with respect to their 1977 survey of the APC HQ site, "Emissions from iron industries were also the primary cause of elevated TSP levels recorded at this site."

King et al. (1976), also studying the Cleveland urban area, did not analyze their results with the degree of spatial resolution given by Graf and Draftz. They contrasted urban and suburban measurements. Some of the relevant conclusions of these authors are that 1) Pb sources in Cleveland are predominantly automotive, 2) there appears to be a local industrial source of Br, and 3) that V, Mn, and Fe concentrations are consistent with those expected from coal combustion.

In the Cleveland measurements from Table A-4, coarse Si and Fe concentrations are elevated, but the Fe/Si ratio is less than 1.0, except on 4/4/81. The Fe may originate from geological material. On 4/4/81, it appears that a regional event took place, because that date is also a high day at Ironton, OH, and Buffalo, NY. However, the Fe concentration was not remarkably high at Buffalo on 4/4/81 ( $2.30 \mu\text{g}/\text{m}^3$  in coarse and  $5.14 \mu\text{g}/\text{m}^3$  in the fine), nor was it an especially high value at Ironton ( $5.65 \mu\text{g}/\text{m}^3$  in the coarse, and  $0.053 \mu\text{g}/\text{m}^3$  in the fine). Neither coarse nor fine Fe were regionally distributed on 4/4/81.

Coarse Ca is in the 6 to  $9 \mu\text{g}/\text{m}^3$  range. Fine Ca is much lower, ranging from 0.4 to  $0.9 \mu\text{g}/\text{m}^3$ . Calcium-containing cement and calcium sulfate aggregate particles (from iron melting operations) are noted in the microscopic analyses of Graf and Draftz as a very minor component of their samples.

Both Graf and Draftz, and King et al. note evidence of local sources of vehicular traffic emissions, including diesel exhaust, Br, Pb, and rubber tire fragments. Modest levels of Br and Pb are found in the present data, however, the Br/Pb ratios are often substantially less than the 0.2 to 0.3 value commonly accepted for aged auto exhaust, and another source of Pb may be of importance.

Sulfate levels in Cleveland range from 6.8 to  $18.5 \mu\text{g}/\text{m}^3$  in the fine fraction with coarse values being considerably less. To check the possibility that a regional-scale event was involved in the highest two

cases,  $18.5 \mu\text{g}/\text{m}^3$  on 7/19/79 and  $17.8 \mu\text{g}/\text{m}^3$  on 9/6/79, sulfate concentrations at three nearby cities were checked: Akron, OH, Chicago, IL, and Buffalo, NY. For two reasons, either that IP measurements had not started yet or that no chemical data were given, Buffalo and Chicago had no information to contribute. At Akron, however, fine sulfate levels were  $20.9 \mu\text{g}/\text{m}^3$  on 7/29/79 and  $13.7 \mu\text{g}/\text{m}^3$  on 9/6/79. Graf and Draftz also found high sulfate readings in a large proportion of their Cleveland samples, and they comment on the difficulty of separating regional-scale events from local phenomena when there are so many coal emission sources close to Cleveland.

Only the 500 mb weather maps were examined for Cleveland. No soundings were available.

On 7/20/79 weak surface high pressure was centered very nearly over Cleveland. The previous three days had been dry, and a stationary front lay along the Atlantic coast on 7/18 and 7/19. On 9/6/79 a low pressure system had moved north along the Atlantic coast causing rain in PA and NY, while a cold front lay to the west. There had been a cold frontal passage on 9/3 with significant rain followed by temporary clearing on 9/5. On 11/5/79 surface high pressure was centered over PA. A frontal passage on 11/2 had brought rain, with partial clearing on 11/3 and 11/4.

On 9/12/80, a cold front was approaching Cleveland from the north, displacing surface high pressure centered over eastern OH on 9/11. Apparently light rain fell at Cleveland by 9/13.

On 4/4/81, the simultaneous high day at Cleveland, Ironton, and Buffalo, a large surface low pressure system was centered over Wisconsin and was moving rapidly northeastward, pushing surface high pressure out to sea. Winds at the surface and aloft were southwesterly and relatively strong, and surface isobars would fall parallel to a line joining Cleveland and Buffalo on the map. Record high temperatures had been recorded over the Great Lakes on 4/2/81.

On 10/13/81, extensive surface high pressure was centered over Montreal, while a cold front approached the western side of the Great Lakes. Conditions had been dry in Cleveland for two days. One day later, on 10/14/81, the situation seemed similar to 4/4/81, with moderately packed isobars sandwiched between a cold front approaching the Great Lakes and surface high pressure lying along the New England coast.

Regional sulfate events on 7/10/79 and 9/6/79 may have enhanced the relatively stagnant conditions in the advance of frontal positions on those days. The situation on 4/4/81 was quite different, with a vigorous storm and heavy rain approaching. The dry conditions preceding the cases of 7/20/79 and 10/13/81 may have enhanced the resuspension of particulate matter earlier deposited at the surface, though Al and Si concentrations for these two days are not elevated with respect to the other Cleveland site-days.

On the highest day of the set of seven, the  $PM_{15}$  mass exceeded the HIVOL by 14%. The  $PM_{15}$  data have been rejected on that day as the  $PM_{15}$ /HIVOL ratio exceeds the EPA/EMSL criterion of 1.1.

#### Philadelphia, PA (9 Site-Days)

The greater Philadelphia area has at one time or another included fourteen IP Network sites. Many of these operated only on a temporary basis during 1979 and 1980.

Neighborhood-scale sources include unpaved roads, a copper smelter, grain loading and mineral handling facilities, a coke oven, and a chemical plant. Three of the sampling sites, T and A Pet, Bridesburg Recreation, and NE Transfer, are located within about a one mile radius near the confluence of the Delaware River and Tacony Creek in the Bridesburg industrial area. Urban-scale sources include a broad range of industrial activities, such as copper, lead, and aluminum smelting, iron and steel foundries, coke ovens, blast furnaces, chemical plants, incinerators, refineries, feed and grain handling, mineral handling, and heavy vehicular traffic.

On 11/20/79, the  $Fe/Si$  ratios, as well as the magnitudes of Fe concentrations (ranging from 2.5 to 4.4  $\mu g/m^3$  in the coarse, and much less in the fine mode) were similar to those expected from geological material. Al was in the vicinity of 3  $\mu g/m^3$  in the coarse mode, and much less in the fine mode. The 11/20/79  $Br/Pb$  ratios in both coarse and fine modes are probably indicative only of auto exhaust, as they range

from 0.19 to 0.25. Cu reached a maximum value of only  $0.1 \mu\text{g}/\text{m}^3$  in the coarse fraction at the T and A Pet site on 11/20/79. The 11/20/79 coarse and fine Ca concentrations are characteristic of geological origins, being in the ranges of  $1.5$  to  $2.9 \mu\text{g}/\text{m}^3$  and  $0.3 \mu\text{g}/\text{m}^3$  to  $0.5 \mu\text{g}/\text{m}^3$ , respectively. On the highest site-day of the set, coarse Mn reached  $6.9 \mu\text{g}/\text{m}^3$  and fine Mn was  $0.9 \mu\text{g}/\text{m}^3$  on 11/20/79 at the T and A Pet site. On other days these concentrations were less than  $0.05 \mu\text{g}/\text{m}^3$ , and in the absence of simultaneously high Fe readings, which would indicate iron and steel processing, this reading may have resulted from a mineral handling operation.

In the 12/5/79 and 12/11/79 cases, the above observations for the Fe concentration, the Fe/Si ratio, the Br/Pb ratio, and the Ca concentration still apply. Fine Cu reached  $0.2 \mu\text{g}/\text{m}^3$  on 12/5/79 and  $0.6 \mu\text{g}/\text{m}^3$  on 12/11/79. Possibly smelting operations are the source, but this does not explain the  $50 - 60 \mu\text{g}/\text{m}^3$  fine mass concentrations on those dates.

The Br/Pb ratios cited above indicate a vehicular traffic contribution to the Philadelphia readings. The sum of Br and Pb coarse and fine contributions is  $2$  to  $3 \mu\text{g}/\text{m}^3$ , and presumably carbonaceous material is also present from the same source. Coarse Al and Ca contributions are not high enough to indicate substantial re-entrainment of either crustal or construction particles.

The three available fine sulfate readings on 11/20/79 were all high, ranging from  $31.4$  to  $35.0 \mu\text{g}/\text{m}^3$ . A very high fine nitrate value for an

eastern station,  $9.2 \mu\text{g}/\text{m}^3$  at the NE Transfer site, was observed on this date, and the minimum value for the date was  $2.5 \mu\text{g}/\text{m}^3$  (fine mode) at Presbyterian Home. Sulfate and nitrate concentrations in nearby Ohio and New York were not measured on 11/20/79 (they were measured on 11/17/79). The meteorological circumstances makes these high sulfate readings appear to be regional.

At the recommendation of the National Climatic Data Center, the Fort Totten, NY, soundings were used for Philadelphia cases. On 11/20/79, the 0000Z sounding shows inversions at 944 mb (695) and 934 mb (1716 M). A warm front was approaching, with cloud decks above 750 mb. Winds up to 850 mb were less than 10 knots at 0000Z; the surface wind was 2 knots out of  $110^\circ$ . High pressure had been a feature of the surface map for at least three days, with dry and unseasonably warm weather.

On 12/5/79 temperatures were much cooler than 11/20/79, and the 0000Z sounding shows an inversion at 810 mb (1850 m). The surface wind was 8 knots out of  $300^\circ$ . Conditions were cool and dry. Surface high pressure on 12/3 gave way as a low pressure system passed to the north of the Great Lakes on 12/5 and 12/6/79.

The 12/11/79 the sounding is very hard to interpret, as it shows a series of inversions all the way up to 500 mb. A stationary front had been shown on the 12/10 surface map, lying along the northern border of PA, but by 12/11 the flow was strictly southwesterly as a cold front approached the Midwest. The surface wind (at Fort Totten) was 4 knots out of  $200^\circ$ .



In summary, conditions were clearly stagnant prior to the 11/20/79 cases, and may also have been stagnant prior to 12/5/79. Both sets of soundings show inversions which tended to confine particulate matter from surface sources to the layer below 850 mb. On 11/20/79 the material may have been confined to an even shallower layer. Clear skies and stagnant, inverted atmospheric conditions clearly enhanced the regional secondary particle episode hypothesized for 11/20/79.

On 10/21/79 at the Bridesburg Recreation Center site the  $PM_{15}$ /HIVOL ratios were 2.27 and 1.11, respectively, and these data are suspect because they exceed the EPA/EMSL acceptance ratio of 1.10. On 3/10/80 at the Presbyterian Home site the fine/coarse ratio was 14.33. On this site day, none of the supporting data can explain the extremely high  $PM_{15}$  fine mass total of  $127.5 \mu g/m^3$ , and furthermore, windy and rainy weather prevailed. In this case it is apparent that an erroneous  $PM_{15}$  fine mass reading has caused a false high site-day identification.

#### Pittsburgh, PA (2 Site-Days)

The highest day for Pittsburgh, 10/30/80, is included, although no elemental or chemical information could be found. Some of the highest  $PM_{15}$  total mass readings in this data base occurred at the nearby Avalon, PA, site, for example  $634.3 \mu g/m^3$  on 2/4/82 and  $431.6 \mu g/m^3$  on 12/6/81. As no supporting chemical, SSI or HIVOL information are available for Avalon, these cases have not been analyzed. Their very magnitudes render them suspect.

Surrounding neighborhood-scale land use is predominantly residential and light commercial. A railroad and the Jones and Laughlin Steel Corp. are located to the west of the site. No urban scale source summary could be found.

On 5/22/81, which was also a high day at Wilmuth Pump, NY, coarse Al and Si concentrations are missing. The coarse Fe concentration was  $7.2 \mu\text{g}/\text{m}^3$  while Mn was elevated at 0.45 and  $0.37 \mu\text{g}/\text{m}^3$  in the coarse and fine fractions, respectively. The fine Fe/Si ratio was 5.45, possibly indicating iron and steel processing as a source. The Br/Pb ratio was 0.13 for the coarse mode and 0.17 for the fine mode, possibly indicating a source of Pb apart from vehicular traffic, as these values are below the typical auto exhaust ratios of 0.2 to 0.3. K and Zn were elevated, especially in the fine mode ( $0.9$  and  $1.3 \mu\text{g}/\text{m}^3$  in coarse and fine, respectively), without an obvious urban source to which they can be attributed. The site survey indicates substantial nearby vehicular traffic (more than 30,000 cars per day), but it does not indicate "dust visibly re-entrained". No construction is indicated which would explain the elevated Ca readings.

The fine sulfate was  $16.3 \mu\text{g}/\text{m}^3$  on 5/22/81. Fine sulfate on the same day at Buffalo (Wilmuth Pump), NY, was  $9.3 \mu\text{g}/\text{m}^3$ ; Buffalo, NY, (P.S. #28),  $12.2 \mu\text{g}/\text{m}^3$ ; Philadelphia, PA, (500 S. Broad),  $5.4 \mu\text{g}/\text{m}^3$ ; and Philadelphia, PA, (Presbyterian Home),  $6.2 \mu\text{g}/\text{m}^3$ . The case of 5/22/81 does not seem to involve a major, if any, regional sulfate episode.

The 5/22/81 Pittsburgh sounding shows a very high inversion at 650 mb (3688 m). Surface winds were 6 knots out of 310°, with high pressure on the surface map centered over southern Ohio. Generally, it was the driest week statewide since the end of January, 1981.

In the case of 10/30/81, the highest day at Pittsburgh, no sounding was obtained, but the maps show high pressure at the surface centered over Pittsburgh. Some precipitation had fallen two to three days before 10/30, but on 10/30 a record low temperature was recorded at Harrisburg, PA, and a wide spread frost was reported. It is likely that a Pittsburgh sounding, if one were available for this day, would show evidence of a radiation inversion close to the surface, given the clear skies and reports of cold temperatures.

On 5/22/81, the strong high pressure over the eastern states probably was the regional factor causing high readings at both Pittsburgh and Buffalo. On 10/30/80, clear skies and high pressure may have resulted in meteorological factors inhibiting the removal and dilution of surface-originating particulate matter, as well as increased demands for residential heating with resultant emissions.

No significant violations of the EPA/EMSL validation criteria are apparent.

#### Hartford, CT (1 Site-Day)

Though the PM<sub>15</sub> concentration on 1/22/81 of 126  $\mu\text{g}/\text{m}^3$  is not one of the highest in the network, this site-day is important in that it represents an eastern city apart from the large industrial centers, such as Buffalo and Philadelphia.

The chemical data for Hartford on 1/22/81 do not show highly elevated concentrations of Fe, Vn, Ni, Br, Pb, Mn, Zn, and Cu, with the possible exception of fine Zn at 0.2  $\mu\text{g}/\text{m}^3$ . The Br/Pb ratio is indicative of auto exhaust, at 0.21 in the coarse and 0.32 in the fine fractions. Si is high, at 9.5  $\mu\text{g}/\text{m}^3$  in the coarse mode, while coarse Al and Fe concentrations are 3.3 and 2.3  $\mu\text{g}/\text{m}^3$ , respectively. Coarse Cl shows one of the highest concentrations seen in this study, at 9.8  $\mu\text{g}/\text{m}^3$ , and K is noteworthy at 0.8 and 0.4  $\mu\text{g}/\text{m}^3$  in the coarse and fine fractions, respectively. Fine sulfate is slightly elevated at 11.1  $\mu\text{g}/\text{m}^3$ . Industrial sources do not appear to be major contributors.

This case may involve the coldest surface temperature of all of the present 50 site days, with a low of 8°F and a high of 36°F reported at Hartford airport on 1/22. Furthermore, 1.1 inches of snow had fallen on 1/16, a trace on 1/17, and a trace remained on the ground on 1/22. Therefore, it seems plausible that both the elevated coarse Cl and the elevated coarse Si could be the result of road sanding and salting operations. There is some substantial local source of coarse particles, as the HIVOL mass is 212.6  $\mu\text{g}/\text{m}^3$  while the FINE-15 is 61.0  $\mu\text{g}/\text{m}^3$ .

Also, it is possible that some of the elevated Cl and most of the elevated K are a result of residential heating in the form of wood burning.

Evidence for regional-scale events is lacking in the 2 typical fine sulfate and nitrate values of 11.1 and 1.32  $\mu\text{g}/\text{m}^3$ , respectively.

A radiosonde sounding from Albany, NY, for 0000Z on 1/22/81 shows a cold surface temperature (18°F) and the lowest of many inversions at 850 to 900 mb (1414 to 962 m). The 0000Z surface wind at Albany was 4 knots out of 30°, and is characteristic of the wind speed and direction at all levels up to 900 mb. The map shows surface high pressure on 1/21, with a cold front and precipitation approaching from the west on 1/22. This appears to be a clear case of a low, radiation-caused inversion with surface high pressure.

#### Chicago, IL (1 Site-Day)

The PM<sub>15</sub> coarse/fine ratio is 1.06 and does not suggest a dominant contribution from either size mode. No data are available from the other IP Network site in Chicago for this date.

In the absence of a sounding, it is still possible to infer the formation of a low-level inversion as skies cleared following a frontal passage on 2/2/81. The high and low temperatures recorded at Chicago O'Hare Airport on 2/3 were 10°F and -5°F, and a trace of snow remained on the ground from the 2.3 inches that fell on 2/1 and 2/2. The pressure was rising at Chicago on 2/3, but it appears to be only a short interlude between storms.

In the absence of other data, it appears that a radiation inversion contributed substantially to this one-time appearance of Chicago on the list of high IP Network site-days.

Ironton, OH (1 Site-Day)

Al, Si, and Fe concentrations were not elevated on 4/4/81 in Ironton, and their ratios are consistent with those of geological material. Zn and Cu concentrations were at typical levels. Coarse Ca was elevated at  $6.27 \mu\text{g}/\text{m}^3$ , as were coarse K and Mn at 0.71 and  $0.23 \mu\text{g}/\text{m}^3$ .

These elements were compared to the masses and the relative fine/coarse proportions at Buffalo and Cleveland on 4/4/81, but the only apparent similarity is with the Ca at Cleveland.

The Ironton Br/Pb ratio for the coarse mode was 0.21, well within the auto exhaust range; however, fine Br was  $1.03 \mu\text{g}/\text{m}^3$ , causing a very unusual Br/Pb fine ratio of 21.0. There is no source information to explain this Br concentration.

As in several previous cases, it is plausible that the elevated coarse Ca derives from local construction. On the other hand, Ironton on 4/4/81 was between storms (in fact, precipitation probably started at Ironton on 4/4/81), and surface conditions probably were not dry enough to encourage resuspension of dust. The elevated K reading may be an indication of residential heating by wood burning, a hypothesis strengthened by the slightly elevated coarse Cl mass of  $0.3 \mu\text{g}/\text{m}^3$ .

The very modest sulfate and nitrate levels for this case do not support the idea of a regional-scale phenomenon.

The weather summary for Ironton is similar to that of Cleveland and Buffalo, showing the imminent approach of a front and southwesterly flow. The Huntington and Buffalo soundings are similar from 960 mb on up. The Ironton temperatures were warmer than those in Buffalo, but they were basically dry-adiabatic from 960 mb up to 770 mb. The Buffalo sounding shows a very shallow inversion near the surface, which is not present on the Huntington sounding. Both show some weak inversion structure in the 700 to 750 mb layer, 2500 to 3000 m MSL at Huntington. Again, what is most noteworthy in the meteorology of all three sites is that heavy rain fell over the states of OH and NY on 4/4/81, following record high temperatures over the Great Lakes on 4/2/81. Despite significant prefrontal southwesterly winds (Huntington 0000Z surface wind was 6 knots at 220°, increasing to 25 knots, 207°, at 850 mb), the rapid approach of the front on 4/4/81 seems to have involved a PM<sub>15</sub> enhancement mechanism at Ironton, as well as in Cleveland and Buffalo.

#### Youngstown, OH (1 Site-Day)

This date comes less than one month after the Hartford, CT, case of 1/22/81 and the Chicago, IL, case of 2/3/81.

Coarse Al, Si, and Fe concentrations suggest a slightly elevated crustal contribution. A check of the HIVOL/PM<sub>15</sub> ratio, 1.66, confirms that large concentrations were present in the coarse and larger fraction

of the particle size distribution. K and Zn were slightly elevated. Coarse Cl and Ca were high at 7.3 and 4.8  $\mu\text{g}/\text{m}^3$ , respectively. The coarse Br/Pb ratio, 0.21, is indicative of auto exhaust. The fine ratio, 0.39, is near the maximum value attributable to unaged auto exhaust.

The elevated Cl concentrations may again indicate road salting. On 2/15/81 about one inch of snow still remained on the ground at Youngstown following a 3 inch snowfall on 2/11. Road sanding may also have contributed to the coarse Al, Si, and Fe concentrations. No information is available to suggest whether or not the coarse Ca mass originated in a local non-industrial, or for that matter, an industrial source.

Regional sulfate episodes are relatively rare in winter. The Youngstown data show an appreciable fine sulfate concentration, 13.4  $\mu\text{g}/\text{m}^3$ , but this value is not in the regional-scale episode category and local coal combustion is probably a simpler explanation.

Intense high pressure formed over the northeastern states on 2/12 and 2/13, following a storm on 2/11. Conditions remained dry, and the high pressure remained over the area until 2/15, when a stationary front is shown on the surface map to the north of the Great Lakes and over NY. A warming trend was in effect at Youngstown from 2/12 to 2/15; on 2/15 the high was 50°F and the low was 22°F. It is likely that a sounding at Youngstown would have shown a radiation inversion and/or a subsidence inversion. The clear skies, high pressure and probable inversion almost



certainly made the difference in placing this case on the list of 50 high site-days.

#### WESTERN SITES

##### Phoenix, AZ (2 Site-Days)

During the first examination of the quarterly summaries, this site, Roosevelt St., provided four possible site days. The second examination provided two more. None of the first four cases were found to have chemical data. The case of 11/6/81, with its very marginal  $PM_{15}$  total mass of  $107.6 \mu g/m^3$ , was retained because chemical data were found. Although elements are lacking, and the  $PM_{15}/HIVOL$  ratio is suspect, the highest day for Phoenix, 6/21/81, is also included in order to round out the profile of this urban area.

The sampling instruments are located on top of a building (County Health Department Complex) which contains a large parking garage and is adjacent to an outdoor parking lot. Vacant lots, residential areas, and a hospital are within a 0.25 mile radius of the sampling location. On the urban-scale, industry in the form of mineral and feed and grain handling, cement works, blast furnaces, and rock crushing are noted.

On 11/6/81 the  $PM_{15}$  coarse/fine mass ratio was 2.56, exceeding the EPA/EMSL criterion which flags any data for which this ratio exceed 1.3. However, the simultaneous HIVOL measurement was  $157.9 \mu g/m^3$ . Since it exceeded the  $PM_{15}$  total mass value by 47% and the SSI value by 36%, there was evidently a large proportion of coarse material on 11/6/81.

In addition, Watson et al. (1981) point out that this criterion is empirical and "...it is possible, though unlikely, that these limits are exceeded under ambient conditions." With this caveat, the case of 11/6/81 will be further analyzed.

For a case where such a large fraction of the mass is apparently in the coarse mode, the crustal species show concentrations barely above background levels. Ca is not even shown in Table 5-7 because the non-reportable data indicated its mass to be at the background level of  $0.02 \mu\text{g}/\text{m}^3$  in both size ranges. There is no evidence of Phoenix's rock crushing or cement industry in these data. Three unusual elements do show elevated levels in the 1 to  $2 \mu\text{g}/\text{m}^3$  mass range P, Ba, and Rb. These non-reportable elements, measured by x-ray fluorescence, are not in excess of detection limits on any other site-day in this study, and their source is not obvious. The difficulty of extracting non-reportable data is an obstacle to checking other Phoenix measurements for these elements and that check has not been made.

The appreciable nearby vehicular traffic, as well as the starting and stopping of engines in the adjacent parking facilities, might cause Pb to be elevated. But the values of  $0.005 \mu\text{g}/\text{m}^3$  for both size ranges are below detection limits. Br is slightly elevated, giving resultant and rather unbelievable Br/Pb ratios in excess of 100.00.

No support for regional-scale sulfate or nitrate episodes follows from the very low levels measured for these species.

The nearest radiosonde data relevant to Phoenix is the sounding from Winslow, roughly 25 miles NNE. On 11/6/81, a broad high pressure region is shown at the surface from New Mexico and Texas to North Dakota and Iowa. Surface trajectories would bring air from southern Texas and the Gulf Coast into Arizona. The high temperature at Phoenix was 87°F, the low was 60°, and the 0000Z Winslow sounding indicates a dry adiabatic atmosphere without inversions up to 550 mb. The 0000Z Winslow surface wind was 4 knots out of 10°, with 10 knots at the 700 mb level. The meteorological picture, then, is one of possible stagnation, as high pressure is shown on the surface for the preceding two days. The subsidence inversion was apparently very high at 540 mb, and there is no evidence of a radiation inversion. Although one may have been present at Phoenix, the nighttime low of 60°F makes this unlikely.

The meteorological situation on 6/21/81 may have allowed advection of material into the Phoenix area from some other location. The simpler explanation seems to be measurement anomaly. The PM<sub>15</sub> mass exceeds the HIVOL by 58%, and the SSI by 169% on 6/21/81.

#### Bakersfield, CA (4 Site-Days)

All four cases in Bakersfield occurred in the winter period, November 1980 to February 1981. Soundings were available for three of the cases, from Vandenberg, CA, roughly 125 miles SW of Bakersfield on the California coast.

The first day, 11/17/80, shows relatively low sulfate and nitrate levels and a fine/coarse ratio of 0.66, while the last three days show much higher sulfate and nitrate levels and fine/coarse ratios between 2.0 and 3.0.

The crustal components, Al, Si, and Fe, were elevated on 11/17/80 and were less so on 12/23/80. Fine Cl, fine Br, and coarse Pb concentrations were higher than normal on both days, and K was elevated in both modes on 11/17/80 as was coarse Ca at  $4.5 \mu\text{g}/\text{m}^3$  on 11/17/80.

The fine sulfate concentrations of the four Bakersfield cases range from 9 to  $45 \mu\text{g}/\text{m}^3$ . The latter is one of the highest sulfate values of all the 50 site-days. The likely precursor of this sulfate is sulfur gases from the pumping and handling of oil in the southern California oil fields. Though the Cl, Br, Pb, K, and Ca concentrations cannot be attributed to a specific industry, the simplest explanation of the sulfate concentrations is an oil industry source.

Non-industrial sources are involved in the 1980 cases. The elevated coarse crustal species probably resulted from re-entrained dust, perhaps from the vacant lot on the corner SW of the sampler. The coarse Br/Pb ratios on 11/17/80 and 12/23/80 are indicative of auto exhaust at 0.24 and 0.20 respectively, but as noted above, fine Br was elevated with respect to Pb on these days, and the Br/Pb ratios were too high for auto exhaust at 2.48 and 3.34. Fine Br concentrations are, in fact, elevated for all four cases. The fine Br concentration of  $2.9 \mu\text{g}/\text{m}^3$  on 2/3/81 is

the highest observed in the 50 cases. Site surveys indicate no Br sources in Bakersfield and this species is not expected from oil extraction. Coarse Ca is also elevated for the two 1980 cases (no data are available for the two 1981 cases) and may indicate nearby construction work.

It is unlikely that sulfate is transported from distant sources since sulfur emissions in other parts of California are lower than they are in the San Joaquin Valley. The four Bakersfield cases show elevated fine nitrate concentrations, reaching a maximum of  $46 \mu\text{g}/\text{m}^3$  on 12/23/80. By comparison, the highest nitrate concentration of the six Rubidoux cases to be discussed below is  $37 \mu\text{g}/\text{m}^3$  in the fine fraction. This may be a Southern California regional event. A fine nitrate concentration of  $33 \mu\text{g}/\text{m}^3$  from the SSI at Fresno on 12/11/80 is noteworthy, but data from 12/23/80 were not found in a search of most southern California sampling sites.

The Vandenburg 0000Z soundings from 12/23/80 and 2/3/81 show prominent, low-level inversions from 950 mb to 1000 mb. The 11/17/80 sounding was taken as a weak cold front approached and it is harder to characterize. On 12/23/80 and 2/3/81, high pressure is shown on the 500 mb maps over the west coast, and the resultant inversions may be a result of subsidence.

11/17/80 may be different from the other three cases. The crustal contribution on this date was noted earlier, and it is probably related to the fact that over 100 homes were destroyed in southern California by

fires fanned by strong "Santa Ana" easterly winds on 11/16/80. The high potassium concentrations,  $2.61 \mu\text{g}/\text{m}^3$  in the coarse fraction and  $1.07 \mu\text{g}/\text{m}^3$  in the fine fraction, confirm this source. The three later cases all involve strong upper level ridging which blocked storms, kept precipitation away, and, at least in the case of 12/23/80, led to markedly warm temperatures compared to averages. These conditions are consistent with the high sulfate and nitrate readings noted above.

#### Rubidoux, CA (6 Site-Days)

The prevailing opinion is that air pollution is usually worse in this area than in other parts of the Los Angeles basin because westerly surface winds tend to move particulate matter toward the eastern side of the valley where the confluence of two mountain ranges, together with frequent subsidence inversions, restrict its removal.

To round out the case studies at Rubidoux, the highest  $\text{PM}_{15}$  reading on 2/22/82 is also included, although no elemental or chemical information is available for that day and there is an indication of erroneous data.

The site survey<sup>1</sup> for Rubidoux shows a well-traveled, paved street, vacant land, and residential areas in the surrounding 0.25 mile radius. An urban-scale source characterization was not available. Atmospheric soundings from Vandenburg and San Diego, CA, were plotted and applied to the analysis of these cases.

The site-days tend to cluster toward the end of the work week (3 on Friday, 1 on Thursday, and 1 on Wednesday), and, as will be discussed

below, three of the cases occurred the day before fronts passed through the northern part of California.

Fe on 10/24/79 was low at 0.04 and  $4 \mu\text{g}/\text{m}^3$  in the coarse and fine modes, respectively. It was also anomalously low on 10/24/79, but on the other days it was significantly higher at 4 to  $10 \mu\text{g}/\text{m}^3$ . K was moderately elevated at 1.5 to  $2.0 \mu\text{g}/\text{m}^3$  in the coarse mode on all days except 10/24/79.

Crustal components contributed moderately and consistently on all days except 10/24/79, with coarse Al/Si/Fe in the rough proportions of 4/1.1/3 ( $\mu\text{g}/\text{m}^3$ ). Substantial coarse Ca was seen on all days except 10/24/79 and may indicate construction somewhere nearby, or possibly industrial cement activity. Cl was slightly elevated in a few cases, and probably originated at the seacoast. Most of the Br/Pb ratios, especially in the coarse mode, were in the 0.2 to 0.3 range, indicative of auto exhaust. The 10/24/79 data are anomalous with a coarse Br/Pb ratio of 0.1.

Around 25% of the  $\text{PM}_{15}$  mass on 10/12/79 and 10/24/79 can be accounted for by the sulfate and nitrate concentrations; lesser contributions were found on other days. In this respect, 10/24/79 is again anomalous in that it shows the second highest fine nitrate concentration of the 50 cases,  $37 \mu\text{g}/\text{m}^3$ . Sulfate and nitrate may not be regionally distributed, but in at least two of the cases they account for large fractions of the  $\text{PM}_{15}$ . Other secondary aerosols may be present, which might account for a major part of the  $\text{PM}_{15}$ .

The San Diego and Vandenburg soundings show subsidence inversions in the 700 to 900 mb interval on all five days. One must regard these soundings with the important caveat that strong on- or off-shore winds may be active below the subsidence inversions.

All cases involve high pressure and dry weather over southern California. Warmer than average temperatures were noted for 10/12/79, 6/20/80, and 8/7/80. On this last day the high was 101°F, and the low was 62°F at Riverside. As noted previously, three of the cases, 10/12/79, 10/24/79, and 5/22/81 occurred on days preceding frontal passages through northern California. On 10/25/79 significant rain reached as far south as central California. The usually stagnant conditions and subsidence inversions seemed to inhibit the removal of PM<sub>15</sub> from the Los Angeles basin on these days.

On the highest day at Rubidoux, 2/22/82, the PM<sub>15</sub> fine/coarse ratio was 3.08, while the PM<sub>10</sub> concentration was a factor of 10 smaller, 19.9  $\mu\text{g}/\text{m}^3$ . The fine/coarse ratio is 3/52. The fine/coarse ratios in the previously discussed five cases did not exceed 1.95. The PM<sub>15</sub> and the PM<sub>10</sub> data for 2/22/82 are probably erroneous.

#### El Paso, TX (3 Site-Days)

Neighborhood-scale influences (in 1979) included busy streets, construction of a ten-story building, and parking lots and garages. Urban-scale influences in El Paso include a refinery, a lime kiln, copper and lead smelting, and iron and steel foundry operations. Watson



et al. (1981) also point out that the city of Juarez, Mexico, just across the Rio Grande River from El Paso, contributes substantial and uncharacterized emissions. Atmospheric soundings from El Paso were plotted for 11/28/79 and 12/11/79.

Na and K were slightly elevated in both size fractions, and Ca was distinctly elevated, especially on 11/29/79, when the coarse concentration exceeded  $14 \mu\text{g}/\text{m}^3$ . The K and Cl values may have resulted from the burning of various materials in Juarez, but very likely the coarse Cl resulted from nearby construction.

Gr/Si ratios were moderately elevated in both cases (in about the ratio 3.7 to 5 on the basis of Fe concentrations in  $\mu\text{g}/\text{m}^3$ ). The Gr/Pb ratios are indicative of auto exhaust, ranging from 0.2 to 0.3.

Sulfate and nitrate levels were very low and there is no evidence of regional scale events.

El Paso soundings at 0000 on both days in 1979 show inversions. On 11/29/79 the surface temperature was a cool 50°F, and a very pronounced subsiding inversion appeared at 700 mb with surface high pressure system over both Mexico and the northern Rockies. On 12/11/79 a weak inversion appeared at 690 mb with a stationary front shown on the surface map over the northern border of New Mexico. Surface temperatures were much warmer in this case (70°F).

On 11/29/79, temperatures were cool enough that residential heating at night may explain the elevated K and Cl values noted earlier. The surface maps for at least four days prior to 12/11/79 indicate dry and

stagnant conditions that would encourage the accumulation of  $PM_{15}$ , even in the absence of a strong inversion.

On 4/29/82, the  $PM_{15}$  total concentration was  $399.6 \mu g/m^3$ ,  $PM_{15}$  fine and  $PM_{15}$  coarse concentrations were 380.5 and  $19.1 \mu g/m^3$ , and the HIVOL concentration was  $104.2 \mu g/m^3$ . The dichotomous sampler data for this day are therefore suspect not only because the total concentration was nearly four times the HIVOL value, but also because the fine/coarse ratio was out of bounds at 19.92.

#### Fresno, CA (1 Site-Day)

This date, 12/11/80, is bracketed by two high site-days at Bakersfield, CA, on 11/17/80 and 12/23/80. Two different meteorological regimes have been hypothesized for the Bakersfield cases.

The Fresno site survey indicates neighborhood-scale influences including busy traffic in a suburban - light commercial neighborhood. No urban-scale influences are noted, although some agricultural activities, such as burning of harvested fields, could be important in the Fresno area.

There was a modest crustal contribution with Al/Si/Fe in the proportions of about 4/12/2  $\mu g/m^3$ . Small elevations appeared in the coarse K and Ca concentrations. The Br/Pb ratios in both the coarse and fine modes were typical of auto exhaust at 0.21 and 0.25, respectively.

A larger fine-mode contribution from local sources is seen in the nitrate concentration of  $29 \mu g/m^3$ . At least three days of high pressure

and clear skies preceded 12/11/80, indicating that other photochemical secondary aerosols may also have contributed to PM<sub>15</sub>.

The 12/11/80 Oakland, CA, sounding is the nearest to Fresno, but it is taken about 180 miles to the north of Fresno at the edge of San Francisco Bay. With this caveat, the sounding indicates a strong subsidence inversion between 850 mb and 950 mb, low enough to substantially trap emissions near the surface. As noted earlier, strong blocking high pressure had been over the west coast since before 12/9/80, and high pressure in the surface map is shown centered over Nevada. Conditions at Fresno are undoubtedly both stable and inverted.

#### San Jose, CA 1 Site-Data

The site description does not contain urban-scale source information. It indicates a neighborhood of vehicular traffic, and parking lots, in a city center-commercial setting. There are probably significant industrial and agricultural activities in the greater San Jose metropolitan area which is at the southern end of the "Silicon Valley" high technology area and San Francisco Bay. In the latter context, it is noteworthy that drying ponds for salt production are seen nearby.

A typical and modest crustal contribution is indicated for Al/Si/Fe, which occurred in the proportions of roughly 3/9/2  $\mu\text{g}/\text{m}^3$ . Cl was slightly elevated, probably originating from either San Francisco Bay or the

ocean shore to the west of San Jose. The K values were more significantly elevated at about  $0.6 \mu\text{g}/\text{m}^3$  in both size ranges, and may have resulted from agricultural burning. The coarse and fine mode Br/Pb ratios were both characteristic of auto exhaust, at 0.25 and 0.29, respectively.

Nitrate was moderately elevated at about  $14 \mu\text{g}/\text{m}^3$  in the fine mode, and as in Fresno, it probably resulted from three days of clear skies, high pressure and sluggish circulation.

The 0000Z Oakland sounding shows the expected subsidence inversion at 830 mb, with warm surface temperatures ( $72^\circ\text{F}$ ) and a surface wind of 3 knots out of  $290^\circ$ . High pressure at the surface and strong ridging aloft were features on the weather maps for at least two days preceding this case. As is often the case with high site-days in California, the common subsidence inversion combined with sluggish winds and warm temperatures to allow considerable photochemical activity and the accumulation of secondary aerosols.

#### Portland, OR (1 Site-Day)

Portland, OR, emerged from the first examination of the quarterly statistical summaries with six high site-days. Another four days were selected in the second examination, but only the highest day and one other of the ten candidate days proved to have chemical information. Further examination of the data revealed an apparently chronic problem

in Portland. Many instances of  $PM_{15}$  exceeding HVDL were noted. Portland's highest  $PM_{15}$  concentration occurred on 10/12/79.

The site description indicates heavy traffic on paved roads near the samplers. The samplers are located in a city center-commercial environment, and urban-scale influences include paper mills, aluminum smelting, iron and steel foundries and arc furnaces, glass furnaces, cement works, and feed and grain handling. Radiosonde observations from Salem, OR, 40 miles south of Portland, are relevant.

Fe, V and W were not elevated. Mn and Zn were slightly elevated in the fine mode at  $0.12$  and  $0.13 \mu g/m^3$ , respectively. Cu was slightly elevated in both modes at about  $0.09 \mu g/m^3$ . Cl and K were slightly elevated, with both showing  $0.2$  to  $0.3 \mu g/m^3$  in the coarse and  $0.5$  to  $0.6 \mu g/m^3$  in the fine modes. The most remarkable concentration of the Portland list was Al at  $43 \mu g/m^3$  in the coarse and  $1 \mu g/m^3$  in the fine mode. Both of these values were more than an order of magnitude higher than the Si concentrations, which in turn were greater than the Fe concentrations, and a crustal origin seems ruled out. With Al smelting operations a major industry in Portland, it is tempting to attribute these concentrations to a valid industrial source. A caveat must be raised, however, in that the Al industries are geographically distant from the sampling site.

To further explore the Al questions, the  $\beta$ -element non-reportable data listing for Al was consulted. As explained earlier, this report groups all Al concentrations for all sites and dates. Quick scanning

this listing, it was noticed that 10/12/79 was not the only example of high coarse Al concentrations from three Oregon sites, Portland, Deschutes County, and Eugene. For example, coarse Al values at Deschutes County on 2/9/80 and 3/28/80 were 61 and 16  $\mu\text{g}/\text{m}^3$ . At Eugene, 16  $\mu\text{g}/\text{m}^3$  of Al were reported on 9/18/80. At Portland, the Al analysis days bracketing 10/12/79, 9/30/79 and 10/24/79 reported 28 and 21  $\mu\text{g}/\text{m}^3$  of Al. Other Al values in Portland on 2/9/80 and 3/28/80 were 27 and 24  $\mu\text{g}/\text{m}^3$ , respectively.

It is not clear that these elevated Al values, more prominent in Oregon than in any other state in the IP Network, can be attributed to the aluminum industry, especially given the elevated readings in other parts of the state. It is suspicious that most of the high readings occurred in Portland, closest to the industrial activity, but judgement on the question must be reserved in light of two caveats.

First, these Al concentrations were taken from the non-reportable XRF analyses, and as mentioned earlier, large inter-laboratory differences have been noted in these data. At this time the question of whether or not all the Oregon data came from one laboratory's Al analyses, and the validation of those analyses, should be raised. It is unlikely, however, that samples covering more than one year from Oregon were analyzed differently from samples taken over the same time period at other IP Network sites. None of these other sites show such high Al values, lending credence to the validity of the measurement process.

Second, Watson et al. (1981) (Table 9.1.5 on page 9-16 of that report) report a coarse Al anomaly at the Big Sister, NY, (near Buffalo) site. Coarse Al concentrations of 44 and 20  $\mu\text{g}/\text{m}^3$  were attributed to collection on the autonomous sampler filters of Al chips from the sampler inlet components. Very small chips, on the order of tenths of millimeters in dimension, can cause the reported Al concentrations. Apart from the Al question there is no convincing evidence in the elemental data to implicate industrial sources.

Si and Pb were present. Their ratios in coarse and fine modes both are quite typical, low level auto exhaust sources. Crustal Si and Fe were present only in low coarse concentrations in the proportion of about 4/2  $\mu\text{g}/\text{m}^3$ , respectively.

Sulfate concentrations exceeded a date, with 12.2  $\mu\text{g}/\text{m}^3$  and 4.1  $\mu\text{g}/\text{m}^3$ , respectively. This high sulfate value occurred at a time of year when sulfur-containing fuels used for heating seems unlikely. In fact, record high temperatures were reported in Oregon on 10/9/79. The large amount of paper manufacturing, both in the Portland Metropolitan area and to the north and south of this area, could be a major contributor of sulfur compounds. These levels are probably more indicative of nearby industrial sources than they are of regional-scale events.

10/12/79 was a high day for both Portland and Rubidoux, causing one to suspect regional-scale weather events. The 0000Z and 1200Z Salem soundings both show subsidence inversions in the 830 to 850 mb layer. High pressure at the surface over the northwestern states and ridging

aloft had been a map feature for three days preceding 10/12/79. On 10/13/79, a weak cold front caused precipitation to start in western Washington. Record high temperatures were recorded at several western stations, with a record high of 81°F at Portland on 10/9/79. Evidence of stagnation is given by the winds below 850 mb in this case. On the 0000Z Salem sounding, the wind was a maximum of 2 knots out of about 340° up to 900 mb, and was 6 knots, 266° at 850 mb. As was the case with most of the California site-days, it appears that warm and dry weather with high pressure, stagnation, and a subsidence inversion contributed to the accumulation of PM<sub>15</sub> in Portland.



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				6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) C. Fred Rogers And John G. Watson				8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Desert Research Institute Reno, NV 89506				10. PROGRAM ELEMENT NO.	
				11. CONTRACT/GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS US EPA Office Of Air Quality Planning And Standards Monitoring And Data Analysis (MD 14) Research Triangle, NC 27711				13. TYPE OF REPORT AND PERIOD COVERED	
				14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES  EPA Project Officer: Thompson G. Pace					
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