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AIRBORNE FINE PARTICULATE MATTER (PM-10) IN SOUTHEAST CHICAGO: PRELIMINARY REPORT II

by Stephen J. Vermette, Clyde W. Sweet, and Sheldon Landsberger

Sponsored by the
Illinois Department of Energy and Natural Resources

Champaign, Illinois
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ABSTRACT

Dichotomous sampling of ambient PM-10 was conducted in Southeast Chicago for the latter half of 1985 and throughout 1987. Samples were collected on Teflon filters and a subset of these filters, screened by wind direction, were subjected to X-ray fluorescence and neutron activation analysis. A small subset of samples were collected on glass fiber filters and analysed for total carbon. Receptor modeling was undertaken to apportion sources of PM-10 mass. While PM-10 concentrations were below the new PM-10 NAAQS, the annual average concentrations approached the Annual PM-10 Standard. Preliminary findings give indication that, while iron and steel mills and related industries make up the bulk of the manufacturing base and of the inventoried emissions, the impact of these stack emissions on annual average PM-10 mass concentrations appears to be small for fine PM-10 when compared to non-steel related contributions, and for coarse PM-10 when compared to urban/industrial fugitive contributions.

1.0 BACKGROUND

The objective of this report is to provide the Illinois Environmental Protection Agency (IEPA) with a preliminary estimate of the relative strengths of sources of inhalable particles for the Lake Calumet area. Inhalable particles (PM-10) are those with diameters less than 10 um. The study area is bound by the Indiana border on the East, the Chicago city limits on the south, 95th Street to the north and Michigan Avenue on the west (Figure 1). The preliminary estimates provided in this report are made to assist IEPA in effectively regulating the new PM-10 National Ambient Air Quality Standard (NAAQS).

The recent PM-10 NAAQS has replaced total suspended particulate matter (TSP) as the ambient standard. Several monitoring sites in the Lake Calumet area have regularly recorded TSP excursions above previous TSP NAAQS (primary standard: annual average TSP < 75 ug/m^3; secondary standard: average TSP < 60 ug/m^3). Since inhalable particles constitute about 60% of TSP in urban areas in Illinois (Kolaz et al., 1986), these sites might be expected to exceed the new PM-10 standards (primary standard: annual average PM-10 < 50 ug/m^3).

Airborne particles are generated by a wide variety of sources including fuel and refuse burning, heavy industry, vehicle traffic, and fugitive emissions. Previous work (Scheff et al., 1984) has identified soil and limestone sources as among the most important contributors to aerosol particle loadings within the Chicago city limits. In that study, coal and refuse burning, vehicles and steel mills were also identified as important sources; however, the sources of almost half of the fine particles were not identified. Fugitive emissions, defined as those emissions that do not pass through a stack, chimney or vent, have been suggested as substantial aerosol sources especially near iron/steel mills.

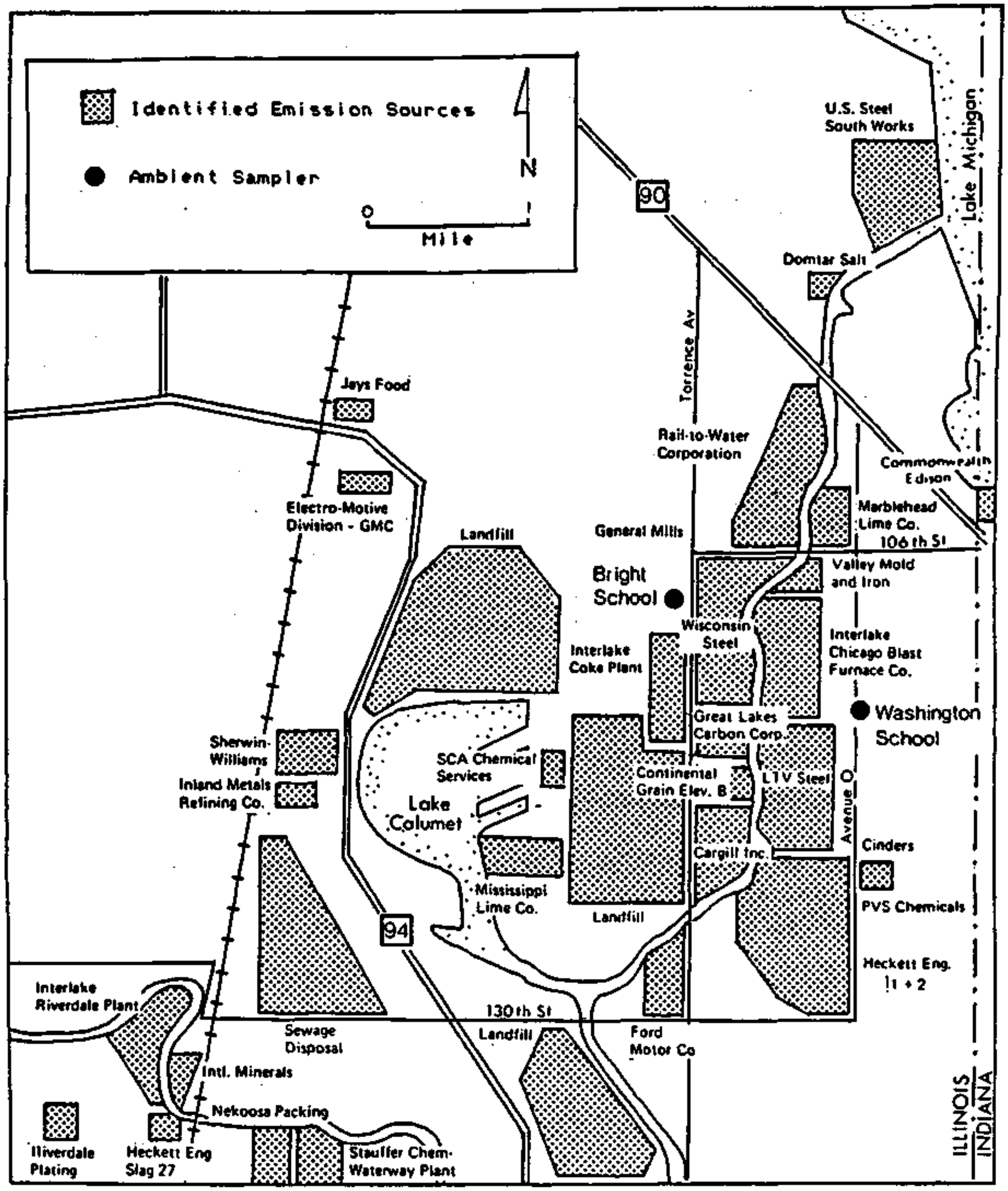


Figure 1. Southeast Chicago study area and industrial location map. PM-10 ambient air sampling sites are also shown.

In the city of East Chicago, IN, the presence of a maxima for steel-related elements upwind of iron/steel mills was interpreted as "arising from re-entrainment of surface dust previously originating from the mills" (Harrison et al., 1971). Khan and Singh (1986) and Lucas and Cassuccio (1987) have attributed > 50% of urban airborne particulate emissions in proximity to iron/steel mills to local fugitive emissions. Other significant components of PM-10 in urban areas include lead-bearing emissions from road dust (IEPA, 1986), secondary sulfate particles as well as elemental and organic carbon (Daisey, 1987) each of which can comprise 25% of the fine particle mass. While sulfate is a regional air pollutant found at elevated concentrations throughout the eastern U.S. (Shaw and Paur, 1983; Tuncel et al., 1985), carbonaceous aerosols are associated with urban areas (Goldberg, 1985).

2.0 METHODOLOGY

2.1 Receptor Modeling Approach

Receptor modeling is a methodology by which contributing sources to air quality are identified from the perspective of the receptor (ambient sampler). Identification is possible assuming that a measured feature at the receptor is linearly additive and follows the principle of conservation of mass. Using Fe as an example, these assumptions may be expressed, relative to the receptor, as:

$$\text{Total Fe} - (\text{Fe})_{\text{soil}} + (\text{Fe})_{\text{steel}} + (\text{Fe})_{\text{road dust}} \quad (1)$$

In addition, the proper identification and/or apportionment of sources is dependent on the proper identification of source specific tracer elements and/or the accuracy of chemical source profiles.

The receptor modeling approach observed in this study is outlined in Figure 2. Individual steps are divided between two general procedures: (1) source identification and (2) source apportionment. Source identification is built upon a series of steps designed with a degree of redundancy, such that an identified source is supported by a number of observations or statistical tests. These steps range from the general observations taken in a study area reconnaissance to the detailed statistical manipulation of receptor data as in factor analysis statistics.

The final output in our receptor modeling approach is the source apportionment of the PM-10 mass. Source profiles were developed for the identified sources and subsequently PM-10 apportionment was determined from chemical mass balance (CMB) statistics.

2.2 Sampling Instrumentation and Site Selection

A dichotomous sampler (Anderson Model 245) capable of collecting fine (<2.5 urn) and coarse (2.5-10 um) fractions of PM-10 was operated at the Bright School site (Figure 2) from October 1985 through to August 1987 (23 months). A recording meteorological station (Climatronics, Inc., Bohemia, NY) was added in 1986 to monitor wind direction, wind speed, temperature, relative humidity and solar radiation. Prior to its installation in 1986 wind speed and direction was provided by IEPA from their meteorological station also located at the Bright School site. The sampling site was moved to Washington School and operated from October 1987 through to September 1988 (12 months). An additional dichotomous sampler was added in July 1988. A third sampling site is scheduled for Carver School, and will operate from October 1988 to July 1989.

Both the Bright and Washington School sites were located in areas thought to be heavily impacted by local industry and a wide variety of urban sources.

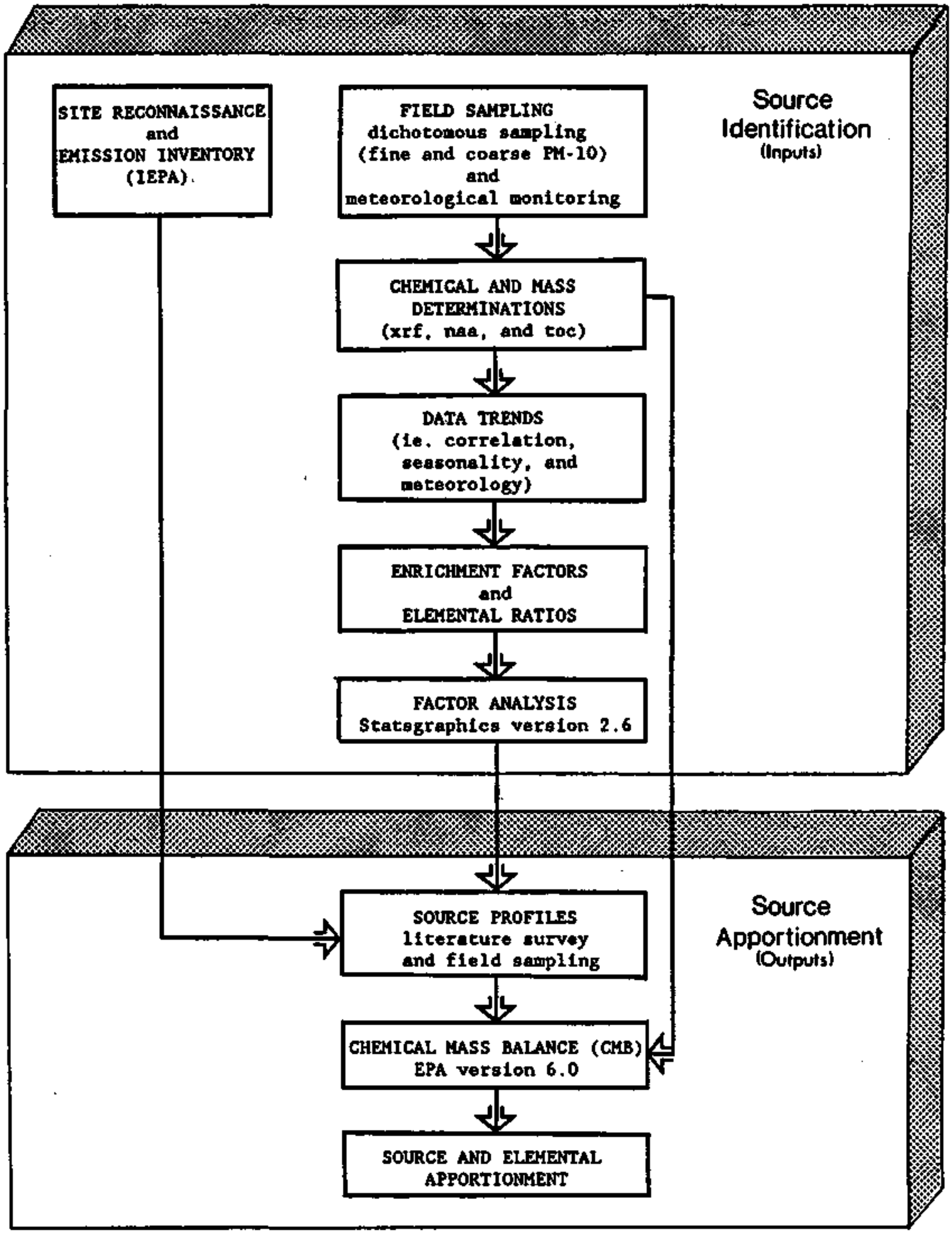


Figure 2. Flow diagram outlining the receptor modeling approach.

Subsequent to to our site selection, preliminary results for dispersion modeling of PM-10 identified the air quality at Bright and Washington Schools as heavily impacted by the local industry and in lieu of sampling on industrial property, these two sites were recommended (Depaul, 1988). The predicted spatial variability of annual ambient concentrations of Chromium (Cr) (PM-10) is shown in Figure 3. The dispersion model appears to predict substantially higher concentrations of Cr than measured at IEPA sites located near the steel mills, however, consistent ratios between modeled and ambient concentrations (dispersion model/IEPA - 25) indicate that while concentrations may be poorly predicted, the spatial variability seems to be consistent with ambient measurements. Predicted and measured concentrations are more closely in line at sites removed from the source (ie. Carver School).

2.3 Filter Analysis

Exposed filters were equilibrated at constant temperature (25°C) and humidity (50%) for at least 24 hours prior to mass determinations. All filter handling and weighing was done in a clean room using a Cahn microbalance enclosed in a humidity controlled chamber.

Selected filter pairs were analyzed using X-ray fluorescence (XRF) by a contract laboratory (NEA, Inc., Beaverton, OR). XRF is non-destructive and 'looks' at the center square centimeter of the filter surface. This technique is based on the atomic excitation of electrons with subsequent emission of characteristic x-rays when electrons from higher levels fill the void spaces. The XRF methods used in this report have been described by Dzubay (1977).

Determination of trace elements was also performed using neutron activation analysis (NAA) at the TRIGA Reactor of the University of Illinois. NAA determinations are used here as a quality assurance check. Unlike XRF

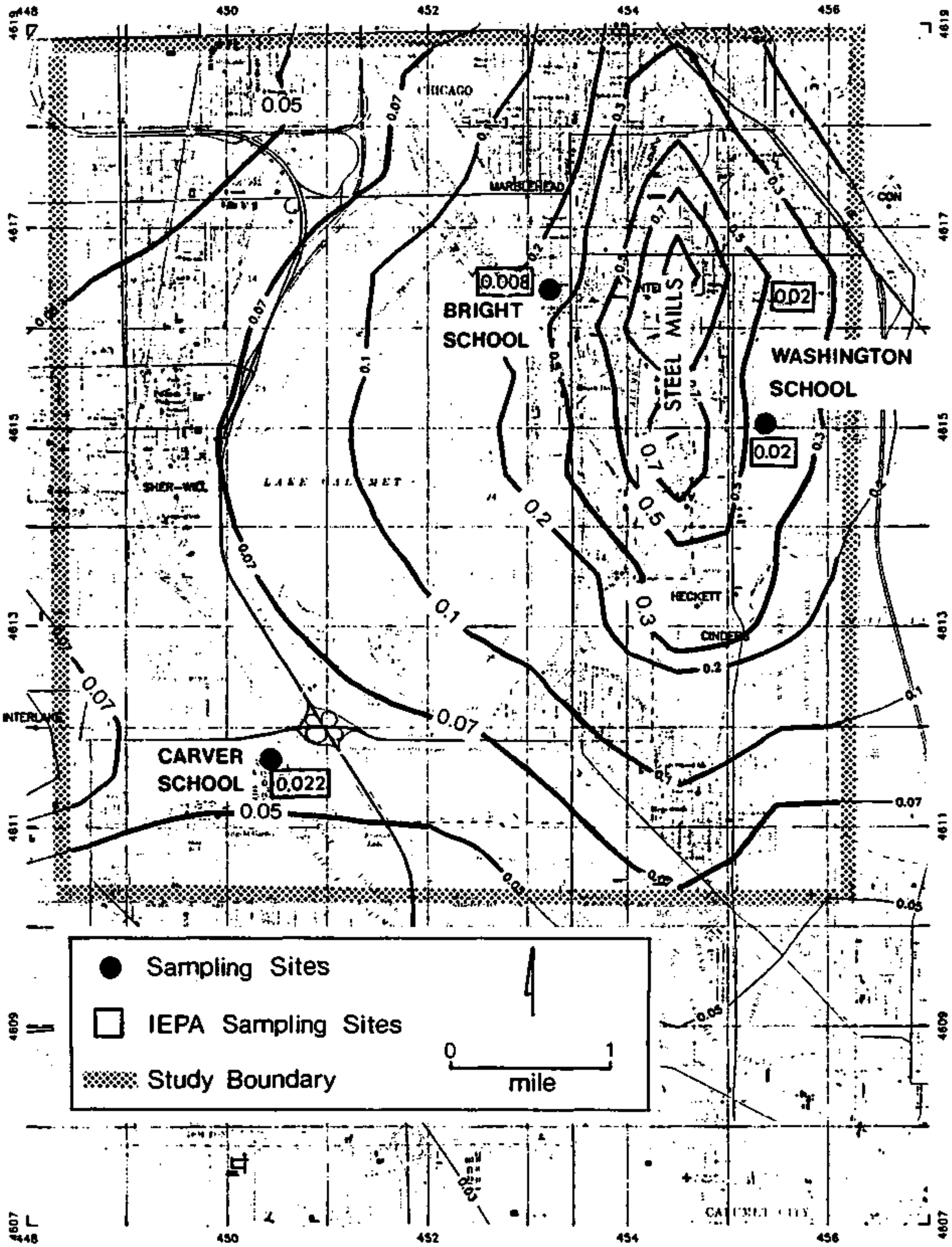


Figure 3. PM-10 sampling sites shown in relation to modeled dispersion of annual average Cr PM-10 concentrations (ng/m^3).

methods, the entire filter medium is subjected to NAA. The outer polyethylene ring of the exposed teflon filter was cut away prior to NAA to avoid its contaminating effects (Sweet and Gatz, 1987). NAA determinations are based on the measurement of induced radioactivity. The radioactive decay of each element emits characteristic energy gamma-rays such that an elemental "fingerprint" can be both identified and quantified. The NAA methods used in this report have been published (Hopke et al., 1988).

2.4 Quality Assurance

Quality assurance procedures for XRF included running NBS Standard Reference Materials, filter blanks and duplicate samples (see Appendix A). Agreement with certified NBS values and between duplicate samples appears to be good and contamination from blank filters is far below the concentrations measured in exposed filters. In addition, analysis of several elements (Cr, Cu, Fe, Mn, V and Zn) from filters analyzed by both XRF and NAA provides a check on the accuracy of the XRF determinations. The inter-method comparisons show good agreement (Figure 4). Discrepancies in some Cu and V comparisons are due to possible NAA contamination or the reporting of XRF values near detection limits, respectively.

3.0 SOURCE IDENTIFICATION

3.1 Site Reconnaissance and Emission Inventory

As a first step in our receptor modeling approach, facility locations and emission inventories were examined for the Lake Calumet area. A summary of the IEPA emission inventory for the area is given in Table 1, and the location of industrial facilities are shown in Figure 1. Not all facilities are listed or shown, but an attempt was made to include all major emission sources.

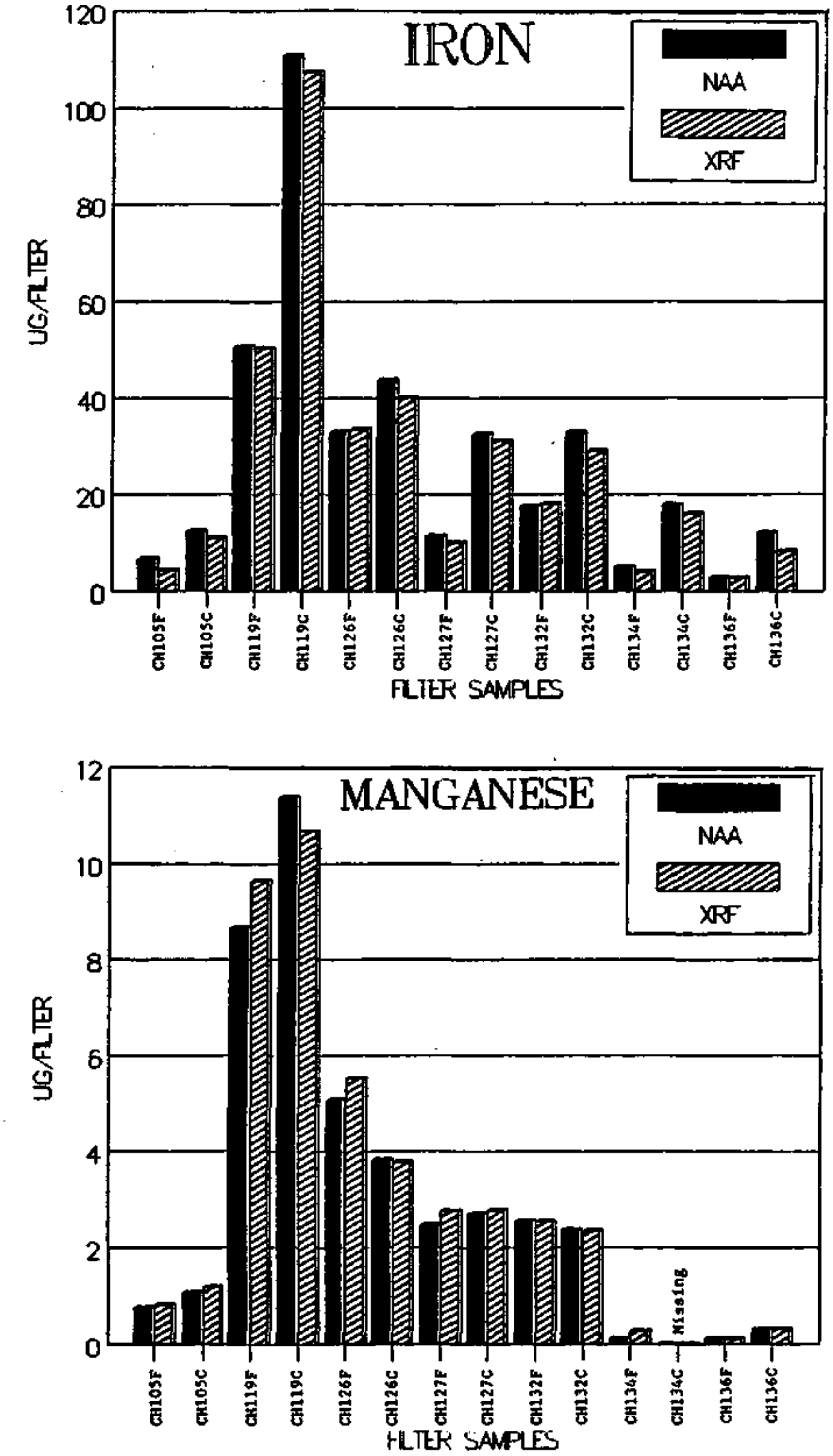
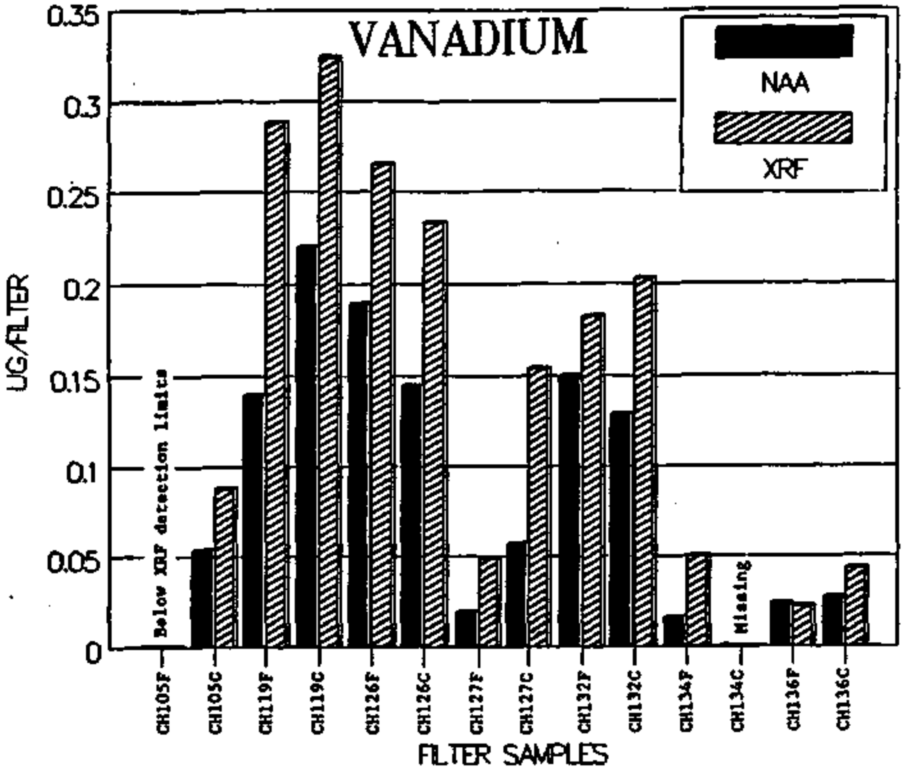
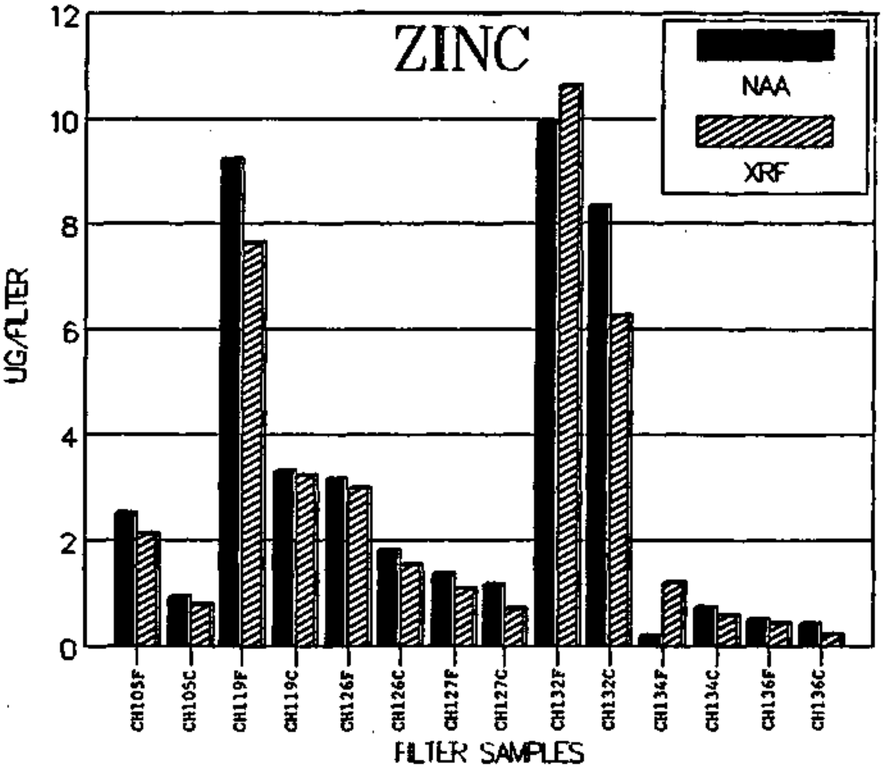
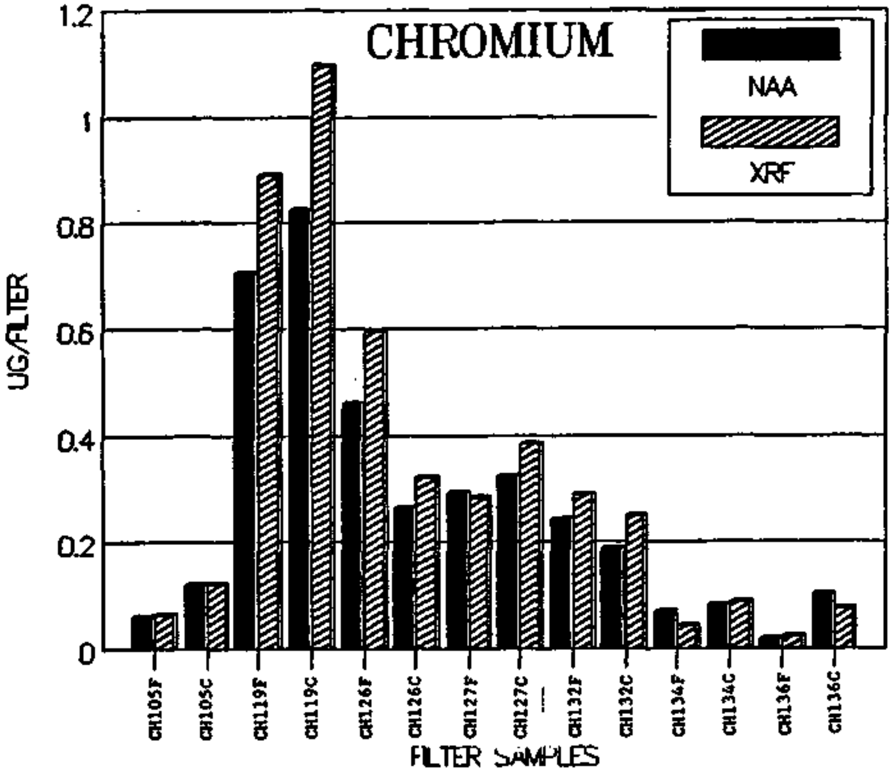


Figure 4. Inter-method comparison of filter elemental determinations.


VANADIUM
NAA
XRF
UG/FILTER
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Below XRF detection limits
Missing
CH105F
CH105C
CH119F
CH119C
CH126F
CH126C
CH127F
CH127C
CH132F
CH132C
CH134F
CH134C
CH136F
CH136C
FILTER SAMPLES


ZINC
NAA
XRF
UG/FILTER
12
10
8
6
4
2
0
CH105F
CH105C
CH119F
CH119C
CH126F
CH126C
CH127F
CH127C
CH132F
CH132C
CH134F
CH134C
CH136F
CH136C
FILTER SAMPLES


CHROMIUM
NAA
XRF
UG/FILTER
1.2
1
0.8
0.6
0.4
0.2
0
CH105F
CH105C
CH119F
CH119C
CH126F
CH126C
CH127F
CH127C
CH132F
CH132C
CH134F
CH134C
CH136F
CH136C
FILTER SAMPLES

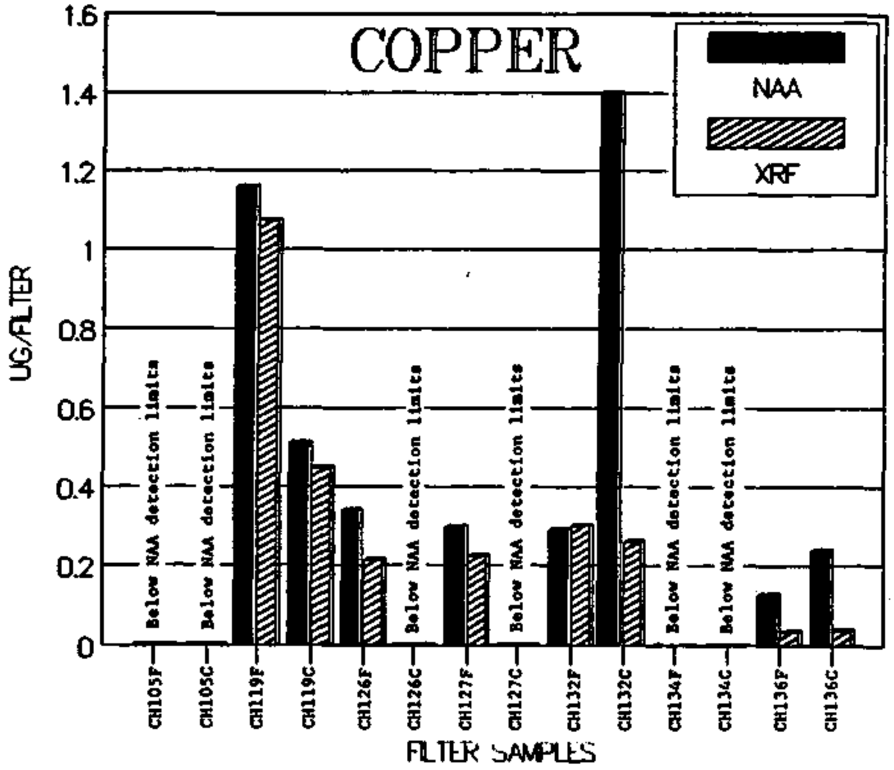

COPPER
NAA
XRF
UG/FILTER
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Below NAA detection limits
Below NAA detection limits
Below NAA detection limits
Below NAA detection limits
Below NAA detection limits
Below NAA detection limits
CH105F
CH105C
CH119F
CH119C
CH126F
CH126C
CH127F
CH127C
CH132F
CH132C
CH134F
CH134C
CH136F
CH136C
FILTER SAMPLES

Table 1. Facilities and Emissions as Summarized from the IEPA Calumet Area Surveillance Report

Industry	Record Dates	Emissions (tons/year) Part	SO$_2$	Significant Others	SIC	Industry Description
Interlake-Rivedale	75-85	373.6#	639.8	695.1 (NOX)	3312	Steel manufacturing
US Steel-Southworks	82-86	110.0	0.1	37.5 (NOX)	3312	Steel manufacturing
Chicago Blast Furn*	80-82	324.2	818.9	2170 (NOX)	3312	Steel manufacturing
LTV Steel*	78-86	515.0#	680.3	420 (NOX) 1713 (CO)	3312	Steel manufacturing
Chicago Coke Plant	80-83	151.6#	437.4	401.6 (HC)	3312	Steel manufacturing
Heckett-Plant 27	81+85	36.5	0	N/S	3295	Slag processing
Heckett Eng.[+]	N/A	76.8	0	N/S	3295	Slag processing
Heckett En. Harsco[+]	N/A	110.9	0	N/S	3295	Slag processing
Cinders[+]	N/A	142.5	0	N/S	3295	Slag processing
Valley Mold & Iron[+]	86	0	0	N/S	3479	Metal Plating
Inland Metals	87	1.2	0	N/S	3341	Refining Nonferrous
Marblehead Lime	81-86	129.7#	532.8	N/S	3274	Lime manufacturing
Domtar Ind.[+]	N/A	12.9	0	N/S	2899	Refining Na Cl
Great Lakes Carbon*	83+86	6.9	376.8	N/S	2999	Petro + Coal Prod
PVS Chemicals	81-86	129.7#	532.8	26.5 (NOX)	2819	Inorganic Chemicals
SCA Chemical	82+83	16.3	0	17.3 (NOX)	4953	Refuse disposal
Electro Motive GMC*	87	0	0	N/S	3743	Locomotive mfg.
Ford Motor Co.*	84+85	9.0	1.9 -	869 (HC)	3711	Auto manufacturing
Rail-to-water	84-87	11.7	0	N/S	4463	Marine Cargo Hand.
Mississippi Line	85	12.4	0	N/S	4463	Marine Cargo Hand.
Int. Minerals[+]	N/A	16.9	0	N/S	4463	Marine Cargo Hand.
Stolt Terminals[+]	N/A	7	0.9	9.8 (NOX) 89.4 (HC)	4226	Warehouse + Storage
Sherwin-Williams	83-87	2.4	0	N/S	2851	Paint manufacturing
Stauffer Chemical*	81-87	20.6	0	N/S	2874	Fertilizer mfg.
Continental-Elv B*	82-87	121.3[#]	1.6	N/S	5153	Marketing grain
Cargill Inc.*	83-86	54.0	0	N/S	5153	Marketing grain
General Mills Inc.*	82+86	154.0	0	N/S	2041	Milling grain
Jay's Foods	81-85	11.6	0	N/S	2099	Food preparation
CID Landfill	84&85	4.4	0	N/S	N/A	Landfill site.
Con-Ed Peaking Units	79-86	6.5	69.5	121.1 (NOX)	4912	Electric power
Riverdale Plating[+]	N/A	19.4	0	N/S	3471	Plating

[#] - Road dust emissions are included in totals

* - Listed emission source were assumed not in operation when hours of maximum and average operation less than 1 hr/1 da/1 wk - not included in emission totals

[+] - Facility not listed in IEPA Calumet Area Surveillance Report

N/A - Not available

N/S - Not significant

Iron/steel and related industries dominate the Lake Calumet area manufacturing base and inventoried emissions. These industries are confined to a north-south strip running either side of the Calumet River (approximately 6 mi^2). A prominent exception is the Interlake Riverdale plant that is located just outside the southwest corner of the study area. Associated with the iron/steel industries are large tracks of land that serve as storage locations for coal, slag, scrap steel and limestone. Other major land uses not related to the iron/steel industry include grain handling and municipal landfills (although slag is also being landfilled). The down-turn in steel production has forced the shut down of a number of operations and the closing of Wisconsin Steel. At the time of this report only Acme (Interlake) Steel approaches full production levels.

Validation of the Lake Calumet emission inventory was made using a simple box model taking into account the study area (25 mi^2) to a mixing height of 0.5 mi (an average of estimated summer and winter mixing heights). PM-10 contributions can be estimated for local industries assuming a constant PM-10 emission rate of 4.11×10^{12} ug/day (60% of TSP, Kolaz et al., 1986) and constant mixing throughout the day and year, an even distribution of emission sources, and an average wind speed of 7.5 mph (Figure 5). Based on the above assumptions, contributions from local industrial sources account for an estimated 2.4 ug/m^3 of ambient PM-10. Average annual PM-10 concentrations are about 40 ug/m^3 (IEPA, 1988). Thus, local industrial contributions account for only 6% of annual average PM-10. While this calculated concentration and percent PM-10 seems small, it is in line with receptor modeling estimates from other industrial areas (Table 2). On days with calm conditions or low wind speeds and/or reduced mixing heights (low ventilation) higher industrial contributions are possible. Removal of a wind component from the box model

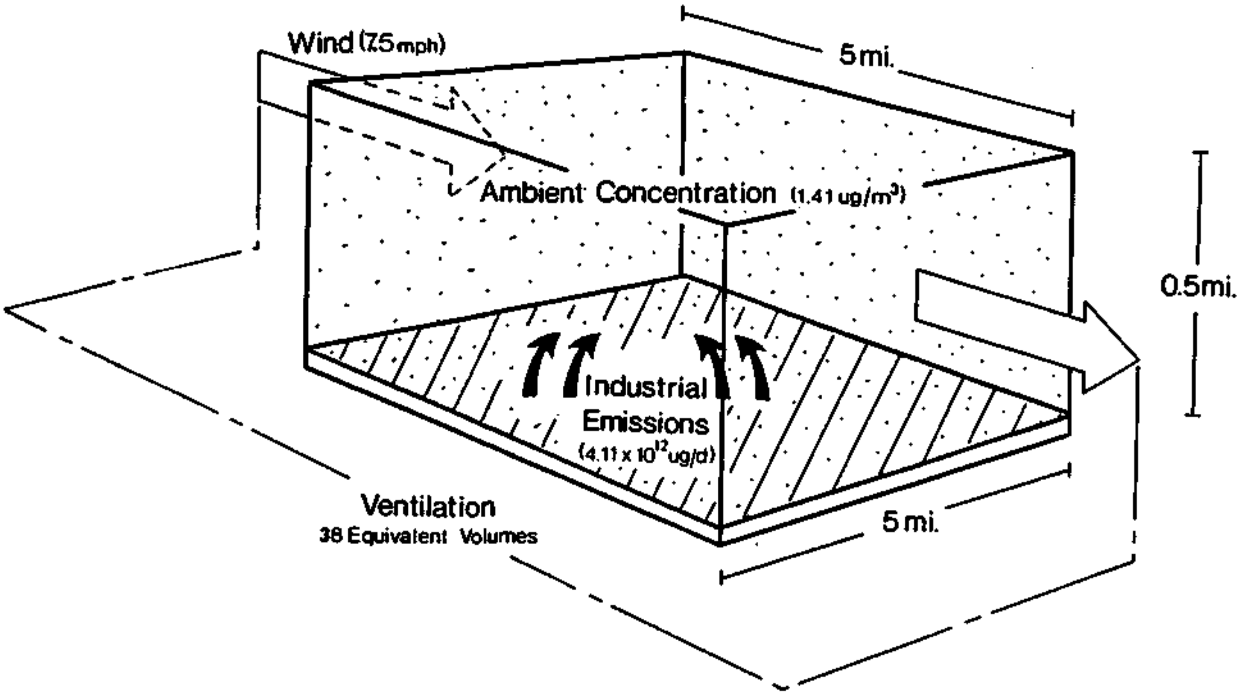


Figure 5. Schematic depiction of variables employed in the Southeast Chicago airshed box model.

Table 2. Receptor Modeling Estimates of Industrial Primary Emissions as Reported in the Literature

Industry	City	% Contribution	Authors
Industrial	Philadelphia[#]	<5% of PM-10	Dzubay et al. (1988)
Industrial	Newark	7% of PM-15	Morandi et al. (1987)
Industrial	Portland	5% of TSP	Cooper and Watson (1979)
Steel	Detroit	12% of CPM[+]	Wolff and Korsog (1985)
Steel	Chicago*	4% of TSP	Gatz (1975)
Steel	N/A	3% to 18% of TSP	Lucas and Casuccio (1987)

Primary emissions from five major stationary sources.

\+ CPM - particles ranging in size from 2.5 um to 10.0 um

* Sampling sites were located upwind (prevailing direction) from iron/steel mill sources.

reduces ventilation and the volume of air which would receive the emissions. Considering a stationary volume of air industrial emmissions account for 68 ug/nrVday or 57% of the worst case PM-10 measured at Bright School (IEPA, 1988). This percent contribution compares well with industrial worst case TSP concentrations (55% of ambient TSP) as determined by Lucas and Casuccio (1987) for the city of East Chicago.

It is apparent that the IEPA emission inventory gives a reasonable account of annual industrial inputs to the Lake Calumet area airshed and that these emissions account for only a small fraction of ambient PM-10. Furthermore, the box model will serve as a useful validation to receptor model estimates of industrial PM-10 inputs to the Southeast Chicago airshed.

3.2 Observed Data Trends

3.21 Mass Loadings

Analysis of filter mass offers useful insights for allocating ambient PM-10 to various sources. In Figure 6, the number of observations of mass concentrations for the study area are compared with mass concentrations from a site that is representative of regional air quality (Bondville, IL). The sampling time frame of the two sites overlap but individual filter samples are not directly comparable. PM-10 mass sampled at Bright School has a mode between 40-50 ug/m3 and a mean of 44 ug/m3. This compares with a mode of 20-30 ug/m3 and a mean of 27 ug/m3 at the regional site. In relation to sampled masses at the regional site, masses measured at Bright School are greater by a factor of 2. Thus, the urban study area has contributed toward a doubling of PM-10 mass. This doubling has not produced violation of the 24 hr PM-10 standard (highest mass concentrations < 90 ug/m3) but does approach the annual PM-10 standard. The implication for control strategies is the need to instigate annual or

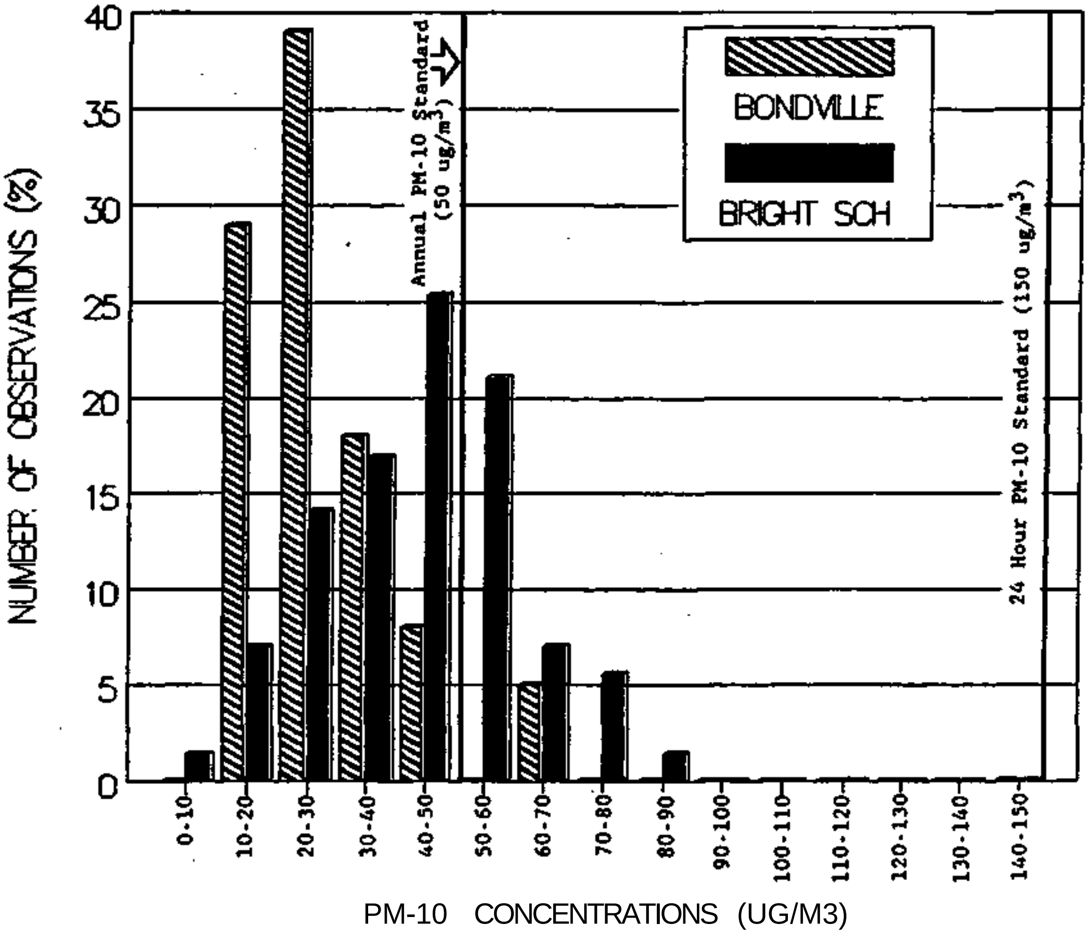


Figure 6. Frequency diagram comparing PM-10 mass concentrations measured at an urban (Bright School) and rural site (Bondville, IL.) Also shown are the PM-10 NAAQS.

seasonal controls to limit average concentrations rather than concentrating controls solely on episodic events (ie. based on meteorological forecasts).

The variability of filter masses by season (1986) is plotted in Figure 7. Examining the winter season first, no correlation is exhibited between fine and coarse PM-10 (r^2 - 0.04). The fine particles dominate winter PM-10 mass and follow a cyclical pattern much like the other seasons. Fluctuations in mass concentration from filter to filter are due to differences in meteorology (variations in wind speed, ceiling heights, etc.). The coarse PM-10 shows less variation in mass concentrations. The decoupling of the two fractions suggests two different sources. Snow cover and general wet conditions in the winter may serve to bind local surface material thereby preventing easy suspension into the airshed. The fine PM-10 may be contributed from more distant sources and/or from combustion processes which are not influenced by ground cover.

In the summer and autumn seasons good correlations (r^2 - 0.73 and 0.72, respectively) are exhibited between fine and coarse PM-10. The correlation is due to meteorology but also demonstrates an active source for coarse PM-10 not observed during the winter season. The coarse PM-10 mass exceeds that of the fine in the summer while in the autumn dominance is reversed and the gap between the two is expanded. If, as in the winter season, coarse PM-10 can be attributed to the suspension of surface materials (crustal and urban dust) then it is apparent that during the summer months suspended surface materials represent the largest fraction of the PM-10 mass. Mass concentrations in the spring appear to be a combination of summer and autumn patterns.

3.22 Trace Elements

Twenty trace elements have been selected as target chemicals for this study. Approximately 400 teflon filter pairs were exposed during 12 and 24

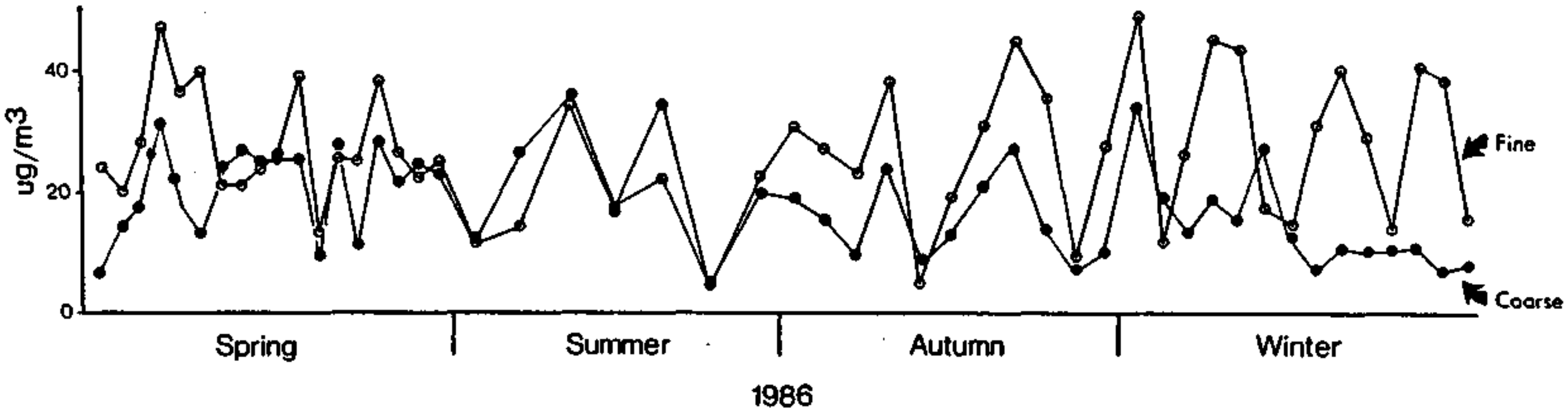


Figure 7. Seasonal variability of fine and coarse PM-10 mass concentrations measured at Bright School.

hour sampling periods at Bright School and from these, 74 pairs were selected for elemental analysis to represent all wind directions (Vermette et al., 1988). Most of the filter pairs correspond to a period of steady wind direction (standard deviation < 20°). Figures 8 and 9 give a break down of the Bright School data by wind direction and season. Average and maximum concentrations of PM-10 mass and elemental determinations are shown for the Bright and Washington School sites (Table 3).

As with PM-10 mass concentrations, examination of elemental seasonal trends reveals useful insights to source identification. The most striking example is seasonal variations of fine chlorine (Cl) concentrations as shown in Figure 10. There is a noticeable decrease in Cl concentrations during the warm months, extending from the last snowfall in the spring to the first snowfall in the autumn. Road salt (NaCl) is used during the cold season to melt snow and ice from the roads and the linkage between road salt usage and the seasonal variability of fine Cl concentrations suggests that road salt is suspended into the study airshed. Variations in Cl concentrations in the cold season are related to the frequency and severity of snowfall/freezing conditions, cleaning of roads by melt waters and periods of surface dryness which facilitate suspension of the road salt.

A second example is the seasonal variability of coarse Si concentrations as shown in Figure 11. Highest concentrations occur during the warm season when surface dust is available for suspension, while in the winter season frozen surfaces limit the availability of surface materials for suspension.

3.3 Enrichment Factor Calculations

A ratio-based calculation used to distinguish local from regional aerosol sources is the enrichment factor (EF) calculation:

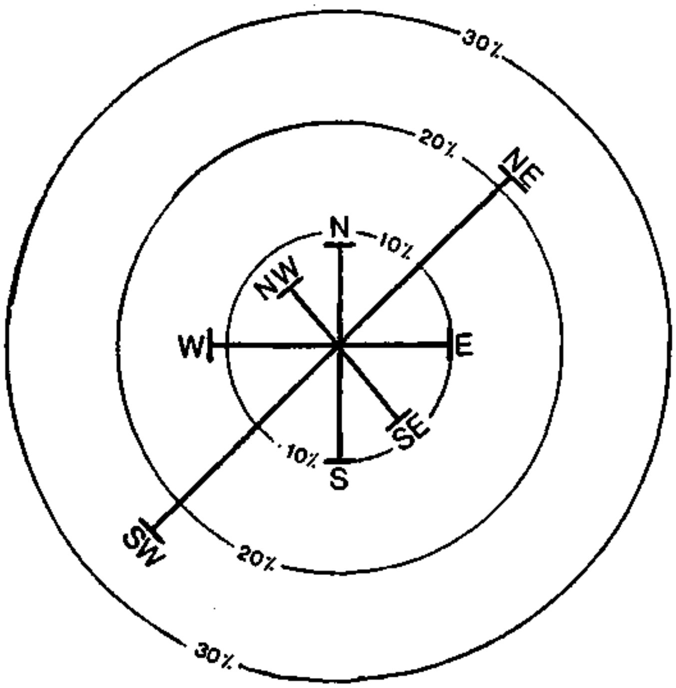


Figure 8. Bright School filter samples showing breakdown by wind direction.

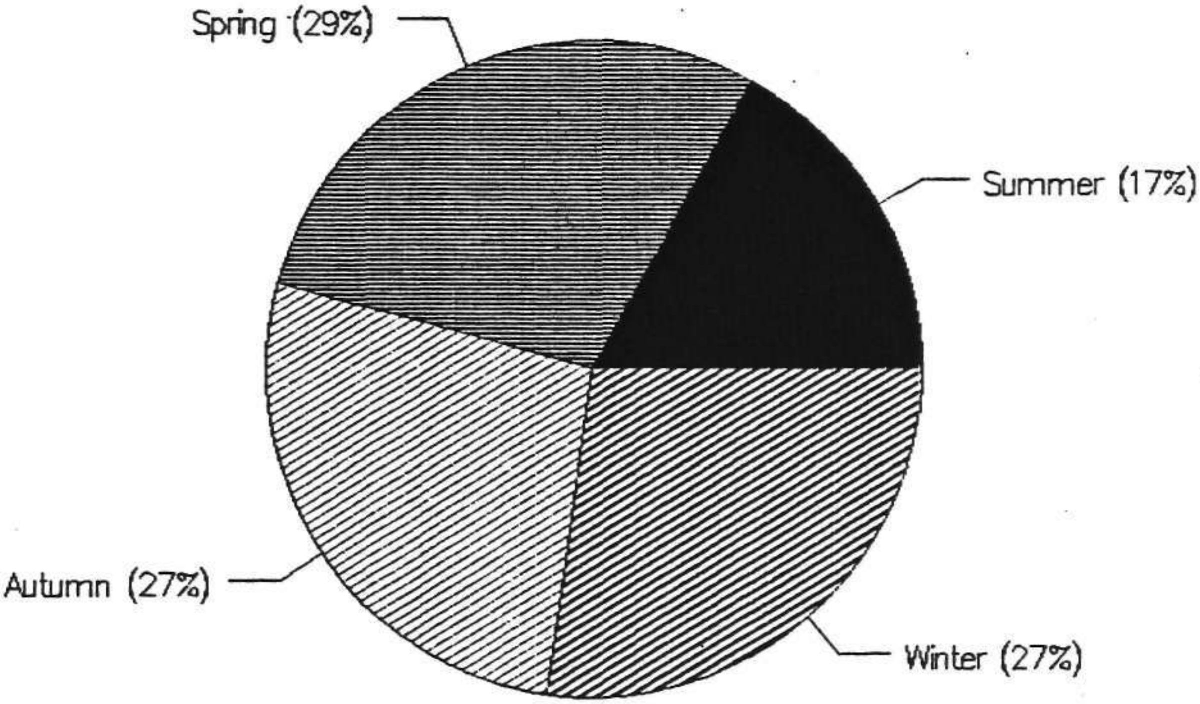


Figure 9. Bright School filter samples showing breakdown by season.

Table 3. Average and Maximum Concentrations of PM-10 Mass and Elemental Determinations in Southeast Chicago[1].

Parameter		Bright School[2]		Washington School[3]	
		Fine[4]	Coarse[5]	Fine	Coarse
PM-10	Avg	25.4	19.2	16.8	13.2
	Max	49.3	80.4	31.2	41.8
Al	Avg	143.8+-19.8	414.5+-56.6	81.7+-11.4	254.5+-35.0
	Max	538.9+-80.9	1762.9+-264.1	175.0+-23.7	1028.7+-138.3
Si	Avg	273.1+-41.6	1327.6+-193.2	137.1+-20.8	830.7+-119.1
	Max	1095.5+-191.2	7739.5+-1189.4	358.7+-53.2	4036.3+-571.7
P	Avg	72.8+-16.3	33.8+-7.8	58.9+-13.3	22.5+-6.4
	Max	372.9+-83.5	169.4+-38.0	148.1+-33.3	50.3+-13.4
S	Avg	2141.6+-241.4	347.7+-42.7	1507.0+-171.2	170.1+-41.0
	Max	6606.9+-748.5	1349.3+-171.6	3191.7+-358.8	509.7+-88.7
Cl	Avg	541.1+-52.6	196.4+-22.3	195.1+-23.6	207.1+-25.5
	Max	3492.8+-391.5	1325.3+-148.5	1135.8+-128.2	947.2+-118.5
K	Avg	135.9+-15.4	109.0+-12.5	107.6+-12.4	86.3+-11.2
	Max	742.1+-83.1	477.4+-53.7	310.4+-35.4	366.5+-42.6
Ca	Avg	109.2+-12.4	1065.5+-119.4	84.4+-9.7	804.3+-91.1
	Max	423.2+-47.4	4356.3+-487.7	477.2+-54.2	2592.8+-293.0
Ti	Avg	8.7+-1.3	31.4+-2.1	5.9+-0.7	25.8+-1.7
	Max	36.7+-9.6	108.5+-9.4	20.1+-4.9	98.8+-5.2
V	Avg	3.4+-0.6	3.9+-0.6	2.0+-0.4	3.2+-0.5
	Max	14.0+-3.9	13.2+-3.7	7.4+-1.9	11.1+-1.5
Cr	Avg	4.9+-0.4	7.2+-0.5	3.1+-0.3	5.7+-0.4
	Max	27.5+-1.5	34.9+-1.8	22.1+-1.3	23.2+-1.5
Mn	Avg	39.3+-2.1	50.3+-2.6	33.0+-1.9	40.2+-2.3
	Max	255.4+-12.8	563.2+-28.3	398.8+-21.2	246.2+-15.7
Fe	Avg	411.6+-20.9	861.3+-43.5	338.6+-18.0	770.4+-40.8
	Max	2012.1+-101.2	3750.2+-188.6	2389.8+-126.1	3195.1+-167.0
Ni	Avg	3.0+-0.3	2.2+-0.3	1.9+-0.3	1.8+-0.3
	Max	13.1+-0.8	10.6+-0.6	9.1+-0.8	6.0+-0.6
Cu	Avg	12.3+-0.8	5.0+-0.4	8.7+-0.7	2.9+-0.4
	Max	128.0+-6.6	43.6+-2.3	53.2+-3.0	12.3+-1.3
Zn	Avg	128.6+-6.6	38.0+-2.0	131.4+-7.0	30.4+-3.0
	Max	571.5+-28.8	213.6+-10.8	1033.3+-54.7	216.4+-19.9

Se	Avg	3.1+-0.3	0.5+-0.2	2.1+-0.3	0.3+-0.2
	Max	9.8+-0.8	12.4+-2.2	5.9+-0.5	0.9+-0.4
Br	Avg	8.8+-0.6	1.8+-0.3	7.7+-0.5	2.2+-0.3
	Max	39.1+-2.0	8.4+-0.5	28.7+-1.5	19.7+-1.1
Rb	Avg	1.6+-0.4	1.3+-0.3	1.2+-0.4	0.9+-0.4
	Max	7.1+-0.8	4.6+-0.7	4.5+-0.8	3.7+-0.7
Sr	Avg	1.9+-0.4	3.4+-0.4	1.3+-0.4	2.7+-0.4
	Max	11.1+-0.8	11.3+-0.8	5.7+-0.9	9.3+-0.9
Sn	Avg	7.4+-4.0	3.7+-3.2	6.1+-3.8	3.8+-3.4
	Max	55.7+-7.1	16.1+-6.3	16.5+-7.7	9.5+-6.5
Pb	Avg	128.3+-6.8	24.6+-1.7	51.8+-3.2	8.6+-1.5
	Max	1372.9+-69.0	224.1+-11.4	459.6+-24.7	27.2+-8.2

1 - PM-10 in ug/m^3, Elements in ng/m^3
2 - Sampling period from 10/85 to 8/87 (N - 74)
3 - Sampling period from 11/87 to 5/88 (N - 30)
4 - (< 2.5 um)
5 - (2.5 to 10 um)

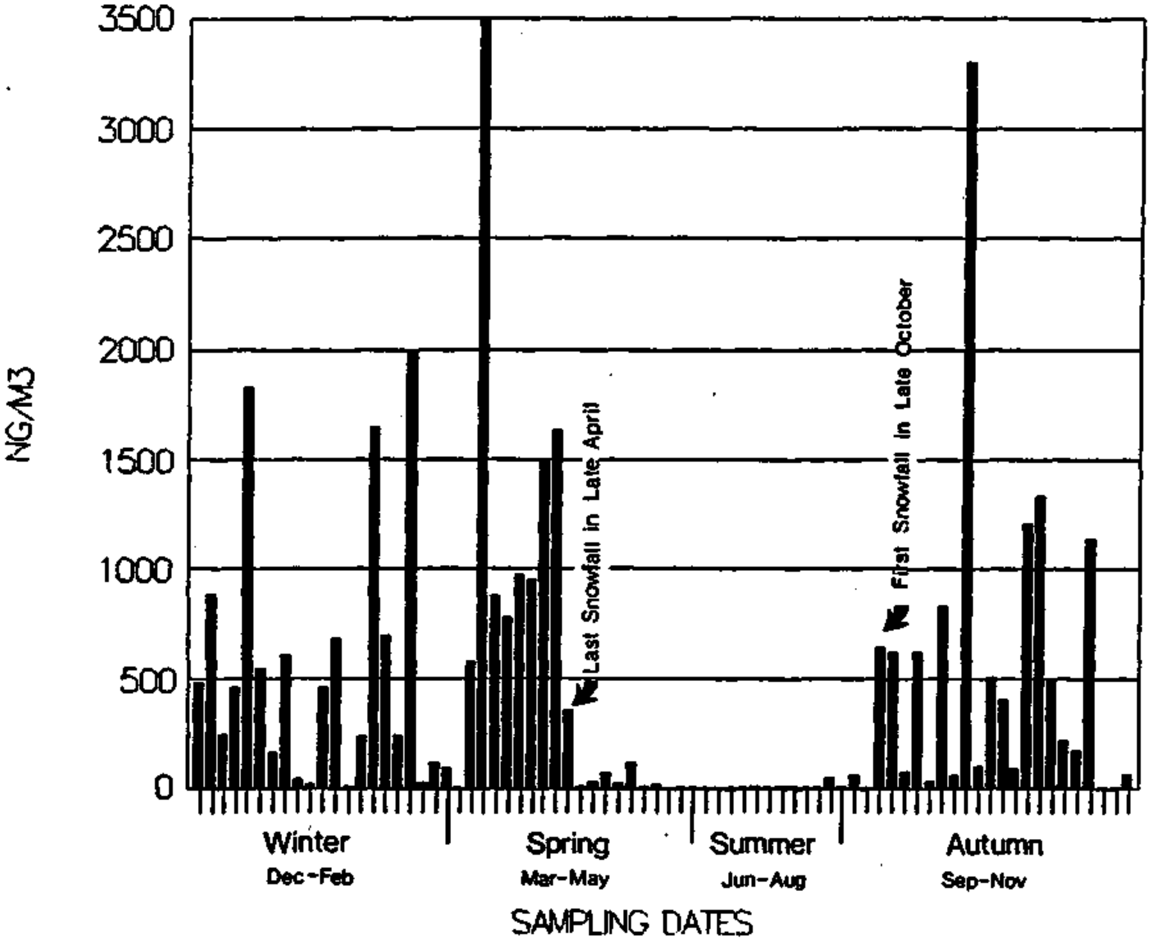


Figure 10. Seasonal variations in fine Cl concentrations as measured at the Bright School site.

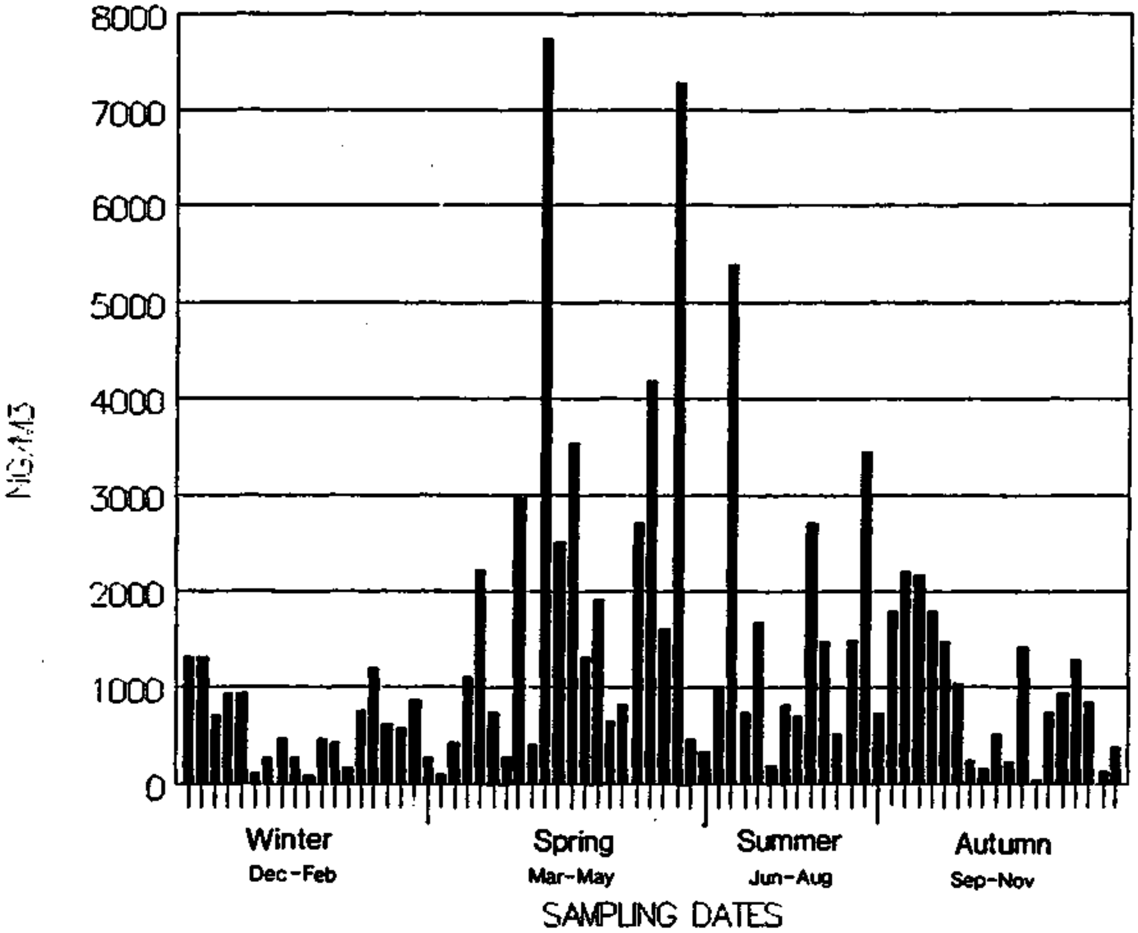


Figure 11. Seasonal variations in coarse Si concentrations as measured at the Bright School site.

$$EF = \frac{X/C\ \text{urban air}}{X/C\ \text{reference material}} \qquad (2)$$

where X is the concentration of the element of interest and C the concentration of the reference element. The value of this calculation in receptor modeling is based on an assumption that similar elemental ratios found between elements in the urban airshed and in the reference material suggest the reference material as a likely source. A crustal reference material (Wedepohl, 1971), with Si used as the reference element, is used in this study to distinguish natural crustal sources (rock and soil) from possible anthropogenic sources. An EF value > 5 represents a five-fold increase from the natural ratio of a given element and suggests a noncrustal source.

Enrichment factor values were calculated for each of the 20 targeted elements on both Bright and Washington School filters. The means and ranges for fine and coarse PM-10 EF are shown in Figures 12 and 13. The elements are ranked in order of increasing mean enrichment. For fine PM-10, Si, Al and Ti can be attributed solely to crustal sources, while V, Mn, Cr, Ni, P, Cu, Cl, Zn, Br, S, Pb and Se are attributed to sources other than crustal. The remaining elements (Ca, K, Sr, Fe and Rb) vary between crustal and noncrustal sources. This variability may depend on meteorology, variations in emmissions, seasonality etc. For coarse PM-10, a larger fraction of the targeted elements are labeled as crustal or variable. Crustal sources contribute to Si, K, Al and Ti, while Cl, Zn, Pb, S and Se are attributed to sources other than crustal. The remaining elements (Sr, Rb, Fe, Ca, P, V, Ni, Mn, Cr, Cu and Br) vary

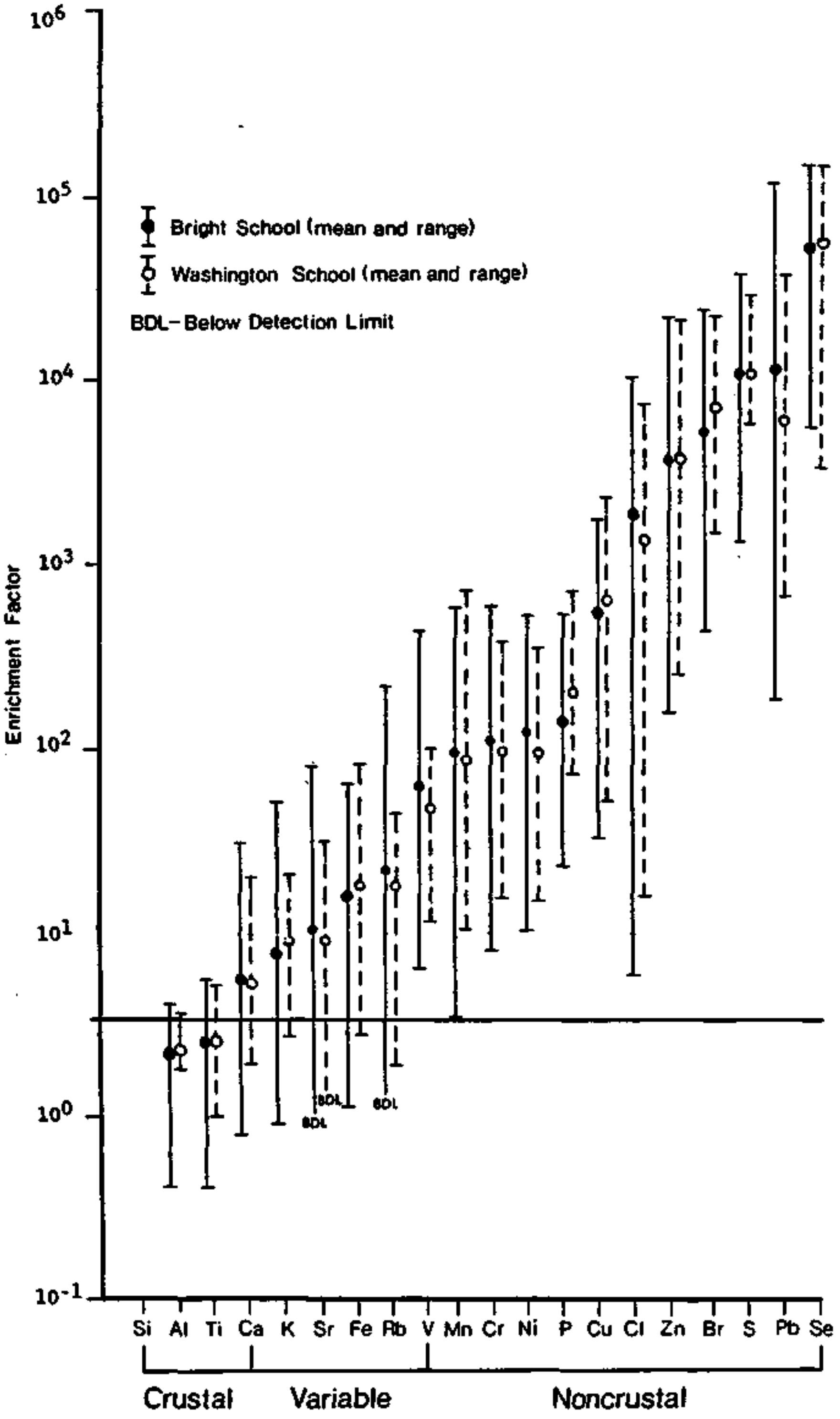


Figure 12. Fine PM-10 enrichment factors (mean and range) calculated for each of the analysed filters.

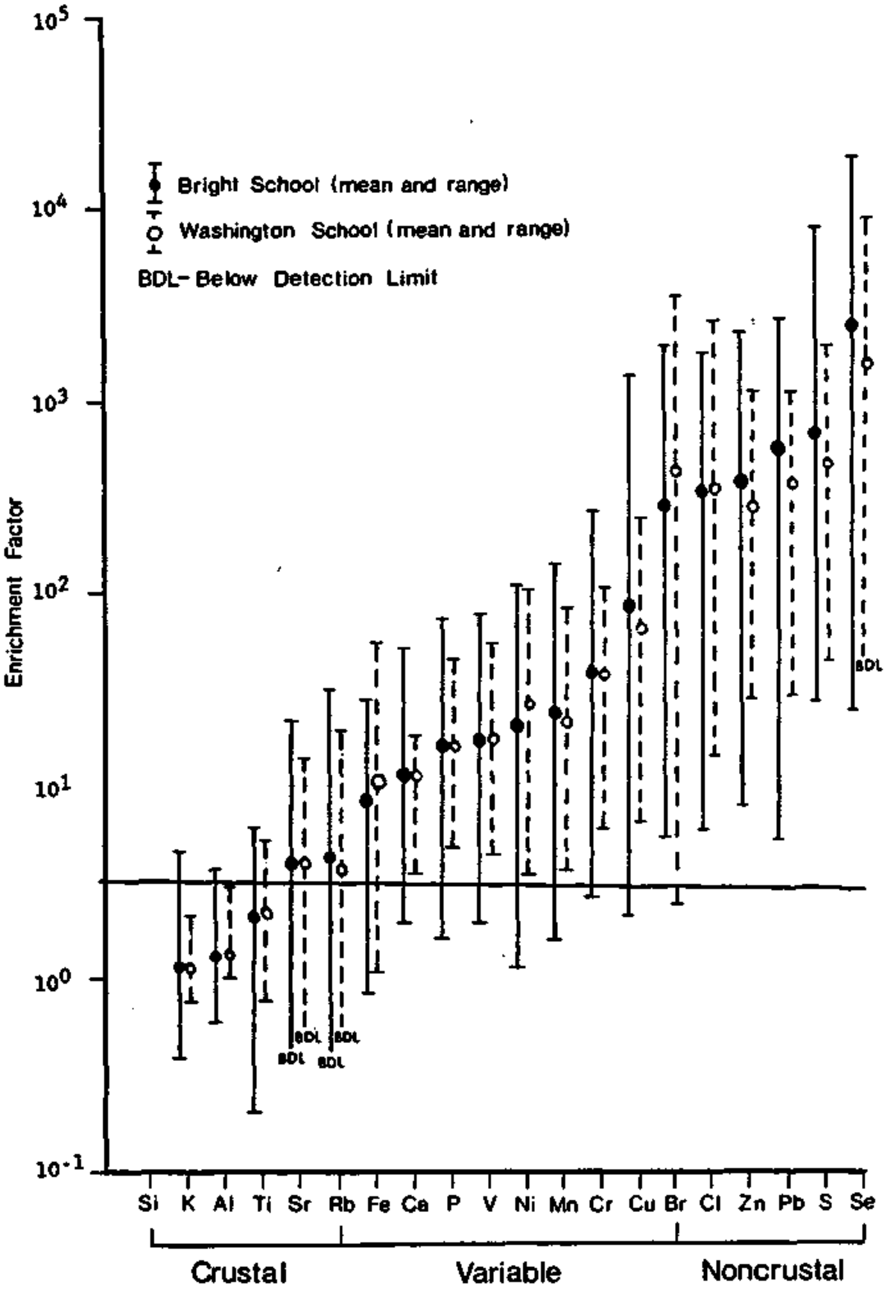


Figure 13. Coarse PM-10 enrichment factors (mean and range) calculated for each of the analysed filters.

between crustal and noncrustal sources.

An example of a mechanism responsible for the variation in sources (crustal or noncrustal) for a particular element is shown for coarse Mn (Figure 14). EF calculations show consistent nonenrichment when air flow is across an urban fetch but near consistent enrichment with air flow across an industrial fetch (steel mills). Manganese is essential in the production of steel (Skinner, 1969) and is an identified emission in steel production (Winchester and Nifong, 1971). In addition, Mn concentrations in the area's soil are considered to be above normal with the highest concentrations in proximity to the iron and steel mills. Contamination of the soil from dust and fumes in that area was considered as a probable cause (IEPA, 1986).

The use of regional air chemistry, instead of crustal material, as a reference material allows for the distinction of sources contributing to the local study airshed from those which contribute to the regional airshed. An EF > 5 suggests the dominance of local sources for a particular element in the urban airshed. Ambient chemistry data collected at Bondville, IL was used to represent the regional airshed.

Enrichment factor calculations were determined from two filter pairs: one pair was influenced by air passing over an industrial fetch; the second pair was influenced by air passing over an urban fetch (Table 4). Apparent in the EF calculations is the substantial enrichment of Fe, Mn, Br(c), Cl, V(c), Cu(c), Zn, Pb and Se(c) from the industrial fetch while only Zn and Pb(c) are enriched from an urban fetch. Elemental abbreviations without subscripts refer to both the fine and coarse fraction of PM-10 while subscripts (f) refer to the fine and (c) to the coarse fraction of PM-10. While these EF calculations do not distinguish between stack and fugitive emissions, the enrichment of some elements in the coarse fraction and not in the fine fraction suggests a

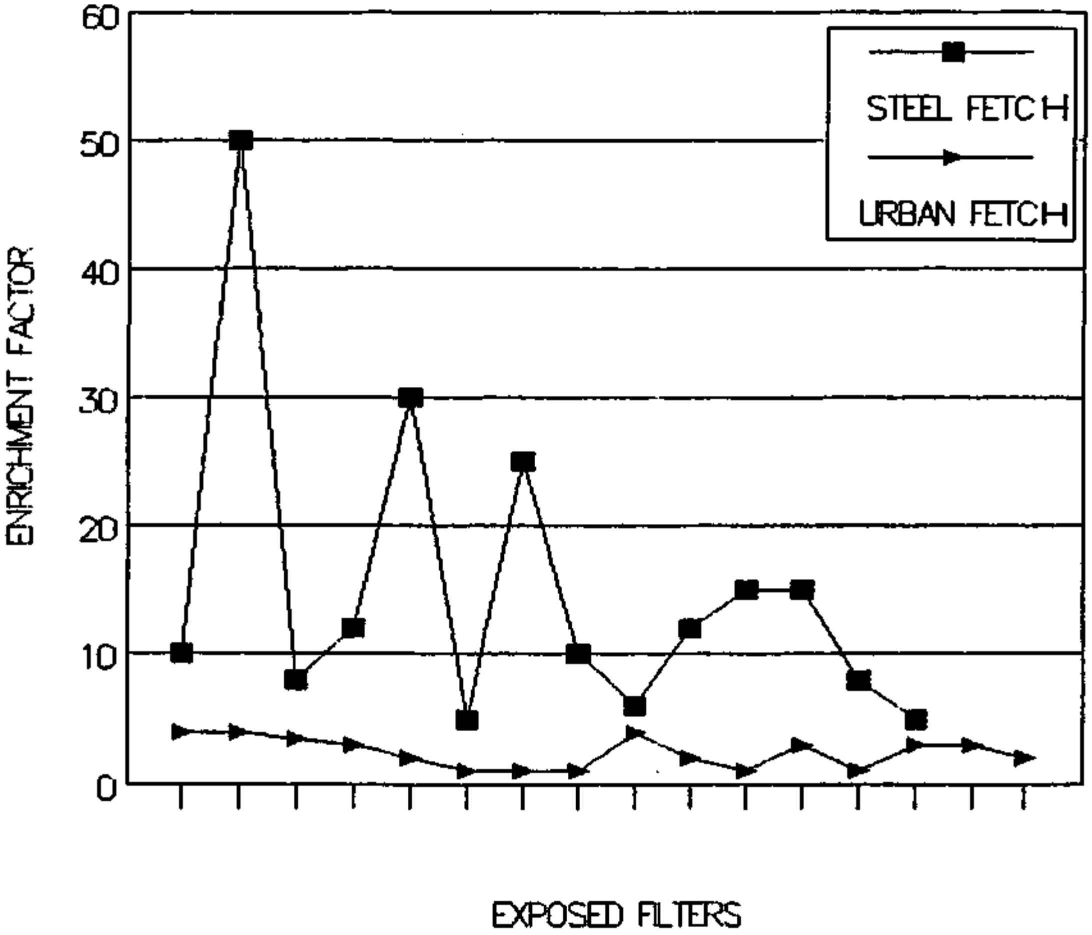


Figure 14. Manganese (Mn) enrichment with wind direction.

Table 4 PM-10 Enrichment Factor Calculations from an Urban and Steel Fetch

	Chicago-Urban		Chicago-Steel	
Element	Fine	Coarse	Fine	Coarse
Al	1.2	1.0	1.1	1.9
Fe	2.6	2.5	20.8	17.1
Ca	0.8	2.6	1.7	3.1
Mn	4.7	2.9	33.0	32.0
Br	1.2	2.8	1.8	7.6
Cl	0.5	1.3	13.3	9.7
P	1.5	1.0	1.1	1.9
K	1.1	1.1	1.3	1.3
Ti	1.7	B/D	2.6	3.9
S	1.8	1.9	0.9	4.6
V	4.3	B/D	4.3	10.1
Cu	1.3	0.9	4.1	13.1
Zn	6.3	8.0	4.5	10.6
Pb	3.5	5.3	17.8	23.8
Se	1.9	2.6	1.4	5.8

B/D - below detection limits

substantial impact from fugitive sources. The lack of significant enrichment for S, Al, Ca, P, K and Ti from both an urban and industrial fetch suggests a strong regional source for those elements.

3.4 Factor Analysis

Factor analysis is a statistical technique which takes a number of measured variables and finds linear combinations of those variables (factors) which explain most of the variance. These factors represent underlying causal parameters which are interpreted in this study as identifying possible emission source categories within the study airshed. In other words, factor analysis reverses the process used to produce the ambient data set. Factor loadings may be considered as 'correlation coefficients' of the original variable (element) with that of a new combination of variables or factors. The closer the factor loading is to 1.0 the more significant the relationship between the individual variable and factor or between the element and a possible source. Factor analysis does not require a priori knowledge of emission source categories and thus is useful in identifying sources previously not considered. While emission sources are identified by factor analysis, the labeling of these sources is based on previous findings, knowledge ef the study area and the scientific literature (see Hopke, 1985 for a more detailed review of factor analysis).

Factor analysis statistics (eigenvalues >1) suggest five and four factors for the fine and coarse fraction data sets, respectively. The varimax-rotated factor loadings corresponding to the first 5 factors for the fine mode are given in Figure 15, while the varimax-rotated factor loadings for the coarse mode are shown in Figure 16. The fine mode factors suggest, in decreasing order of variance, the presence of a strong steel/industrial process source, a sulphate and coal-fired boiler source, an unidentified source of Br, Cl, Rb and

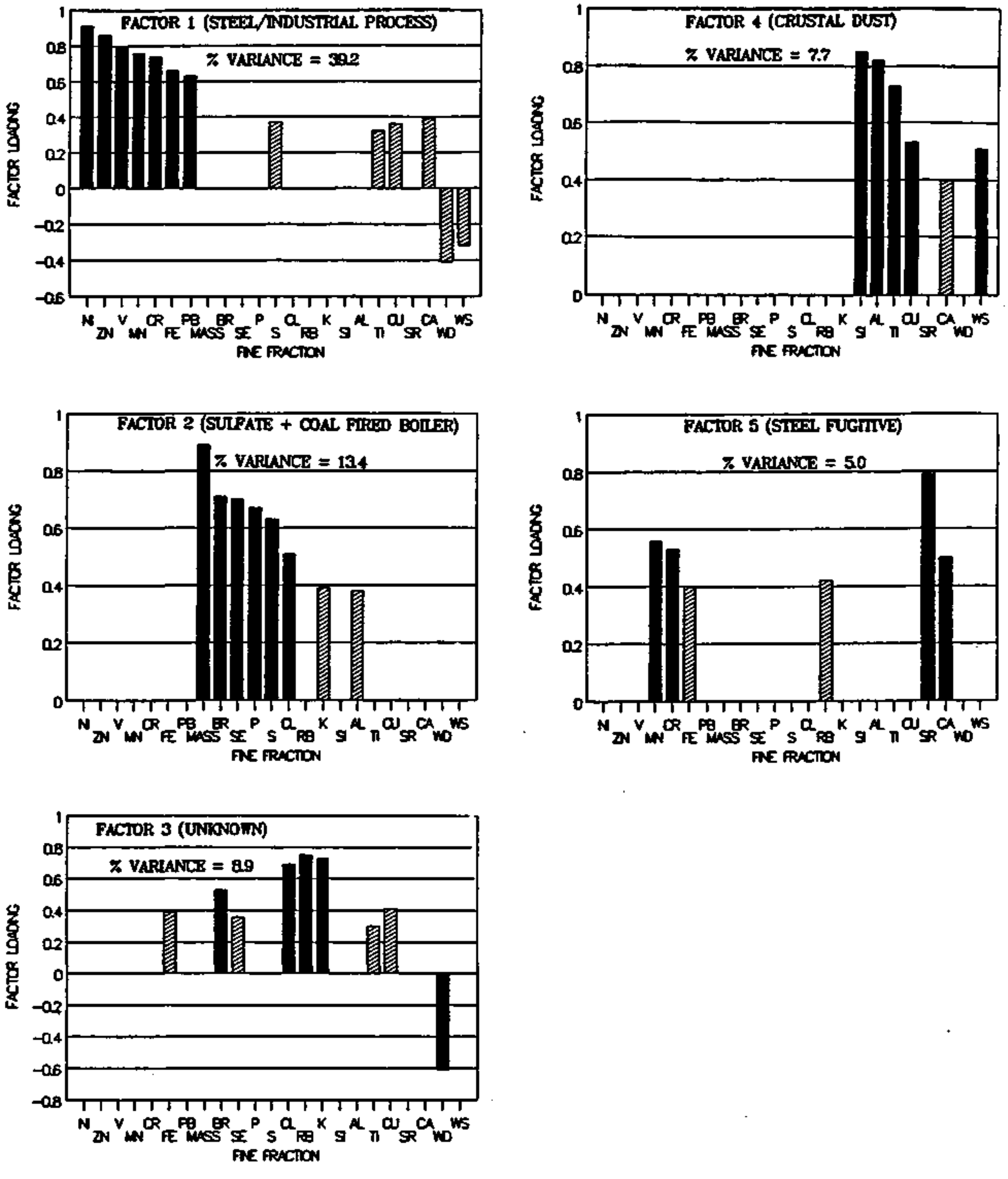


Figure 15. Graphic presentation of factor loadings and identified source categories for fine PM-10. Factor loadings > 0.5 are shown as solid bars.

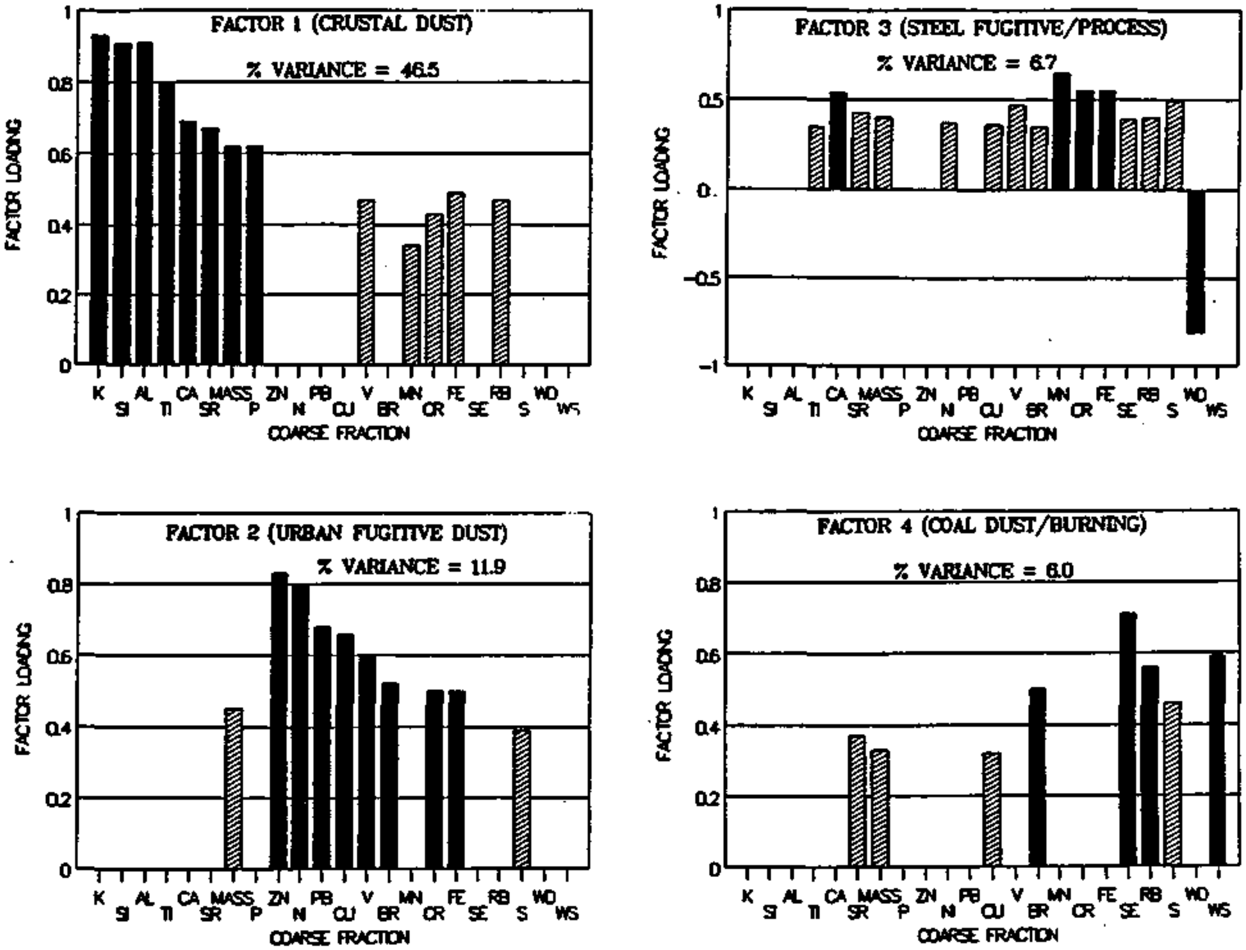


Figure 16. Graphic presentation of factor loadings and identified source categories for coarse PM-10. Factor loadings > 0.5 are shown as solid bars.

K (possibly automobile emissions), a crustal dust source, and a steel mill fugitive source. The coarse mode factors include a crustal dust source, an urban fugitive dust source, a steel fugitive dust/process source, and a coal dust/burning source. Factor analysis sources identified as fugitive (crustal and urban / industrial) appear to account for most of the coarse fraction variance and for a smaller but significant portion of the fine fraction.

4.0 SOURCE APPORTIONMENT

4.1 Chemical Mass Balance Model

The Chemical Mass Balance (CMB) Model, using a procedure known as least square estimates, 'sorts out' the contributions of emission source categories to the ambient air sample. Mass balance equations are written for each fitting element. Prior to CMB usage, an inventory of sources (source identification) and a knowledge of the composition of these sources is required.

Source categories have been identified in previous sections but the composition of these sources needs to be identified. Using source profiles from the literature, an early attempt by Hopke et al (1988) noted that an insufficient amount of the total mass was accounted for by the measured elements. The species that was obviously missing was carbon, especially when considering the proximity of Bright School to coking operations, coal storage areas and several large grain handling operations.

4.11 Carbon Determinations

While no carbon determinations were made for filters collected at the Bright School site, subsequent sampling at the Washington School site has included total carbon (TC) analysis. The glass fiber filters that were subjected to TC analysis were collected in sequence with the teflon filters.

The filters were treated with acid to remove carbonate and combusted at 800°C to convert elemental and organic carbon into CO_2 for measurement. The glass fiber filters represent a distinct 12 or 24 hour sampling period occurring either before or after a filter used for elemental analysis and therefore, direct comparisons with elemental determinations are not possible. However, comparisons between the TC mass and aerosol mass show that carbon comprises a substantial fraction of the aerosol mass (Figure 17). As a percentage of aerosol mass TC varied from 14.5 to 53.0% (average —25.2%). There appears to be no significant difference between fine and coarse filters where carbon accounts for an average of 24.0% and 26.5% of the aerosol mass, respectively. Combustion is usually indicated as the principal source of carbon (Shah et al., 1986; Huntzicker et al., 1986). The high abundance of TC in the coarse filters may indicate other sources such as grain handling (30% TC - Taback et al., 1979), coal storage/handling (Illinois coal 67% TC - Gluskoter, 1977) and other fugitive emissions.

4.12 Urban Dust Chemical Profile

In our review of facility locations, it was noted that large tracks of land serve as storage locations for coal, slag, scrap steel and limestone. Fugitive emissions produced in these areas combine with those from other sources, namely road dust, open lots and industrial yards, creating a complex mosaic of fugitive sources to PM-10. Generic source profiles for industrial processes or specific materials are primarily not site specific and are thus useful for preliminary receptor modeling. Fugitive source profiles, on the other hand, are more site specific and prone to misspeciation particularly when in proximity to industrial fugitive sources.

Prior to CMB modeling urban dust was sampled within the study area (Figure

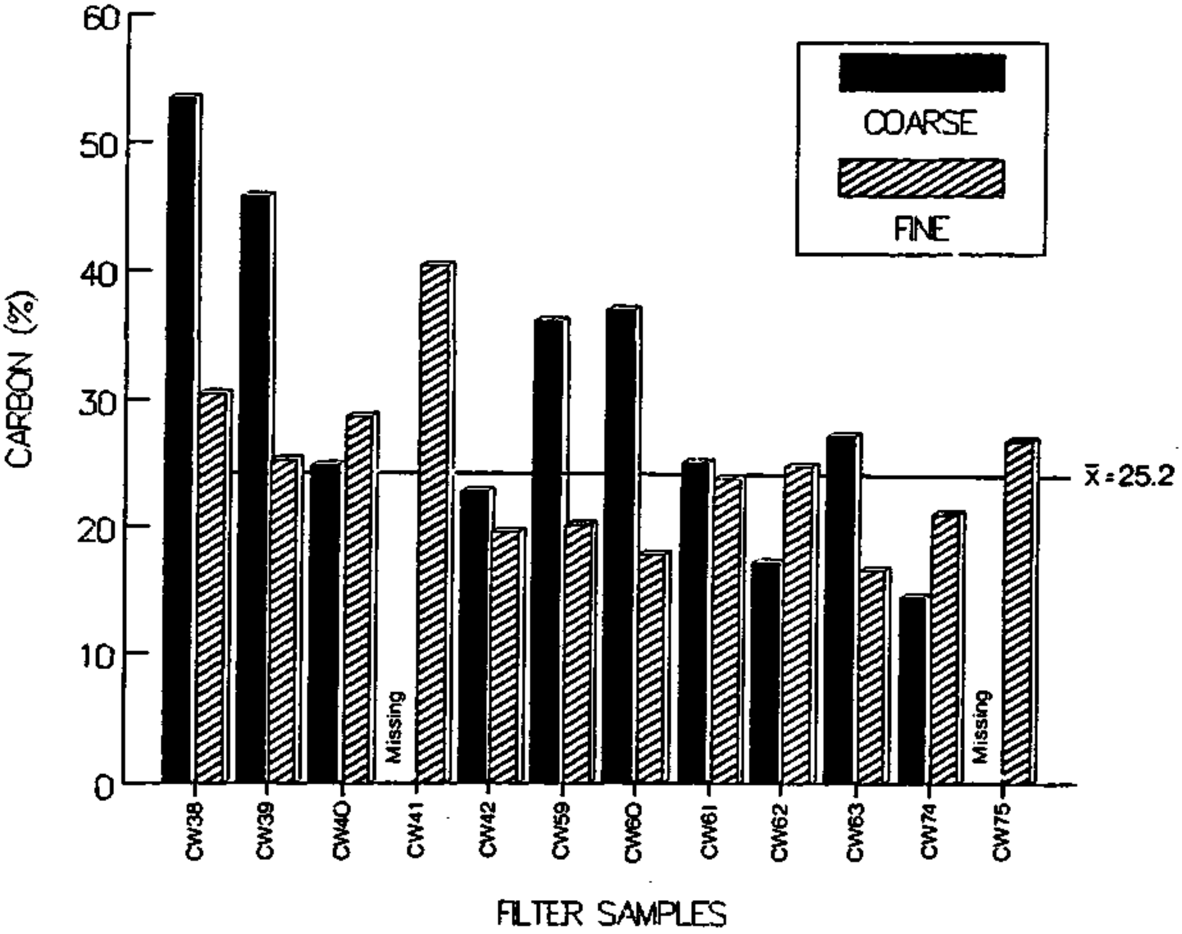


Figure 17. Carbon mass expressed as a percent of filter mass. Samples were measured at the Washington School site.

18). Of the seven samples collected to date, three (samples 3, 5 and 6) have been subjected to XRF and carbon analysis on fine and coarse PM-10. Determinations for these three samples comprise the urban dust (UDUST) source profile (Table 5) used in the CMB model.

The importance of characterizing the chemical composition of urban/industrial fugitive sources is demonstrated for Mn in Figure 19. It is apparent that usage of paved and unpaved road dust profiles provided by the USEPA Source Library could not adequately represent Mn concentrations from the sampled fugitive emissions. High Mn concentrations from an unpaved track in the study area (Figure 20) reinforce our need to rely on an indigenous UDUST source profile but also illustrates the variability of urban dust sources within the study area. The high Mn concentration is close to that reported for slag (a waste product of steel production). At present, an inadequate number of urban dust samples does not allow for distinction between urban dust profiles and will, no doubt, reduce the model fit.

Other source profiles used for the CMB Model are listed in Table 6. It should be noted that only the STEEL and UDUST source profiles were measured in the Chicago area. The source profile REGION was derived from mean concentrations of ambient PM-10 sampled at a rural site (Bondville-approximately 8 mi southwest of Champaign, IL) and is used in the CMB Model to account for sources contributing to regional PM-10 (Table 7). CDUST sources can be distinguished from REGION sources by considering the latter a mean value and the former accounting for daily ranges, at least for crustal sources. Ambient carbon concentrations were assumed to be 25.0% of the filter mass, 20% for UDUST (this study) and 30% for STEEL (an estimate).

4.13 Source Contribution Estimates

Source contribution estimates are shown graphically from an average of 10

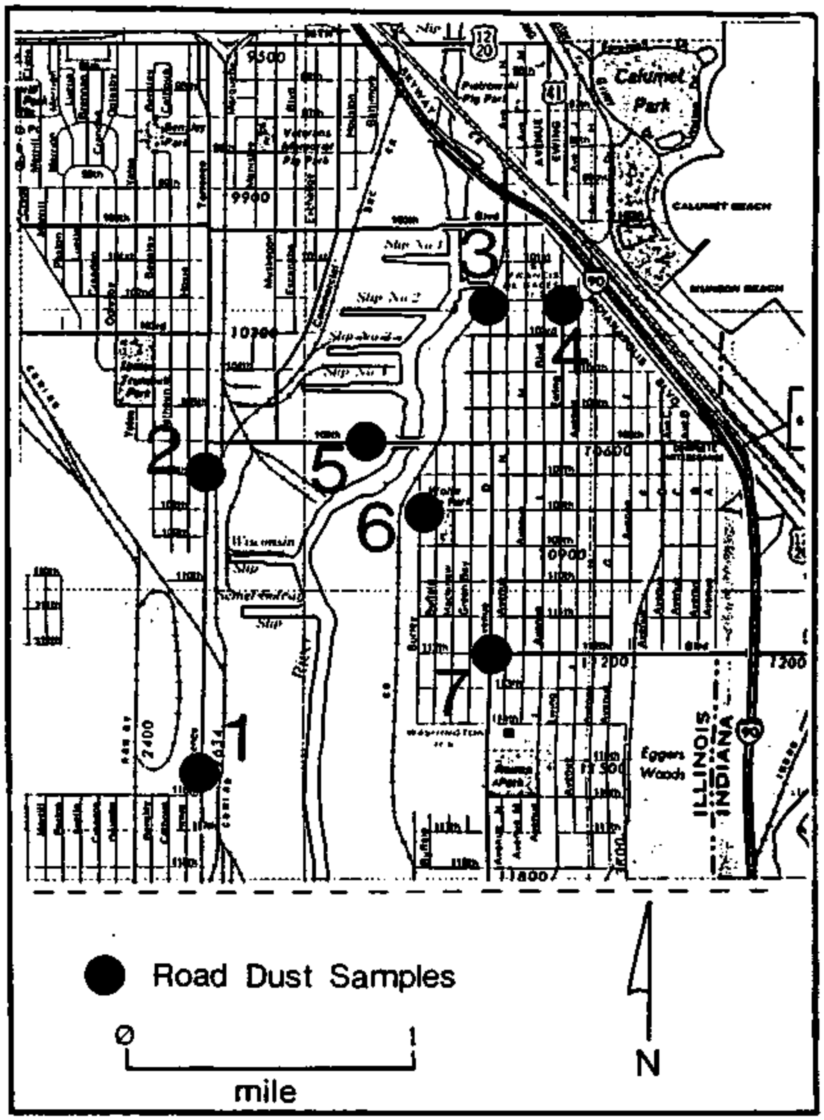
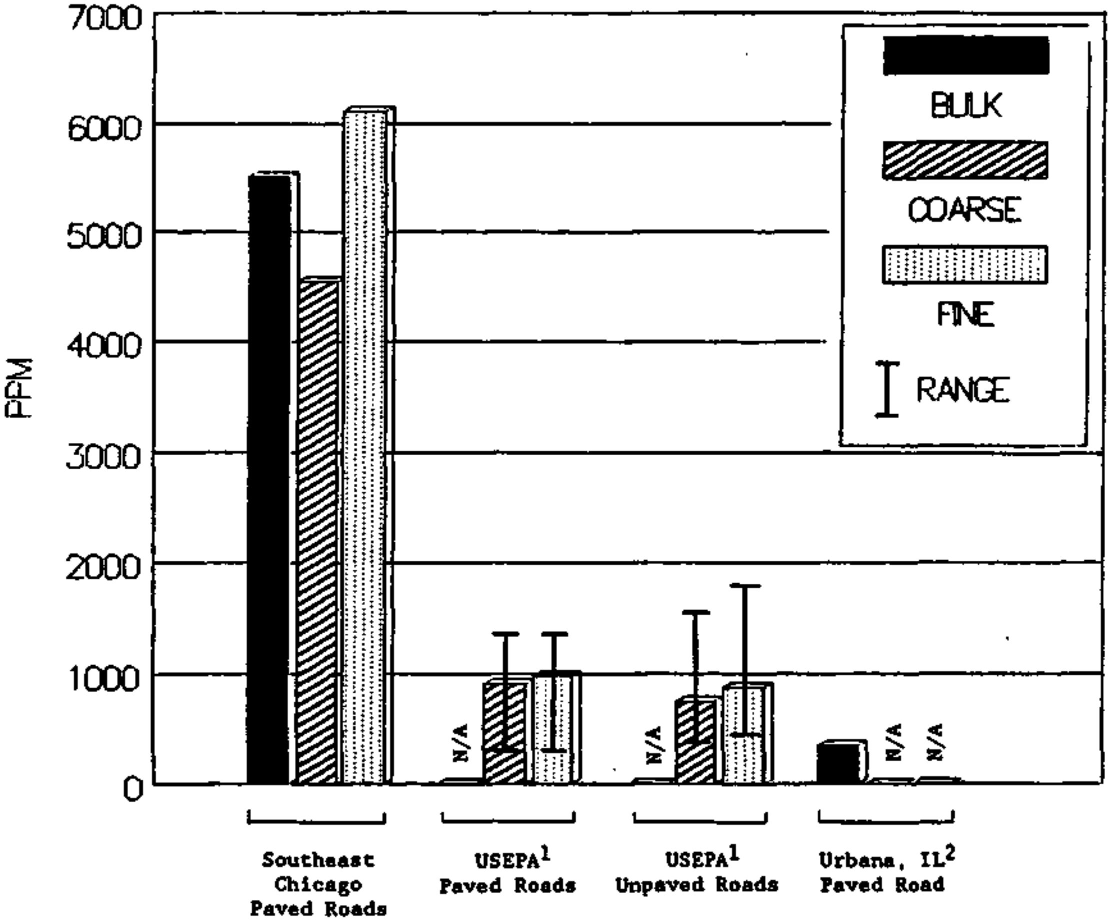


Figure 18. Urban dust sampling sites. With the exception of site #3 ('dirt' track), samples were collected off of paved roads.

Table 5. Southeast Chicago Urban Dust (UDUST) Chemical Profile

Parameter	% Fine Fraction	% Coarse Fraction
Al	2.187	1.818
Si	6.226	5.787
S	1.231	1.217
Cl	0.890	1.411
K	0.385	0.305
Ca	11.709	11.108
Ti	0.182	0.147
V	0.017	0.014
Cr	0.045	0.086
Mn	1.360	1.081
Fe	5.281	4.265
Ni	0.015	0.009
Cu	0.021	0.016
Zn	0.233	0.139
Br	0.005	0.003
Pb	0.103	0.071
Carbon*	20.000	20.000

* Measured from bulk sample



[1] U.S. Environmental Protection Agency Source Library (USEPA, 1984)

[2] Hopke et al., 1980

N/A: Not Available

Figure 19. Southeast Chicago paved road dust Mn concentrations as compared to values reported in the literature.

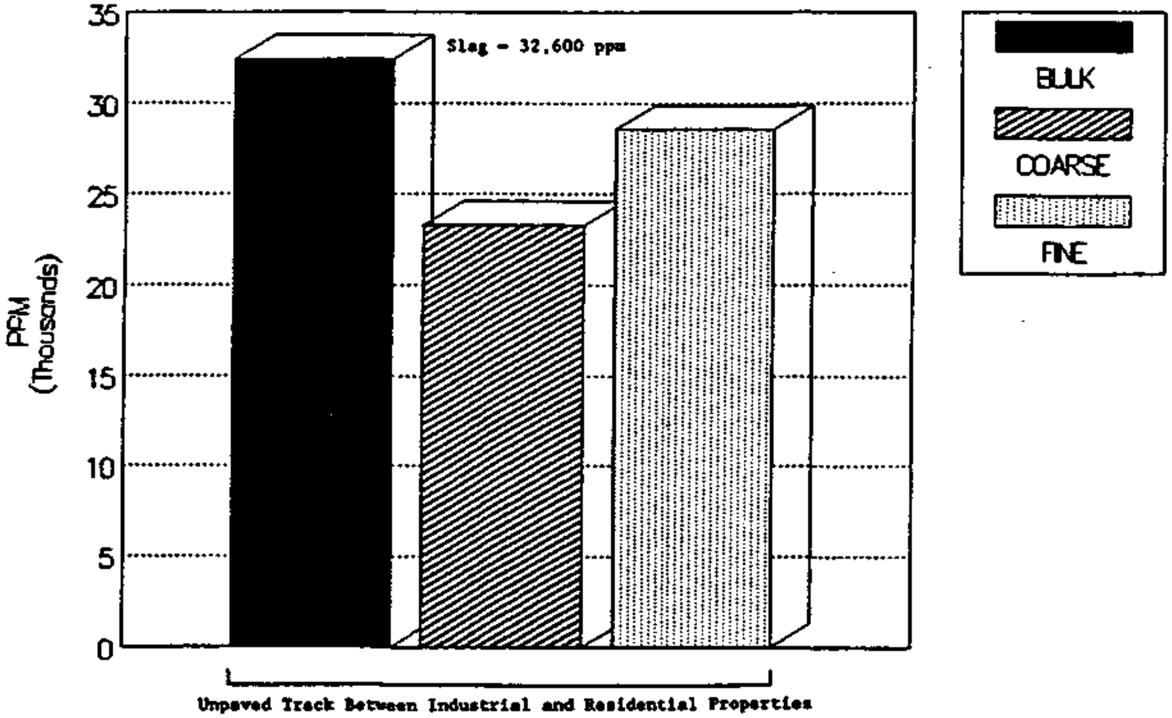


Figure 20. Bulk (< 2 mm), fine and coarse PM-10 Mn concentrations as measured from urban dust sampled at site #3.

Table 6. CMB PM-10 Source Category Profiles

Profile	Description	Source
REGION	Average regional air chemistry	This study
UDUST	Southeast Chicago urban dust	"
SALT	Road Salt	"
CARBON	Total Carbon	"
STEEL	Chicago Steel stack emissions	Scheff et al (1984)
AUTOPB	Automobile emissions	U.S. EPA, 1984
BLASTF	Blast Furnace	"
COALB	Coal Burning	"
COALD	Coal Dust	"
COALF	Coal Flyash	"
COKED	Coke Dust	"
CDUST	Crustal Dust	"
1NCIN	Incinerator	"
ROADS	Winter Road Dust (sand + salt)	"
ROADD	Road Dust (Uncontaminated by Chicago industry)	"
$S0_4$	Sulphate	"

Table 7. Southeast Chicago Regional (REGION) Chemical Profile

Parameter	% Fine Fraction	% Coarse Fraction
Al	0.554	2.610
Si	1.032	10.247
S	10.380	1.694
CI	0.117	0.343
K	0.342	0.827
Ca	0.302	3.033
Ti	0.025	0.154
V	0.005	0.009
Cr	0.004	0.009
Mn	0.020	0.050
Fe	0.306	1.395
Ni	0.026	0.005
Cu	0.016	0.021
Zn	0.115	0.075
Br	0.025	0.005
Pb	0.106	0.034
Carbon*	10.000	10.000

* Estimate

model runs (Figures 21a and b). The quantity of mass predicted ranged from 63 to 110%, with both the fine and coarse mass being equally accounted for. Closer examination of the average coarse fractions suggests that fugitive sources account for a much larger fraction of the mass than emission sources. Of the fugitive sources urban dust and coal dust account for the largest fraction. The contribution of the coal dust is based on its high carbon content. Steel emissions account for the largest fraction of the emission sources (50%) but this represents only a small proportion of the coarse mass (7%). Other significant sources include crustal dust, sulfate, incinerators, road salt and oil burning. While the latter three were not identified specifically in factor analysis they were identified in previous sections of this report.

Examination of source estimates for the mean fine fraction show the regional source as the largest single contributor. Included in this source is crustal dust, sulfate and various anthropogenic emissions. Local sources probably contribute to what we are calling regional pollution if the ratios of the targeted elements are similar to those found in regional pollution. In fact, such urban sources are major causes of regional air pollution. In the cases of steel, urban dust, road salt, automobile and oil burning sources, elemental ratios are sufficiently different from regional air pollution to quantify these components of urban air pollution. Source contribution estimates for urban dust are considerably smaller in the fine fraction than in the coarse fraction and steel emissions contribute to a larger proportion of the fine mass than the coarse.

A closer look at some of the individual runs reveals a range of source contributions depending, at least in part, on wind direction. With airflow from the southeast the steel mills are downwind of Bright School. As shown in Figures 22a and b, urban dust (59%) and coal dust (27%) accounts for the

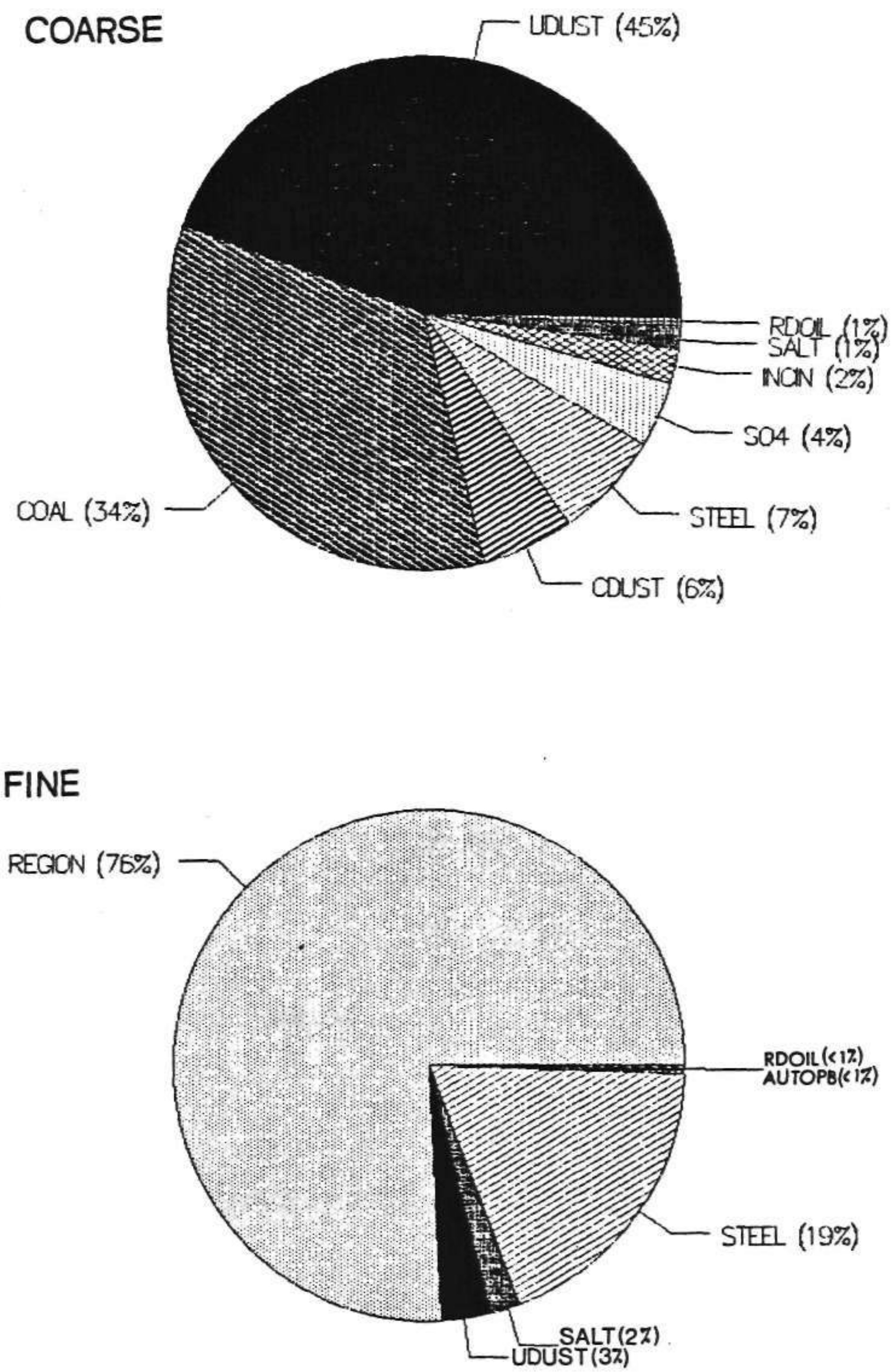


Figure 21. Average percent source contribution estimates for (A) coarse and (B) fine PM-10 mass.

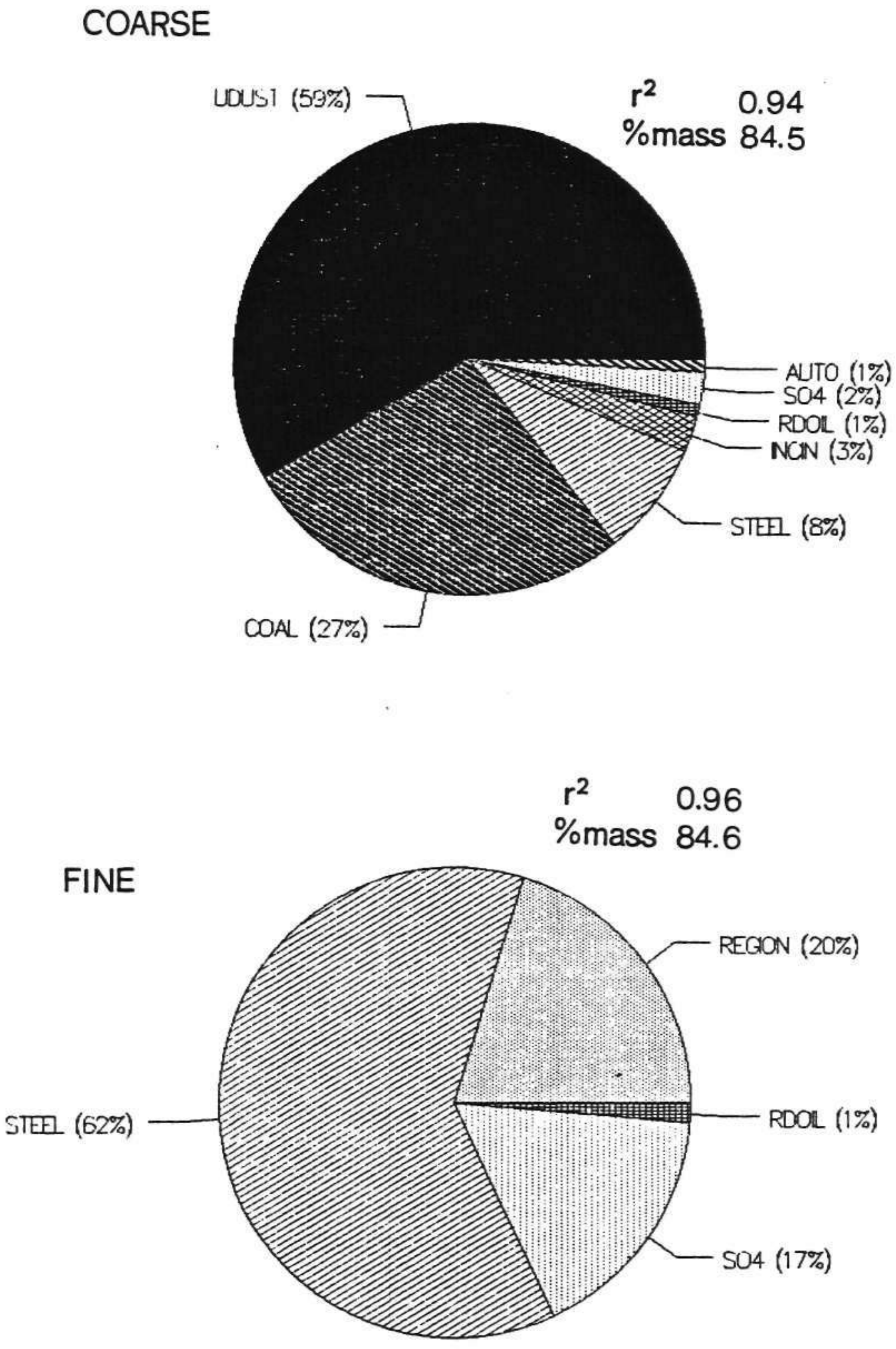
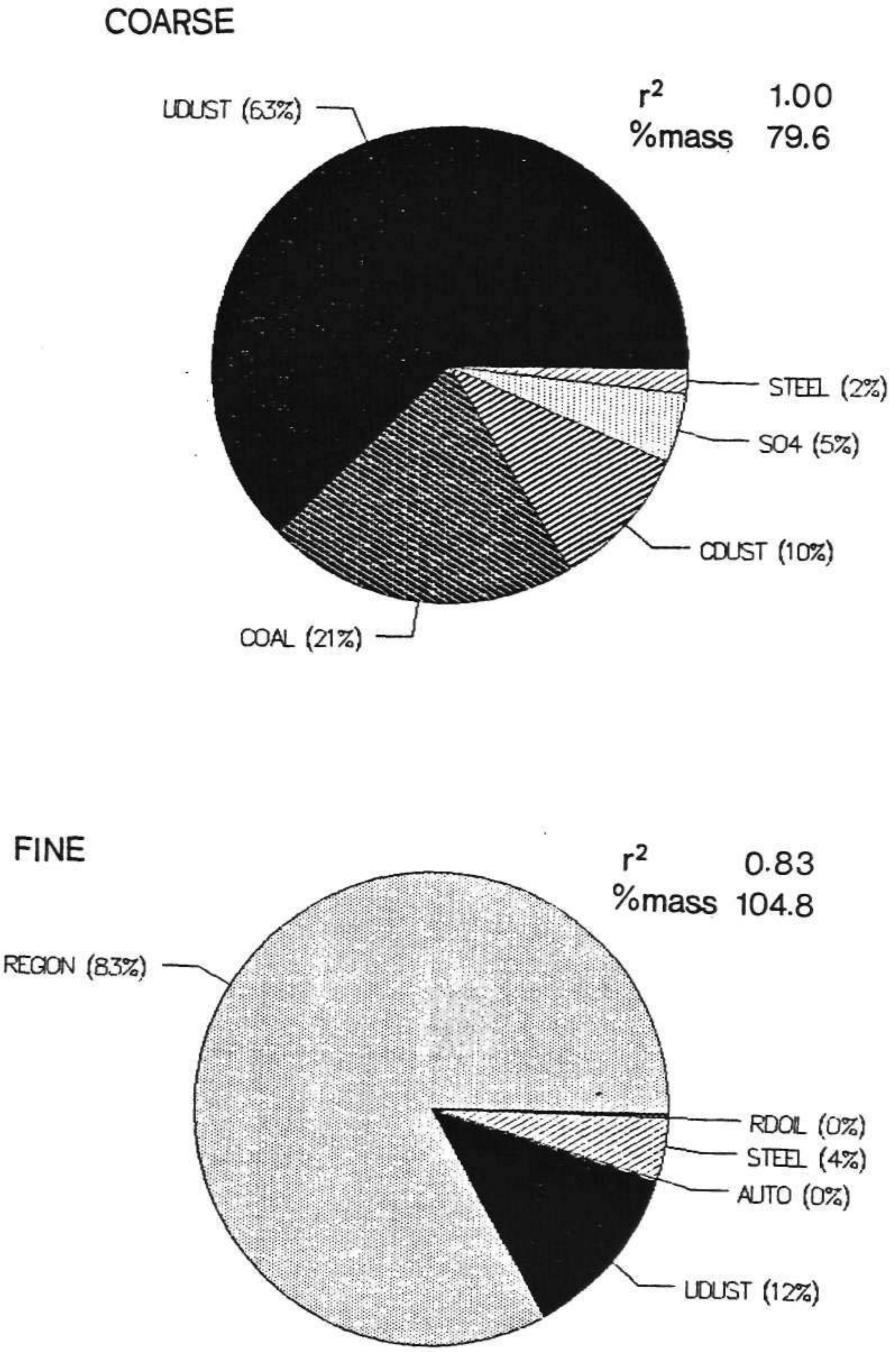


Figure 22. Percent source contribution estimates for (A) coarse and (B) fine PM-10 mass (sample CH-126). Airflow was from the southeast (passing over the iron and steel mills) 60% of the sampling time.

largest share of the coarse mass, with steel emissions accounting for only 8%. On the other hand, steel emissions account for the largest share of the fine mass (62%) along with sulfate (17%), while urban dust does not appear to contribute.

With airflow predominantely from the northeast (numerous slag, coal and other storage piles), urban dust accounts for an even larger share of the coarse mass (63%) with the steel emissions reduced to 2% (Figure 23a). The UDUST source profile employed in previous runs gave a poor accounting and was replaced with urban dust sample #3 (see Figure 18) which was sampled upwind to the northeast of Bright School and is likely a slag material (see Figure 20). With airflow from the northeast, the contribution of steel emission sources is reduced from 62% to 4% of the fine mass while the urban dust (slag) source increased from <1 to 12% (Figure 23b).

Airflow predominantly from the west does not pass over most of the steel mills. The one exception is Acme (Interlake) Steel located just outside the western boundary of the study area (see Figure 1). The urban dust source profile does not account for any of the coarse PM-10; rather a road dust source (USEPA Source Library), not contaminated by Chicago industrial emissions, accounts for the largest share of the coarse mass (Figure 24a). Surprisingly, a steel source also contributes to the coarse mass (7%). The coal dust source profile poorly fit the ambient data set but a substantial unknown carbon source was required to account for mass. In the fine fraction (Figure 24b), the regional source accounts for the largest fraction of mass (95%), with road salt, steel, urban dust and incinerators accounting for a total of only 5%.


COARSE

FINE

Figure 23. Percent source contribution estimates for (A) coarse and (B) fine PM-10 mass (sample CH-22). Airflow was from the northeast (passing over coal and slag storage piles) 75% of the sampling time.

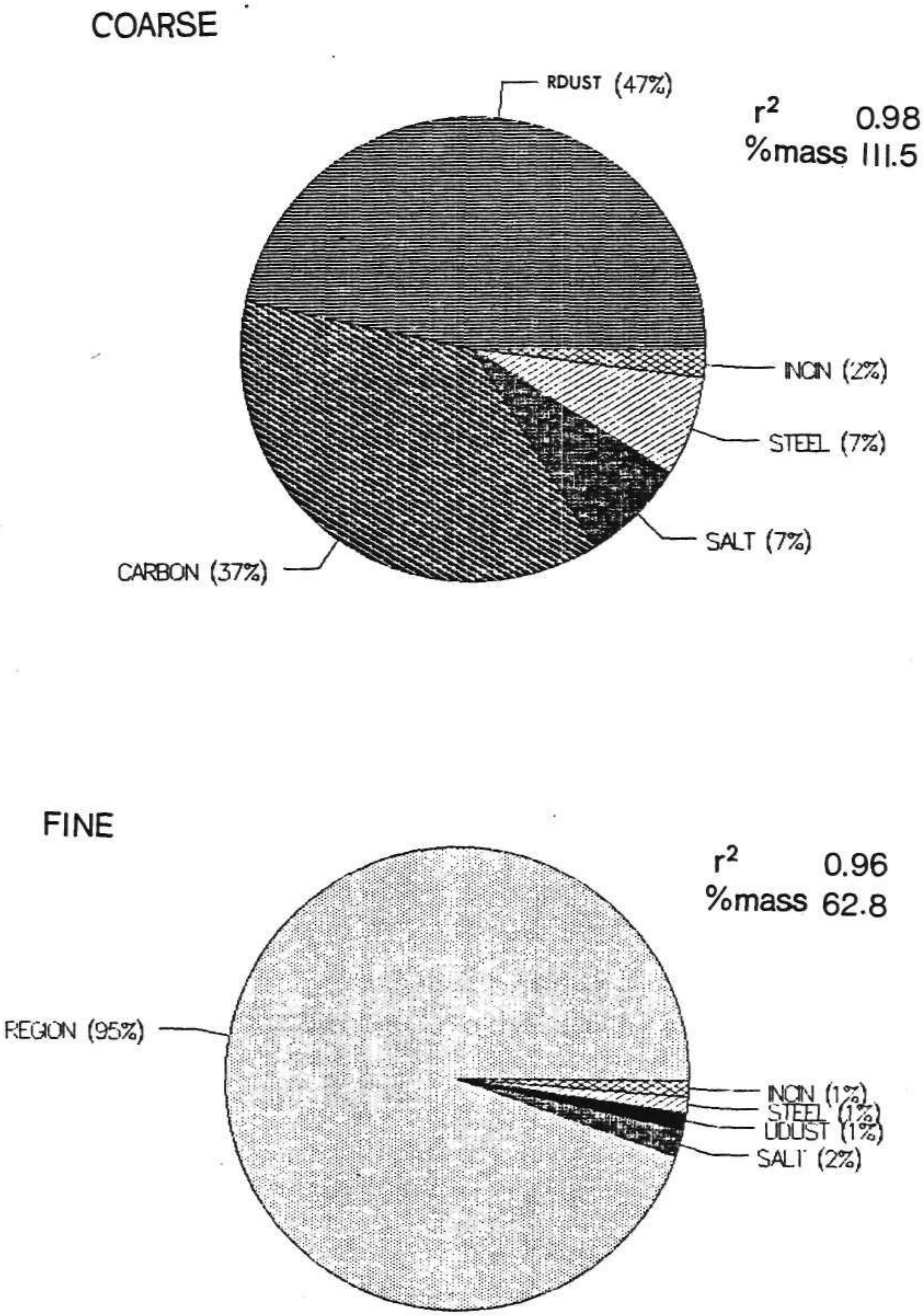


Figure 24. Percent source contribution estimates for (A) coarse and (B) fine PM-10 mass (sample CH-31). Airflow was from the Northwest 100% of the sampling time.

5.0 CONCLUSION AND RECOMMENDATIONS

PM-10 concentrations measured at Bright School have remained in compliance with the new PM-10 NAAQS, but the annual average concentrations do approach the Annual PM-10 Standard of 50 ug/m^3. There appears to be a seasonal variation in the percent contribution of fine and coarse PM-10 mass. Coarse PM-10 dominates in the summer, while fine PM-10 dominates in the autumn and winter months. Differences in percent contribution are greatest during the winter months. Iron and steel mills and related industries make up the bulk of the Southeast Chicago area manufacturing base and of the inventoried emissions, however, the impact of these stack emissions on annual average PM-10 mass concentrations appears to be small for fine PM-10 when compared to non-steel related source categories, and for coarse PM-10 when compared to urban and industrial fugitive emissions source contributions. Similarily, automobile emissions do not appear to substantially impact PM-10 mass concentrations.

Control strategies instigated in the Southeast Chicago study area should strive to control annual or seasonal emissions of PM-10 mass rather than concentrating controls solely on episodic events (ie. based on meteorological forecasts). Further control of iron and steel mill emissions will reduce PM-10 mass during specific short term periods but will have little impact on annual average PM-10 mass concentrations. A far greater percent decrease in annual average PM-10 mass concentrations, at a substantially lower cost, will be obtained by controlling urban and industrial fugitive emission sources. Control methods include the liberal spraying of dust retardents, street sweeping and functional landscaping designed to restrict wind erosion around industrial complexes.

Final recommendations outline further research needed to better apportion PM-10 mass in Southeast Chicago and to better resolve the urban dust source.

The first of these, routine sampling of ambient carbon, has already been implemented at the Washington School and is planned for the Carver School site. The second and third recommendations are outlined in more detail in Appendix A and B. These include the chemical analysis of industral dust samples already collected in Southeast Chicago. This proposed data base will better define industrial fugitive emissions within the study area. The third proposal is the establishment of an Illinois rural air quality network designed to reduce a significant gap in our knowledge of regional air quality and to better assess sources and control strategies for PM-10.

REFERENCES

Cooper, J.A. and Watson, J.G., 1979: *Portland Aerosol Characterization Study*. Final Report to the Oregon State Department of Environmental Quality.

Daisey, J.M., 1987: Chemical Composition of Inhalable Particulate Matter-Seasonal and Intersite Comparisons, *In: Toxic Air Pollution: A Comprehensive Study of Non-Criteria Air Pollutants*. J.M. Daisey and P.J. Lioy (Eds.), Lewis Publishing, Chelsea, MI, p 294.

Depaul, T., 1988: Personnal Communication.

Dzubay, T.G., 1977: *X-ray Fluorescence Analysis of Environmental Samples*. Ann Arbor Science Publishers, Ann Arbor, MI, p 310.

Dzubay, T.G., Stevens, R.K., Gordon, G.E., Olmez, I., and Sheffield, A.E., 1988: A Composite Receptor Method Applied to Philadelphia Aerosol. *Environ. Sci. Technol.*, 22, 46-52.

Gatz, D.F., 1975: Relative Contribution of Different Sources of Urban Aerosols: Application of a New Estimation Method to Multiple Sites in Chicago. *Atmos. Environ.*, 9, 1-18.

Gluskoter, H.J., Ruch, R.R., Miller, W.G, Cahill, R.A., Dreher, G.B., and Kuhn, J.K., 1977: *Trace Elements in Coal Occurrence and Distribution*. Illinois State Geological Survey. Circular 499, Urbana, IL 61801

Goldberg, E.D., 1985: *Black Carbon in the Environment*, John Wiley & Sons, New York.

Harrison, P.R., Rahn, K.A., Dams, R., Robins, J.A. Winchester, J.W., Bran, S.S. and Nelson, D.M., 1971: Areawide Trace Metal Concentrations Measured by Multielemental Neutron Activation Analysis. *J. Air Pollution Control Assoc.*, 21, 563-570.

Hopke, P.K., 1985: *Receptor Modeling in Environmental Chemistry*. John Wiley & Sons, New York.

Hopke, P.K. , Wlaschin, W. , Landsberger, S., Sweet, C, and Vermette, S.J'., 1988: *The Source Apportionment of PM-10 in South Chicago*. Presented at the Air Pollution Control Association PM-10 Specialty Conference, San Francisco, CA, March 21-24.

Huntzicker, J.J., Heyerdahl, E.K., McDow, S.R., Rau, J.A., Griest, W.H., MacDougall, C.S., 1986: Combustion as the Principal Source of Carbonaceous Aerosol in the Ohio River Valley. *J. Air Pollution Control Assoc*. 36, 705-709.

Illinois Environmental Protection Agency, 1986: *The Southeast Chicago Study: An Assessment of Environmental Pollution and Public Health Impacts*. Report IEPA/ENV/86-008. IEPA Division of Environmental Programs, Springfield, IL 62706.

Illinois Environmental Protection Agency, 1988: 1987 Annual Air Quality Report, Report IEPA/APC/88-022, Division of Air Pollution Control, Springfield, IL 62794-9276.

Khan, A. and Singh, L. , 1986: Fugitive Emissions and Their Role in New Source Review. Presented at the 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, June 22-27.

Kolaz, D.J., Sweitzer, T.A., and Bromke, D.L., 1986: Illinois PM-10 Measurements: Mass and Chemical Composition. Presented at the 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, June 22-27.

Lucas, J.H. and Casuccio, G.S., 1987: The Identification of Sources of Total Suspended Particulate Matter by Computer Controlled Scanning Electron Microscopy and Receptor Modeling Techniques. Presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, June 21-26.

Morandi, M.T., Daisey, J.M., and Lioy, P.J., 1987: Development of a Modified Factor Analysis/Multiple Regression Model to Apportion Suspended Particulate Matter in a Complex Urban Airshed. Atmos. Environ.. 21:8, 1821-1831.

Roscoe, B.A., Hopke, P.K., Dattner, S.L., and Jenks, J.M., 1982: The Use of Principal Component Factor Analysis to Interpret Particulate Composition Data Sets. J. Air Pollution Control Assoc. 32, 637-642.

Scheff, P.A., Wadden, R.A., and Allen, R.J., 1984: Development and Validation of a Chemical Element Mass Balance for Chicago. Environ. Sci. Technol., 18:12, 923-931.

Shah, J.J., Johnson, R.L., Heyerdahl, E.K., and Huntzicker, J.J., 1986: Carbonaceous Aerosol at Urban and Rural Sites in the United States. J. Air Pollution Control Assoc. 36, 254-257.

Shaw, R.W., and Pauer, R.J., 1983: Composition of Aerosol Particles Collected at Rural Sites in the Ohio River Valley. Atmos. Environ., 17:10, 2031-2044.

Skinner, B.J., 1969: Earth Resources. Prentice-Hall Inc., Englewood Cliffs, New Jersey.

Sweet, C.W. and Gatz, D.F., 1987: Atmospheric Research and Monitoring Study of Hazardous Substances: Third Annual Report. Report for Hazardous Waste Research and Information Center, Illinois Department of Energy and Natural Resources, Savoy, IL 61820.

Taback, H.J., Brienza, A.R., Macko, J., and Brunetz, N. , 1979: Fine Particle Emissions from Stationary and Miscellaneous Sources in the South Coast Air Basin. Report No. KVB 5806-7 83, KVB Inc., Tustin, CA.

Tuncel, S.G., Olmez, I., Parrington, J.R., Gordon, G.E., and Stevens, R.K. , 1985: Composition of Fine Particle Regional Sulfate Component in Shenandoah Valley. Environ. Sci. Technol., 19:6, 529-537.

U.S. EPA, 1985: Receptor Model Source Composition Library. EPA 450/4-85-002, U.S. EPA, Research Triangle Park, NC 27711.

Vermette, S.J., Sweet, C.W., and Landsberger, S., 1988: Southeast Chicago PM-10 Data base (October 1985 to May 1988), Illinois State Water Survey, Atmospheric Chemistry Section, Champaign, IL 61820-7495.

Wedepohl, K.H., 1971: Geochemistry. Holt, Rinehart and Winston, New York.

Winchester, J.W. and G.D. Nifong, 1971: Water Pollution in Lake Michigan by Trace Elements from Pollution Aerosol Fallout, Water. Air, and Soil Pollution, 1, 50.

Wolff, G.T., and Korsog, P.E., 1985: Estimate of the Contribution of Sources to Inhalable Particle Concentrations in Detroit. Atmos. Environ.. 19:9, 1399-1409.

APPENDIX A

NBS Standard Reference Materials SRM 1832 and 1833

Element	N	XRF Determinations (ug/cm^2)	Certified Value (ug/cm^2)
Al	22	14.2 +- 0.9	15.0 +- 1.0
Si	22	35.0 +- 3.1	36.7 +- 2.4
K	22	18.5 +- 1.2	18.9 +- 1.9
Ca	22	19.1 +- 1.0	19.4 +- 1.3
Ti	22	13.4 +- 0.6	13.6 +- 2.0
V	22	4.4 +- 0.3	4.7 +- 0.5
Mn	22	4.3 +- 0.2	4.5 +- 0.5
Fe	22	14.9 +- 0.4	15.2 +- 0.5
Cu	22	2.4 +- 0.1	2.4 +- 0.2
Zn	22	5.4 +- 0.2	5.6 +- 0.3
Pb	22	16.1 +- 0.5	16.9 +- 0.9

Filter Blanks and Duplicate Analysis[1]

		Sample Filter				Sample Filter			
Parameter	Blank	Fine		Coarse		Fine		Coarse	
	(n-4)	First[2]	Second[3]	First	Second	First	Second	First	Second
Al	7+-18	2273+-135	2207+-133	4659+-251	4270+-234	2008+-118	1943+-114	10786+-556	10379+-535
Si	3+-U	3313+-177	3379+-180	15583+-789	15123+-766	4698+-246	4857+-251	40699+-2049	40385+-2027
P	7+-11	1806+-362	1824+-366	804+-162	739+-149	793+-160	564+-114	2896+-581	2011+-403
S	178+-55	40548+-2079	40278+-2065	17479+-909	17635+-915	14789+-761	16041+-824	3447+-190	3809+-214
Cl	6+-23	418+-103	20+-99	1021+-80	975+-79	BDL	69+-40	581+-40	711+-50
K	11+-10	1199+-69	1123+-66	1159+-69	1172+-69	979+-53	954+-53	3214+-167	3267+-171
Ca	19+-8	849+-48	799+-45	13490+-679	13273+-668	1190+-63	1234+-66	16910+-853	17644+-887
Ti	<1	45+-6	55+-7	290+-17	276+-17	BDL	BDL	226+-67	102+-84
V	4+-3	22+-4	20+-5	38+-6	32+-6	BDL	BDL	BDL	BDL
Cr	<1	40+-5	11+-5	55+-5	13+-5	38+-5	32+-5	61+-5	63+-6
Mn	<1	164+-11	150+-10	176+-11	185+-11	86+-5	76+-6	197+-11	218+-13
Fe	74+-9	1260+-67	1227+-65	4710+-240	4637+-236	1221+-65	1148+-61	5897+-300	5559+-282
Ni	<1	49+-5	52+-6	39+-5	42+-5	18+-3	18+-3	19+-3	22+-3
Cu	37+-5	7694+-387	7615+-383	1464+-75	1457+-75	42+-5	50+-5	43+-5	38+-4
Zn	<1	2466+-131	2536+-134	2355+-119	2353+-119	287+-16	298+-17	159+-10	142+-9
Se	<1	75+-6	75+-6	15+-3	18+-4	41+-4	27+-3	15+-3	13+-3
Br	5+-4	178+-11	160+-11	70+-6	70+-7	158+-9	98+-7	56+-5	42+-4
Rb	4+-6	42+-7	36+-7	40+-6	19+-7	24+-5	12+-4	30+-5	20+-4
Sb	<1	232+-135	255+-153	190+-133	193+-156	35+-5	10+-5	77+-7	59+-6
Sn	35+-88	739+-75	725+-82	BDL	BDL	BDL	BDL	BDL	BDL
Pb	19+-14	3548+-181	3582+-183	1475+-77	1441+-76	732+-40	632+-35	323+-21	266+-18

1 - ng/filter
2 - First determination
3 - Second determination
BDL - Below Detection Limit