WMRC Reports
Waste Management and Research Center

Toxic Trace Elements in Urban Air in Illinois

Clyde W. Sweet,
Stephan J. Vermette,
Donald F. Gatz

Illinios State Water Survey

RR-E42
January 1990
Electronic Version

HAZARDOUS WASTE RESEARCH & INFORMATION CENTER
One East Hazelwood Drive
Champaign, Illinois 61820
(217)333-8940

HWRIC RR-042

Toxic Trace Elements in Urban Air in Illinois

by

Clyde W. Sweet
Stephen J. Vermette
and
Donald F. Gatz

Illinois State Water Survey
Champaign, Illinois

Printed January 1990
Reprinted April 1991

Illinois Department of
Energy and Natural Resources

Toxic Trace Elements in Urban Air in Illinois

by

Clyde W Sweet
Stephen J Vermette
and
Donald F Gatz

Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820

Prepared for

The Illinois Hazardous Waste Research and Information Center
HWRIC Project Number 88006

Printed January 1990
Reprinted April 1990

Printed by Authority of the State of Illinois 91/100

CONTENTS

ACKNOWLEDGEMENTS

We thank Dave Kolaz and Bob Hutton of the IEPA for providing wind data and trace element data from the IEPA network and for their help in siting equipment We also thank Dr Sheldon Landsberger and Dr Phil Hopke of the University of Illinois for their help with sample analysis and data interpretation Mike Richman provided statistical advice, Greg Dzurisin, Joe Wlaschin, and Tom Channic helped with computer analysis of data, and Paul Nelson and Mike Snider handled filter processing and sampler calibration Finally, Joyce Fringer provided expert typing of the manuscript

TABLES

FIGURES

ABSTRACT

The airborne concentrations and sources of 17 toxic trace elements were evaluated in three polluted urban areas in Illinois: southeast Chicago, East St Louis, and Granite City Concentrations and meteorology were monitored between September 1985 and June 1988 Particle size distributions and vapor-particle partitioning were also measured during this period Using the existing emissions inventories for the study areas, we applied factor analysis and chemical mass balance analysis to the data This statistical analysis together with our monitoring data show that most of the airborne trace elements in excess of background concentrations come from stack and fugitive emissions from heavy industry within the study areas Elevated levels of chromium and manganese are caused by steel-related activities in Chicago and Granite City Airborne cadmium, lead, zinc, and copper come from emissions from smelters in East St Louis and Granite City In all of these areas, fugitive emissions from wind-blown dust, materials handling, and vehicle traffic are important sources of airborne toxic trace elements We conclude that existing standards for airborne inhalable particles do not adequately control the levels of many toxic trace elements and that the first step in the control of these pollutants is to identify the sources of individual elements rather than sources of particulate matter in general

EXECUTIVE SUMMARY

This report provides comprehensive evaluation of the concentrations and sources of a group of 17 toxic trace elements in three urban areas in Illinois The study areas were southeast Chicago, East St Louis, and Granite City These areas were chosen because they have the worst air quality in Illinois in terms of airborne particulate matter (IEPA, 1987) and because they have a wide variety of potential sources of toxic trace elements These sources include steel mills (Chicago and Granite City), nonferrous metal smelters (East St Louis and Granite City), and hazardous waste incinerators (Chicago and East St Louis) A rural site near Champaign (Bondville) was used to evaluate regional background levels of airborne trace elements

The list of elements chosen for analysis was compiled from a variety of sources These elements all have the potential for toxic effects at typical ambient levels Several have been implicated as major contributors to carcinogenic (cadmium, chromium, arsenic) and neurotoxic (lead, mercury) health risks from polluted air In general, toxic elements, with the exception of lead and some of the carcinogens, are not routinely monitored in urban air in Illinois, so this study provides new information on the airborne levels of many toxic pollutants

At each study site, samples of inhalable particles and meteorological data were collected between September 1985 and June 1988 Over 600 filters were analyzed for trace elements using X-ray fluorescence A subset of 150 of these filters was analyzed by neutron activation analysis to provide information on additional elements We also carried out experiments to evaluate particle size distribution, vapor-particle partitioning, and source identification in each of the study areas

The overall objective of this project is to provide an in-depth chemical and physical characterization of airborne toxic trace elements and to identify important sources of these pollutants in three selected urban areas in Illinois The approach taken was to develop a toxic trace element data base using a variety of sampling and analytical techniques We also developed an emissions inventory combining existing information on point sources with experimental work on fugitive emissions Receptor modeling and other statistical methods were then used to verify and quantify the contribution of individual sources to the amount of a particular airborne toxic element

Toxic Trace Element Data Base

Data for the 17 toxic elements that could be measured in this study are summarized in Table 1 In most cases, concentrations found at the rural background site (Bondville) are similar to levels measured in a national network and are used as an estimate of regional background levels The major exception is lead Both urban and rural levels of this element have dropped markedly during the last ten years with the introduction of unleaded gasoline At the urban sites, trace element concentrations are generally 2 to 10 times higher than at the rural site The exceptions are selenium and mercury These two elements have a significant vapor phase component that is not reflected in data from airborne particles

In terms of health risk, two elements are of particular concern Cadmium concentrations in East St Louis are more than ten times higher than "normal" urban levels Since cadmium has been identified as an important carcinogen at typical urban levels, the elevated concentrations in East St Louis need to be lowered Airborne chromium is also an important carcinogen at typical urban levels so health risks could also be reduced by better control of this pollutant

Table 1. **Average toxic trace element concentrations ($\mu g/m^3$) in inhalable airborne particles.**[a]

Element	Bondville	Chicago	E. St. Louis	Granite City	U S Average[b] Urban/Rural
Vanadium (V)	002	007	006	004	021/ 008
Chromium (Cr)	002	011	006	010	011/ 007
Manganese (Mn)	010	086	025	045	038/ 020
Nickel (Ni)	001	005	004	004	010/ 003
Copper (Cu)	005	015	135	026	-
Zinc (Zn)	039	166	131	096	160/ 040
Selenium (Se)[c]	002	003	006	002	-
Molybdenum (Mo)	< 001	003	001	001	002/ 001
Silver (Ag)	001	.002	003	002	-
Cadmium (Cd)	002	006	025	008	002/ 001
Tin (Sn)	002	011	016	009	-
Antimony (Sb)	003	011	010	011	-
Barium (Ba)	004	010	013	011	030/ 010
Mercury (Hg)[c]	001	002	001	001	-
Cobalt (Co)	< 001	001	001	< 001	-
Lead (Pb)	022	127	209	122	580/ 084
Arsenic (As)	001	003	004	005	-
Total PM10	28	41	41	47	

[a] Particle diameter <10 μm, concentrations are in $\mu g/m^3$
[b] USEPA Data (Evans et al , 1984)
[c] Substantial amounts of Hg and Se are in the vapor phase

Particle-size Distributions

Inhalable particulate matter (PM-10) can be divided into two size fractions: coarse (10 to 2.5 μm) aerodynamic diameter and fine (less than 2.5 μm). Coarse particles are generated by mechanical processes such as wind erosion, vehicle traffic, and materials handling, while fine particles usually result from the condensation of vapors in the emissions of high temperature processes. Coarse particles predominate in fugitive emissions (uninventoried, nonstack emissions) and fine particles are more important in stack and tailpipe emissions. The trace elements that are found mostly on fine particles from combustion sources are selenium, lead and copper. The other 14 elements are found on both coarse and fine particles indicating that they are emitted from a variety of sources. Size distribution profiles measured on samples collected downwind of steel mills and nonferrous metal smelters show that toxic elements are concentrated on coarse particles in emissions from these sources. This indicates that for these industries fugitive emissions are a major source of these toxic elements. Such emissions are often related to the surface contamination of the area surrounding the plant and may not reflect the current operations at the plant.

Vapor Phase Trace Elements

Using special vapor traps, the vapor phase samples of mercury, selenium and arsenic were collected from filtered air. Between 20 and 80 percent of the mercury and 15 to 30 percent of the selenium in urban samples were present in the vapor phase. No vapor phase arsenic could be detected.

Source Identification and Receptor Modeling

Source identification begins with site reconnaissance and emissions inventories to generate a list of major sources. Subsequent evaluation of averages, trends, enrichment factors and wind direction in the trace element data base further characterizes and identifies sources. Particle size distributions show the relative importance of fugitive versus stack emissions.

Receptor modeling is a statistical method for characterizing the underlying structure of complex data. The first step, factor analysis, is used here to verify that the complex mixture of trace elements that we find in the atmosphere of the study areas does result from the previously identified sources. Factor analysis can also identify sources that were not found in the initial analysis. Table 2 lists the major sources identified in the urban study areas and verified by factor analysis. These sources are industrial stack and fugitive emissions and resuspended urban dust. Vehicle emissions, coal burning and regional sulfate are also important sources in the study areas.

The final step in receptor modeling is to quantify the contribution of a given source to the concentration of individual elements in the atmosphere using chemical mass balance (CMB) techniques. For each site, CMB was carried out on average concentrations to evaluate the average conditions. We also performed CMB analyses on data from a few filters with very high levels of trace elements to evaluate conditions when maximum concentrations occurred.

The results of CMB analysis indicate that in Chicago most of the chromium (Cr) and manganese (Mn) comes from steel-related emissions and resuspended dust. Selenium (Se) and arsenic (As) are related to coal burning and coke production. The other elements are attributed to a variety of different sources including oil combustion, soil and incinerators. The attribution of most of the lead (Pb), zinc (Zn) and cadmium (Cd) to incinerator emissions in CMB analysis is almost certainly erroneous because of other strong evidence that most of these elements come from steel emissions and vehicle exhaust. The failure of CMB to allocate emissions to sources accurately in this case probably is due to inaccurate source profiles for Chicago steel emissions.

Table 2. Summary table of emission sources

Identified Sources	Southeast Chicago		Granite City		East St Louis	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
Soil (crustal)	X	X	X		X	
Iron and Steel (Stack)	X		X		X	
Iron and Steel (Dust)	X	X		X		X
Oil Burning	X		X		X	
Coal-derived	X	X		X		
Cu Smelter			X	X	X	X
Zn Smelter			X	X	X	X
Pb Smelter			X	X		
Al smelter			X			
Vehicle Emissions	X		X		X	
Urban/Road Dust		X	X	X	X	X
Sulfate	X		X		X	
Road Salt	X			X		

In Granite City, Cr and Mn come from steel emissions and resuspended urban dust Se and As are coal related and Zn, Cu , As, and Cd are related to smelter emissions The predominant source of Pb and As is resuspended contaminated soil and urban dust In East St Louis, Mn and Cr levels are still steel related, but other sources such as coal burning are relatively more important The nonferrous metal smelters are the sources of Cu, Zn, and Cd, and coal burning is the source of Se Lead is derived from auto emissions and resuspended urban dust, and nickel and vanadium are due to oil combustion

Conclusions

By combining a thorough site inventory and monitoring program with receptor modeling, it is possible to evaluate source contributions of airborne toxic trace elements to a complex urban area In the three urban areas studied in this project, current regulatory practices permit unhealthful levels of several toxic elements in the atmosphere even though standard air quality objectives are met To achieve adequate control, major sources of specific elements need to be identified so that appropriate control measures may be taken Special attention should be given to resuspended fugitive dust because these seem to be a major source of toxic elements from industrial areas

CHAPTER 1. INTRODUCTION

Toxic materials are emitted into the atmosphere as part of many human activities Increased awareness of air pollutants and new potential sources of airborne toxic chemicals has brought a concern that toxic air pollutants[1] may be a health hazard It is difficult to assess the magnitude of problems caused by toxic air pollutants or to suggest possible solutions because most of these chemicals are not routinely monitored in ambient air, and very little information is available on average or peak concentrations Likewise, little is known about the relative importance of various sources to the burden of toxic air pollutants in urban air The study described here is an effort to fill some of these knowledge gaps for three polluted urban areas in Illinois

For toxic air pollutants to be a health hazard to the general population of an urban area, airborne concentrations of these chemicals must be high enough to give rise to some toxic effect Of the many toxic effects that might be considered, carcinogenicity and neurotoxicity are most important because many toxic chemicals can cause these effects at very low concentrations Several years ago the U S Environmental Protection Agency (Thomson et al, 1985) conducted a study of cancer risks posed by selected toxic air pollutants A major finding of this study was that most of the cancer risk from urban air can be attributed to approximately 15 pollutants Of these 15 pollutants, 12 fall into two general categories: trace elements and volatile organic chemicals The three pollutants with the highest cancer risk, benzene, carbon tetrachloride, and chromium, fall into these two categories Lifetime individual risks of contracting cancer by breathing ambient urban air with typical concentrations of each of the 15 pollutants in the study ranges from 10^{-3} to 10^{-9} A lifetime individual risk of 10^{-3} means that if 1,000 people were exposed to a carcinogen for 70 years, it would cause cancer in one of them Aggregate risk from breathing urban air containing a mixture of all 15 chemicals at typical ambient concentrations results in a lifetime risk of about 10^{-3} to people living in urban areas In other words, it is estimated that about 1500 cases of cancer occur in the U S each year as a result of toxic air pollutants in ambient air To put this in perspective, there are about 850,000 total cases of cancer each year in the U S (Anon , 1983); so only about 0 2 percent of all cancers are due to toxic air pollutants Obviously, carcinogenic air pollutants are not a major health threat; however, this group of chemicals gives rise to a small but quantifiable health risk to the general public

No comprehensive study has been done on the neurotoxic effects of toxic air pollutants However, one criteria pollutant, lead, can cause neurological damage in children in urban areas (Boeckx, 1986) Lead uptake occurs via several pathways including breathing lead-bearing suspended particles or ingestion of urban dust contaminated by the fallout of such particles Recognition of the importance of these pathways in producing high lead levels in children (Elias, 1986) has led to the elimination of lead in gasoline, the major source of airborne lead, and the establishment of air quality standards for lead In addition to lead, several other trace elements are neurotoxins Whether the concentrations of these chemicals in ambient air are high enough to cause any toxic effect is not known at this time

Since most of the currently recognized health risks due to toxic air pollutants have been attributed to toxic trace elements and toxic volatile organics, this study has focused on these two chemical groups Table 3 lists 19 trace elements that occur in ambient air The concentrations of many of these have risen dramatically over the last few decades to the point where they are now seen as possible health threats (Galloway et al, 1982) Less is known about past and current concentrations of toxic volatile organics in ambient air Table 4 lists the most important toxic volatile organic chemicals found in urban air (Brodzinsky and Singh, 1983) and their potential health effects

---

[1] *"Toxic air pollutants" here are differentiated from ozone, sulfur dioxide and other "criteria" pollutants for which health effects, ambient levels and sources are well known and for which air quality standards have already been established*

Table 3. Toxic trace elements

Element	Major Source	Health Effects[b]	Analysis Method[c]
Thallium (Th)	Coal	Carcinogen	NA
Beryllium (Be)	Coal, Metallurgy	Carcinogen	NA
Vanadium (V)	Coal, Oil	Irritant	XRF/INAA
Chromium (Cr)[a]	Coal, Steel	Carcinogen	XRF/INAA/PIXE
Manganese (Mn)	Steel	Neurotoxin, Mutagen	XRF/INAA/PIXE
Nickel (Ni)	Coal, Oil, Metallurgy	Carcinogen	XRF
Copper (Cu)	Metallurgy	-	XRF/PIXE
Zinc (Zn)	Metallurgy Incineration	-	XRF/INAA/PIXE
Arsenic (As)[a]	Coal, Metallurgy	Carcinogen	INAA
Selenium (Se)	Coal, Metallurgy	Metabolic Toxin	XRF/INAA
Molybdenum (Mo)	Coal, Metallurgy	-	XRF
Silver (Ag)	Coal, Incineration	Mutagen	XRF
Cadmium (Cd)[a]	Metallurgy, Incineration	Carcinogen	XRF
Tin (Sn)	Metallurgy	Neurotoxin	XRF
Antimony (Sb)	Metallurgy	-	XRF/INAA
Barium (Ba)	Coal	-	XRF
Mercury (Hg)	Coal	Neurotoxin	XRF
Lead (Pb)	Gasoline, Metallurgy	Neurotoxin, Mutagen	XRF/PIXE
Cobalt (Co)	Coal, Metallurgy	Carcinogen	INAA

[a] significant cancer risk at ambient levels (Thomson et al, 1985)
[b] References: Nelson, 1984; NAS, 1973, 1974a, 1974b, 1975, 1976
[c] NA = Not analyzed; XRF = X-ray fluorescence
INAA = Instrumental neutron activation analysis; PIXE = Proton-Induced X-ray Emission

Table 4. Toxic volatile organics

Compound	Major Source	Health Hazard[a]	Analysis Method[b]
Benzene	auto exhaust, chemical and steel industry	SC	GC/FID
Methyl chloride	-	BM	GC/FID
Methylene chloride	solvent	BM	GC/FID
Chloroform	water treatment	SC	GC/ECD
Carbon tetrachloride	chemical industry	SC	GC/ECD
1,2 dichlorothane	chemical industry	SC	GC/ECD
1,2 dibromoethane	auto exhaust	SC	GC/ECD
1,1,1 trichlorothane	solvent	BM	GC/ECD
Trichlorethylene	solvent	SC	GC/ECD
Tetrachloroethylene	dry cleaning	SC	GC/ECD
Chlorobenzene	industry	BM	GC/FID
o-dichlorobenzene	chemical industry	BM	GC/ECD
Acrylonitrile	chemical industry	SC	HPLC
Butadiene	chemical industry	SC	GC/FID
Ethylene oxide	sterilizers, chemical industry	SC	HPLC
Styrene	chemical industry	BM	GC/FID
Vinyl chloride	chemical industry, landfills	SC	GC/FID

a) SC = suspected carcinogen
BM = bacterial mutagen
(Brodzinsky and Singh, 1983)

b) GC = gas chromatography
FID = flame ionization detection
HPLC = high pressure liquid chromatography
ECD = electron capture detection

The overall objective of the project was to provide an in-depth chemical and physical characterization of airborne toxic trace elements and toxic volatile organics and to identify important sources of these pollutants in three selected urban areas in Illinois Preliminary results were discussed in three previous interim reports (Gatz and Sweet, 1985; Sweet and Gatz, 1986, 1988) This final report contains the findings, conclusions and recommendations of the project on the toxic trace elements The ambient concentrations, particle size distributions, vapor-particle partitioning, and the important sources of target elements are discussed based on monitoring data collected from September 1985 to June 1988 Monitoring of volatile toxic organics is continuing in 1988 and 1989, and the findings of the project in this area will be covered in a later report

CHAPTER 2. SAMPLING LOCATIONS AND STUDY AREAS

Four study areas and six sampling locations were used in this work The three urban study areas were chosen because they have the worst known air quality in Illinois in terms of criteria pollutants such as total suspended particles (TSP) and because they contain a wide variety of industrial point sources including many known to emit toxic air pollutants These areas have the potential for levels of airborne toxic materials higher than at other locations in Illinois For comparison, the fourth study area is in a rural location near Champaign This site was chosen to be representative of regional air quality and provides an estimate of background concentrations of toxic air pollutants in Illinois The locations of the four study areas are shown in Figure 1 In this section, site maps and point source emissions inventories are described for each of the urban study areas

The Chicago study area is a 64 square kilometer area in southeast Chicago bounded by 95th Street to the north, the Indiana state line to the east, the Chicago city limits to the south and State Street to the west Iron and steel and related industries dominate the study area's manufacturing base and inventoried emissions These industries are largely confined to a north-south strip running either side of the Calumet River Associated with the iron/steel industries are large tracts of land that serve as storage locations for coal, slag, scrap steel, limestone and other raw materials Other significant facilities include numerous landfills and waste disposal sites Air quality was measured at two sites in the study areas: Bright Elementary School at 10740 S Calhoun, from October 1985 to August 1987, and Washington Elementary School at 3611 E 114 Street, from December 1987 to June 1988 The locations of these sites along with the locations of major point sources are shown on the map in Figure 2 A list of these sources and an emissions inventory is given in Table 5

The Granite City study area is bounded by the Mississippi River to the west and northwest, and Horseshoe Lake to the southeast and includes the municipalities of Granite City, Madison, and Venice The city of East St Louis is located to the south and the city of St Louis to the southeast Like southeast Chicago, iron/steel industries dominate the manufacturing base of Granite City In addition to iron and steel, lead smelting and lead recycling facilities are located within the study area Air quality was measured at 20th and Adams streets in Granite City between January 1986 and December 1987 The site map and emissions inventory for the Granite City study area are in Figure 3 and Table 6

The East St Louis study area is bounded by the Mississippi River on the west and includes the municipalities of East St Louis, Sauget, and Cahokia The city of St Louis is located to the west of the study area, across the Mississippi River The dominant manufacturing activities in the study area are copper and zinc smelting and organic chemical production Air quality was measured at two sites in this area: the Illinois Environmental Protection Agency (IEPA) trailer at 13th and Tudor streets from September 1985 to August 1987 and the Kerr-McGee lot at Little Avenue and 19th Street in Sauget from September 1987 to June 1988 A map with these sites shown and a table of major point sources and emissions inventories are given in Figure 4 and Table 7

The fourth site in this network is in a rural area near Champaign 8 km south of Bondville, IL This site was chosen to be representative of regional air quality and is also used in several national air and precipitation monitoring programs There are no point sources within 10 km and the site is at least 50 km downwind of urban areas during times of prevailing northwest and southwest winds In this location, concentrations of airborne toxic air pollutants should be representative of conditions in most of rural Illinois and provide an estimate of the contribution of regional background to urban pollution Samples were collected between September 1985 and September 1987

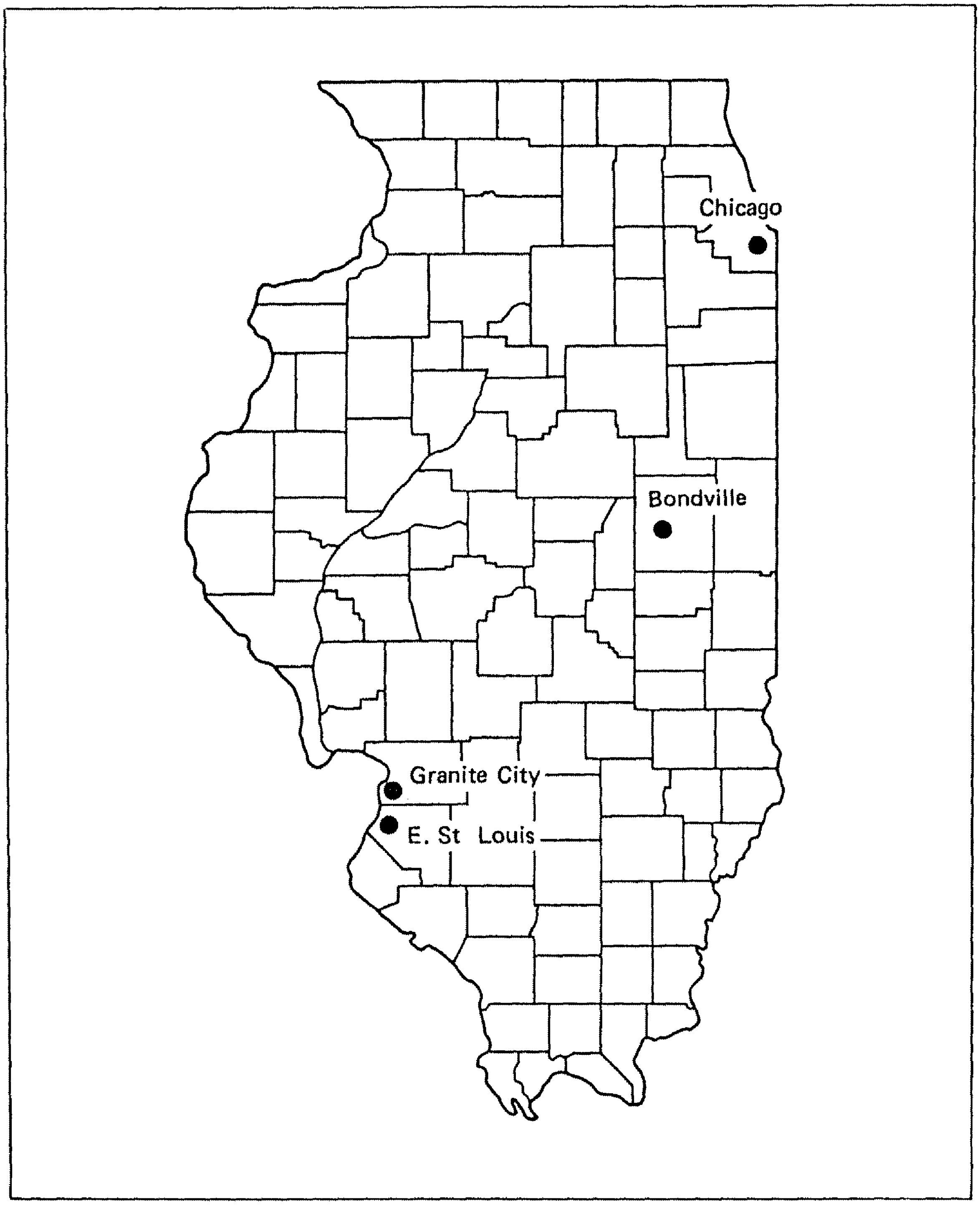


Figure 1 Air toxics monitoring sites

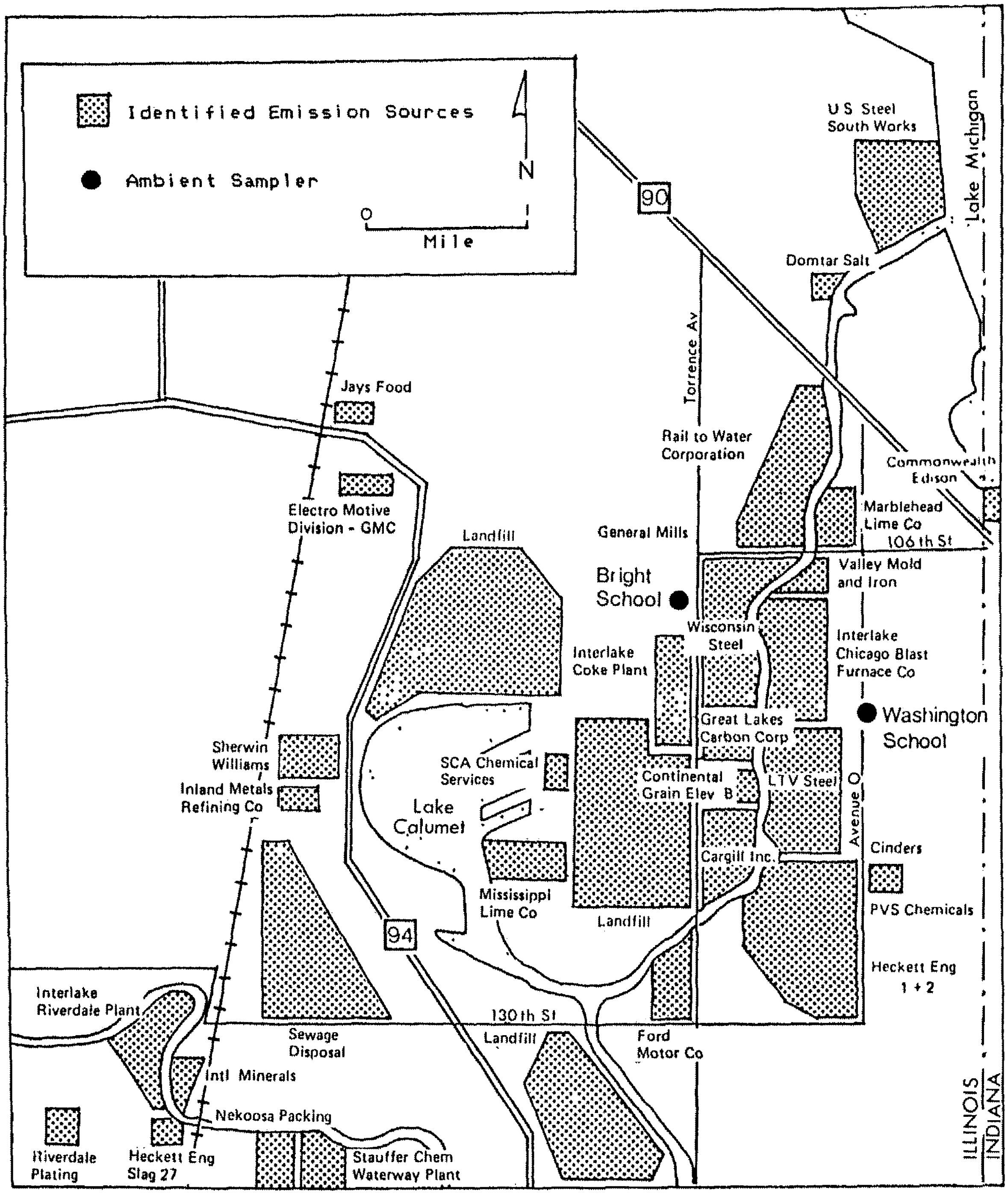


Figure 2 Southeast Chicago study area

Table 5. Point source inventory -- southeast Chicago[a]

Emissions (tons/year)

Industry Name	Particulate Matter	SO_2	Significant Others	SIC[b]	Description
Interlake-Rivedale	373 6	639 8	695 1 (NOX)	3312	Steel manufacturing
US Steel-Southworks	110 0	0 1	37 5 (NOX)	3312	Steel manufacturing
Chicago Blast Furn	324 2	818 9	2170 0 (NOX)	3312	Steel manufacturing
LTV Steel	515 0	680 3	420 0 (NOX) 1713 0 (CO)	3312	Steel manufacturing
Chicago Coke Plant	151 6	437 4	401 6 (HC)	3312	Steel manufacturing
Heckett-Plant 27	36 5	0	-	3295	Slag processing
Heckett Eng	76 8	0	-	3295	Slag processing
Heckett En Harsco	110 9	0	-	3295	Slag processing
Cinders	142 5	0	-	3295	Slag processing
Inland Metals	1 2	0	-	3341	Refining nonferrous
Marblehead Lime	129 7	532 8	-	3274	Lime manufacturing
Domtar Ind	12 9	0	-	2899	Refining Na Cl
Great Lakes Carbon	6 9	376 8	-	2999	Petro & coal prod
PVS Chemicals	129 7	532 8	26 5 (NOX)	2819	Inorganic chemicals
SCA Chemical	16 3	0	17 3 (NOX)	4953	Refuse disposal
Ford Motor Co	9 0	1 9	869 (HC)	3711	Auto manufacturing
Rail-to-water	11 7	0	-	4463	Marine cargo hand
Mississippi Line	12 4	0	-	4463	Marine cargo hand
Int Minerals	16 9	0	-	4463	Marine cargo hand
Stolt Terminals	7	0 9	9 8 (NOX) 89 4 (HC)	4226	Warehouse & storage
Sherwin-Williams	2 4	0	-	2851	Paint manufacturing
Stauffer Chemical	20 6	0	-	2874	Fertilizer mfg
Continental-Elv B	121 3	1 6	-	5153	Marketing grain
Cargill, Inc	54 0	0	-	5153	Marketing grain
General Mills, Inc	154 0	0	-	2041	Milling grain
Jay's Foods	11 6	0	-	2099	Food preparation
CID Landfill	4 4	0	-	N/A	Landfill site
Con-Ed Peaking Units	6 5	69 5	121 1 (NOX)	4912	Electric power
Riverdale Plating	19 4	0	-	3471	Plating

a) Source: Illinois Environmental Protection Agency, Emissions Inventory, unpublished data

b) Standard Industrial Code

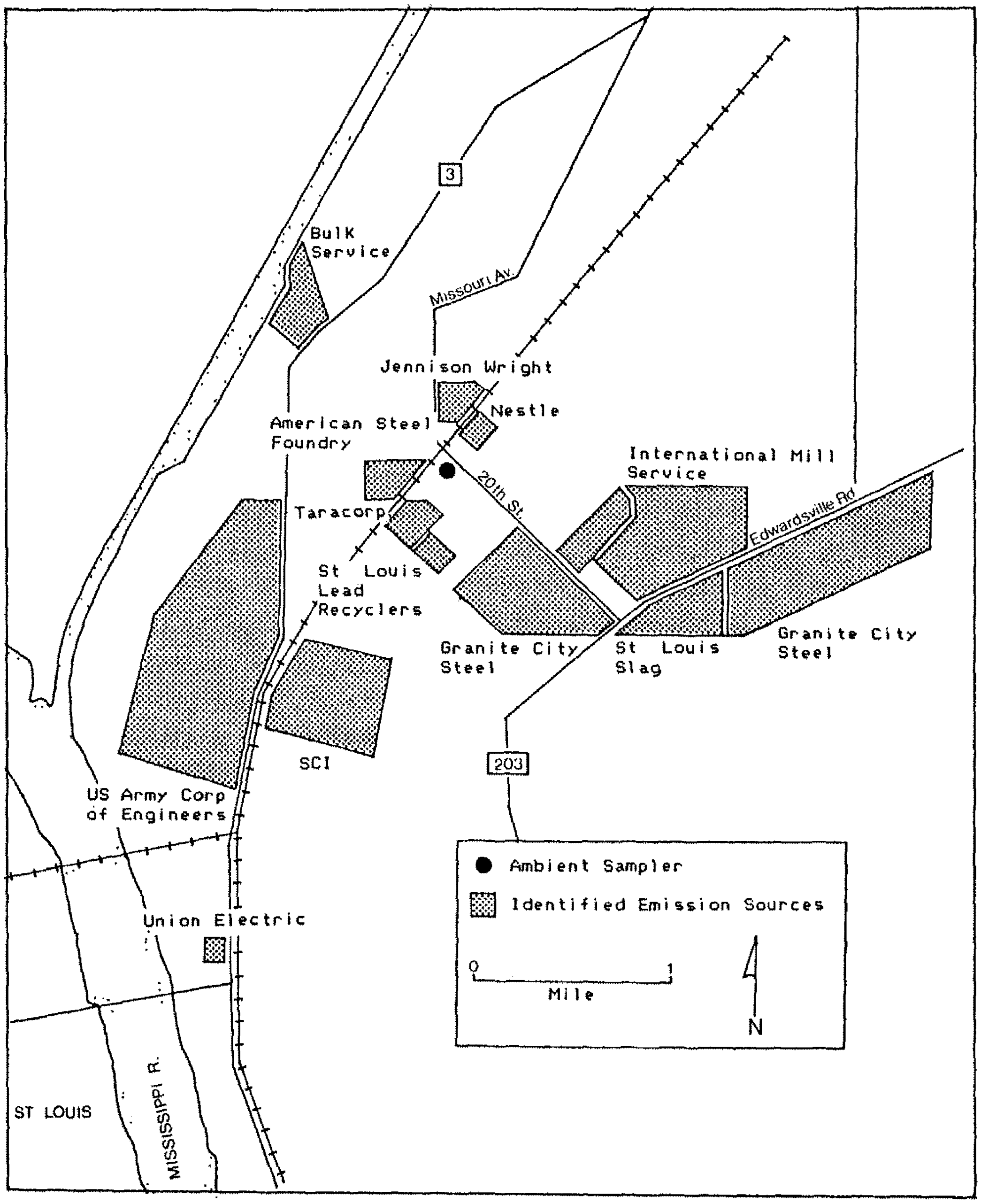


Figure 3 Granite City study area

Table 6. Point source inventory -- Granite City/Madison/Venice[a]

	Emissions (tons/year)				
Industry Name	Particulate Matter	SO_2	Significant Others	SIC[b]	Description
Granite City Steel	2282 0	8641 0	3473 0 (NOX) 172 0 (HC)	3312	Steel manufacturer
St Louis Slag Products	242 0	-	-	3295	Slag processing
Bulk Service	104 0	-	-	4463	Marine cargo handling
Archer Daniels Midland	107 0	14 0	52 4 (NOX) 33 5 (HC)	2075	Soybean processing
U S Army	9 6	110 0	47 5 (NOX)	9711	Construction
Nestle Co	35 9	28 7	51 2 (NOX)	2099	Food manufacturer
Tara Corp	74 4	-	17 3 (NOX)	3341	Secondary lead smelter
Corn Sweeteners, Inc	2 4	10 5	11 6 (HC)	2087	Grain processing
International Mill Service	48 8	-	-	3295	Ground minerals
St Louis Lead Recyclers	5 4	-	-	5093	Lead recycling
SCI	51 5	0 2	48 7 (NOX)	3341	Secondary A1 smelter
Kerr-McGee	8 4	-	61 6 (HC)	2491	Wood preserving
Union Electric	7 7	8 2	113 0 (NOX) 8 4 (HC)	4911	Coal fired Power plant
American Steel Foundry	0 3	-	-	3325	Steel foundry
Jennison Wright Corp	12 7	-	4 1 (HC)	2491	Wood preserving

a) Source: Illinois Environmental Protection Agency, Emissions Inventory, unpublished data

b) Standard Industrial Code

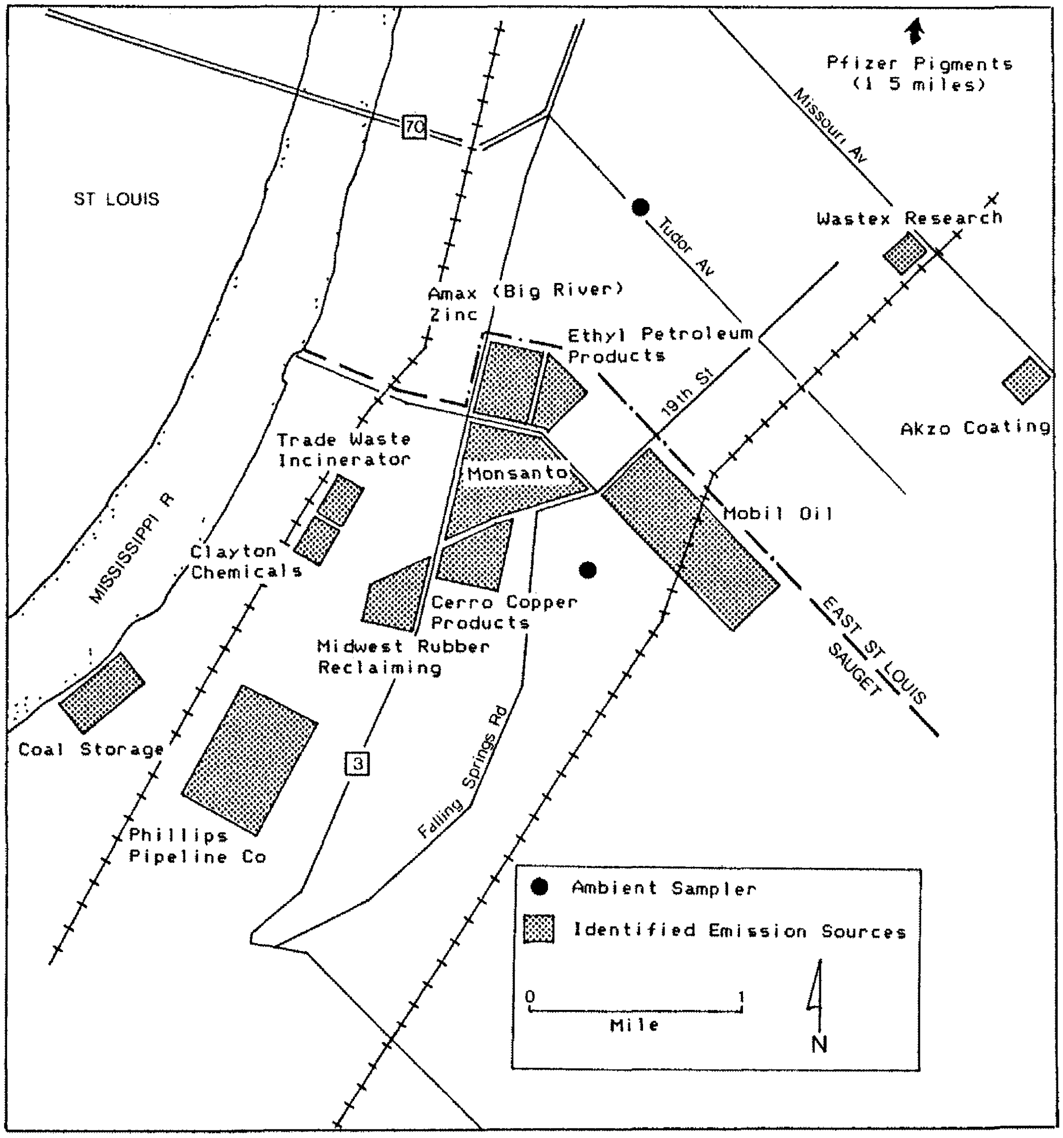


Figure 4 East St Louis study area

Table 7. Point source inventory--East St. Louis/Cahokia/Sauget[a].

Emissions (tons/year)

Industry Name	Particulate Matter	SO_2	Significant Others	SIC[b]	Description
Cerro Copper Products	49 1	-	3 2 (NOX)	3341	Secondary Copper Smelter
Amax (Big River) Zinc	120 1	3 2	7 2 (NOX)	3333	Zinc Smelter
Monsanto	168 3	5112 0	185 0 (HC) 1011 0 (NOX)	2869	Organic Chemicals
Midwest Rubber Reclaiming	376 0	110 0	5 5 (HC)	3031	Reclaimed Rubber
Trade Waste Incinerator	71 1	-	8 9 (HC)	4953	HW Incineration
Pillsbury	132 0	-		4463	Grain Handling
Mobil Oil	-	-	328 0 (HC)	5171	Petroleum Products
Clayton Chemicals	0 2	6 6	62 4 (HC)	2869	Organic Chemicals
Ethyl Petroleum Products	3 3	1129 0	327 9 (HC)	2869	Organic Chemicals
Wastex Research	-	-	20 4 (HC)	2869	Organic Chemicals
Atro Coating	-	-	31 9 (HC)	2899	Chemicals Preparation
Central Soya	45 0	-		5151	
Phillips Pipeline Co	1 3	4	1350 0 (HC)	5171	Petroleum Terminal
Pfizer Pigments	156 7	108 0	246 5 (NOX)	2816	Inorganic Pigments

a) Source: Illinois Environmental Protection Agency, Emissions Inventory, unpublished data

b) Standard Industrial Code

It is important to recognize that for all three urban study areas the existing emissions inventories are only a starting point for identifying important sources of toxic air pollutants. The many sources that are not inventoried here include fugitive dust from many point sources and emissions from area sources such as transportation, construction, and materials handling. Major point sources outside the study areas in Missouri and northwest Indiana can affect the study areas when the wind is from the right direction. Finally, there are point sources within the study area that are not included in the official emissions inventory either because they are too new or because they were missed.

The significance of the "unaccounted for" emission sources can be demonstrated using a simple box model of the study areas. Model variables and assumptions include: the study area (64 km^2), a mixing height of 0.8 km (an average of estimated warm and cold season mixing heights); a constant PM-10 emission flux (60% of TSP, Kolaz et al., 1986); a constant mixing height throughout the day and year; an even distribution of emission sources; and an average annual wind speed. Based on these assumptions, contributions from inventoried industrial sources account for an estimated 2.7 $\mu g/m^3$ (Chicago), 3.1 $\mu g/m^3$ (Granite City), and 1.4 $\mu g/m^3$ (East St. Louis). These estimated concentrations account for only 6.1 percent (Chicago), 6.6 percent (Granite City), and 3.3 percent (East St. Louis) of the average annual PM-10 concentrations (see Table 9, p. 20) in the respective airsheds. The percent contributions are in reasonable agreement with estimates of industrial primary emissions as reported in the scientific literature (Table 8). On days with calm conditions (low wind speeds and/or reduced mixing heights) higher concentrations from the inventoried emission sources are likely. Under calm conditions with wind speed equal to zero in the model, inventoried emissions account for 69 percent (Chicago), 70.1 percent (Granite City), and 25.2 percent (East St. Louis) of the "worst case" PM-10 concentrations for each of the respective cities. Of the three cities studied, the impact of non-inventoried emissions appears greatest for East St. Louis.

Table 8. Receptor modeling estimates of industrial primary emissions.

Predominant Industry	City	% Contribution	Authors
Industrial	Philadelphia[a]	<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[b]	Wolff and Korsog (1985)
Steel	Chicago	4% of TSP[c] 15.2% of TSP 16.6% of RP[d]	Gatz (1975) Scheff _et. al_ (1984) Scheff _et. al_ (1984)
Steel	N/A	3% to 18% of TSP	Lucas and Casuccio (1987)

[a] Primary emissions from five major stationary sources
[b] CPM = particles ranging in size from 2.5 um to 10.0 um
[c] Sampling sites were located upwind (prevailing direction) from iron/steel mill sources
[d] RP = respirable particles (< 2μm)

CHAPTER 3. METHODS AND QUALITY ASSURANCE

In this section sampling and analysis methods for the trace elements will be discussed in detail along with quality assurance procedures Methods for the volatile organics were covered in an earlier report (Sweet and Gatz, 1988) and will not be discussed here Additional quality assurance results are included in Appendix A

3 1 Sampling Methods

3 1 1 Dichotomous Virtual Impactor Samples

Samples were collected for 12 or 24-hour periods using an automatic dichotomous virtual impactor fitted with a PM-10 inlet made by Andersen Samplers, Inc , Atlanta, GA (Series 245) This sampler is designed to separate particles less than 10 μm in diameter into two size fractions, a fine particle fraction (<1 to 2 5 μm) and a coarse particle fraction (2 5 to 10 μm) It samples at a flow rate of 0 0167 m^3/minute and has the capability of exposing up to 20 filter pairs automatically U S EPA tests of this system have demonstrated good precision and accuracy for PM-10 measurements (Rodes et al, 1985)

The filters used are 37 mm diameter Teflon disks with a polyethylene support ring They have an average pore size of 2 0 μm According to the manufacturer, these filters collect all particles with diameters greater than 0 2 μm from the air passing through them, according to the manufacturer (Gelman Sciences, Ann Arbor, MI) Filters are equilibrated for 24 hours at 50 percent relative humidity before weighing All filter handling and weighing is done in a clean room in a laminar flow clean bench Using a Cahn microbalance, the precision (standard deviation) of duplicate weighings under these conditions is $\pm$5 μg

In normal field operation, the samplers are run for 1 to 2 weeks collecting 10 to 15 pairs of filters A chart recorder verifies normal operation of the sampler pump and filter changes Any filters for which the sampler did not operate normally are discarded To operate this sampler in the winter, a supplementary heater was installed in the filter chamber to maintain temperatures above freezing (Conley and Buckman, 1987) After filters are exposed, they are equilibrated at room temperature and 50 percent relative humidity for 24 hours before reweighing Once a month the samplers are calibrated to insure a total flow of 0 0167 m^3/min (1 00 m^3/hour) using a mass flow meter (Model 715, Sierra Instruments, Inc , Carmel, CA) Deviations in flow were usually within ± 5 percent; if the deviation was more than 5 percent, an average flow rate was calculated and the volume corrected Measured masses were corrected for dichotomous sampler error according to the formula supplied by the manufacturer and sample volumes were corrected for differences between the ambient temperature and the standard temperature for the calibrator (21^{o}C)

Filters were chosen for analysis after evaluation of meteorological data for the sampling period In general, the sampling periods selected were those in which the standard deviation of the wind direction was less than 20 degrees An attempt was made to include filters representing the widest possible variety of wind directions and meteorological conditions (see Chapter 4)

3 1 2 Cascade Impactor Samples

To determine particle size distributions, samples were taken using a standard high-volume sampler fitted with a six stage cascade impactor and PM-10 inlet (Models 236 and 321A, Andersen Samplers, Inc , Atlanta, GA) The collection substrate was uncoated Whatman 41 filter paper The performance characteristics of this device have been published in Willeke, (1975) and show that it effectively fractionates PM-10 particles into six size classes Milford and Davidson (1985) have pointed out that a potential problem with cascade impactors is that large particles may fail to lodge in the upper stages of the impactor in a phenomenon called "particle bounce " Small particles do not bounce because the impaction surface is very rough on the scale of PM-10 particles (Willeke, 1975) The PM-10 inlet on this device removes larger particles from the airstream which minimizes bounce-related skewing of the size distribution Indeed, scanning electron microscopic examination of this filter revealed that most particles were within the theoretical size ranges for the impactor stage where they were caught and that no large particles were on the back stages of the impactor

The sampler was calibrated before each run with a manometer-type calibrator (Andersen Samplers, Inc) This PM-10 sampler was also evaluated by Rodes et al (1985) and found to be within acceptable standards of precision and accuracy Samples were collected over a twenty-four hour period at a flow rate of 34 cubic meters per hour

There has been some discussion in the literature regarding fine particle losses when Whatman 41 filters are used in high volume sampling (Watts, et al, 1987) In this work, however, we found no detectable difference in the amount of fine particle elements such as Se and Zn between samples collected on Whatman 41 and samples collected on Teflon filters (See Appendix A)

3 1 3 Streaker Samples

The "streaker" sampler is a low-volume, dichotomous, PM-10 sampler developed at Florida State University (Courtney et al, 1978) Air is sampled continuously at one liter per minute for a period of one week Large particles are caught on a coated-membrane impaction surface and fine particles collected on a 0 4 μm Nuclepore filter This system is designed to be used with Proton-Induced-Xray-Emission (PIXE) spectroscopy for trace element analysis The advantage of this method is the excellent time resolution that can be obtained Trace element concentrations can be determined over intervals as short as one hour This allows determination of short term fluctuations and a more accurate determination of the relationship of concentration and wind direction However, due to the small amount of sample collected, this method is only capable of detecting a few trace elements

3 2 Analytical Methods

All trace element analyses were done by contract laboratories NEA, Inc of Beaverton, Oregon carried out X-ray fluorescence (XRF) analysis of Teflon filters Whatman 41 and some Teflon filters were analyzed by instrumental neutron activation analysis (INAA) by Dr Sheldon Landsberger of the University of Illinois, Urbana, Illinois Streaker samples were analyzed by PIXE at Element Analysis Corp , Tallahassee, Florida Teflon filters were shipped in special plastic holders (Petrieslides^{TM}, Millipore Corp , Bedford, Massachusetts) to ensure sample integrity was maintained during transport During the initial stages of this work, approximately 50 Teflon filters were reweighed after shipment and XRF analysis No change in the mass on the filters carrying fine particles could be detected In some cases, a loss of coarse particles was measurable but this amounted to no more than 10% of the total deposit The other filters are less subject to losses, but this could not be checked because of the destructive nature of PIXE and INAA analysis

3 2 1 XRF Methods

The XRF analyses were carried out using an ORTEC TEFA III energy dispersive X-ray fluorescence analyzer Each filter was analyzed three times in each of three different excitation conditions optimizing the sensitivity for specific elements as indicated below:

A1, Si, P, Fe	Mo anode, no filter, 15 KeV, 200 μ amps
S, C1, K, Ca, Ti, V, Cr, Mn, Fe	W anode, Cu filter, 35 KeV, 200 μ amps
Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Ba, La, Hg, Pb	Mo anode, Mo filter, 50 KeV, 200 μ amps

Filter blanks were analyzed and an average blank spectrum was used as a background subtraction for each sampled filter The raw analytical data were reviewed by a laboratory supervisor at the contract laboratory before processing was completed Sample data were then corrected for spectral interferences, particle size and deposit absorption effects

The 2-sigma detection limits achieved by the use of this method are listed in Appendix A (Table 4, p 95) These detection limits are based on blank filters with aerial densities of 1 0 mg/cm^2 similar to the ring mounted Teflon filters used with the dichotomous samplers

The laboratory's approach is based on a well established, validated standard operating procedure (SOP), an X-ray analysis QA plan and validated standards The SOP has been validated through numerous interlaboratory and intermethod comparisons including an EPA validation of XRF calibration films for NBS certification In addition, over 100 of the filters analyzed by NEA with XRF were also analyzed with NAA which provided intermethod comparisons for Cr, Mn, Fe, Cu, and Zn on both fine and coarse filters The results of this intercomparison study are given in Appendix A (Table A-9, p 99)

At least one quality control sample was analyzed for every eleven filters which provides excellent continuity in the analysis over many different runs The precision (one standard deviation) is 2 percent or less when counting statistics are not the limiting factor The accuracy is 5 percent or less as demonstrated by blind interlaboratory and intermethod comparisons (Table A-9, p 99)

3 2 2 INAA Methods

Elemental concentrations for the air filters were determined using the following instrumental neutron activation analysis procedures The support ring around the filter was removed before analysis This was not necessary with XRF, because only the center portion of the filter is analyzed For the short-lived radioisotopes (Al, Ba, Ca, Cu, In, Sr, Mn, V, Tl, Cl, Na) filters were wrapped in plastic and placed in rabbit carriers and irradiated for a period of five minutes at a flux of 1 5 X 10^{12} n/cm^2/sec After the return of the carrier the filter was removed from its plastic wrapping and carefully placed in an acid washed 7 cc polyethylene vial and presented for counting in front of a hyper-pure germanium counter Typical delay times were of the order of 4 to 5 minutes Samples were counted for 10 minutes Deadtime corrections were evaluated by using a 60 Hz pulser Variations in neutron flux were monitored using sulphur standards every several hours throughout the day Flux variations (1 percent or less) were constant during the day, but varied up to 5 percent for different days All variations were normalized to the standard calibrations

For the medium-lived (As, Sb, La, Sm, Mo) and long-lived isotopes (Se, Zn, Cr, Fe, Ni, Sc, etc) filter samples were irradiated for six hours at a flux of 4 5 X 10^{12} n/cm^2/sec Delay times of 3-4 days and counting times of 30-60 minutes were used To obtain better sensitivities for Mo the samples were recounted 4-5 days later to allow the sodium to adequately decay The remainder of the long-lived isotopes were counted for a period of 20,000 seconds (5 55 hours) after a 3-4 week decay Flux variations ± 5 percent were monitored every three hours using cobalt flux wires Calibration was performed using liquid standards from atomic absorption solutions NBS coal samples and blank filters were run with each group of filters The results of standard analyses are given in Appendix A (Table A-7, p 98)

3 2 3 PIXE Methods

The methods used in PIXE analysis have been described (Johansson et al, 1975) Briefly, the sample is irradiated in a proton beam resulting in the emission of x-rays from excited atoms in the sample A spectrum is obtained with peaks corresponding to specific elements Due to the small filter area irradiated (2 x 10 mm) and the low filter loadings, the sample size is very small Only about four toxic elements (Mn, Zn, Cu and Pb) are detectable in most samples Standards and filter blanks were analyzed with each group of filters

CHAPTER 4. TOXIC TRACE ELEMENT DATA BASE

4 1 Average Trace Element Concentrations

The toxic trace element data base used in this work consists of weather data and analytical results from 314 pairs of coarse and fine dichotomous filters Approximately 1,000 filter pairs were collected at six sampling locations in the four study areas between September 1985 and June 1988 Those selected for analysis generally coincided with steady wind direction (standard deviation ≤ 20°) However, we attempted to include a representative sample of all wind directions and meteorological conditions in the data base Concentrations of 34 elements including 17 toxic elements are in the data base X-ray fluorescence was used to determine all of the elements except for Sb, As, Co, Mo, Ag, Ba, and V which were determined by neutron activation Table 9 provides a statistical summary of the concentrations of the 17 toxic elements and total PM-10 mass in each of the four study areas Averages, standard deviations and maxima are given The values for PM-10, V, Cr, Mn, Ni, Cu, Zn, Se, Hg, and Pb are based on 50-100 filter pairs per site For these elements, more than 90% of the values are above XRF detection limits For Cd and Sn, only about 25% of the values are above the XRF detection limit, and their average average concentrations were computed by using one-half the detection limit for below detection limit values The concentrations of As, Co, Sb, Mo, Ag, and Ba were nearly all below XRF detection limits At two stations, Chicago and Granite City, approximately 50 filter pairs were analyzed by INAA At the other two stations, 5-10 filter pairs were analyzed by INAA The values for these six elements are based on the NAA data rather than the XRF data

Comparison of the concentrations found at the rural site to those in the urban areas provides an estimate of the contribution of regional pollution to urban air quality At all three urban study areas, the average PM-10 mass on the filters is only about 50 percent higher than that found at a rural site well removed from any significant local sources

The samples in this data base were selected to provide trace element information under a wide range of meteorological conditions In addition, most of the samples chosen were collected under steady wind conditions to maximize the amount of directional information in the data base A breakdown of the analyzed filter samples by wind direction and season is shown for each of the study sites (Figure 5 and 6) The distribution of analyzed filters closely reflects average wind direction at the sites This analysis protocol means that the data base averages do not necessarily represent true annual averages However, a comparison with Illinois Environmental Protection Agency (IEPA) data (IEPA 1986, 1987) from a systematic air sampling network is shown in Table 10 In general, the ISWS data agree quite well with IEPA averages even though entirely different sampling protocols and analytical methods were used This indicates that the data base does provide a good estimate of average conditions at the site

The concentrations of individual elements vary considerably between sites In a few cases (Se and As), regional levels are nearly as high as urban levels indicating that local sources of these elements are not very important The concentrations of most other toxic elements are three to ten times higher in urban air than in rural air For these elements, significant local sources are present The concentrations of toxic elements found in this study can be compared with concentrations found in national urban air monitoring networks (Evans et al, 1984; Saltzman et al, 1985) Only two elements are substantially higher in the study areas than in other U S urban areas There is about four times as much airborne manganese in southeast Chicago as in other urban areas around the country Levels of airborne cadmium in East St Louis are 5 to 10 times higher than in most urban areas Both of these toxic elements are closely associated with emissions from major industries (steel and smelters) in the study areas

Table 9. Average and maximum concentrations of trace elements in Illinois[a]

		Bondville		Chicago		E. St. Louis		Granite City	
		Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
PM10	Avg	16±6	12±10	23±11	18±11	23±14	18±10	24±16	23±19
	Max	32	47	49	80	100	44	99	96
V	Avg	0 8±0 4	1 2±1.3	3 0±2 7	3 7±2 7	3 0±2 4	3.0±2 0	2.0±2 2	2 4±1 7
	Max	2 0	9 1	14	13	13	10	12	9
Cr	Avg	0 7±0 4	1 2±1 1	4 4±4 7	6 8±6 2	2 0±1 9	3 7±2 7	2.1±2 0	8.2±10.4
	Max	1 8	6 9	28	35	14	17	9 2	71
Mn	Avg	3 5±1.8	6 6±5 1	38±57	48±70	9 3±8.7	15±11	11±11	33±30
	Max	8	28	399	563	55	65	69	253
Ni	Avg	0 5±0 3	0 7±0 5	2 7±2.6	2 1±1 0	2 1±1 4	1 8±1 5	1 7±1.5	1 9±1 5
	Max	1 5	2 1	13	11	5 7	9.0	7.7	6.3
Cu	Avg	2 7±2 1	2 7±5 1	11±15	4 4±5 3	112±249	23±40	19±27	7 0±8 1
	Max	10	29	128	44	1611	224	156	41
Zn	Avg	19±10	9 5±9 0	130±161	36±37	120±152	111±177	57±48	39±34
	Max	43	45	1033	216	771	1142	250	174
As	Avg	0 8±0 4	0 5±0 3	1 5±1 1	1 0±10 9	1 9±2 6	1 6±1 8	3 4±3 7	1 5±2 6
	Max	1 2	0 9	5 4	2 7	8	5	21	19
Co	Avg	15± 1	1± 1	0 4±0 4	0 4±0 3	0 5±0 6	0 4±0 4	0 1±0 1	0 2±0 2
	Max	0.3	.2	1 0	0 7	1 7	1 2	0 3	0 6
Se	Avg	1 8±1 0	0 3±0 2	2 8±2 0	0 4±0 4	4.7±6 8	1 2±3 8	2 2±1 4	0 4±0 3
	Max	7 2	1 1	9 8	2 2	38	22	7 7	1 2
Mo	Avg	0 1±0 4	0 1±0 4	2 0±4 9	0 6±2 2	0 5±1 1	0 7±1 6	0 5±1 5	0 5±1 1
	Max	1 6	2 2	22	16	4 9	9 3	8.2	6 5
Ag	Avg	0 4±0 5	0 3±0 4	1 0±1 3	0 7±1 1	1 1±1 5	1 4±1 6	1 4±2 0	0 9±1 3
	Max	1 5	1 7	4 7	4 3	6 7	8 5	10	6 5
Cd	Avg	1 4±0 6	0 6±1 1	3 2±1 5	2 5±1 1	15±24	9 7±18	4 8±5.7	2 8±2 5
	Max	2 9	4 5	9 7	5 9	115	97	70	18
Sn	Avg	1 6±0.6	1 4±0 5	7 1±7 2	3 7±2 2	12±21	4 3±4 2	6 4±49	2 5±2 9
	Max	3 5	2 7	56	16	169	38	25	10
Sb	Avg	1 7±2 0	1 1±1 4	6 4±5 9	4 1±4 6	6 3±6 4	4 1±5 2	5 4±5.2	5.2±8.1
	Max	7 4	5 2	27	18	28	28	21	49
Ba	Avg	2 4±4 5	1 6±3 4	4 1±7 3	5 6±7 8	8 3±16	5 0±8 9	5 0±7 6	5 8±8 0
	Max	15	13	7 4	32	107	35	36	34
Hg	Avg	0 3±0 2	2±0 1	1 0±1 0	0 5±0 3	0 7±0 4	0 5±0 4	0 7±0.6	0 4±0 3
	Max	8	5	7.0	1 5	2 0	1 9	3 8	1 6
Pb	Avg	18±10	4 4±3 0	107±188	20±33	148±176	61±102	75±89	47±79
	Max	42	14	1372	224	854	489	417	355

[a] PM-10 in µg/m^3, Elements in ng/m^3

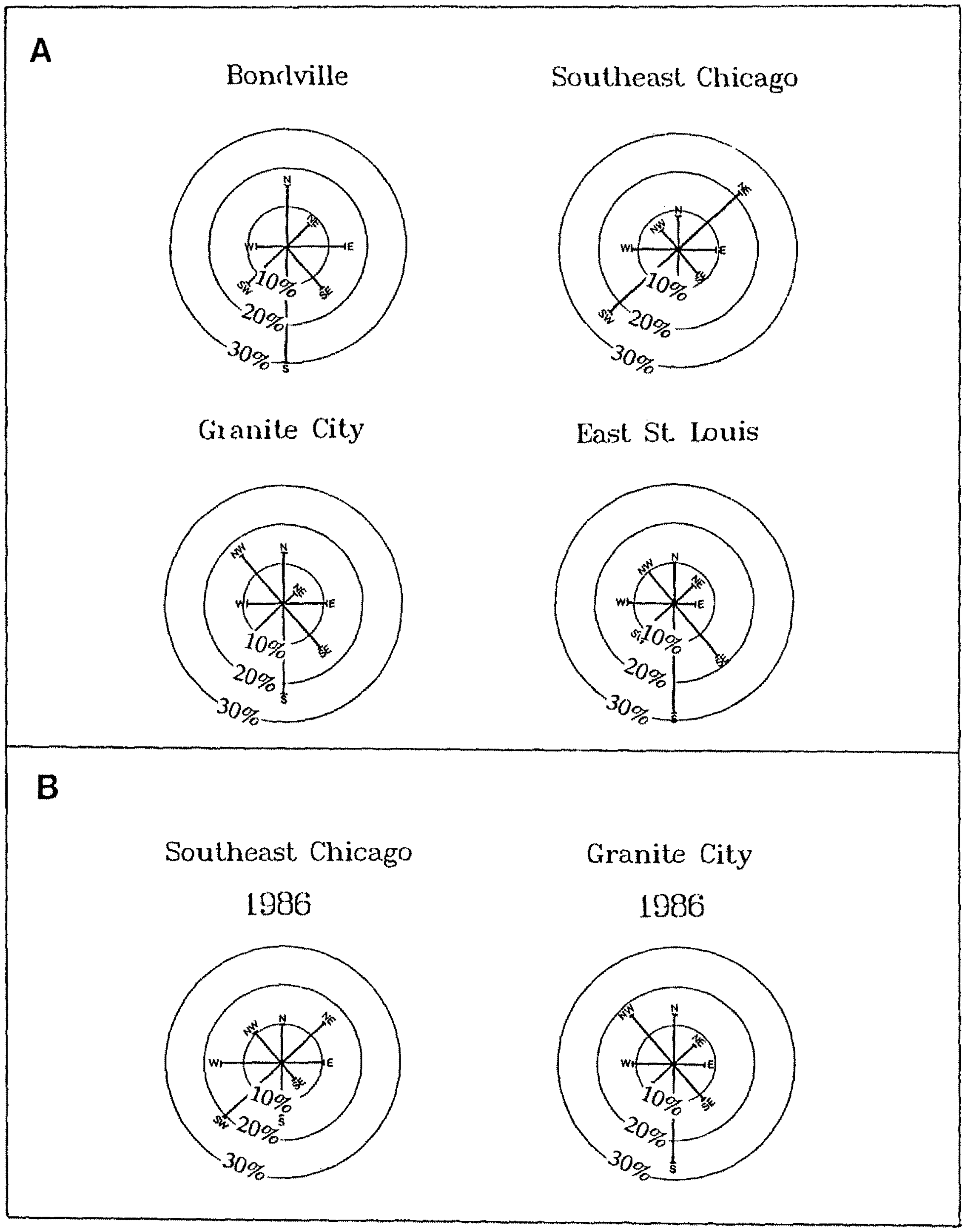


Figure 5 Percentages of data base filters corresponding to different wind directions (A) and wind roses (B)

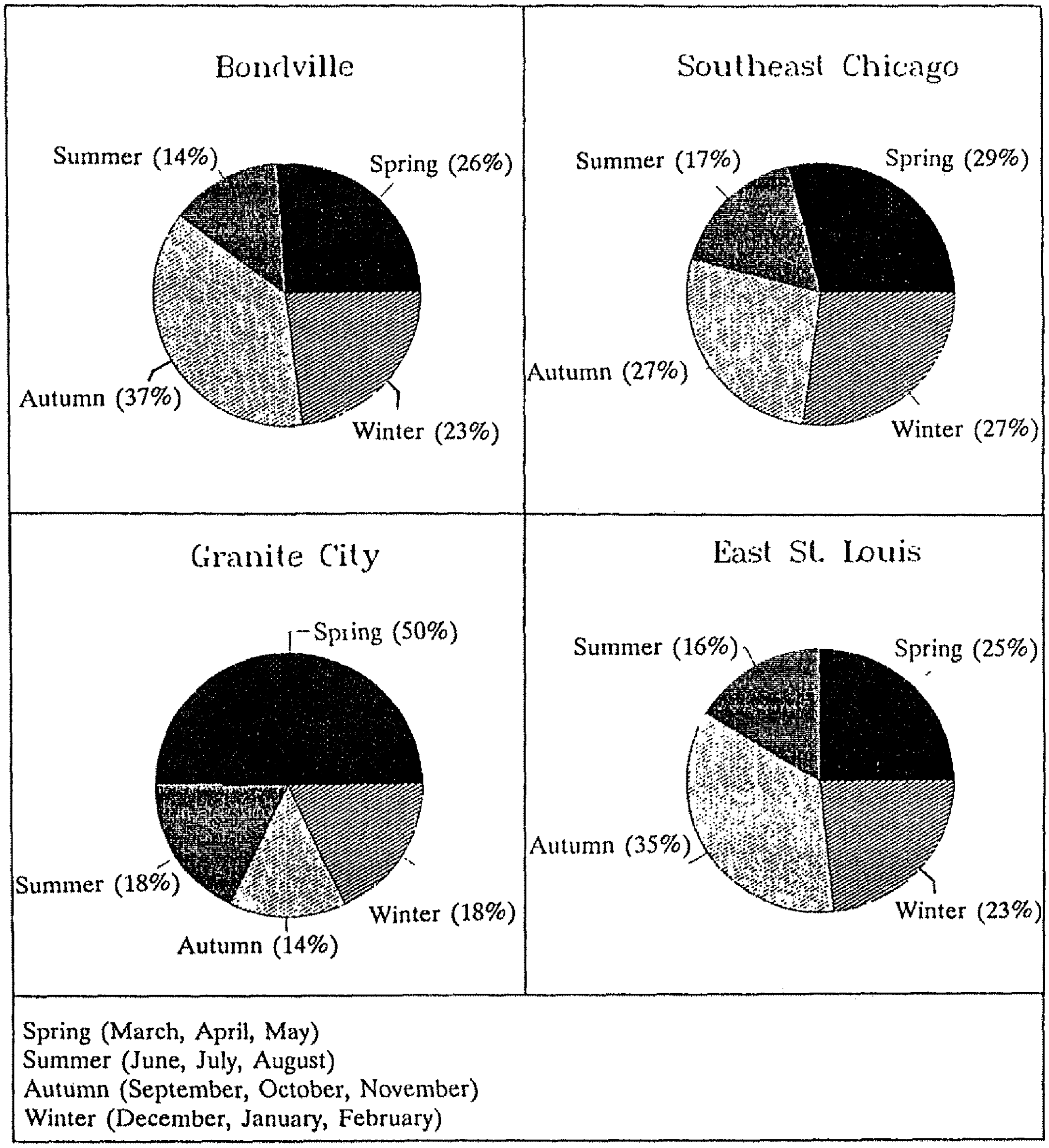


Figure 6 **Seasonal distribution of data base filters**

Table 10. **Average ambient concentrations of airborne trace elements (ng/m^3) during 1986-87[a].**

	Southeast Chicago		East St Louis		Granite City[b]	
	IEPA	ISWS	IEPA	ISWS	IEPA	ISWS
Se	2 0	3 2	2 5	5 9	2 0	2 6
Ni	3 5	4 9	3 5	3 6	5	3 6
Mn	76	86	34	24	160	44
Cr	8	11	4 5	5 7	16	10 3
Cd	1	5 7	29	25	9 5	7 6
Pb	150	130	220	210	180	122
PM-10	39	41	47	41	46	47

a) ISWS: Illinois State Water Survey data from this study
IEPA: Illinois EPA data for the same sites in 1986 and 1987

b) Granite City IEPA site was within 1km, but not colocated

The fact that such large variations in the amounts of individual toxic elements are found in urban air calls into question the strategy of controlling total inhalable particle mass as a surrogate for toxic materials carried on the particles In many cases, the total mass of particles in the urban areas is only slightly higher than that of clean rural air Concentrations of individual elements, however, can be ten times higher In the case of a carcinogen like Cd, this almost certainly leads to an increased health risk

4 2 Trends

The data were examined for seasonal, weekly and diurnal trends No clear trends for any of the toxic elements could be found This is consistent with the fact that urban sources of airborne particles such as industrial stack emissions and vehicle traffic are fairly constant An interesting pattern was noted for two of the nontoxic elements Figure 7 shows the seasonal variation of airborne chlorine (C1) at Bright School High C1 levels coincide almost exactly with the snow season and road salt application This illustrates the potential for resuspension of fine particles by vehicular traffic A similar pattern appeared in the Granite City data but not in the East St Louis data A second pattern was observed for airborne silicon in Chicago (Figure 8) Higher concentrations were present during the spring Other crustal elements varied in the same way Since none of the urban pollution elements showed this pattern, the particles presumably come from uncontaminated wind-blown dust from the surrounding region

The duration of this study was not long enough to determine long term trends However, limited IEPA trace element data collected a decade ago, indicate that Pb, Fe, and Mn in Chicago and Granite City were considerably higher than at present (Gatz and Sweet, 1985) This is almost certainly due in large part to the reduction in steel industry activity and the phaseout of leaded gasoline over the period

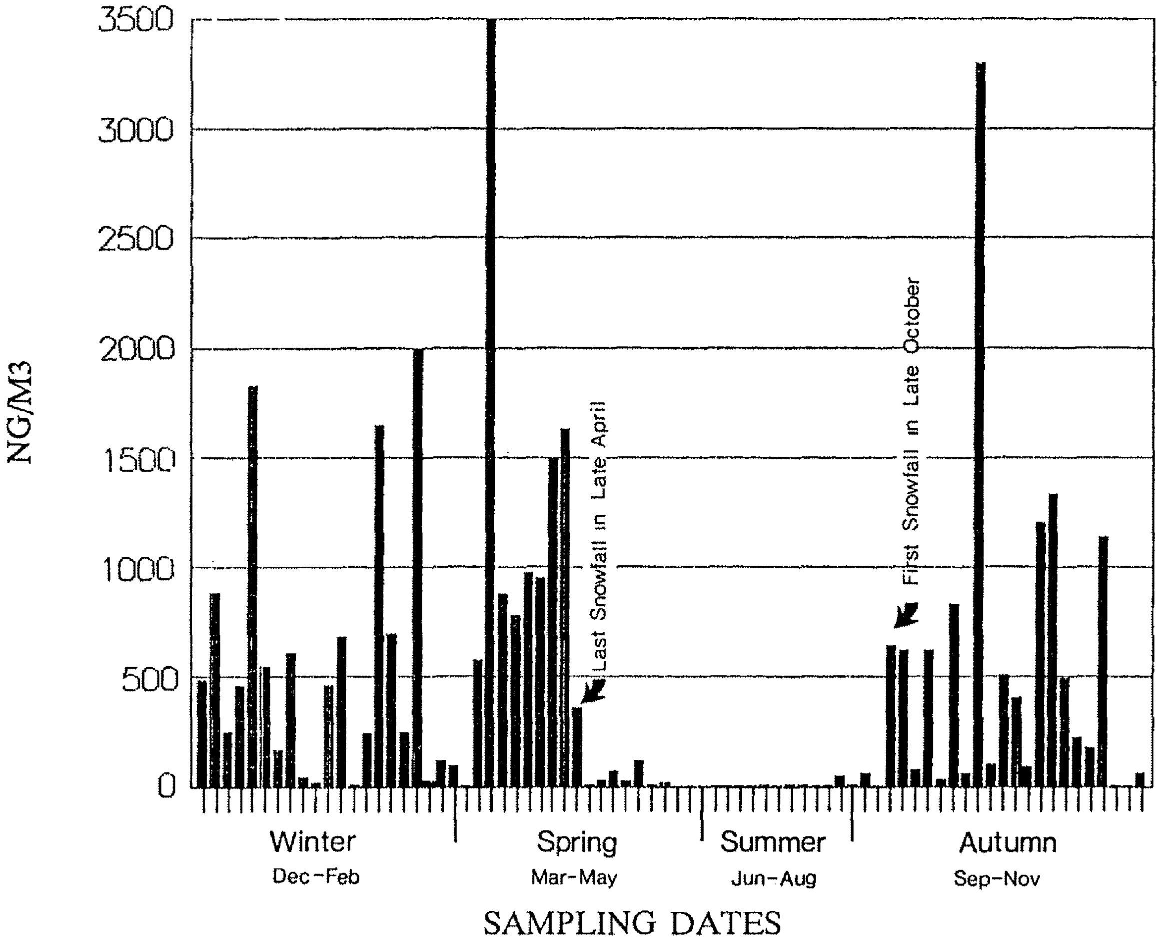


Figure 7 Seasonal variation of chloride in southeast Chicago

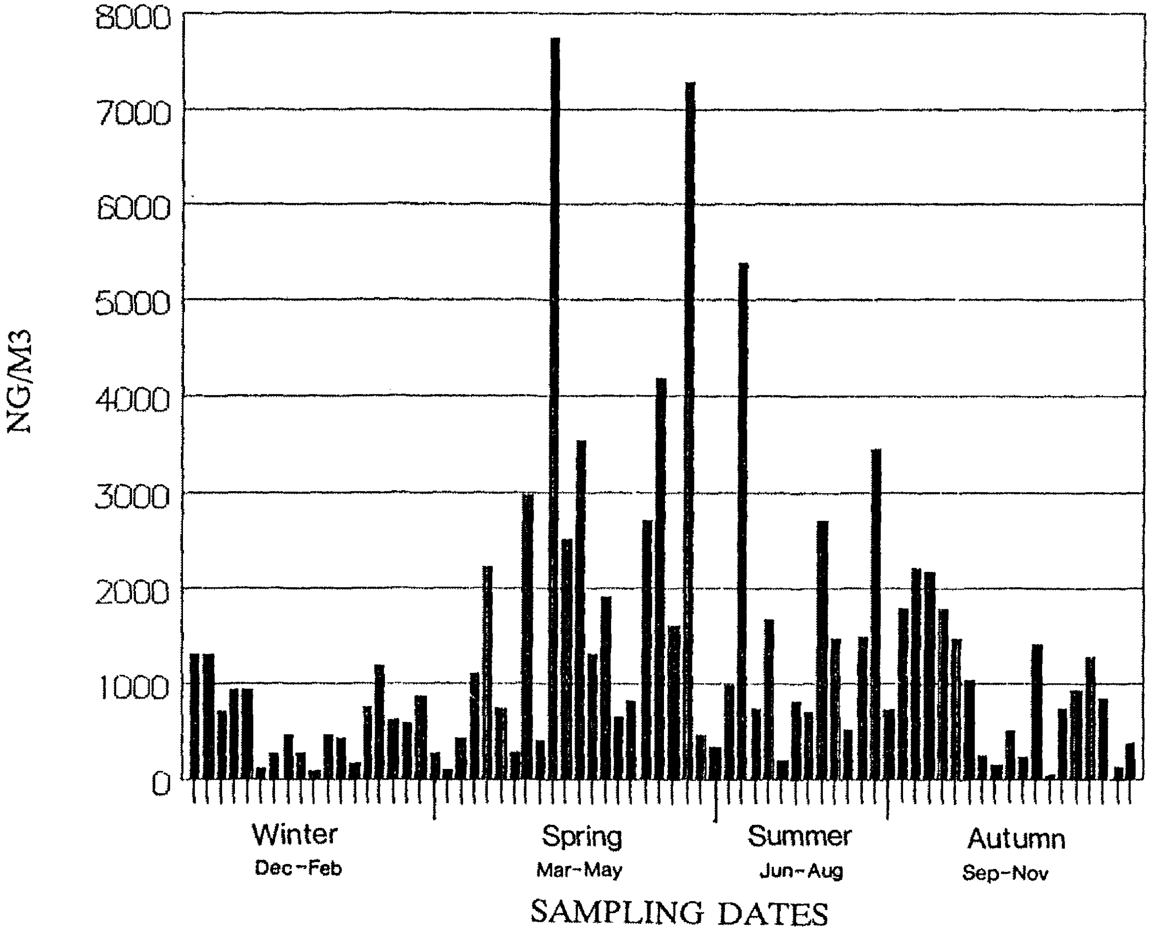


Figure 8 Seasonal variation of airborne silicon in southeast Chicago

4.3 Wind Direction

Analysis of the data, based on wind direction, yields information on the sources and the types of emissions that generate toxic trace elements. The Bright school (see map in Figure 2, p. 7) data were divided into four groups on the basis of wind direction. Several steel mills are near this site. Table 11 shows the average concentrations of several steel related elements for the four wind sectors. Different sources contribute airborne particles in each of these sectors. The northeast, southeast and southwest sectors have most of the nearby steel industry while wind from the NW passes over a long fetch of urban area with no nearby heavy industry. Of the existing steel mills, those to the east and southeast had active blast furnace operations during the sampling period. The other mills in the area were either closed or operating at a low level during 1986 and 1987. The steel related elements (Cr, Mn, and Fe) are significantly higher in the fine fraction only when the wind is from the southeast, the direction of active blast furnace operations. In contrast, the concentrations of these elements in the coarse fraction are similar when the wind is blowing from either active steel mills or inoperative ones. Presumably Cr and Mn from slag piles, contaminated soil and urban dust are resuspended and contribute to the airborne concentrations of Mn and Cr. When the wind is from the southwest or northwest, the concentrations are lower because steel related industries are much further away in these directions and exert much less influence on the air quality.

Table 11. Concentrations of trace elements at Bright School in relation to wind sector[a]

Element		Wind Direction NE (0-90°)	SE (90-180°)	SW (180-270°)	NW (270-360°)
Cr	Fine	4.9 ± 4.2^{a}	11.6 ± 8.0^{b}	3.8 ± 3.0^{a}	2.1 ± 1.8^{a}
	Coarse	8.9 ± 8.2^{a}	12.5 ± 8.5^{a}	6.0 ± 4.8^{a}	2.4 ± 2.4^{b}
Mn	Fine	49 ± 37^{a}	103 ± 81^{b}	26 ± 33^{c}	7.8 ± 7.6^{c}
	Coarse	75 ± 110^{a}	91 ± 68^{a}	33 ± 31^{b}	10.5 ± 10.5^{c}
Fe	Fine	539 ± 407^{a}	922 ± 542^{b}	288 ± 228^{c}	103 ± 96^{d}
	Coarse	1054 ± 834^{a}	1520 ± 876^{a}	692 ± 452^{b}	312 ± 300^{c}
Zn	Fine	183 ± 149^{a}	237 ± 130^{a}	81 ± 44^{b}	67 ± 51^{b}
	Coarse	35 ± 20^{a}	84 ± 57^{b}	30 ± 24^{a}	21 ± 19^{a}
Pb	Fine	106 ± 113^{a}	387 ± 404^{b}	105 ± 171^{a}	32 ± 20^{c}
	Coarse	71 ± 17^{b}	53 ± 63^{b}	24 ± 40^{a}	18 ± 28^{a}

a) Values in ng/m^3 with the standard deviation. For each row, values with different superscripts are statistically different from each other at the 95% confidence level using a one tailed F-test.

The high levels of steel related elements in fine particles collected during northeast winds is somewhat puzzling. Very little active steel making took place at the mill located in this direction during the sampling period, and there are no other sources northeast of the site. The explanation may be related to lake - land breeze effects. In areas near large bodies of water, winds can shift rapidly as the land cools at night and heats up during the day relative to the water. These effects plus the "heat island" effects of a large city can cause pollutants to circulate and refumigate the source areas (Lyons, 1970). Alternatively, complex curved wind trajectories may be bringing in steel related elements from plants in northwestern Indiana. Samples taken during northeast wind flows therefore may not always be representative of sources in that direction at the Bright School site.

Two other toxic elements, Zn and Pb, are also elevated at Bright School when the wind is from the industrial sectors. Both of these elements are normally associated with the fine fraction indicating high temperature sources. However, the presence of elevated concentrations of these elements in the coarse fraction with southeast winds, indicates that they are present in fugitive emissions from this area as well.

Similar patterns are evident in the East St. Louis data. Average concentrations of a group of smelter related trace elements are shown in Table 12. Highest levels of both fine and coarse fractions of these elements occur when winds are from the southwest, the direction of the smelters. This indicates that both stack and fugitive emissions from this area carry these toxic elements. Since the prevailing winds in this area are from the southwest, the smelters will have a large impact on average air quality in East St. Louis.

Table 12 Concentrations of trace elements in East St. Louis in relation to wind sector[a].

Element		Wind Direction			
		NE (0-90°)	SE (90-180°)	SW (180-270°)	NW (270-360°)
Zn	Fine	88±63^{a}	95±87^{a}	221±209^{b}	76±80^{a}
	Coarse	52±29^{a}	74±103^{a}	287±290^{b}	51±60^{a}
Cu	Fine	11±10^{a}	86±146^{b}	208±270^{c}	30±50^{a}
	Coarse	7.1±5.6^{a}	12±18^{a}	44±55^{b}	6.2±6.9^{a}
Cd	Fine	3.5±1.0^{a}	10.8±10.5^{b}	39.5±37.5^{c}	10.4±16.3^{b}
	Coarse	2.8±0.9^{a}	4.8±6.8^{a}	29.8±29.2^{b}	5.4±9.2^{a}
Sn	Fine	9.0±7.3^{a}	6.6±7.1^{a}	19.6±36.4^{b}	7.5±8.1^{a}
	Coarse	9.1±11.1^{a}	3.7±2.2^{b}	4.0±3.2^{b}	3.5±1.8^{b}
Pb	Fine	112±84^{a}	70±71^{a}	292±251^{b}	100±66^{a}
	Coarse	21±12^{a}	51±69^{a}	156±168^{b}	29±23^{a}

a) Values in ng/m^{3} with the standard deviation. For each row, values with different superscripts are statistically different from each other at the 95% confidence level using a one tailed F-test.

CHAPTER 5. PARTICLE SIZE DISTRIBUTION

Determination of the particle size distributions of toxic trace elements is important for two reasons The first is that much can be inferred about the source of a particular trace element by its particle size distribution Atmospheric particle masses and surface area typically show a bimodal distribution with respect to particle diameters (Seinfeld, 1986) Particles below 1 μm in diameter are derived from the condensation of hot vapors and the chemical conversion of gasses to materials with low volatility The sources of these particles are mostly stack and tailpipe emissions resulting from high-temperature combustion In contrast, particles greater than 2 μm in diameter result from mechanical processes These can be anthropogenic processes like fugitive emissions from vehicle traffic or materials handling or natural processes like wind-blown dust and plant particles The dichotomous sampler is designed to take advantage of this characteristic distribution of airborne particles It collects two fractions for each air sample, a fine particle fraction with diameters below 2 5 μm and a coarse particle fraction with diameters greater than 2 5 μm

The second reason for determining particle size distributions of toxic trace elements is that movement of the element through the environment is controlled by size distribution Coarse particles are removed from the atmosphere much more rapidly than fine particles For this reason, some elements like Se and Pb which are concentrated on fine particles are more likely to be present in regional pollution due to long-range transport of urban emissions On the other hand, elements such as Mn and Co found on coarse particles are more likely to settle out near the source and give rise to contamination in surface dusts Particle size is also an important factor in human exposure since smaller particles penetrate more deeply into the respiratory tract This fact has resulted in promulgation of ambient air quality standards for inhalable particles (those below 10 μm in diameter or PM-10) Although the particles themselves may not be harmful, they often carry materials such as toxic trace elements which can damage delicate tissues or be absorbed into the bloodstream

Two sampling methods were used in this project to provide information on the size distribution of airborne particles The dichotomous sampler data listed in Table 9 (p 20) include average values for both fine and coarse particles For most elements, significant concentrations are found in both size fractions indicating contributions from both types of particle generating processes For a few elements, (Zn, Se, and Pb) the fine fraction predominates These are elements whose sources are principally high-temperature anthropogenic emissions In the case of Zn, incinerators and smelters are the most important sources Se is produced during coal combustion Pb is produced in auto exhaust and smelter emissions Many of the trace elements that are found in the coarse particles were probably originally emitted as fine particles from stacks Subsequent wet and dry deposition has contaminated urban dust and surface soils so that resuspended fugitive emissions often are substantially enriched with trace elements A substantial portion of the airborne toxic trace elements is derived from such emissions (see Receptor Modeling Section)

The second sampling method that provides particle size information was the cascade impactor Samples of PM-10 were taken at all four sampling locations using a cascade impactor to separate the particles into six size fractions Four types of samples were collected: 1) rural samples were collected at the Bondville site, 2) urban samples were collected at Bright School in Chicago during NW wind flow, these samples reflect average urban conditions and are not influenced by local industrial sources, 3) steel-influenced samples were collected at Chicago and Granite City when the sampling sites were downwind of nearby steel mills, 4) smelter-influenced samples were collected at East St Louis when this site was downwind of nearby copper and zinc smelters

The size distributions for the toxic trace elements that could be analyzed by neutron activation analysis are shown in Figures 9 to 11 The type of sample (rural, urban, steel influenced or smelter influenced) is shown on each graph along with the total concentration of a particular element The curves are not smoothed so that the size range for each fraction can be seen The ordinate in these plots is the normalized distribution function:

$$(\Delta C/C_T)/\Delta \mathrm{logdp} \qquad (1)$$

where ΔC is the airborne mass concentration of the element in a given size range (which extends from the maximum particle size, dp_{max}, to the minimum particle size, dp_{min}, for a given impactor stage) The term C_T is the total concentration of the element in all size ranges, and $\Delta \log dp$ is the difference, $\log dp_{max} - \log dp_{min}$ The aerodynamic diameter of a particle, dp, is the size of a unit density sphere with aerodynamic transport characteristics identical to those of the original particle The area under the curve between any two particle diameters is proportional to the fraction of airborne mass in that size interval

The concentrations of several elements were much higher when the wind was blowing from nearby industrial sources Smelters are important emitters of Zn, Cu, and As (Figure 9) These elements are found in both large and small particles In smelter-influenced samples, a large proportion of the airborne mass of these elements is in the coarse fraction when compared to urban or rural emissions Similarly, samples heavily influenced by steel sources are enriched in Cr, Mn, Ni, V, and Co (Figures 10 and 11) These elements are also concentrated on the coarse particles The source of this material is presumably wind-blown dust from vehicle traffic and materials handling Much is probably resuspended surface dust which has been contaminated by fallout from past emissions Trace elements on fine particles, on the other hand, are mostly derived from high-temperature emissions from stacks and tailpipes

These data indicate that there can be substantial differences in the particle size distributions of trace elements In general, the emissions of trace elements from nearby industrial sources have a relatively higher proportion of toxic trace elements on coarse particles than is the case with urban or rural samples This is reasonable in view of the fact that coarse particles are removed from the atmosphere by wet and dry deposition more rapidly than fine particles Rural samples that mostly reflect long-range transport from distant sources would then have relatively more of a given element on fine particles

The other elements detected in this study are not particularly enriched in the samples influenced by local industry There are probably many different sources of these elements that contribute to these trace element concentrations giving a wide range of particle sizes The particle size distributions found in this work for urban and rural samples are generally similar to those reported elsewhere (Milford and Davidson, 1985)

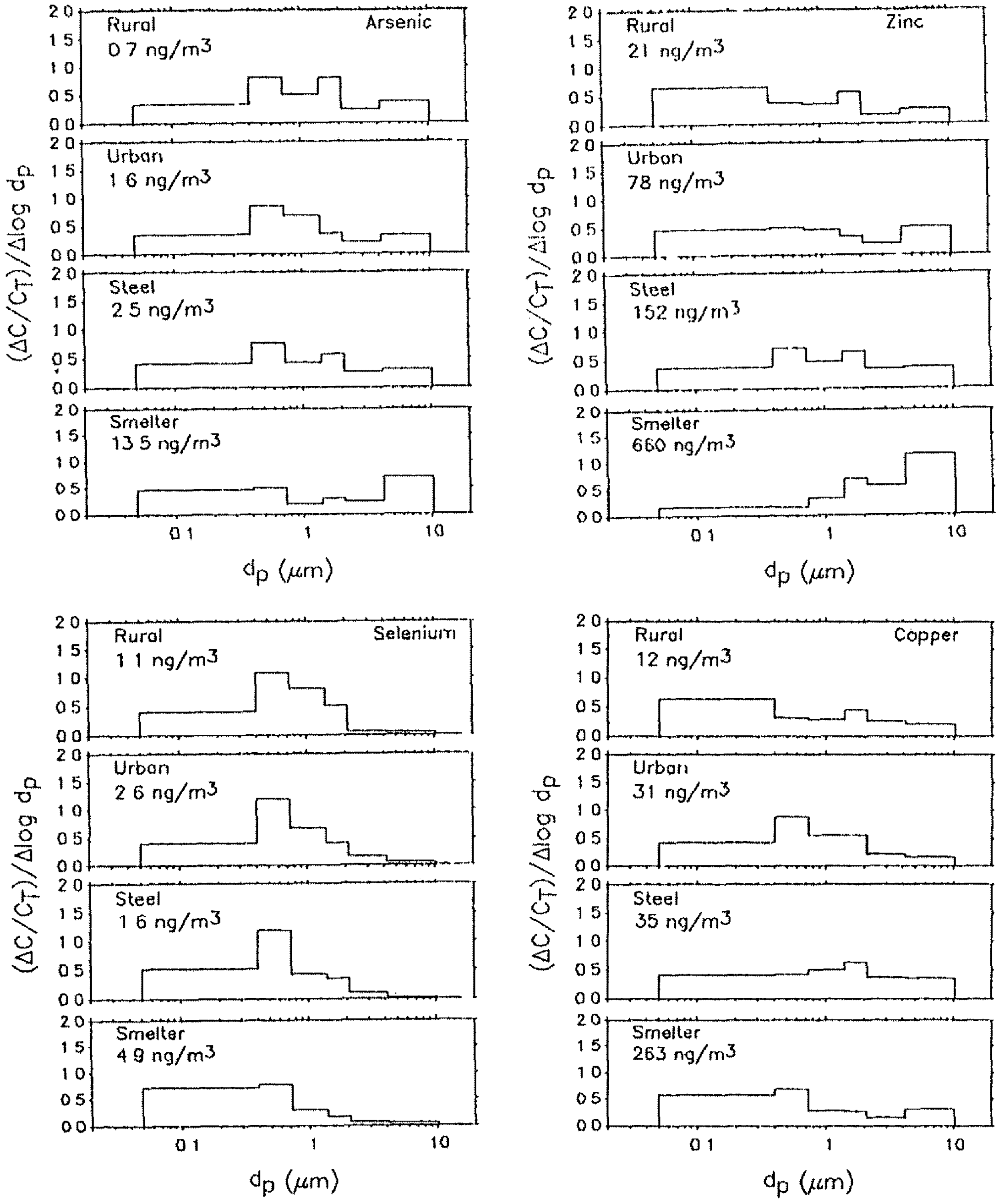


Figure 9 Particle size distributions for arsenic, zinc, selenium and copper

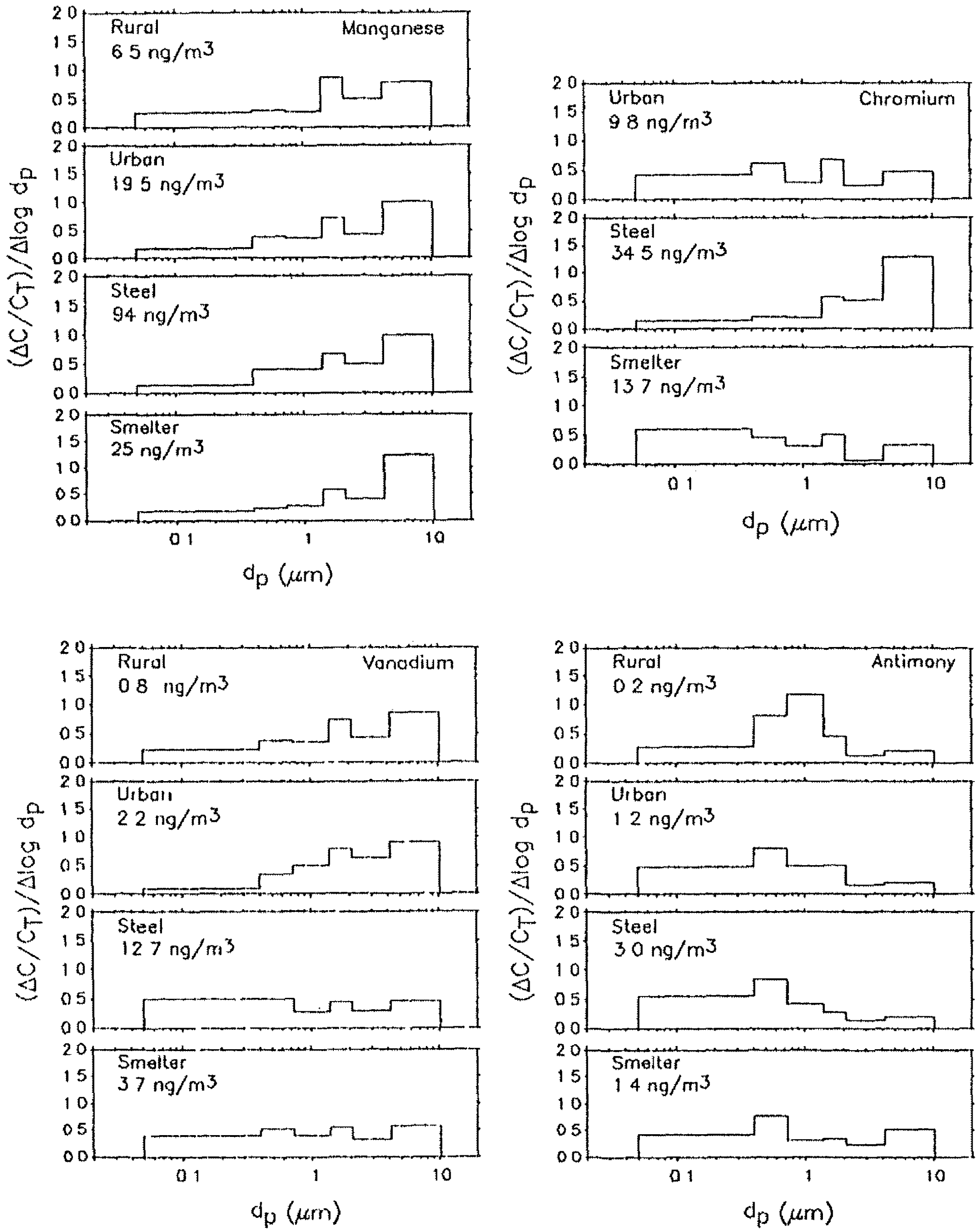


Figure 10 Particle size distributions for manganese, chromium, vanadium and antimony

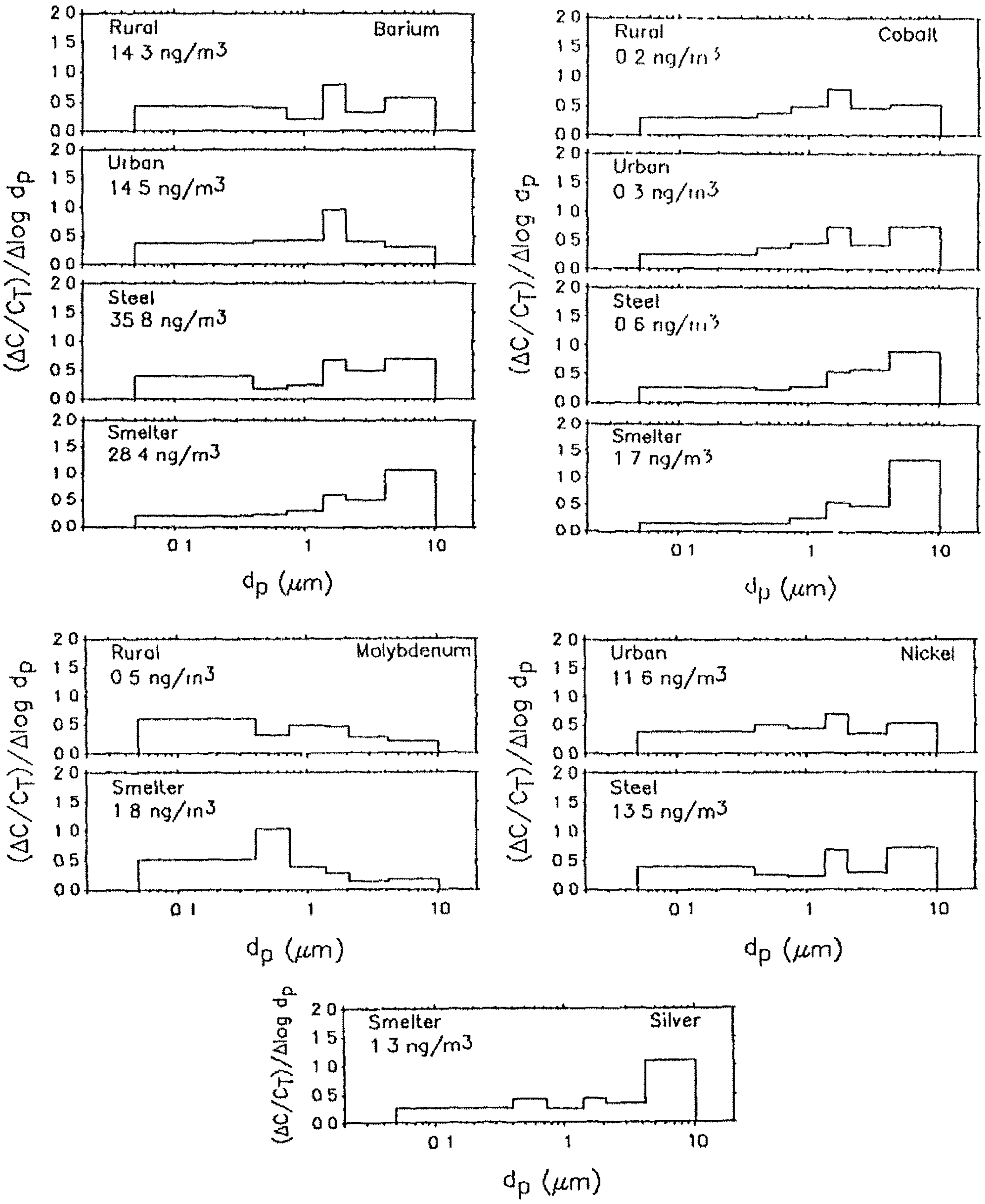


Figure 11 Particle size distributions for barium, cobalt, molybdenum, nickel and silver

CHAPTER 6 VAPOR PHASE TRACE ELEMENTS

Among the toxic trace elements studied in this project, there are three that may have a significant vapor-phase component under ambient conditions Airborne mercury (Hg) occurs as a number of volatile chemical species, including elemental Hg, $HgCl_2$, and alkylated mercury compounds As a consequence of this, the particle-bound fraction of Hg in the atmosphere is often less than 10 percent of the total (Braman, 1983) Arsenic (As) is another element with a significant vapor component in the form of arsenic oxide or methylated arsenic Appel, et al (1984) have suggested that using particle filtration techniques alone may lead to a significant undersampling of As Finally, selenium (Se) can exist in a variety of vapor forms including elemental Se, SeO_2, and organo-selenides (Ross, 1984) Indeed, Pillay, et al (1971) found that about 60 percent of atmospheric selenium passes through aerosol filters

Two of these elements, As and Hg, have been specifically designated as hazardous air pollutants by the U S EPA and are undergoing review to set emission standards (Cannon, 1986) Although Se levels in the atmosphere are probably not high enough to be a health concern, little is known about vapor-particle partitioning of this element Concentrations of particle-bound Se are relatively high in Illinois and show little variation between urban and rural sites This suggests that the air near source areas is enriched in vapor-phase Se that is transformed into particulate material during transport in the atmosphere Because of the potential health effects of these three elements, it is important to measure their vapor phase concentrations Exposure to these elements may be greater than that estimated from particle measurements alone

Two types of impregnated filters were used to trap volatile trace elements in this work The first is a cellulose filter (Whatman 41) soaked in a 10 percent solution of tetrabutylammonium hydroxide (TBAH) for collection of several chemical forms of airborne As (Walsh, et al, 1977) The second is a commercial filter consisting of a Whatman 41 cellulose filter impregnated with activated charcoal This filter is highly efficient in collecting vapor phase Se (Mosher and Duce, 1983) Activated charcoal is also a very useful absorbent for the collection of atmospheric Hg (Schroeder, 1982) The filters are mounted in plastic holders and positioned downstream from the Teflon filters in the dichotomous samplers With this arrangement, particulate matter and vapor phase elements are collected separately from the same air Typically about 100 cubic meters of air are filtered, this should contain up to several hundred nanograms (10^{-9} g) of each element A second (back-up) filter was used to detect breakthrough of the gaseous species

Both particle and downstream absorbent filters were analyzed by neutron activation analysis (NAA) for As and Se, and cold vapor atomic absorption for Hg NAA provides data on total As and Se present on the filters All chemical forms of Hg present in the sample are reduced to elemental Hg before atomic absorption analysis Therefore, the data only indicate the total amount of vapor-phase elements collected, not the individual chemical species present The definition of vapor-phase elements used here is an operational one in that all material passing through the particle filter and trapped on the vapor traps is termed vapor-phase

The data from individual experiments are shown in Table 13 Arsenic was detected on only one TBAH vapor trap sample, equaling about 3 percent of the total As In all other samples, the As in the vapor trap was below the detection limit and could have amounted to no more than a few percent of the total Se was captured on the charcoal vapor traps No Se was found on the second trap, indicating that vapor-phase Se is efficiently trapped by the charcoal-impregnated filters The levels of vapor-phase Se reported here are similar to those found in other urban samples (Pillay, et al, 1971; Mosher and Duce, 1983)

Table 13 Vapor-phase arsenic, selenium and mercury (ng/m^3).

Sampling Site	Arsenic		Selenium		Mercury	
	Particle	Vapor	Particle	Vapor	Particle	Vapor
Bondville	0 7	< 1	1 8	<0 1	0 4	1 5
					0 2	0 5
Chicago	1 5	< 1	0 6	0 3	0 2	0 4
			4 1	1 0		
East St Louis	2 5	< 1	1 8	0 3	1 3	4 6
	4 4	< 1	3 2	0 9	0 3	0 6
Granite City	1 9	< 1	1 3	0 3	1 5	1 7
	3 1	0 1			3 0	0 7

The charcoal traps were not so effective in trapping Hg In all cases, substantial amounts of Hg broke through to the second filter Typically about two-thirds of the total vapor-phase Hg was found on the first filter Assuming an equal collection efficiency on each filter stage, an overall collection efficiency of about 60 percent can be calculated The data in Table 13 have not been corrected for collection efficiency and should be considered a minimum estimate of vapor-phase Hg levels The percentage of Hg found in the vapor phase varies considerably from sample to sample In urban areas, high concentrations of airborne Hg were found both bound to particles and present as vapor

The effectiveness of particle sampling for determining total trace element concentrations differs for each of the volatile trace elements measured here Arsenic was almost entirely bound to particles Although other workers (Walsh, et al, 1977) have reported that up to 20 percent of airborne As is in the vapor phase in some urban samples, the results reported here showed no significant vapor-phase arsenic in urban samples taken for this study The presence of vapor-phase Se in urban air is not unexpected because several chemical forms of this element (Se, SeO_2) have appreciable vapor pressures at ambient temperature (Ross, 1984) The absence of this vapor-phase Se in the rural sample may indicate that volatile Se becomes bound to particles as air masses age and move away from Se sources (coal-fired boilers and smelters) A similar relationship is seen between volatile SO_2 and particulate sulfate in air samples taken at urban and rural sites in Illinois (IEPA, 1987) Finally, particle sampling may miss the majority of the Hg in ambient air Although more Hg is bound to particles in polluted urban environments than in rural samples (Schroeder, 1982), most of the airborne Hg in urban areas may still be in the vapor state The technique used here is not suitable for accurate determination of vapor-phase Hg, but gives a minimum estimate for volatile forms of Hg

CHAPTER 7. STREAKER SAMPLES

The "streaker" sampler described by Courtney et al (1978) is a low-volume dichotomous sampler (1 0 liter/min) designed to operate automatically for periods of up to one week Particles are deposited in narrow strips and analyzed by proton-bombardment The major advantage of this sampler is that concentrations can be measured over periods as short as one to two hours Such short averaging times provide a much better estimation of peak concentrations than the 12 to 48 hours needed to collect a typical dichotomous sample A second advantage is that wind direction is likely to be much less variable over shorter sampling periods This provides a better estimation of the direction of local emission sources The major disadvantage of the streaker is that fewer elements are detectable using this method because of the small sample size

We collected one week streaker samples in each of the three urban study areas Segments of the streaker filter corresponding to a 2-hour sampling period were analyzed by proton-induced X-ray emission (PIXE) Six toxic elements could be detected The analysis resulted in 10 to 50 data points per element Table 14 lists the maximum concentrations found for these elements Because of the short sampling times, streaker data gives a better estimate of peak concentrations than the 12 and 24-hour dichot samples In most cases, these concentrations are well above the maximum concentrations found in standard dichotomous samples (see Table 9, p 20) An example of the temporal variations seen is shown in Figure 12 Here concentrations of fine and coarse lead in Granite City are plotted against time for the one week streaker sampling period Peaks in the concentration of fine lead occurred several times during the week and were associated with winds from several directions This is consistent with the widespread nature of auto exhaust, the source of most fine lead Coarse lead, on the other hand, occurred only with southerly winds and high wind speeds The source in this case is probably fugitive emissions from battery storage piles and contaminated dust at nearby lead industries

Another way of depicting streaker data is by plotting "pollution roses " These are circular plots of concentration and wind data constructed so that wedges corresponding to high concentrations of airborne pollutants point toward the sources In Figure 13, the pollution rose for coarse lead is superimposed on a map of the Granite City study area with the center of its axes at the sampling site The predominance of coarse lead from the south through the southwest is apparent

When measurements from two sites are available, streaker data can identify the location of sources as well as the general direction In Figure 14, pollution roses for fine manganese are shown on a map of the Chicago study area The two facilities with active blast furnace operations, Chicago Blast Furnace Co and LTV Steel, are clearly indicated as sources During the week the streaker was run at Washington School, fine manganese also came from the northeast There are no sources in this direction However, steel related pollutants could have been carried out over Lake Michigan from the study area or from the steel mills in northwest Indiana These pollutants, then could move back overland as part of the land-lake breeze phenomenon seen in this area (Lyons, 1970)

Pollution roses for fine zinc and fine copper are shown on maps of the East St Louis area (Figures 15 and 16) The zinc smelter is a major source of fine zinc here, but there are other sources indicated to the southwest in St Louis and to the north The zinc source to the north may be galvanizing operations at Granite City Steel For fine copper, some contribution is made by the copper smelter located in the study area, but there seems to be a major source of fine copper outside the study area to the southwest

Additional pollution roses for all of the toxic trace elements analyzed and a more complete description of their meaning are provided in Appendix B In analyzing this streaker data, it is important to recognize that each pollution rose represents a one-week "snapshot" of conditions at the site These conditions may or may not be representative of typical conditions The information derived from streaker data is most useful as corroborative evidence used to confirm the findings from analysis of the dichotomous filter data base

Table 14 **Maximum concentrations of trace elements at urban sites in Illinois (ng/m^3)**

	Chicago		East St. Louis		Granite City	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
Mn	1800	980	30	65	35	110
Pb	2200	1350	700	375	200	160
Zn	875	210	500	170	95	15
Cr	12	32	5	8	<5	50
Ni	32	<2	10	<2	4	6
Cu	48	<5	475	<5	90	<5

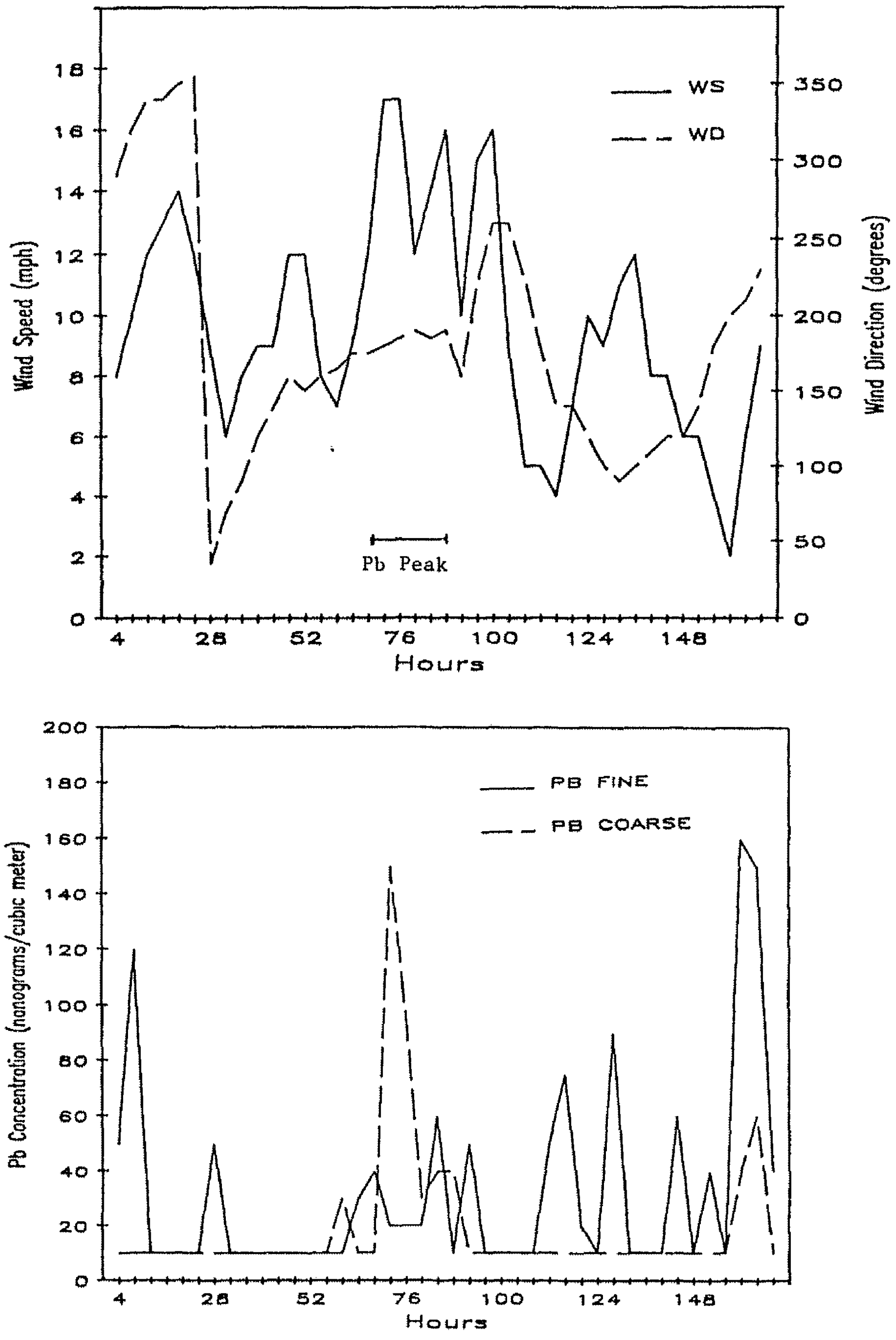


Figure 12 Variation in airflow and lead concentration at Granite City over a one-week period

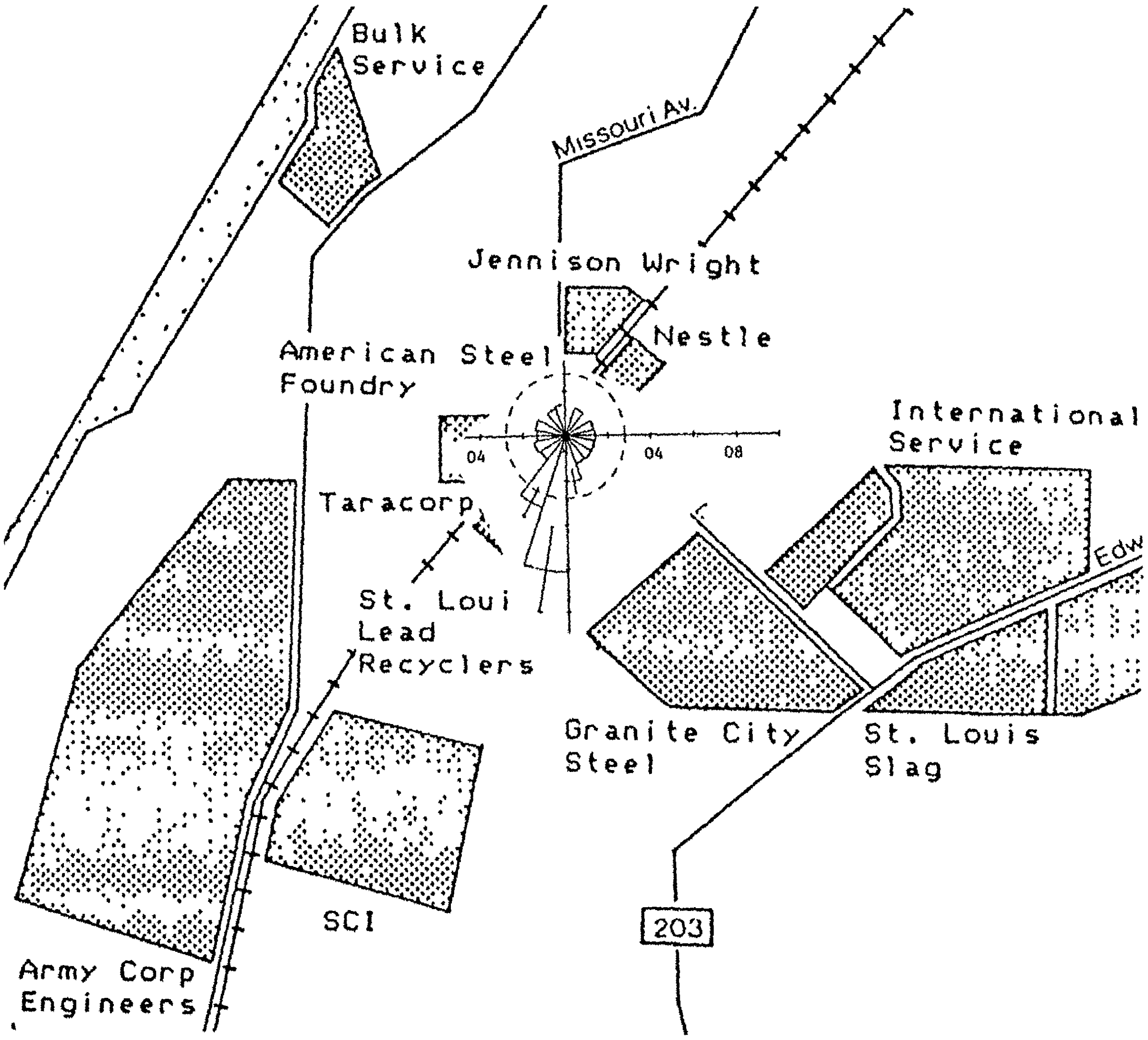


Figure 13 Mean concentrations of coarse lead as a function of wind direction in Granite City ($\mu g/m^3$)

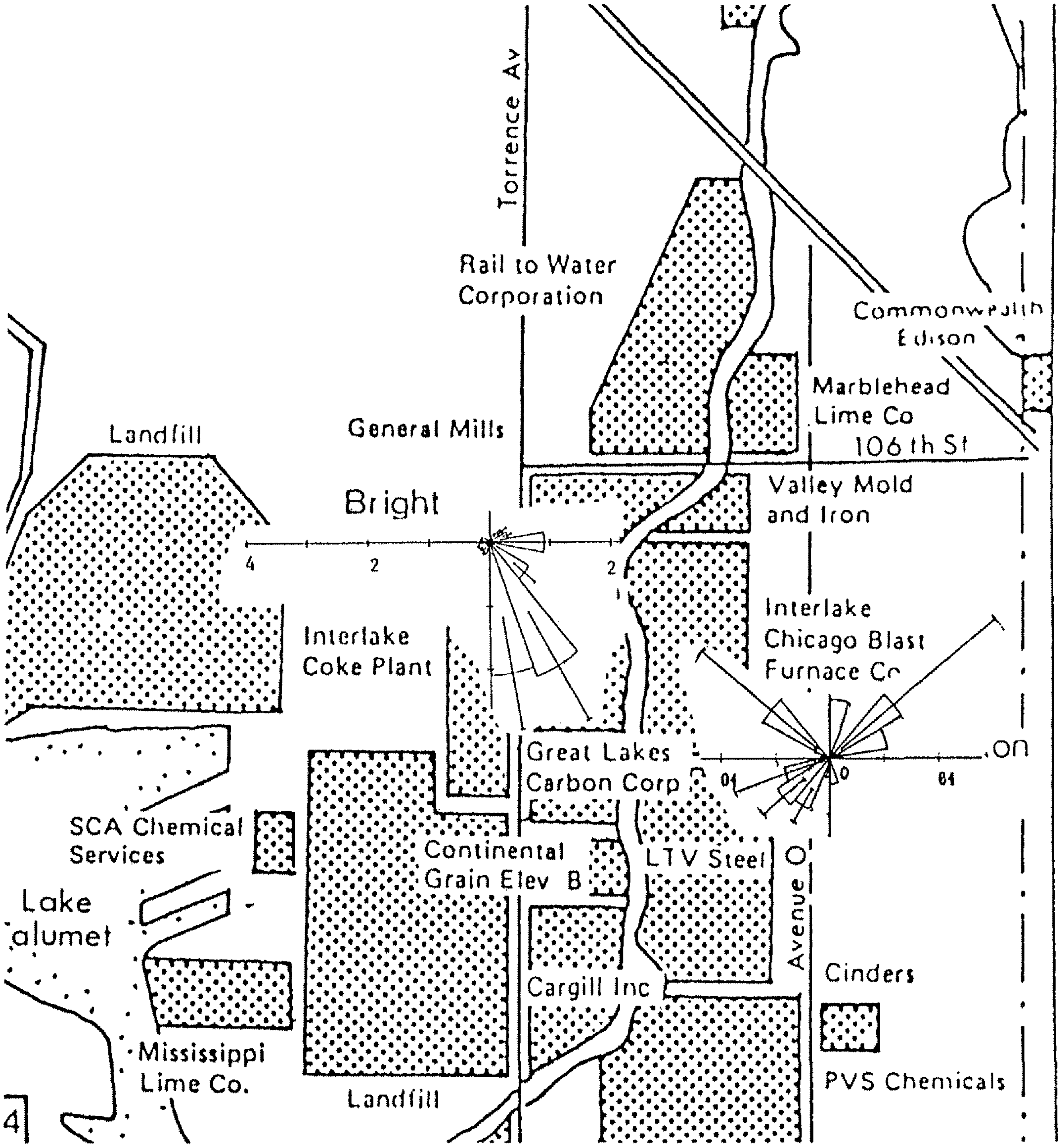


Figure 14 Mean concentrations of fine manganese as a function of wind direction for two sampling sites in Chicago ($\mu g/m^3$)

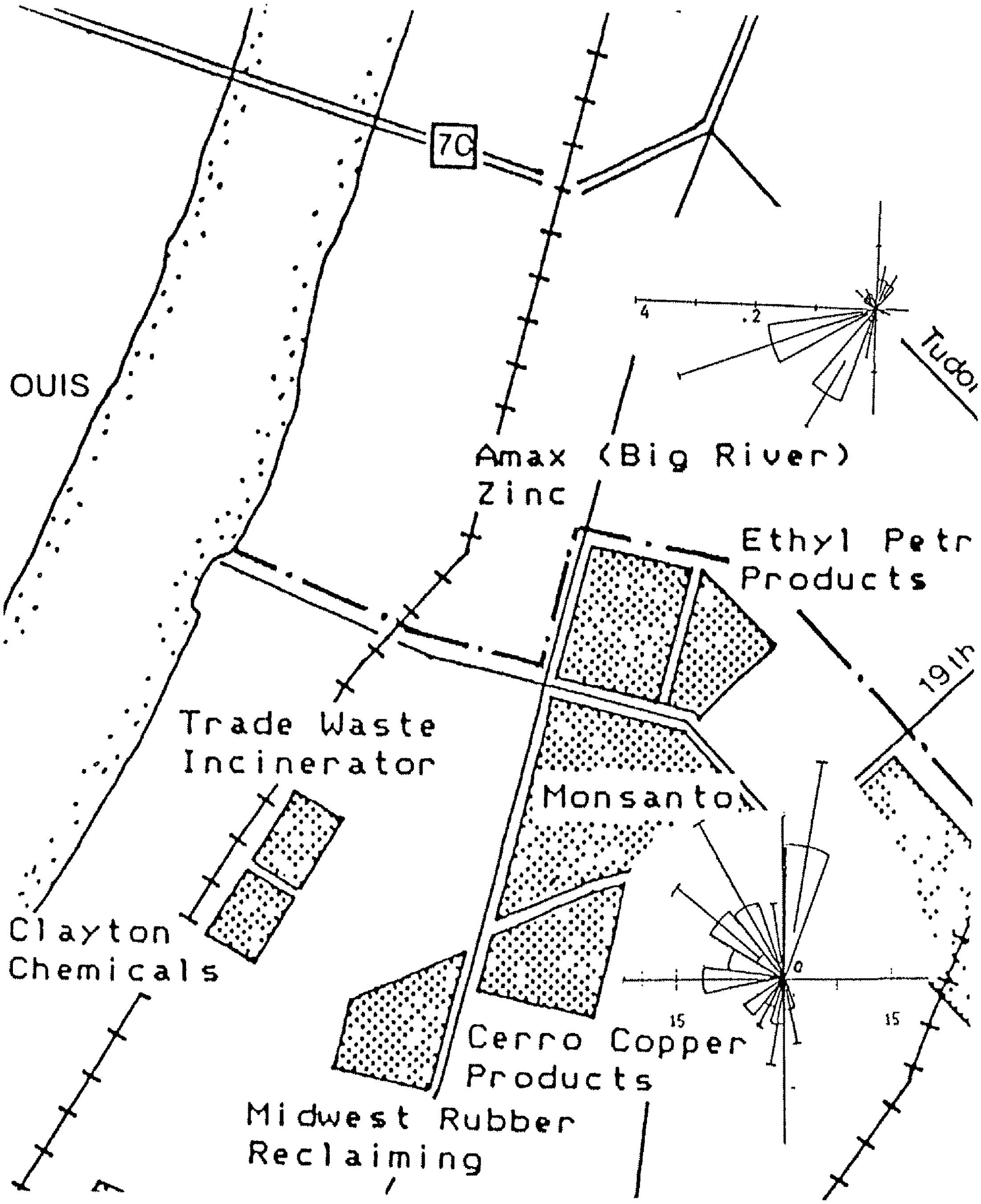


Figure 15 Mean concentrations of fine zinc as a function of wind direction at two sampling sites in East St Louis and Sauget ($\mu g/m^3$)

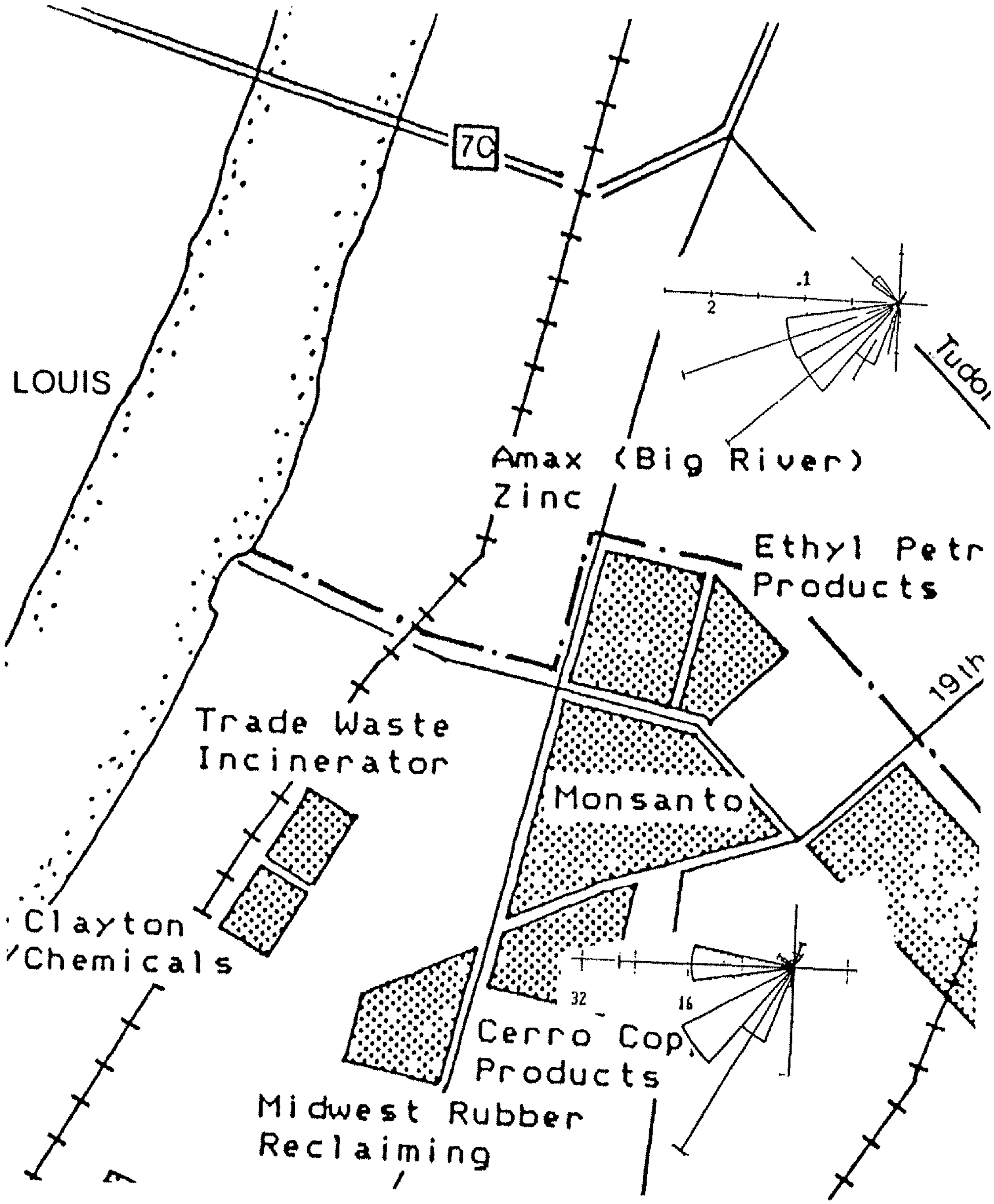


Figure 16 Mean concentrations of fine copper as a function of wind direction at two sampling sites in East St Louis and Sauget ($\mu g/m^3$)

CHAPTER 8 RECEPTOR MODELING

Receptor modeling is a technique by which sources contributing to air quality are identified from the perspective of the receptor (ambient sampler) Identification is possible assuming that a measured compound 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:

$$\text{Total Fe} = (\text{Fe})_{\text{soil}} + (\text{Fe})_{\text{steel}} + (\text{Fe})_{\text{road dust}} \qquad (2)$$

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

The receptor modeling approach observed in this study is outlined in Figure 17 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 source identification is supported by a number of observations or statistical tests In addition, both toxic and non-toxic elemental measurements are used to best identify inhalable particulate matter (PM-10) sources

Source identification does not begin in this section It started with site reconnaissances (Figures 2 through 4, pp 7-12) and emission inventories (Tables 5 through 7, pp 7-12) Source information was also gained through the characterization of the trace element data base (averages, trends and wind direction), in sampling particle size distributions and in the evaluation of streaker samples This section will build on those previous findings using enrichment factor and factor analysis statistics

8 1 Source Identification

Prior to the use of enrichment and factor analysis let us review the , emission source information discussed in the previous sections of this report Arsenic and Se concentrations varied little between urban and rural sites suggesting no significant local sources Fine and coarse Cr, Mn, and Fe were attributed, in Southeast Chicago, to iron/steel related emissions, while fine Zn and Pb were attributed to stack sources and auto exhaust within the industrial area In Granite City coarse Pb concentrations are strongly associated with south winds, the source likely a battery storage pile and contaminated dust at a nearby lead industry In East St Louis, highest levels of both fine and coarse Zn, Cu, Cd, Sn, and Pb were attributed to smelters but Zn and Cu were also attributed to additional unidentified sources outside our study area in St Louis In all three urban study areas, fugitive emissions appear to be major sources of airborne toxic pollutants

8 1 1 Enrichment Factor Calculations

Enrichment factor (EF) calculations have been used to distinguish between natural and anthropogenic emission sources EF values are calculated as follows:

$$EF = \frac{(X/C)_{\text{urban air}}}{(X/C)_{\text{reference material}}} \qquad (3)$$

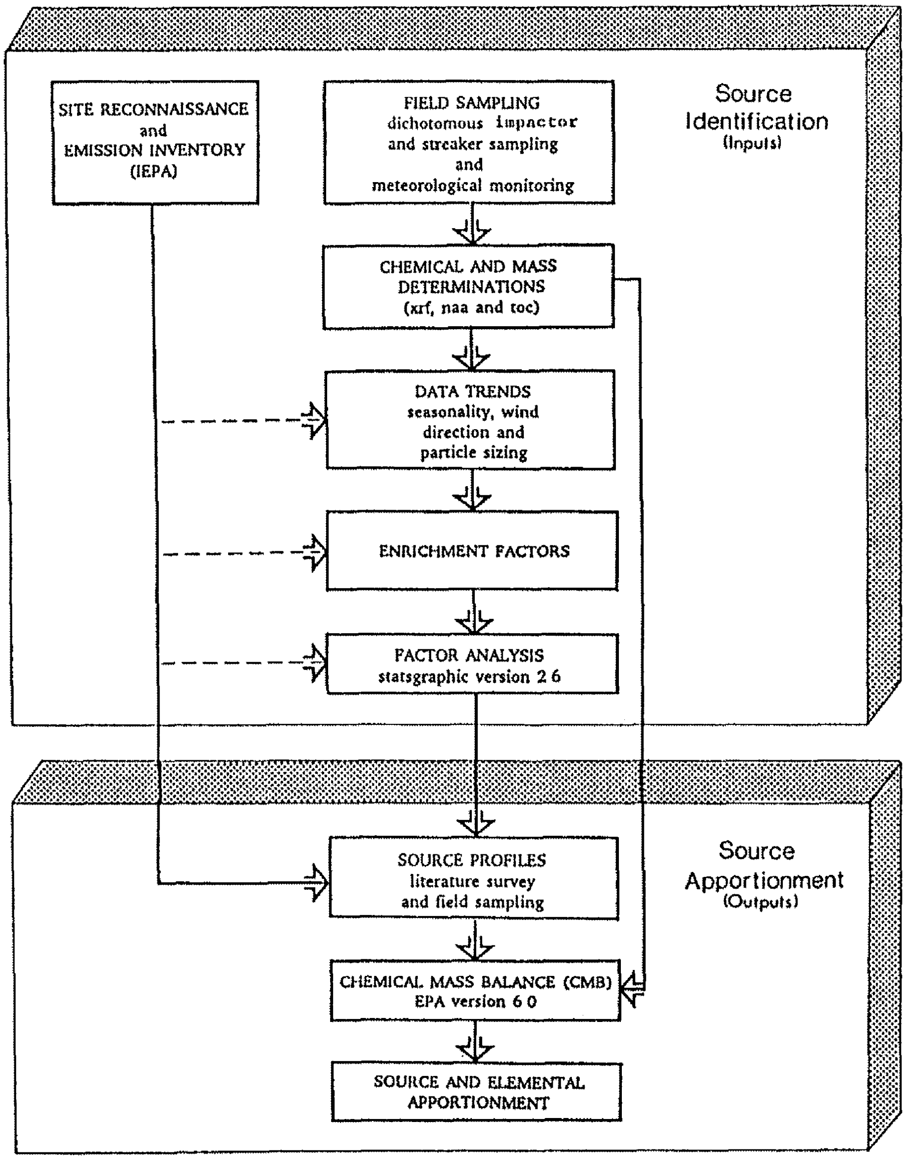


Figure 17 Receptor modeling flow diagram

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 atmospheric samples and in the reference material suggest the reference material as a likely source Crustal weathering and soil erosion are thought to be the prevalent natural sources of aerosol 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 anthropogenic sources An EF value greater than 5 represents a five-fold increase from the natural ratio of a given element and suggests a noncrustal source (assumed anthropogenic)

8 1 1 1 Bondville

The mean and range for fine and coarse PM-10 are presented in Figures 18 Fine and coarse Si, Al, and Ti, and coarse Cl and Fe are attributed primarily to soil (crustal) sources; fine and coarse Zn, Br, Pb, S, and Se, and fine Cr, P, Cu, and Ni are attributed primarily to anthropogenic sources; and the remaining elements vary between soil and anthropogenic sources The toxic elements, with the exception of Mn and V, are grouped as primarily anthropogenic, and reach the site by long-range transport

The Bondville data show that anthropogenic emission sources reach well beyond urban and industrial boundaries The enrichment of S and Se is a signature for regional sulfate; Br and Pb are indicators of motor vehicle emissions; and V and Ni are related to oil combustion Elemental enrichment factors plotted by wind direction show no real discrimination for a particular wind sector, with the exception of fine and coarse Zn and Cu, and coarse S and Br The heightened enrichment for Zn, Cu, and S with winds from the WSW to WNW (Figure 19) implicates the cities of Decatur and/or Bloomington as pollution sources Extension of the urban plume from the St Louis area is possible but less likely Similarly, the influence of Champaign/Urbana and perhaps Chicago may be responsible for the higher yet variable enrichment shown from the northeast The lower enrichments with airflow from the south are not surprising as this fetch is removed from areas with large urban concentrations Coarse Br shows heightened enrichments from the northeast (Champaign/Urbana) but, unlike Zn, Cu, and S, there is no enrichment in air from the west

8 1 1 2 Southeast Chicago

The mean and range for fine and coarse PM-10 are presented in Figures 20 Fine and coarse Si, Al, and Ti, and coarse K and Sr are attributed primarily to soil (crustal) sources; fine and coarse Br, Cl, Zn, Pb, S and Se and fine V, Mn, Cr, Ni, P, and Cu are attributed primarily to anthropogenic sources; and the remaining elements vary between soil and anthropogenic sources Generally, enrichments are heightened over that of Bondville, especially in the coarse fraction The heightened enrichment is most apparent for Pb, Mn, Fe, Cr, and V suggesting strong local sources, in relation to regional sources, for these elements

Elemental enrichment factors plotted by wind direction are used to better define the elemental sources impacting the Bright School sampling site Fine and coarse Mn and Fe, and coarse Ca show heightened enrichments with southeasterly airflow from the iron and steel mills (Figure 21) Fine Zn and Ni show a distinct enrichment in air coming from the mills but indicate additional sources to the north There is a hint in the enrichment plots of: blast furnace contributions (Chicago Blast Furnace Co , 130° to 165°) for fine Mn, Fe and Pb; incinerator contributions (SCA Chemical Services, 237° to 244°) for fine Pb and Zn; and power plant or coal contributions (Commonwealth Edison/coal storage piles, 38° to 62°) for coarse S (Figure 21)

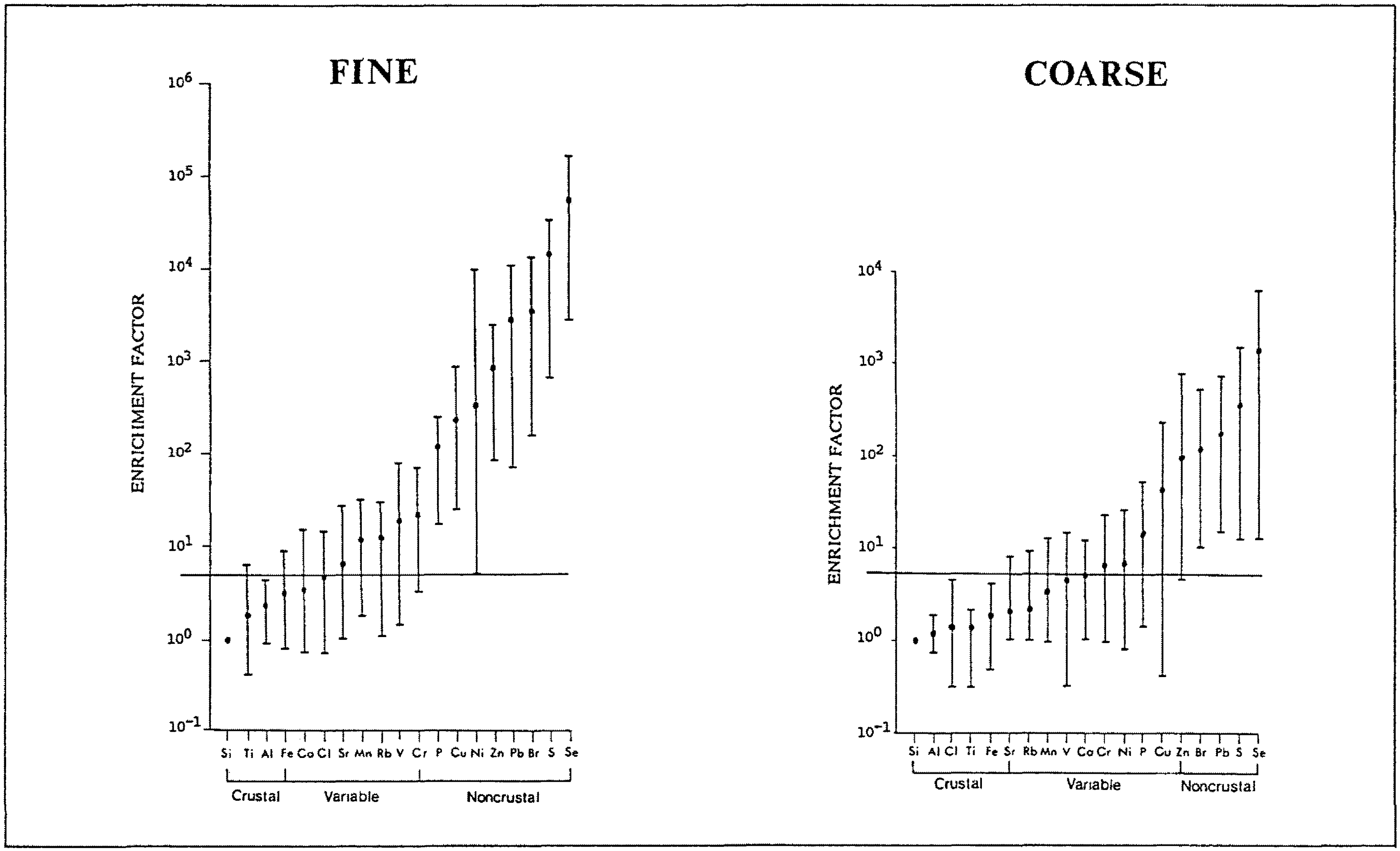


Figure 18. Enrichment factors - Bondville.

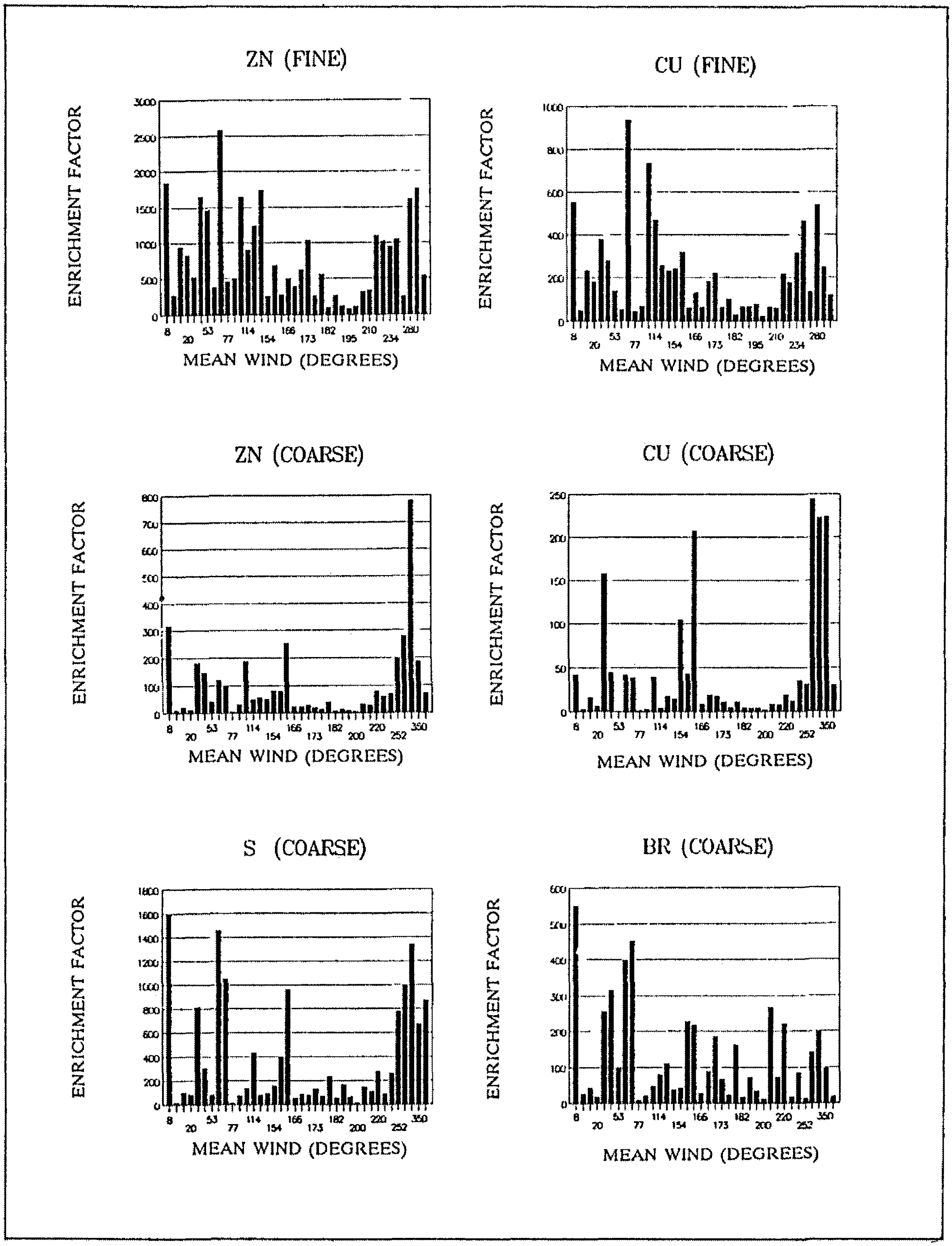


Figure 19 Wind direction and enrichment factors - Bondville

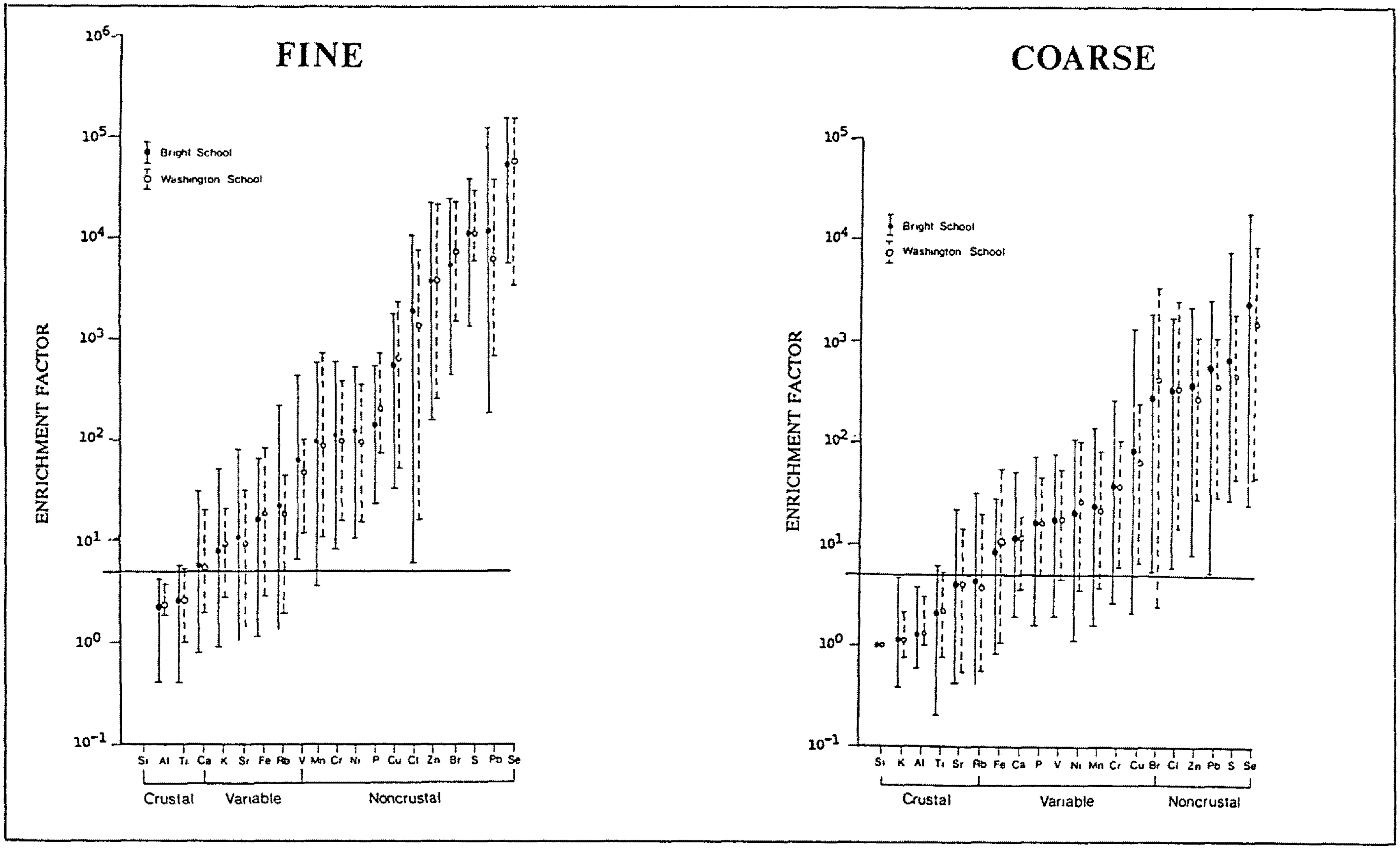


Figure 20. Enrichment factors - Chicago.

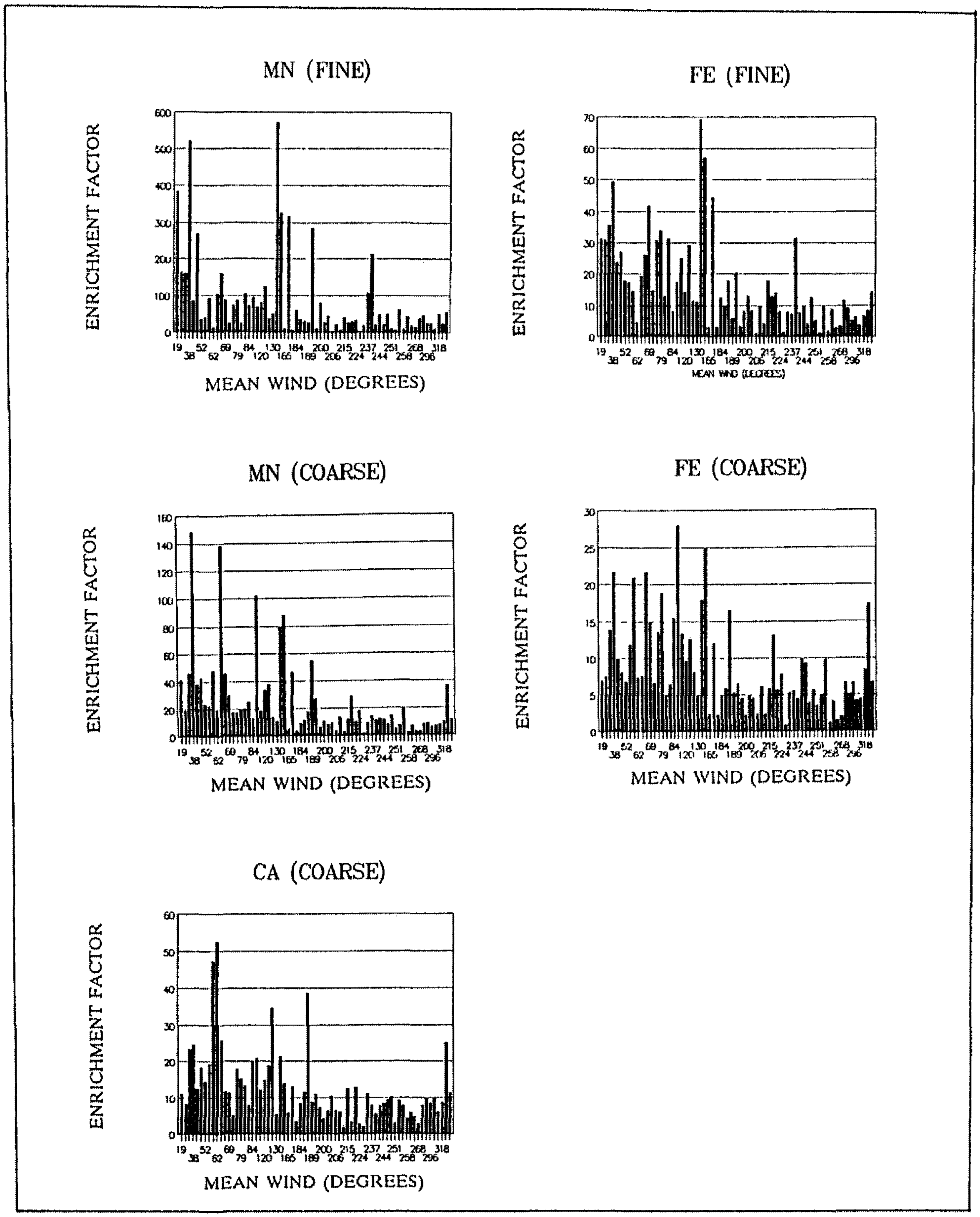
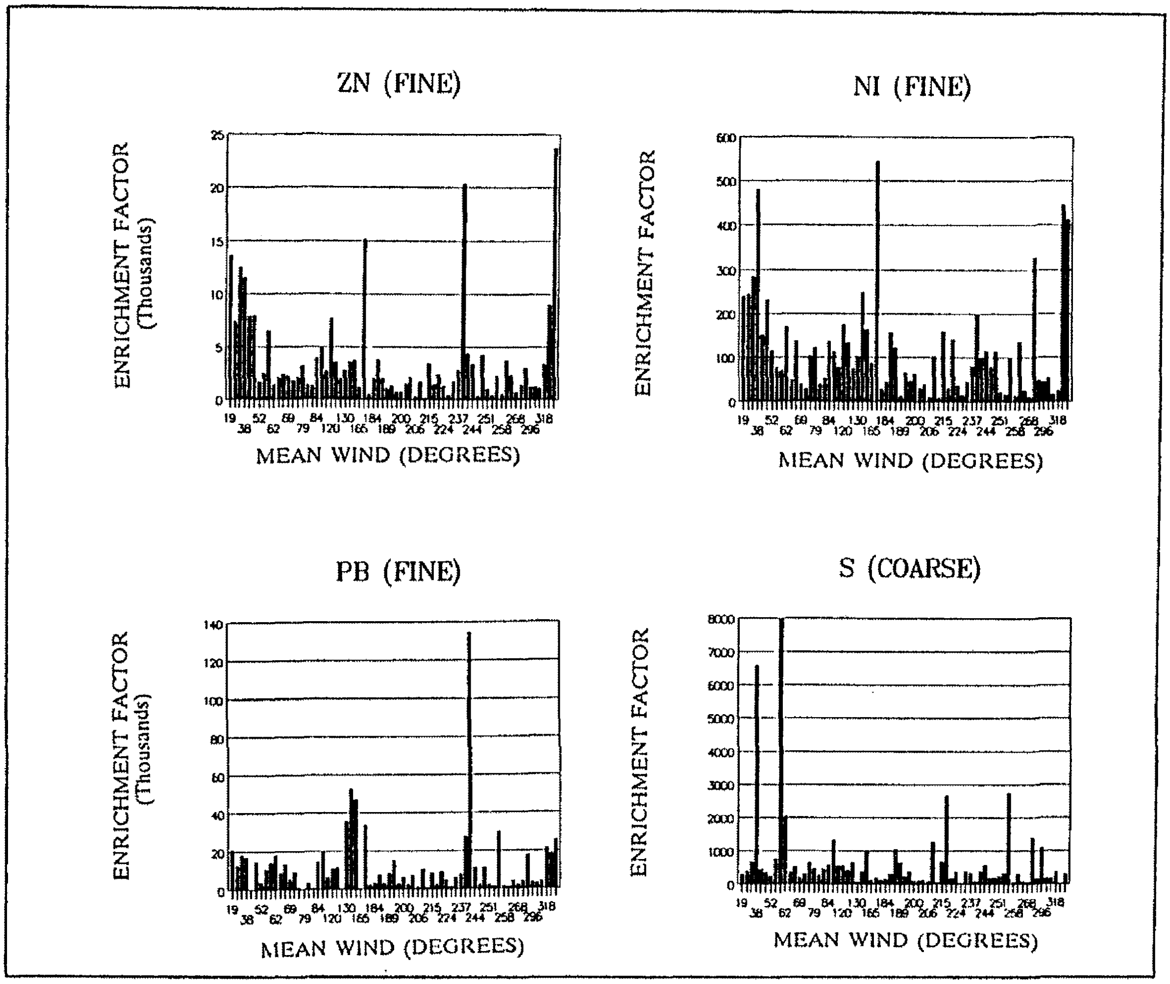


Figure 21 Wind direction and enrichment factors - Chicago

Figure 21 (Continued)



8 1 1 3 Granite City

The mean and the range for the fine and coarse components of PM-10 are presented in Figure 22 Fine and coarse Si, Ti, and Al, and coarse Na and K are attributed primarily to soil (crustal) sources; fine and coarse Cr, Cu, Br, Cl, Zn, S, As, Sb, Pb, Sn, Se, and Cd are attributed primarily to anthropogenic sources; while the remaining elements vary between soil and anthropogenic The toxic elements, again with the exception of Mn and V, are grouped as primarily anthropogenic

Elemental enrichment factors plotted by wind direction are used to better define the sources of enrichment By way of example, fine and coarse Pb, and fine Cu, Cl, Ni, and V (Figure 23) show heightened enrichments with airflow from the south The inclusion of coarse Pb in this list suggests that the local Pb smelter and recycling facility are a source of at least the coarse Pb The heightened enrichment of fine Cl may be linked to the Al smelter (Al does not show a specific directional pattern as natural sources dominate) The enrichments of Cu, Ni, V, and to a lesser degree, Zn are likely attributed to the smelters and other industries located in East St Louis and St Louis In addition, enrichment values hint of Cu, V, and Ni sources to the north (refineries and metallurgical industries are located in Wood River and Alton)

Heightened enrichments of fine and coarse Mn and Fe, as well as coarse S and Se (Figure 23) are apparent with airflow from the northeast and southeast after having passed over Granite City Steel and related industries A further distinction of sources can be made between steel-related facilities Located to the southwest of the sampler are the Granite City Steel mills The enrichment of Fe is restricted to times when airflow is over the mills Located to the northeast of the sampler are large tracts of land utilized for slag and coal storage The enrichment of Mn and Se is greatest with airflow over both the mills and slag Heightened enrichments of fine S and Zn are found with airflow from both the east and south of the sampler Galvanizing operations at Granite City Steel to the east and a Zn smelter to the south are likely sources of fine Zn

8 1 1 4 East St Louis

The mean and range for the fine and coarse components of PM-10 are presented in Figure 24 Fine and coarse Si, Al and Ti, and coarse K are attributed primarily to soil (crustal) sources; fine and coarse P, Cl, Cu, Br, S, Sn, Zn, Pb, and Se are attributed primarily to anthropogenic sources; the remaining elements vary between crustal and anthropogenic The grouping of these elements between soil and anthropogenic is similar to that of Southeast Chicago and Granite City

As for Granite City, enrichment factors plotted by wind direction are shown to be a sensitive indicator of emission sources for East St Louis Enrichments show a pattern of heightened enrichment of fine and coarse Cu, Zn, Cd, Pb, and Se, fine Sn and coarse S with airflow from the south to SSW, in line with the Zn and Cu smelters and industries within the city of St Louis (Figure 25) This pattern is best shown in the coarse fraction The Sauget sampler shows heightened enrichments of coarse Zn from the NW, confirming a Zn smelter source, however, fine Zn is shown to be primarily from sources to the W and SW (Figure 26) A copper smelter is in this direction along with a municipal incinerator farther west in St Louis Trade Waste Incinerator does not appear to be a substantial source of fine Zn The indication of Zn sources from the SW is in agreement with observations from the streaker data (see Streaker Section) and with the general observations made by the simple box model (see Chapter 2, p 13) Heightened enrichments for fine and coarse Cu and fine Pb from the SW are attributable to the Cu smelter and/or St Louis sources Location of the Sauget sampler does not allow for discrimination between the two Coarse Cd and fine Se show enrichments that indicate both the Zn smelter, the Cu smelter and in East St Louis and other unidentified sources in St Louis are important

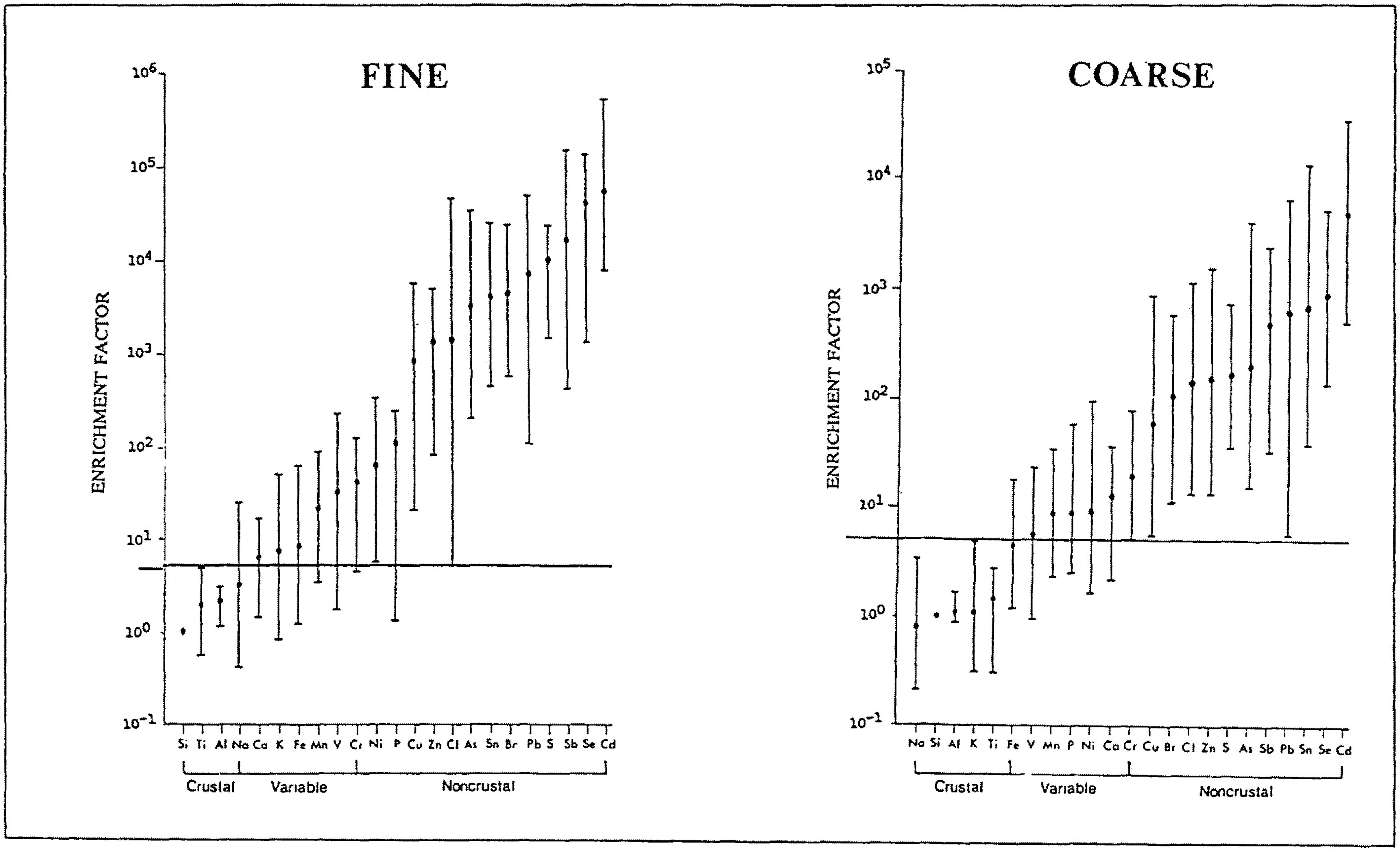


Figure 22. Enrichment factors - Granite City.

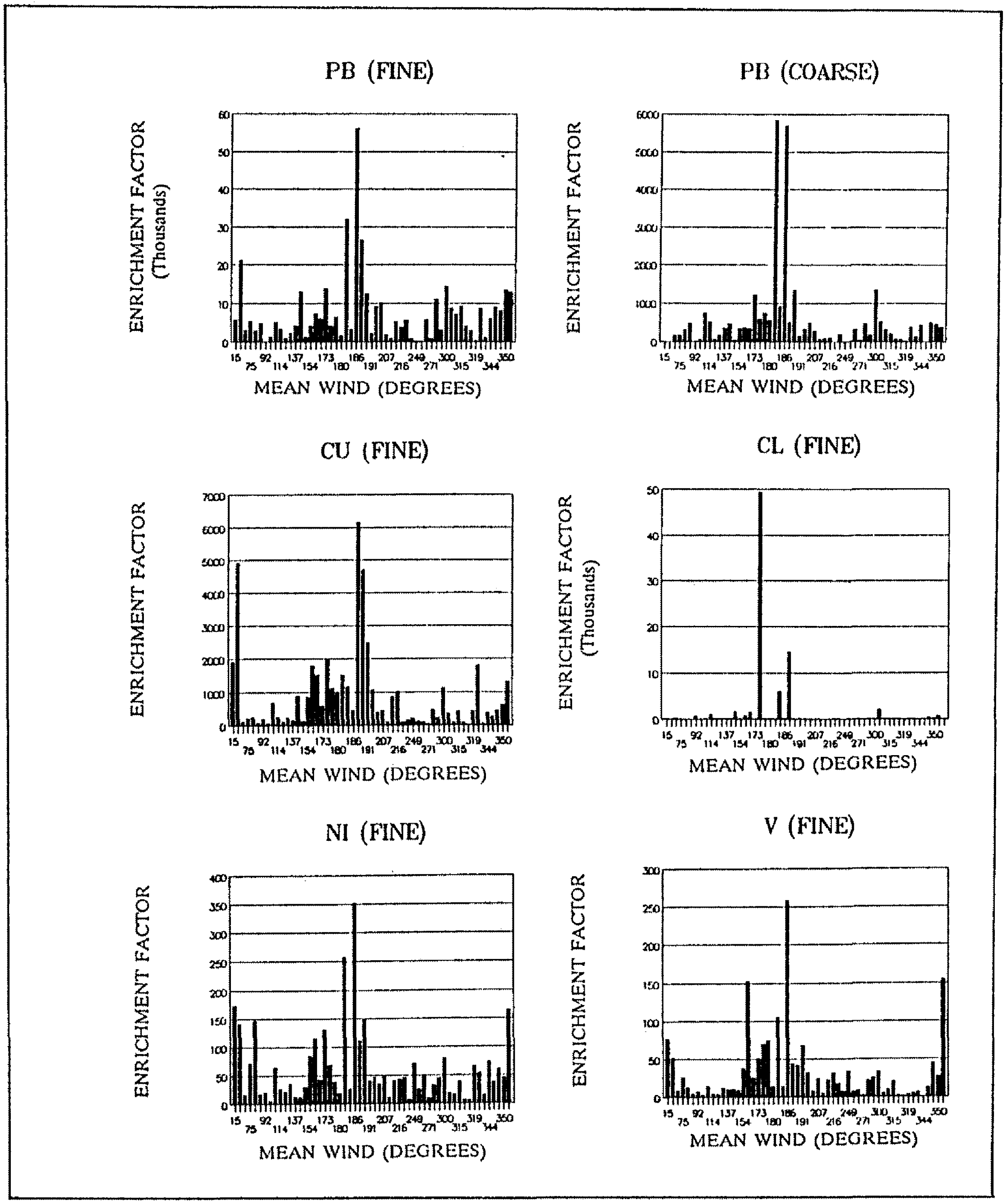
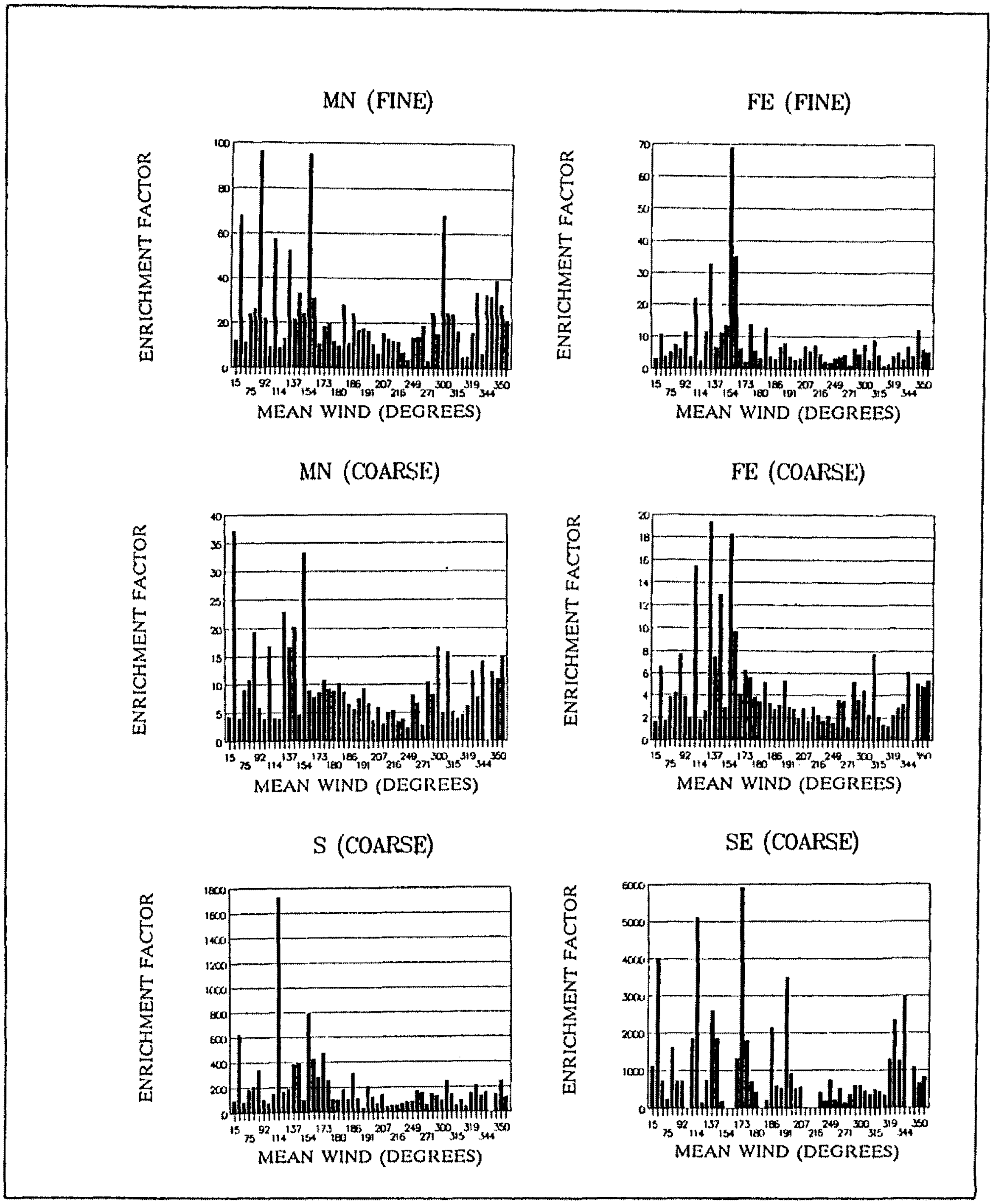


Figure 23 Wind direction and enrichment factors - Granite City

Figure 23 (Continued)



MN (FINE)

FE (FINE)

MN (COARSE)

FE (COARSE)

S (COARSE)

SE (COARSE)

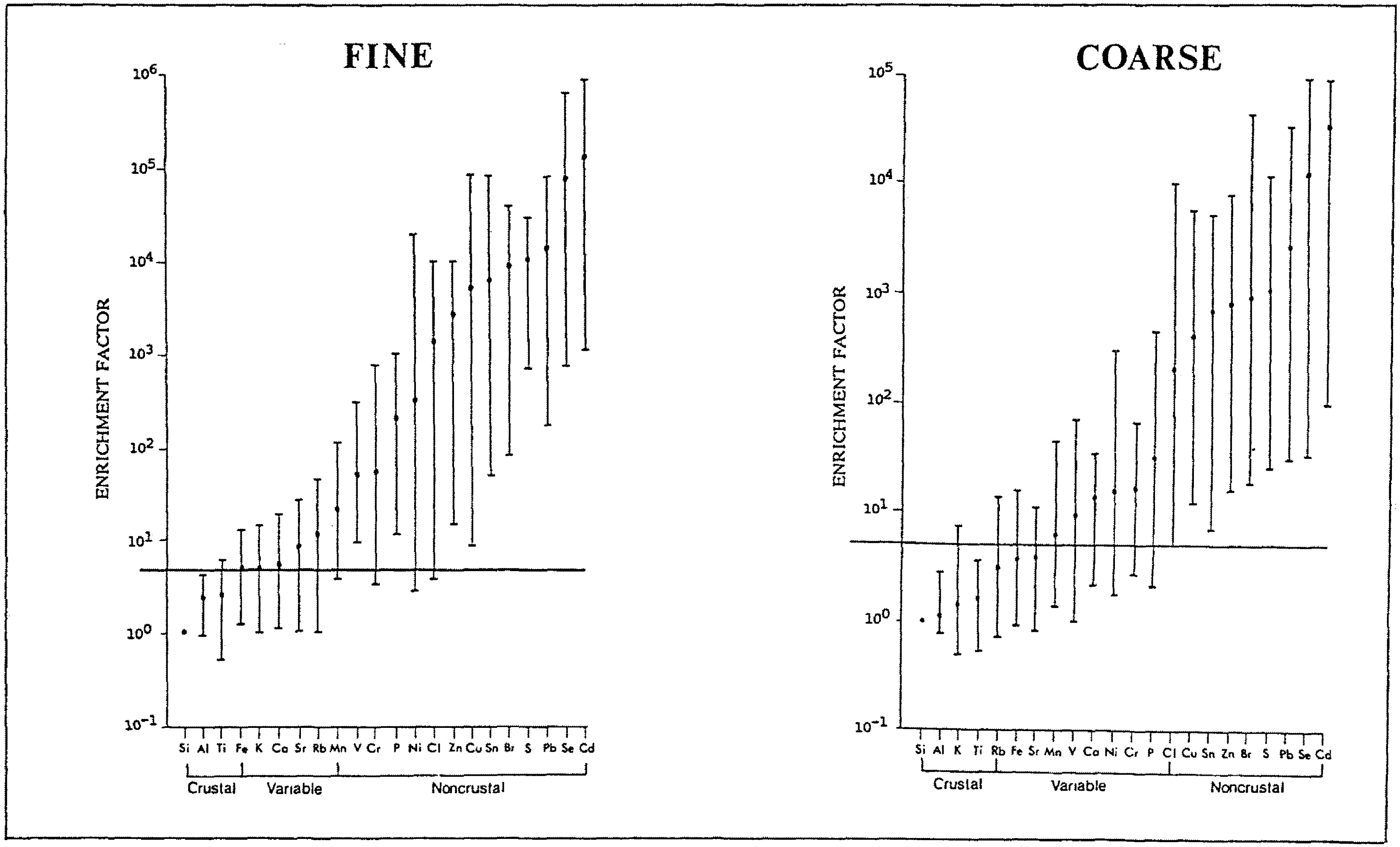


Figure 24. Enrichment factors - East St. Louis.

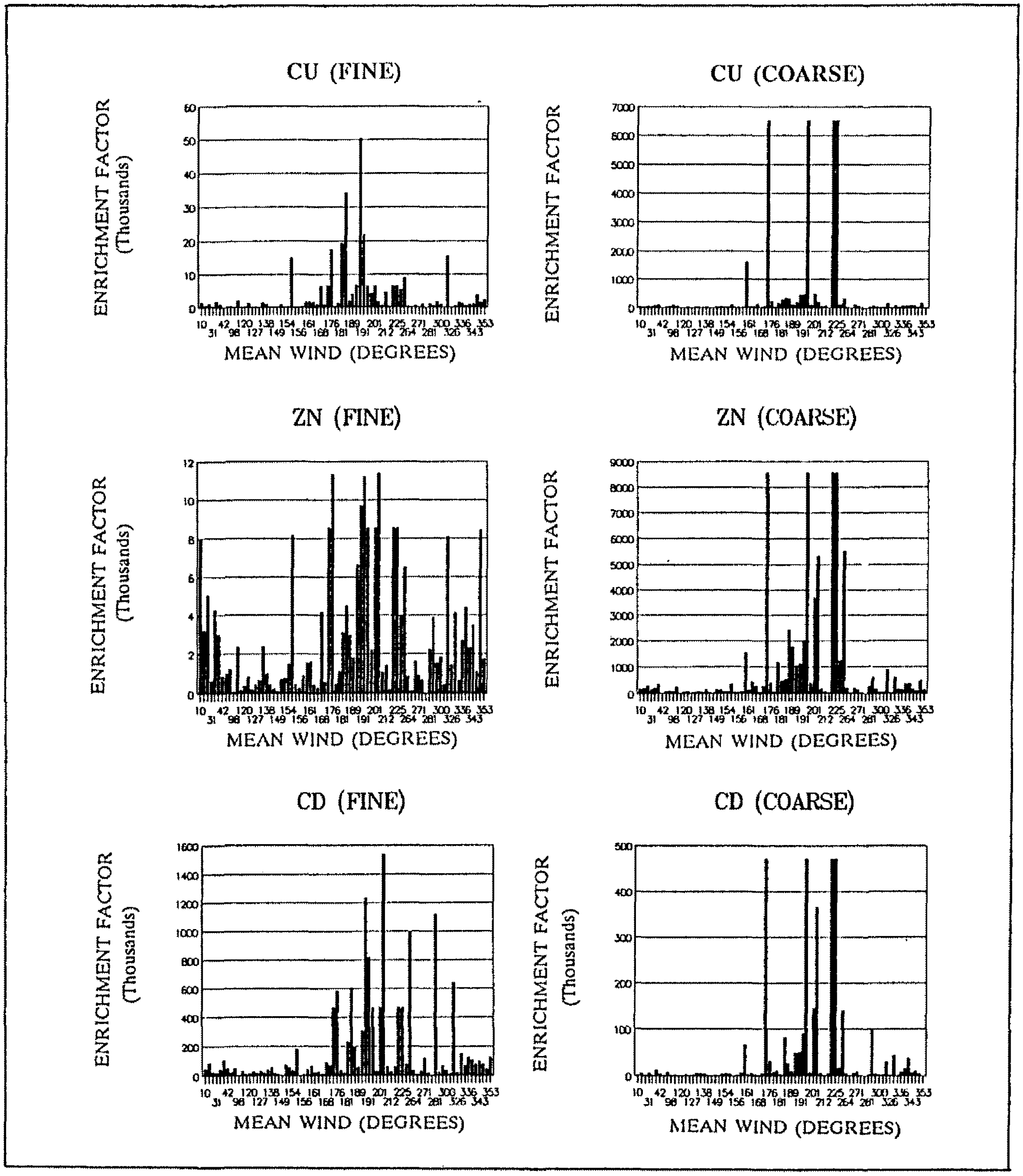
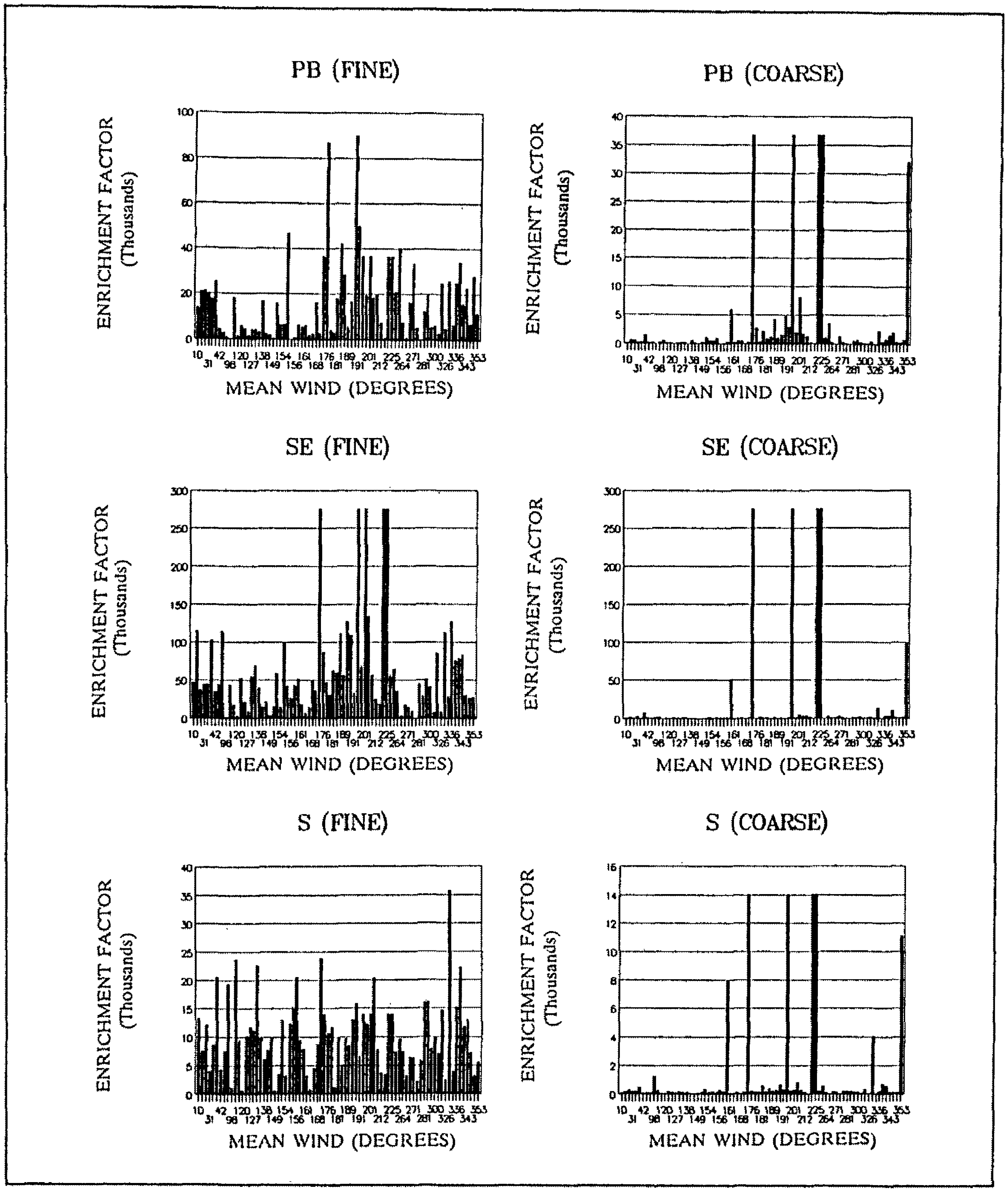


Figure 25 Wind direction and enrichment factors - East St Louis

Figure 25 (Continued)



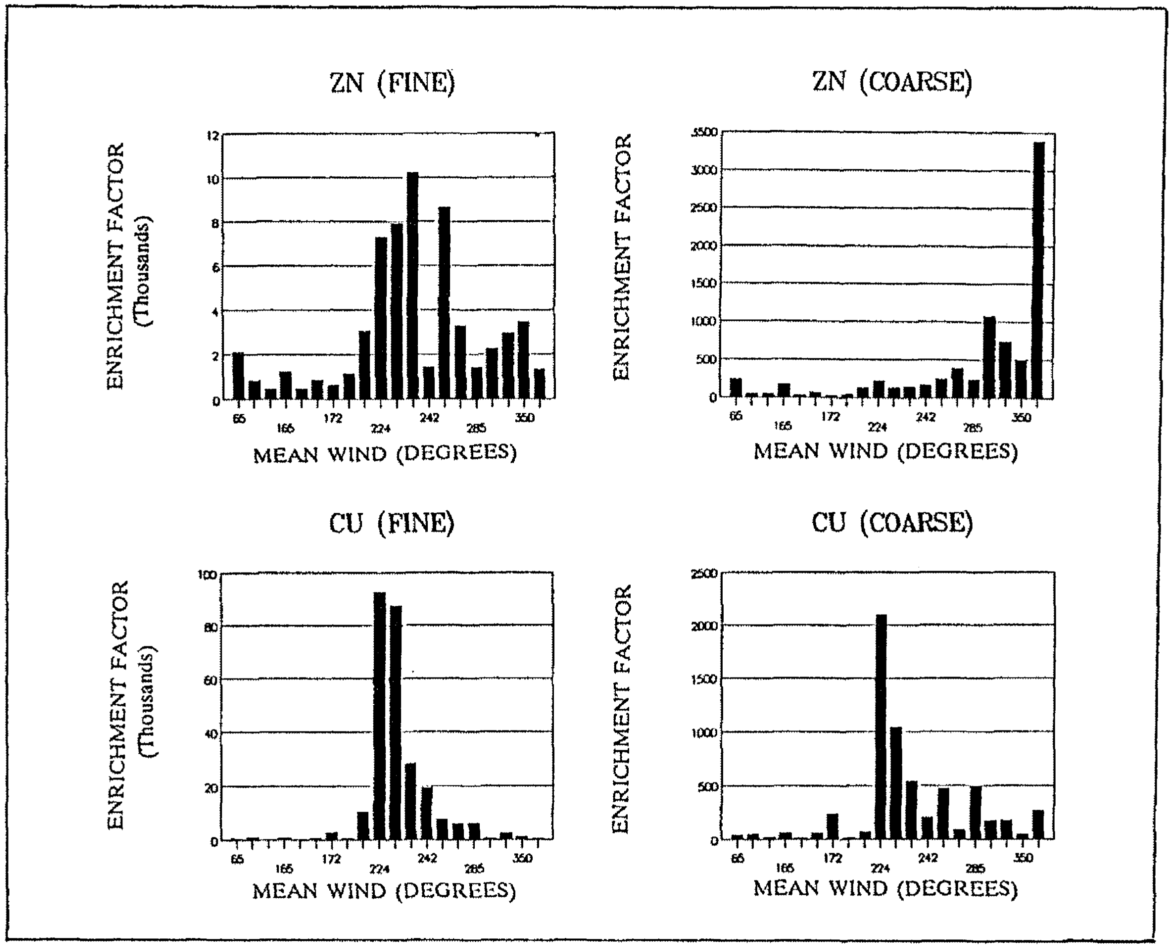
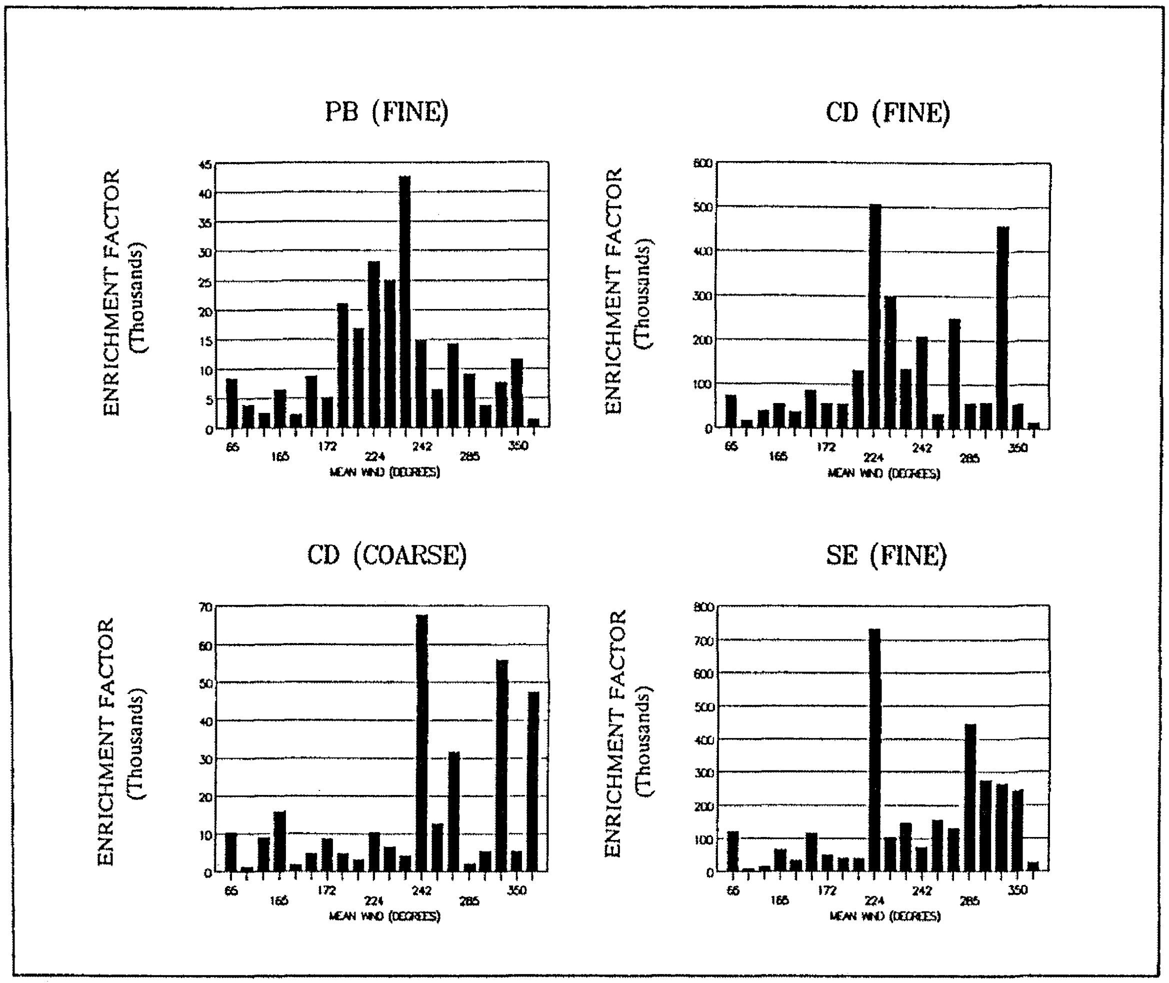


Figure 26 Wind direction and enrichment factors - Sauget

Figure 26 (Continued)



8.1.2 Factor Analysis

Factor analysis is a statistical technique for characterizing complex data sets and is commonly used in atmospheric chemistry for pollution source identification (Gaarenstroon, et al, 1977; Gatz, 1975, Gordon, 1988; Lioy, et al, 1989). It takes a number of measured variables and finds linear combinations (factors) of those variables that explain most of the variance. These factors represent underlying causal parameters that can be interpreted as identifying possible emission source categories within the study area (Hopke, 1985). 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 requires no a priori knowledge of emission source categories and thus is useful as an independent method for suggesting emission sources not inventoried or previously considered. However, identifying and labeling of these sources is based on previous findings, knowledge of the study area and known emission source characteristics taken from the scientific literature.

A number of "rules of thumb" exist in choosing the number of factors to be interpreted in factor analysis. The most common rule is to keep factors with eigenvalues $\geq$ 1. By way of definition, eigen vectors define a plane in a matrix that contains some data points and an eigenvalue indicates the dimensionality of that plane. Other methods include keeping only those factors with +/- errors that do not overlap (Kendal/North criteria) and plotting eigenvalue curves (scree plots) (see Hopke, 1985 and Richman, 1986 for more detailed reviews). To maximize the identification of possible sources a maximum number of factors that were physically meaningful were retained (Hopke, 1985). In practice, this approach matched an eigenvalue $\geq$ 1 criterion.

The results of factor analysis and factor identifications derived from statistical manipulation of the data base are discussed for each of the monitoring sites separately. In the plots of factor loadings, those loadings above 0.5 (highly significant) are indicated by a solid bar and those loadings between 0.3 and 0.5 are indicated by a light bar. While the inclusion of wind direction in FA can be problematic (i.e., 0° is the same as 360°), it is included in our final FA runs. Two iterations (with and without wind direction) showed little differences in factor numbers and elemental character, yet the inclusion of wind direction offers useful insights for source identification. This approach may have worked in this case because no major sources at any of the sites are near the 0°/360° overlap. Factor identifications were made by comparing significant elements and other parameters to known source characteristics.

8.1.2.1 Bondville

Factor analysis statistics, shown in Figure 27, suggest that for Bondville the fine component of PM-10 is influenced by the following sources:

Factor 1: Soil (crustal), characterized by Al, Si, and Ti

Factor 2: Urban/industrial, characterized by Mn, Cu, Zn, and Cr

Factor 3: Unknown, characterized by Rb and Sr

Factor 4: Urban/industrial combustion, characterized by Pb, Br, V, and Cl

Factor 5: Regional sulfate, characterized by S

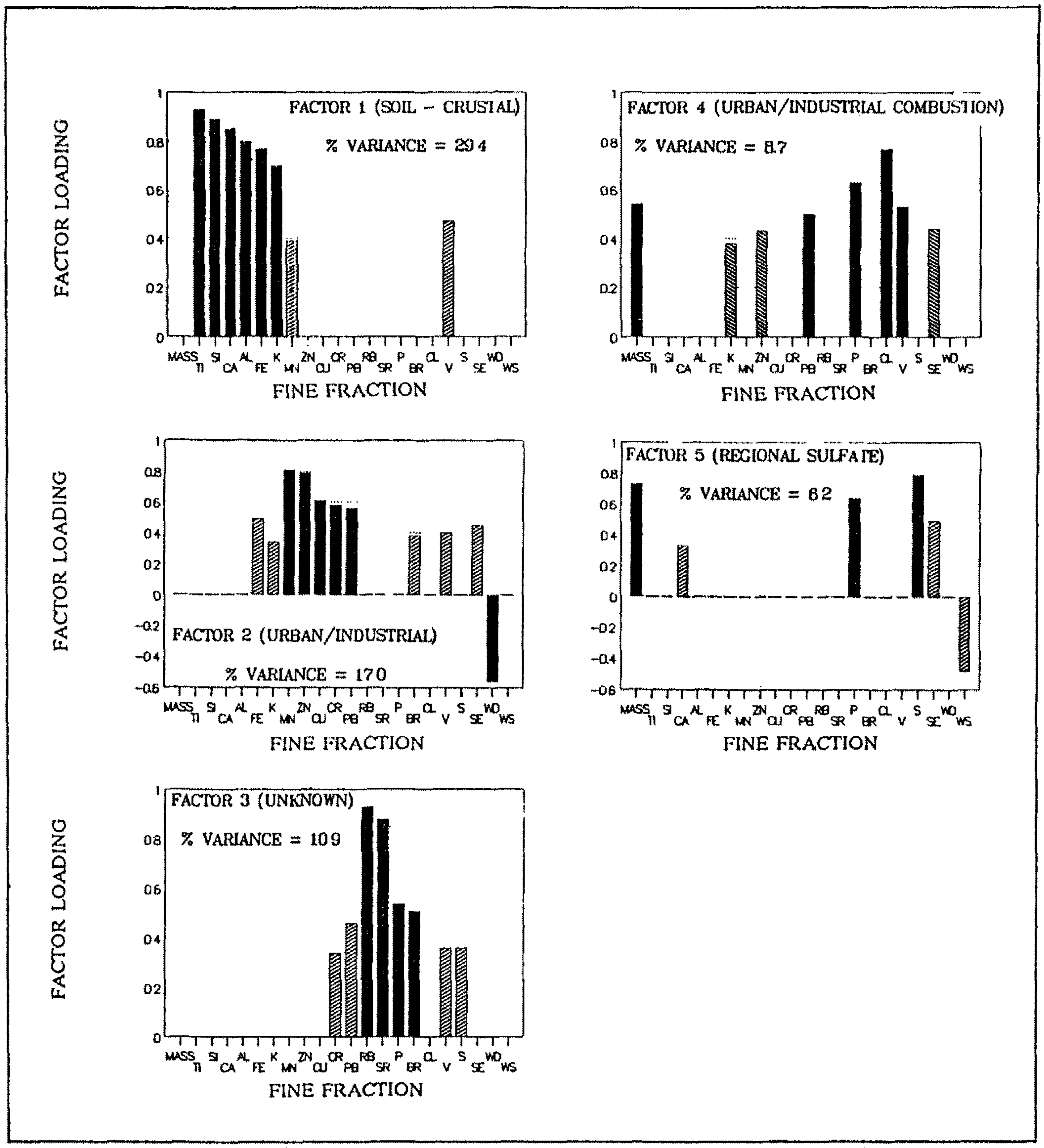


Figure 27 Fine particle factors for Bondville

Factor 1, dominated by nonenriched soil related elements, suggests a soil source (cultivated fields) The lack of any association with wind speed suggests soil transport over some distance The soil source accounts for only 29 4% of the sample variance and for a small fraction of the fine PM-10 variability The regional siting of Bondville and low absolute concentrations in the air do not preclude anthropogenic influences Factor 4 and Factor 5 are identified as coal and gasoline combustion sources and are correlated with the fine PM-10 mass Factor 2, dominated by metallic elements, suggests urban/industrial sources distinct from combustion sources Both source types are likely to be in urban areas and the distinction shown here may be related to transport characteristics One factor (Factor 3) remains unexplained Its presence may be an artifact of factor analysis, resulting from concentrations often at or below detection limits

Factor analysis statistics, shown in Figure 28, suggest that for Bondville the coarse component of PM-10 is influenced by the following sources:

Factor 1: Soil (crustal), characterized by Al, Si, Ti, and high wind speeds

Factor 2: Regional sulfate, characterized by S
Urban/industrial, characterized by Zn, Cu, and Ni

Factor 3: Urban/industrial combustion, characterized by Pb, Br, and Se

Factor 1, as in the case of the fine particles suggests a soil source but accounts for a larger percent of the variance than found for the soil in the fine particle fraction This factor is also correlated with mass in coarse particles An association with wind speed suggests local influences Factor 2 and Factor 3 are identified as urban/industrial sources Enrichment calculations have shown the elements associated with these factors to be anthropogenic A better resolution of sources, for both the fine and coarse components of PM-10, is not possible at Bondville and this would not be expected considering the distance of possible sources

8 1 2 2 Southeast Chicago

Factor analysis statistics, shown in Figure 29, suggest that for Southeast Chicago the fine component of PM-10 is influenced by the following sources:

Factor 1: Iron and steel mill emissions characterized by Mn, Fe, Cr, Pb, and easterly winds
Oil burning and/or steel emissions, characterized by V and Ni
Other unidentified sources characterized by Pb and Zn

Factor 2: Sulfate and coal-related characterized by S and Se

Factor 3: Unknown source, characterized by Br, Cl, Rb, and K

Factor 4: Soil (crustal), characterized by Al, Si, and Ti

Factor 5: Iron and steel mill dust, characterized by Mn, Cr, and Fe

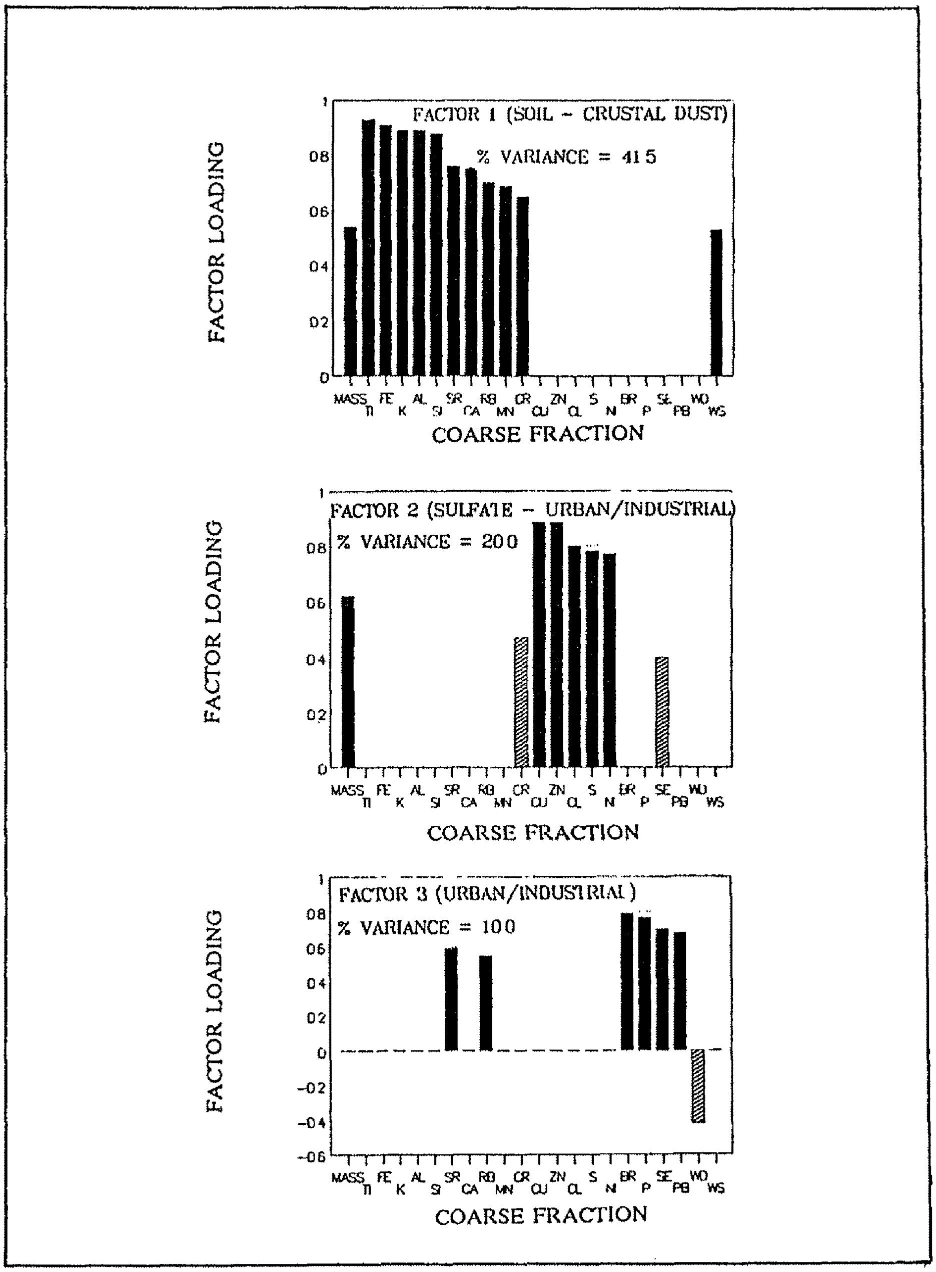


Figure 28 Coarse particle factors for Bondville

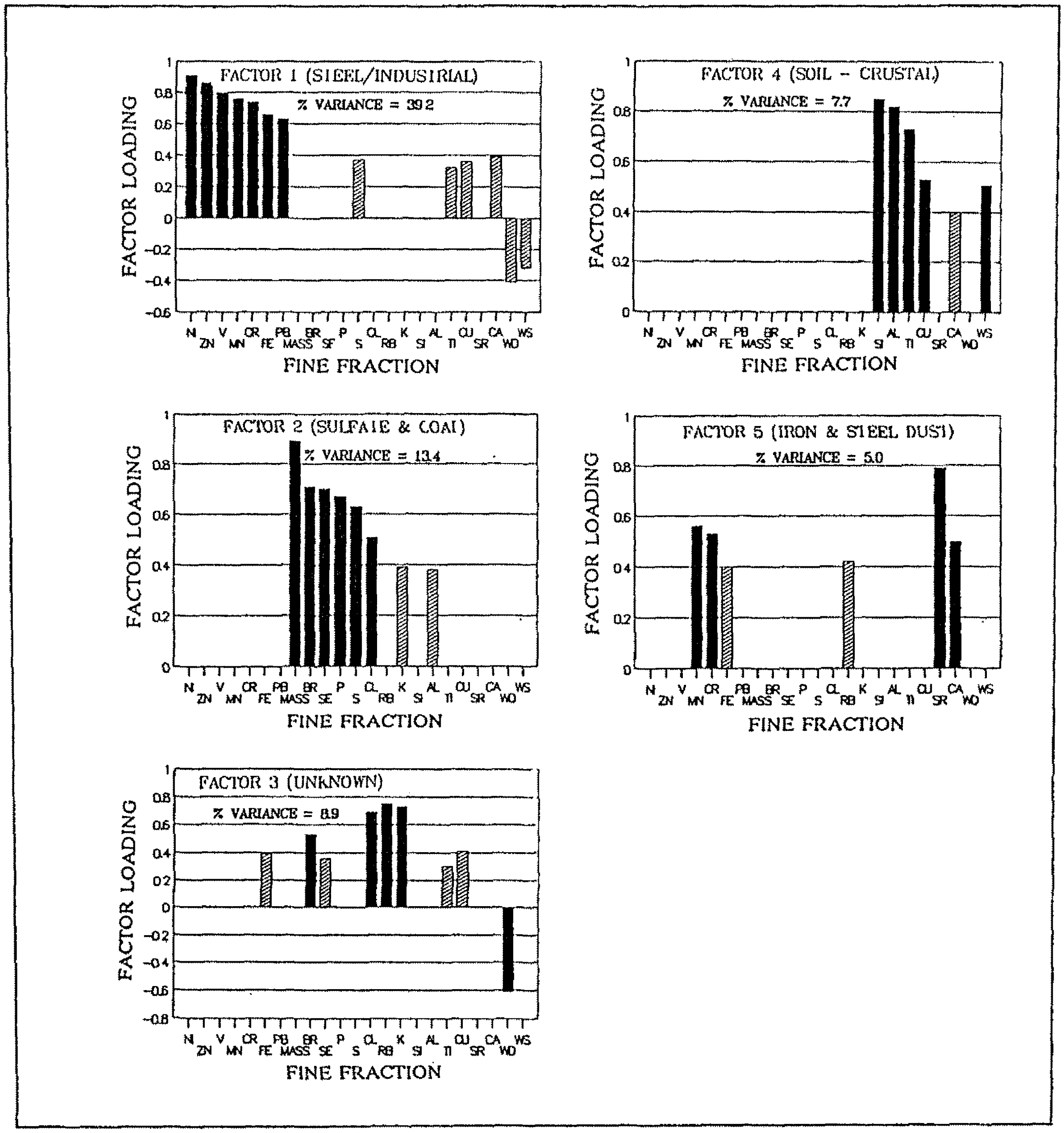


Figure 29 Fine particle factors for southeast Chicago

Factor 1, dominated by metallic elements (ie Fe, Mn, and Cr) in association with easterly winds (iron and steel mill fetch) and weak airflow (poor ventilation), suggests stack emissions, particularly iron and steel, as a source Emissions from oil burning (Ni and V) and other unidentified sources (Pb and Zn) co-vary with the mill emissions Constituent elements of Factor 1 account for most of the fine particle variance but regional sulfate sources (Factor 2) correlates with the fine particle mass Two of the factors (Factor 4 and Factor 5) suggest fugitive emission sources Factor 4, dominated by Al, Si, and Ti, suggests a soil (crustal) source and Factor 5, dominated by the enriched metallic elements Mn, Cr, and Fe suggests iron and steel-derived fugitive dust The source distinction between Factor 4 and Factor 5 is reinforced by the positive loading of wind speed with a soil source suggesting wind erosion as the suspension mechanism The lack of a similar relationship with the iron and steel-derived dust supports a mechanical method for dust suspension (e g truck traffic) Toxic elements are associated, in part, with each of the identified sources No auto emissions could be isolated by factor analysis even though they are a source of Pb in Chicago This is probably due to the fact that airborne Pb levels have been greatly reduced in recent years and that auto exhaust covaries with steel emissions and other Pb sources

Factor analysis statistics, shown in Figure 30, suggest that for Southeast Chicago the coarse component of PM-10 is influenced by the following sources:

Factor 1: Soil (crustal), characterized by Al, Si, and Ti

Factor 2: Contaminated urban dust (road dust), characterized by Fe, Cr, Pb, Br, Cu, and Zn

Factor 3: Iron and steel mill dust, characterized by Fe, Cr, Mn and easterly winds

Factor 4: Coal-derived dust, characterized by Se and high wind speeds

Fugitive emission sources account for nearly all of the coarse PM-10 variability and are correlated with total mass in Southeast Chicago It is reasonable to assume that urban activities in proximity to urban ambient air samplers contribute a substantial fraction of resuspended dust Factor 1, identified as soil (crustal), may include as sources local landfills and road dust uncontaminated by industry Fugitive dusts related to the iron and steel mills are identified as: road dust contaminated from iron and steel related sources (truck spillage, track on, atmospheric fallout); dust entrained from iron and steel industry properties; and coal dust Some uncertainty exists in the labelling of Factor 2 and Factor 3, however, it is apparent that a number of iron and steel related sources (enriched Fe, Mn, and Cr) affect the coarse PM-10 The toxic elements are associated with the fugitive dusts from the iron and steel mills

8 1 2 3 Granite City

Factor analysis statistics, shown in Figure 31, suggest that for Granite City the fine component of PM-10 is influenced by the following sources:

Factor 1: Soil (crustal), characterized by Al, Si, and Ti
Regional sulfur, characterized by S

Factor 2: Oil burning characterized by V and Ni
Motor vehicle emissions, characterized by Pb and Br
Smelters, characterized by Cu, Zn, Pb, and As

Factor 3: Iron and steel-related, characterized by Mn, Fe, Zn, Se, and easterly winds

Factor 4: Unknown, characterized by Rb and Sr

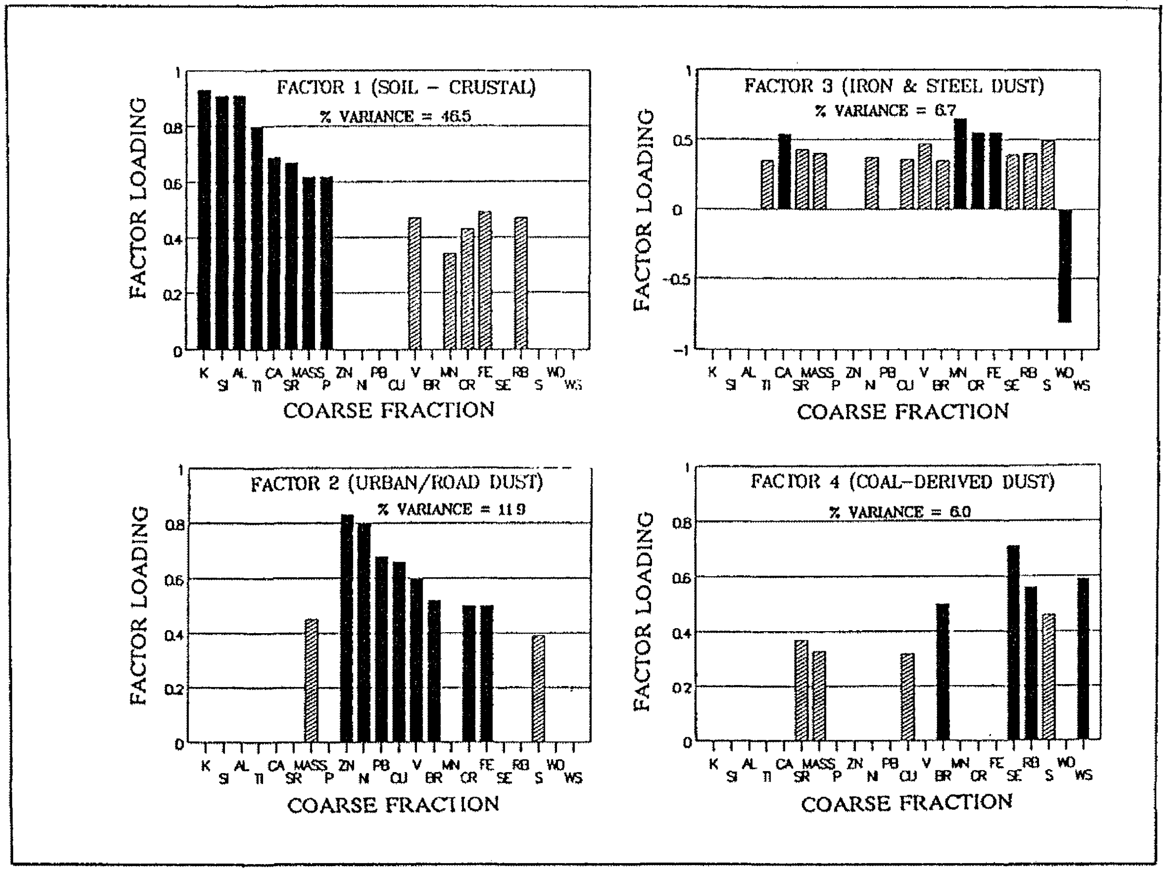


Figure 30 Coarse particle factors for Southeast Chicago

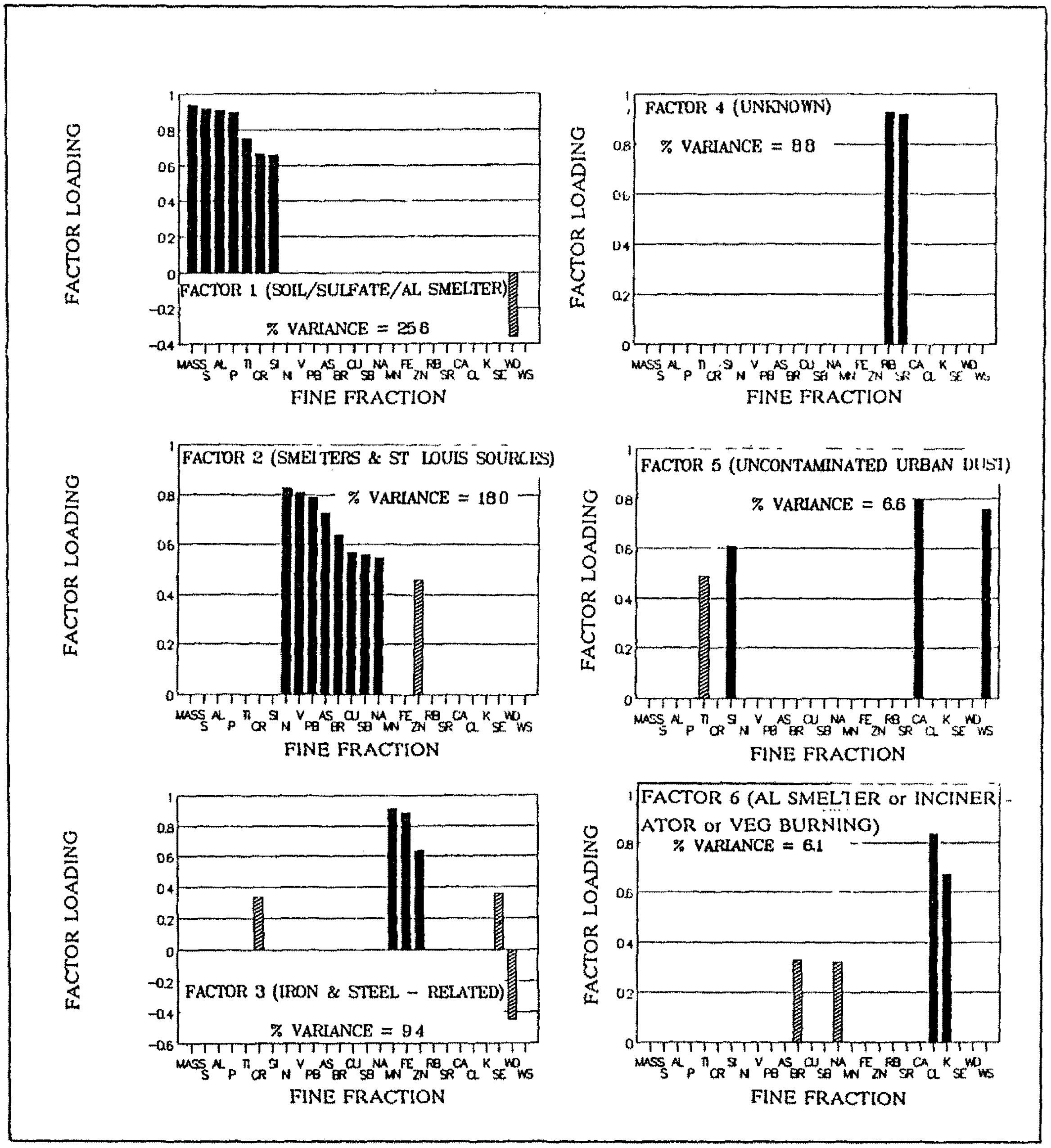


Figure 31 Fine particle factors for Granite City

Factor 5: Limestone, characterized by Ca and high wind speeds

Factor 6: Al smelter/incinerator/vegetation burning, characterized by K and Cl

Factor 1 and Factor 2 elemental loadings suggest sources in each that co-vary and thus cannot be distinguished from one another This co-variation of sources within a factor suggests either variations in concentrations controlled by a common source or variations controlled by transport (sources from outside the study area) Factor 1 is unique in that soil-related elements and regional sources (tillage and regional sulfur) co-vary but it is puzzling why such a factor is found only for Granite City The proximity of an aluminum smelter with Al and S emissions, in combination with soil sources, may explain Factor 1 An Al smelter is also suggested in Factor 6 In addition to Al and S, emissions from Al smelters include substantial amounts of Cl, K and Na (Hopke, 1985), but vegetation burning or incinerators also may produce airborne K and Cl Factor 2 suggests a number of anthropogenic sources related to industry and urban areas in general: oil burning, motor vehicle, and smelter emissions Factor 3 suggests a more specific source, attributed to iron and steel-related emissions The limestone source (Factor 5) shows no contamination of toxic and/or industrially related elements and thus indicates a Ca-enriched emission source (e g parking lot) likely near the sampler One factor (Factor 4) remains unexplained

Factor analysis statistics, shown in Figure 32, suggest that for Granite City the coarse component of PM-10 is influenced by the following sources:

Factor 1: Urban/iron and steel-related dust, characterized by V, Mn, Fe, Cr, Zn, and high wind speeds

Factor 2: Smelter, characterized by Cu, As, and Pb

Factor 3: Coal-derived or smelter, characterized by Se

Factor 4: Road salt, characterized by Cl and Na

Factor 5: Industrially-derived, characterized by S

Factor 1, dominated by nonenriched soil elements (Al, Si, and Ti) in association with enriched signature elements for iron and steel (Mn, Fe, and Cr), suggests a fugitive source of contaminated urban dust The positive relationship between the associated elements and wind speed reinforces the fugitive dust hypothesis and further, it suggests a local source The contaminating source appears to be dominated by Granite City Steel and related industries, although smaller sources likely contribute as well Factor 1 accounts for most of the variability of the coarse PM-10 mass and a large percentage of the elemental variance Factor 2, dominated by Pb, Cu and As, suggests a unique fugitive dust source related to the lead smelter and recycling operations located to the south of the sampler Coal-derived or smelter (local smelters utilize Se bearing ores) emission sources are identified in Factor 3 The resolution, based on the factor loadings, does not allow for the separation of sources Similarly Factor 5, characterized by S, does not allow for the identification of a more specific source type, other than industrially-derived An additional fugitive source suggested in the factor analysis statistics is road salt (Factor 4) High concentrations of Cl for January and February lend support to a road salt source, as does the association of Na and Cl with Pb

8 1 2 3 East St Louis

Factor analysis statistics, shown in Figure 33, suggest that for East St Louis the fine component of PM-10 is influenced by the following sources:

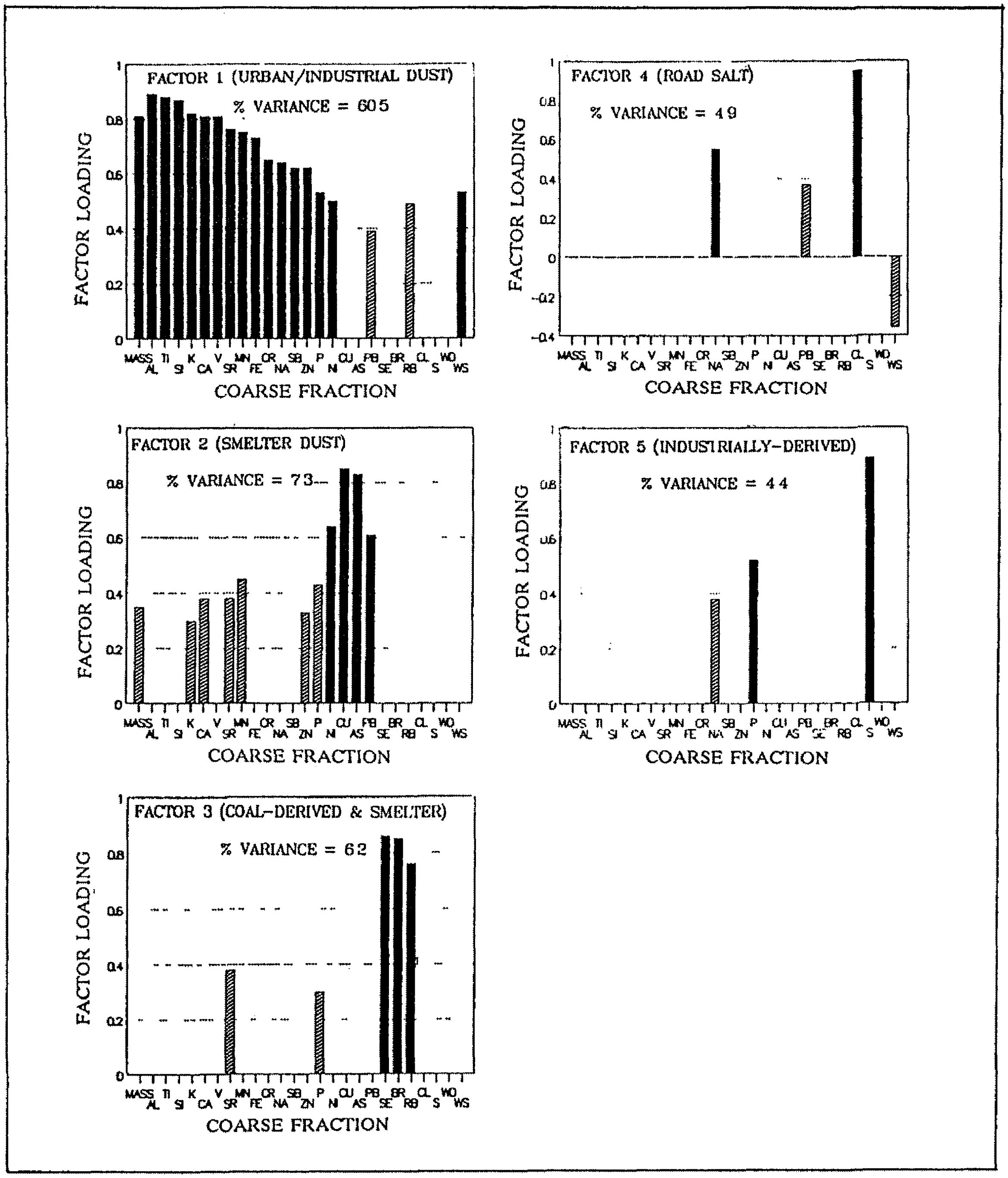


Figure 32 Coarse particle factors for Granite City

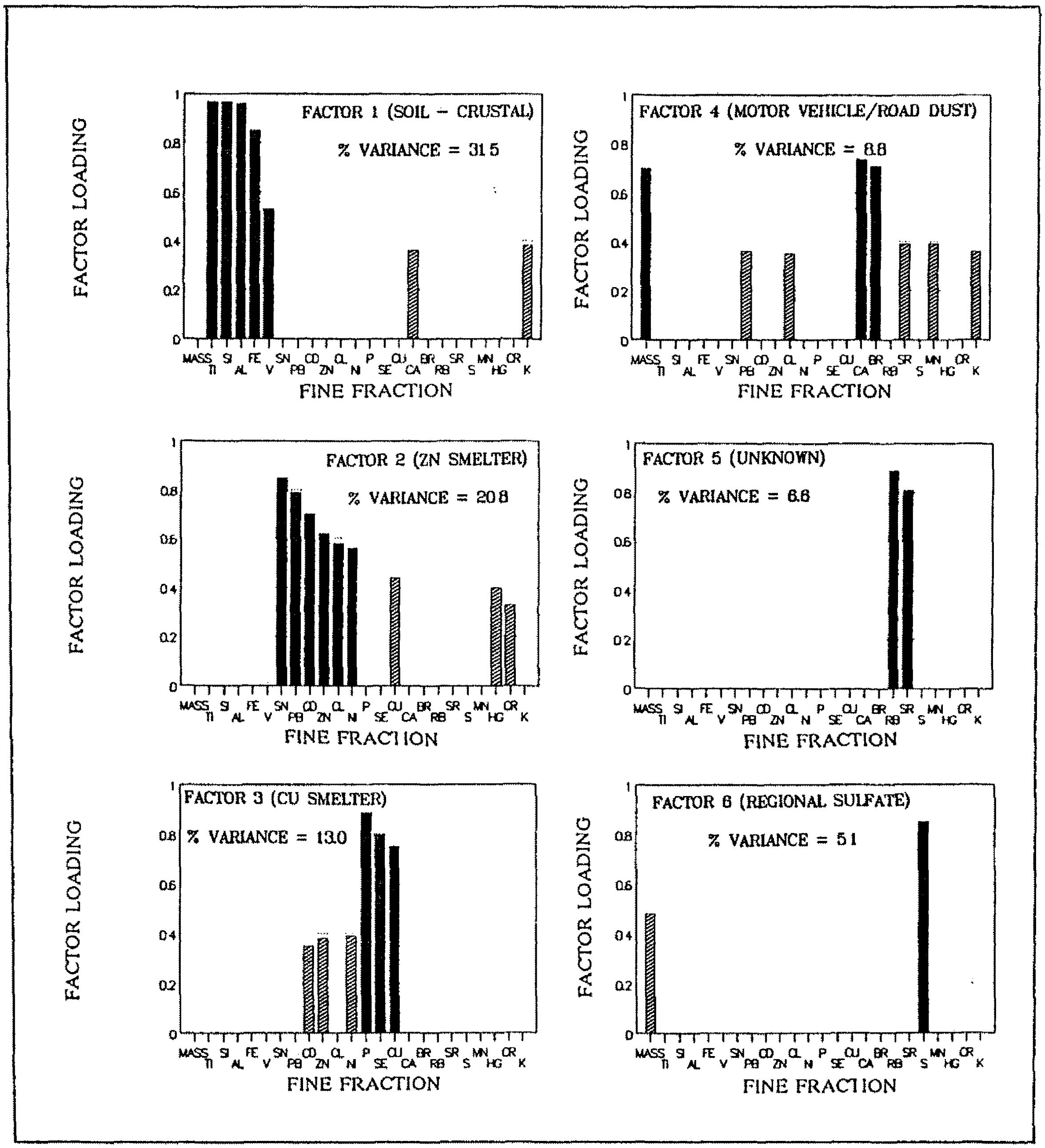


Figure 33 Fine particle factors for East St Louis/Sauget

Factor 1: Soil (crustal), characterized by Al, Si, and Ti

Factor 2: Zn smelter, characterized by Zn, Cd, Pb

Factor 3: Cu smelter, characterized by Cu

Factor 4: Motor vehicle emissions characterized by Br and Pb
Road dust, characterized by Ca

Factor 5: Unknown, characterized by Rb and Sr

Factor 6: Regional Sulfur, characterized by S

Factor 1, characterized by Al, Si and Ti, suggests an uncontaminated soil source which, unlike Granite City, is separate from that of regional sulfur (Factor 6) The influences of the Zn and Cu smelters within the study area are distinguished from one another The overlap of Cu, Zn, Ni, and Cd factor loadings between Factors 2 and 3 attest to a smelter source type The dominance of Zn in Factor 2 suggests a Zn smelter source while the dominance of Cu in factor 3 suggests a Cu smelter source A motor vehicle exhaust / road dust source is suggested for Factor 4 The East St Louis sampler was located on a roadway median, and it is not surprising that road dust accounts for most of the variability in PM-10 fine mass, surpassing that of regional sulfur which traditionally dominates

The large number of samples collected in East St Louis allowed for separate factor analysis runs based on wind direction (northeast, southeast, southwest and northwest) The sources above are reidentified but additional sources include: oil burning (southwest and northwest winds, characterized by V and Ni); iron and steel (northeast winds, characterized by Fe and Mn); incinerator (northwest winds, characterized by Zn, K, and Pb); and a Ti source (northwest winds, characterized by Ti) This last source is somewhat puzzling Traditionally Ti is associated with Si and Al as representative of soil (crustal) sources and this association has, with this one exception, carried through in our research Dzubay (1980) has identified the source of Ti as a paint pigment factory in St Louis but this factory has been closed since 1979 The toxic elements are associated with five of the identified sources: Zn smelter; Cu smelter; residual oil; incineration; and iron and steel mill emission sources

Factor analysis statistics, shown in Figure 34, suggest that for East St Louis the coarse component of PM-10 is influenced by the following sources:

Factor 1: Soil/road dust, characterized by Al, Si, Ti, Fe, Mn, and Cr

Factor 2: Steel industry dust, characterized by Fe, Cr, and Mn
Coal-derived and/or smelter, characterized by Se

Factor 3: Zn smelter, characterized by Zn, Cd, and Pb

Factor 4: Cu smelter, characterized by Cu

Both Factor 1 and Factor 2 include enriched metallic elements Linkage with soil related elements in Factor 1 suggests a contamination of indigenous urban dust This factor may represent a road dust source with metallic elements contributed by roadside debris or fallout Factor 2 loadings, on the other hand, do not include soil related elements (Al, Si and Ti) suggesting a second metallic source The association of Se and S with the metallic elements suggests an industrial source such as Granite City Steel or unidentified industrial sources within the city of St Louis As with fine PM-10, both the Zn and Cu smelters are identified from other sources and are distinguished from one another

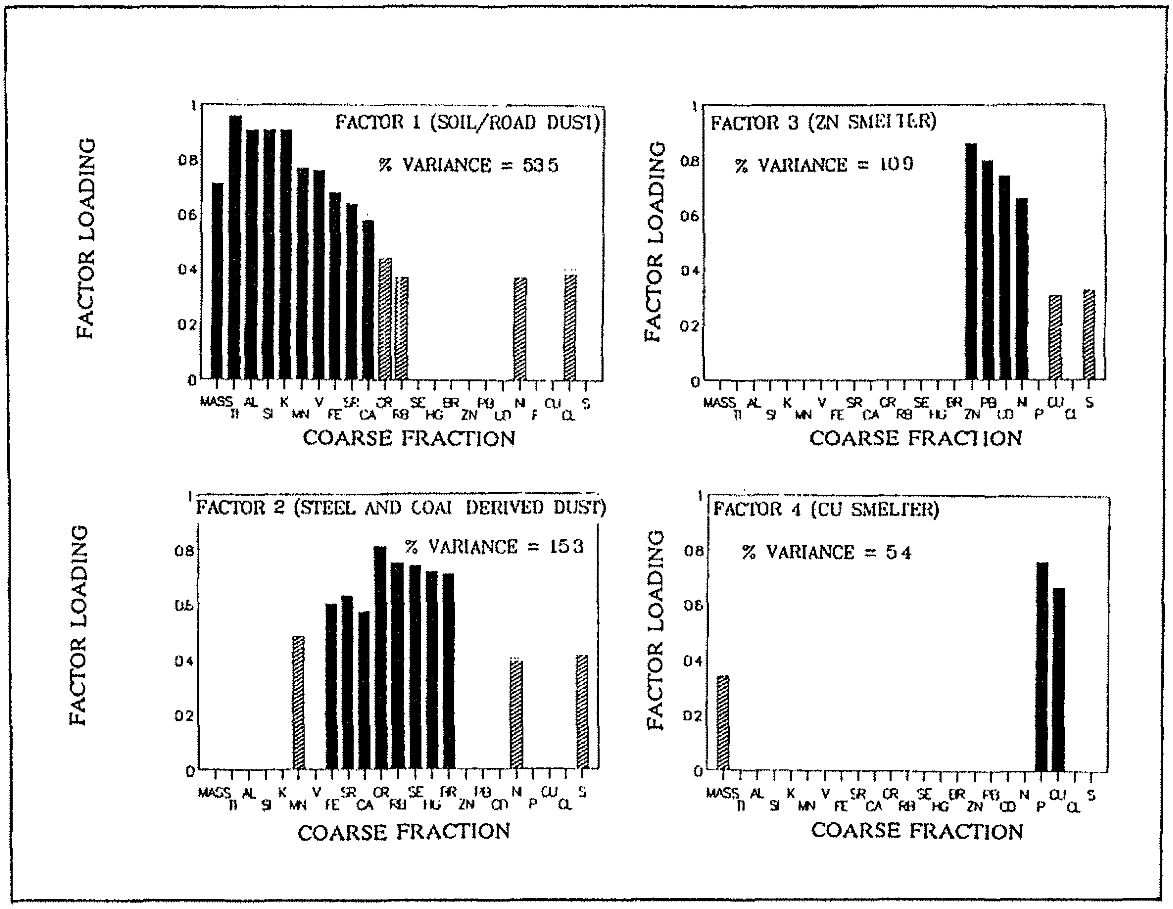


Figure 34 Coarse particle factors for East St Louis/Sauget

Separate factor analyses based on wind direction were made for the coarse PM-10 The sources above were reidentified but additional sources include: soil (northeast winds, characterized by Al and Si); iron and steel mills (northeast winds, characterized by Mn, Cu, Fe, and Zn); an unidentified industrial ferrous metal source (southwest, characterized by Fe, Mn, and Se); Pb smelter and/or Pb recycling (northeast, characterized by Pb); and sulfur (southwest winds, characterized by S) The toxic elements are associated with five of the identified sources: road dust; iron and steel mills and ferrous metal sources from St Louis; Cu smelter; Zn smelter; and Pb smelter/recycling emission sources

A summary table of emission sources is presented in Table 15

Table 15. Summary table of emission sources

Identified Sources	Southeast Chicago		Granite City		East St Louis	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
Soil (crustal)	X	X	X		X	
Iron and Steel (Stack)	X		X		X	
Iron and Steel (Dust)	X	X		X		X
Oil Burning	X		X		X	
Coal burning and dust	X	X		X		
Cu Smelter			X	X	X	X
Zn Smelter			X	X	X	X
Pb Smelter			X	X		
Al smelter			X			
Vehicle Emissions	X		X		X	
Urban/Road Dust		X	X	X	X	X
Sulfate	X		X		X	
Road Salt	X			X		

8 2 Chemical Mass Balance Model

The final output in our receptor modeling approach is the source apportionment of the toxic trace elements Source profiles were developed for the identified sources and toxic air pollutant apportionment was determined from chemical mass balance (CMB) statistics (Axetell and Watson, 1987)

The Chemical Mass Balance (CMB) model, using a calculation 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 element Source contribution estimates (by element) are calculated for the period represented by the ambient data The CMB model generates two statistics used to evaluate the "fit" between the model and the data The first, r^2, should be at least 0 8 and as close to one as possible The second statistic, X^2 (Chi squared), should be less than four and as close to one as possible The model also predicts the total airborne mass resulting from the modeled emission sources The model should generally predict a mass within 20% of the measured value The degrees of freedom (D F) are needed to evaluate the X^2 statistic

Normally, CMB is carried out on single filters This approach has the advantage that the number of sources that need to be considered are minimized If the wind direction is constant during the sampling period, only upwind sources affect the sampling site The major disadvantage is that a single filter represents only the time period sampled, not average conditions In order to reflect average conditions, CMB would have to be done on a very large number of filters representing all meteorological conditions in proportion to their actual occurrence throughout the year Even then, some filters representing calm or variable wind conditions with high airborne trace element concentrations would not be represented In addition, CMB analysis of single filters can easily be distorted by analytical or weighing errors

Our approach is to carry out CMB on the average results reported earlier (Table 9, p 20) We have already shown these to reflect average conditions at the sites, and analytical or weighing errors in a few individual filters will not be as significant when averaged into a large data base Although all sources impacting on the sites need to be considered, we have already narrowed the list considerably using wind trajectory analysis (pp 26-27, 39, 45-61) and by factor analysis (pp 62-75) As a check on the average results, CMB was also run on typical filters representing high impact from major pollution sources at the various sites

To carry out CMB analysis, source profiles are selected from a data base that has been compiled from the literature and from direct measurements The selection of sources is based on the emissions inventories, wind trajectory analysis of ambient measurements and on factor analysis results Combinations of these sources are then analyzed until a statistically reasonable fit is obtained that reflects known major sources The distribution of toxic elements among the source categories can then be calculated Generally, all detectable elements were used as fitting species in CMB analysis In a few cases, however, particular elements were deleted because they were not included in available source profiles or were below detection limits in the ambient data There are many uncertainties in CMB analysis so these results should be regarded as only an approximation of the actual distribution of toxic elements among sources

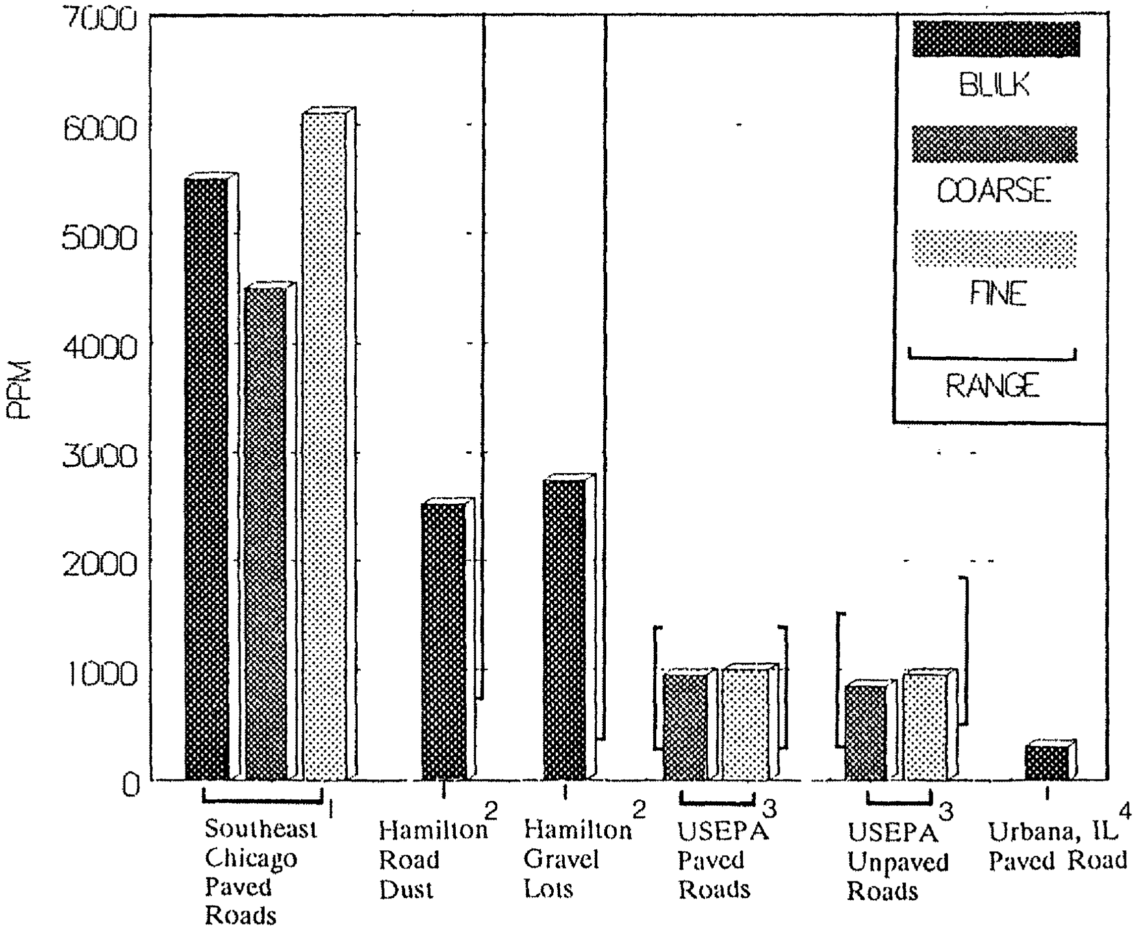
Those sources identified in previous sections of this report were used for the model runs The chemical signatures for emission sources were obtained from the scientific literature and from data collected in this work They are listed in Table 16 With the exception of the "urban/steel dust" source signatures for Southeast Chicago and several fugitive dust profiles from Granite City, the emission source signatures used in the CMB model were not sampled from the study areas Sources are often site specific and thus source apportionment numbers based on generic source profiles should be viewed with caution In addition, the source profiles used varied between specific batch processes to overall industrial composites which may or may not have been best suited for the identified source

Table 16. **CMB source profiles**[a]

Profile	Source
Crustal Dust (T41319)	USEPA, 1984
Steel Blast Furnace (T28302)	"
Coal Dust (T21204)	"
Coal Burning (T11201)	"
Coke Dust (T21203)	"
Copper Secondary Smelter (T29203)	"
Lead Slag Dust (T21501)	"
Incinerator (T17106)	"
Oil Burning (T11501)	"
Motor Vehicle Exhaust (T33003)[b]	"
Steel Composite Emissions	Scheff et al, 1984
Urban/Steel Dust (Southeast Chicago)	Vermette et al, 1988
Steel Slag Dust	"
Zinc Smelter	Hopke, 1985
Aluminum Secondary Smelter	"
Power Plant	"
Lead Secondary Smelter	"
Fugitive Dust (Granite City)	Vermette and Williams, 1989

[a] Complete profiles are listed in Appendix C
[b] Pb and Br modified to reflect 1987 values (Chang et al, 1988)

A number of sources identified in the three urban areas studied were labeled as fugitive dust Fugitive source profiles can be very site specific Under contract with the Illinois Department of Energy and Natural Resources (IDENR) and Illinois Environmental Protection Agency (IEPA) dust samples were collected from roads within the Chicago and Granite City study areas Analytical results from these samples were used in this report as an urban fugitive dust profile (urban/steel dust) The importance of site specific fugitive source profiles, especially in proximity to dust laden industrial sources (e g steel mills), is demonstrated for Mn in Figure 35 It is apparent that use of paved and unpaved road dust profiles provided by the United States Environmental Protection Agency (USEPA) 1984 Source Library could not adequately account for the Mn concentrations



[1] This Study

[2] Vermette et al, 1987

[3] U S EPA Source Library, 1984

[4] Hopke et al, 1980

Figure 35 Manganese concentrations in urban dust

The average percent contribution of identified sources to the toxic elements are presented for Southeast Chicago, Granite City and East St Louis (Tables 17 through 19) The results are reported as a percent of the calculated total source contribution Model statistics generally show good general agreement between measured and calculated elemental concentrations Sources identified in the model runs that have no toxic elements (e g road salt and sulfate) are not listed The "goodness of model fit" for each of the toxic elements is shown as a ratio between calculated and measured average ambient concentrations Generally, good agreement is shown for V, Cr, Mn, Ni, Cu, Zn, and Pb while As, Se, Cd and Sn show a poorer fit The poorer fit is due both to ambient concentrations and/or source concentrations at or near detection limits and also from inaccuracies in the generic source profiles used

In southeast Chicago (Table 18), it is apparent that most of the Cr, Mn, Cu, and As on fine particles comes from steel-related stack and fugitive sources Coal burning is important for Se The attribution of most of the Zn and Pb in fine particles to an incinerator source is probably inaccurate We know from wind trajectory analysis (Table 11, p 26) and from the coarse particle CMB, that the steel mill area coarse particle Cr, Mn, Cu, and Ni are due primarily to steel-related fugitive emissions Wind trajectory analysis also shows that steel-related emissions are also an important source of Zn and Pb This is not reflected in available source profiles for steel-related emissions and leads to unreliable model estimates for these elements Total mass tends to be underpredicted in fine particles compared to the individual elements This probably indicates that the source data for carbon are inaccurate

Average CMB results for Granite City shown in Table 18, indicate that the toxic elements in fine particles originate from a wide variety of sources In order to get a good fit, additional sulfur as sulfate and Fe as Fe_2O_3 had to be added (this was also true in Chicago) More of these two elements is present in Granite City fine particles than can be explained by available source profiles Steel-related stack and fugitive emissions account for most of the Cr and Mn Incinerator emissions are responsible for the majority of the Zn Smelter emissions from the East St Louis area seem to contribute most of the Cd and Cu This is somewhat surprising because these sources are about 15 km away However, Granite City is downwind from these smelters during SW wind flow so they might be expected to have an impact on average air quality Coal burning produces most of the Se and auto exhaust is the source of fine Pb in Granite City The only element poorly predicted here is As The reason is that many of our source profiles did not include As Total mass was under predicted in this model We have found large amounts of carbon in many samples of ambient air and resuspended dust taken from Granite City (Vermette and Williams, 1989) This high carbon level is not reflected in many of the generic profiles used Table 18 also shows the sources of toxic elements in coarse particles in Granite City Steel-related stack and fugitive emissions were responsible for most of the V, Cr, Mn, and Zn Resuspended urban dust contaminated by past fallout from the local lead smelter (not operating during this study) was the primary contributor of coarse Pb Finally, power plant emissions seem to be an important source of Cu on coarse particles

In East St Louis (Table 19), toxic elements were also attributed to a wide variety of sources No excess sulfate or iron was needed to get good CMB solutions, which indicates this problem may be related to steel mills in Chicago and Granite City Long-range transport of steel related emissions was responsible for most of the Cr and Mn Smelters cause most of the airborne Cu, Zn, and Cd Coal burning is the most important source of Se Finally, auto emissions are responsible for most of the Pb The relatively poor model prediction for Cd could be because a major source of this element has not been identified However, the close association of Cd and Zn in the rest of this work makes it more likely that the literature value for Cd in Zn smelter emissions is much lower than the true value for East St Louis Likewise, Pb in fine particles, although well-predicted by CMB, is not attributed to smelter emissions in contrast to wind trajectory analysis (Table 12, p 27) In addition, Br is poorly predicted by the model indicating that motor vehicles are not the only source of fine Pb

Table 17. Southeast Chicago average source contributions to toxic trace elements

Fine Fraction

R^2 = 0.96
χ^2 = 4.20

D.F. = 12
Predicted Mass = 61.5%

Element	Calculated / Measured	Coke Dust	Steel (Stack and Fugitive)	Incinerator Mass	Regional Background & Sulfate	Coal Burning
V	0.42	23.1%	26.7%	0.0%	28.6%	22.1%
Cr	0.94	5.6%	78.8%	4.0%	7.1%	5.4%
Mn	0.59	0.0%	92.5%	0.8%	6.3%	0.0%
Ni	0.96	0.6%	10.8%	12.1%	70.6%	6.7%
Cu	0.86	69.8%	2.9%	14.8%	11.4%	1.2%
Zn	0.98	4.2%	2.5%	85.9%	6.3%	0.2%
As	1.02	36.1%	0.0%	0.0%	46.8%	19.0%
Se	0.74	0.0%	0.0%	1.7%	37.3%	61.5%
Cd	1.41	17.7%	0.0%	61.8%	22.2%	0.9%
Sn	1.29	0.3%	0.0%	99.7%	0.0%	-
Pb	0.94	6.5%	3.8%	89.0%	0.1%	-

Coarse Fraction

R^2 = 0.98
χ^2 = 2.74

D.F. = 10
Predicted mass = 117%

Element	Calculated / Measured	Urban[a] Dust	Blast Furnace	Steel[b]	Motor Vehicle
V	0.71	63.8%	30.0%	6.1%	0.0%
Cr	1.03	35.7%	42.9%	21.3%	0.0%
Mn	0.85	71.3%	2.1%	26.5%	0.0%
Ni	1.11	55.2%	38.4%	6.6%	0.1%
Cu	1.04	43.6%	20.5%	35.1%	0.3%
Zn	1.00	93.3%	0.0%	6.6%	0.1%
Pb	0.79	59.9%	5.4%	12.9%	22.1%

[a] Road dust contaminated by industrial sources (primarily steel and coke

[b] Steel emission composite (blast furnace, coal burning, etc.)

Table 18. **Granite City average source contributions to toxic elements**

Fine Fraction

$R^2 = 0.97$
$\chi^2 = 3.55$

D.F. = 11
Predicted Mass = 65.5%

Element	Calculated/Measured	Steel Stack Emissions	Urban/Industrial Dust	Auto Exhaust	Regional Background + Sulfate	Incin-erator	Coal Burning	Smelter
V	0.56	28.9%	20.9%	0.0%	17.6%	0.0%	22.8%	9.6%
Cr	1.12	47.8%	26.8%	0.0%	6.0%	2.0%	7.6%	9.5%
Mn	0.94	3.2%	56.1%	0.0%	0.0%	0.0%	1.4%	31.0%
Ni	1.24	15.3%	12.9%	1.2%	50.0%	4.8%	7.5%	10.6%
Cu	1.03	0.0%	0.0%	0.0%	3.1%	2.3%	0.0%	91.4%
Zn	1.04	15.4%	0.0%	0.0%	7.6%	61.3%	0.0%	10.5%
As	0.40	2.3%	8.5%	0.0%	28.5%	0.0%	19.3%	41.5%
Se	0.93	0.4%	0.0%	0.0%	20.9%	0.0%	56.8%	22.2%
Cd	0.89	0.7%	0.0%	0.0%	12.8%	20.9%	0.9%	62.7%
Sn	0.87	0.5%	0.0%	0.0%	13.4%	47.2%	0.0%	38.5%
Pb	0.92	0.4%	1.2%	45.2%	6.0%	37.5%	0.2%	9.0%

Coarse Fraction

$R^2 = 0.98$
$\chi^2 = 2.54$

D.F. = 14
Predicted Mass = 129%

Element	Calculated/Measured	Steel Stack Emissions	Urban/Industrial Dust	Lead Contaminated Urban Dust	Power Plant
V	1.37	20.7%	37.3%	26.8%	15.2%
Cr	0.81	37.3%	24.7%	14.9%	23.2%
Mn	1.01	2.1%	58.1%	37.0%	3.6%
Ni	1.30	27.5%	33.2%	0.0%	0.0%
Cu	1.07	9.1%	10.9%	13.2%	66.7%
Zn	1.00	9.1%	55.4%	14.9%	29.4%
Pb	1.01	1.4%	7.4%	75.8%	16.4%

Table 19 East St Louis average source contributions to toxic trace elements

Fine Fraction

R^2 = 0 96
χ^2 = 3 67

D F = 12
Predicted Mass = 71 8%

Element	Calculated Measured	Regional Background	Coal Burning	Steel	Zinc Smelter	Copper Smelter	Motor Vehicle Exhaust
V	0 46	54 8%	35 2%	7 0%	1 3%	0 0%	1 7%
Cr	0 96	29 7%	18 8%	43 5%	1 3%	5 8%	1 3%
Mn	1 00	31 9%	2 8%	62 6%	2 2%	0 0%	1 0%
Ni	1 15	81 7%	6 3%	1 7%	0 0%	8 4%	2 0%
Cu	0 99	2 1%	2 1%	0 1%	0 9%	95 0%	0 2%
Zn	1 03	13 8%	0 4%	0 7%	85 6%	0 2%	1 5%
Se	0 01	42 6%	57 8%	0 0%	0 0%	0 0%	0 3%
Cd	0 36	38 3%	1 5%	0 0%	52 5%	3 5%	5 0%
Pb	0 90	11 8%	0 1%	0 8%	1 8%	0 3%	84 7%

Coarse Fraction

R^2 = 0 95
χ^2 = 5 73

D F = 9
Predicted Mass = 81 5%

	Calculated Measured	Crustal Dust	Urban[a] Dust	Zinc Smelter	Copper Smelter
V	0 56	15 9%	81 1%	1 3%	0 0%
Cr	0 59	9 0%	85 9%	5 3%	0 2%
Mn	1 38	9 1%	90 1%	1 0%	0 0%
Ni	0 66	17 9%	72 2%	0 0%	10 2%
Cu	1 00	0 4%	7 5%	5 1%	87 5%
Zn	1 06	0 2%	7 5%	92 6%	0 0%
Cd	0 33	0 0%	5 2%	93 9%	8 9%
Pb	0 87	0 1%	95 4%	4 6%	0 1%

[a] Road dust contaminated by industrial sources, (smelters and steel)

The CMB analyses presented up to this point have been based on average filter results and should reflect the average impact of major sources on ambient air quality For each study area, a set of individual filters was selected to reflect conditions of high airborne trace element concentrations The filters selected had the highest concentrations of trace elements coincident with steady winds from source areas The results of CMB analysis on these filters are shown in Figures 20 through 22 In general, the major sources are the same as those identified in the average CMB analysis

Steel and urban dust account for most of the Cr and Mn in Chicago when winds are from the southeast Fugitive emissions of these elements from steel mill areas are the most important sources Lead and zinc are not well predicted, indicating the source signature data for these elements are inaccurate Mass is underpredicted in fine particles as with the average data

The individual filters chosen from Granite City represent southerly winds from the steel mill and lead smelter areas The important sources of toxic elements and general characteristics of the CMB solution are very similar to those seen in the analysis of average results

In East St Louis, high trace element levels occur when winds are from the southwest CMB analyses of individual filters taken during southwest winds are almost identical to average results The similarity between these single filter CMB's and average CMB results indicates that the sources associated with episodes of high trace element pollution play an important role in average airborne trace element concentrations in the study areas

Table 20. Southeast Chicago source contributions to toxic elements during pollution episodes

Fine Fraction

R^2 = 0 99
χ^2 = 1 87

D F = 7
Predicted Mass = 66 1%

Element	$\frac{\text{Calculated}}{\text{Measured}}$	Steel (Stack & Fugitive)	Power Plant	Coke Dust	Oil Burning
V	0 86	30 0%	1 4%	1 7%	66 4%
Cr	0 98	96 6%	0 2%	0 5%	0 4%
Mn	0 75	99 7%	0 2%	0 0%	0 0%
Cu	0 71	35 6%	1 5%	60 4%	2 1%
Zn	0 24	85 4%	0 4%	10 0%	2 4%
Pb	0 08	88 8%	0 0%	5 0%	0 0%

Coarse Fraction

R^2 = 0 96
χ^2 = 4 65

D F = 9
Predicted Mass = 84 3%

Element	$\frac{\text{Calculated}}{\text{Measured}}$	Urban/ Steel Dust	Steel (Stack & Fugitive)	Coal Dust	Oil Burning
V	0 63	31 1%	4 9%	0 0%	64 7%
Cr	1 08	79 3%	20 5%	0 0%	0 5%
Mn	1 01	87 6%	12 9%	0 0%	0 0%
Cu	1 11	45 9%	52 4%	0 0%	1 8%
Zn	1 01	92 5%	7 5%	0 0%	0 9%
Pb	0 22	68 6%	27 2%	4 1%	0 9%

Table 21. Granite City source contributions during pollution episodes

Fine Fraction

$R^2 = 0.97$
$\chi^2 = 3.97$

D.F. = 11
Predicted Mass = 67.5%

Element	Calculated Measured	Urban Dust	Steel	Regional Background & Sulfate	Power Plant	Smelters
V	0.68	2.2%	34.0%	34.3%	19.7%	4.0%
Cr	0.92	3.1%	83.7%	7.2%	1.6%	7.4%
Mn	0.96	1.8%	80.0%	5.2%	8.9%	9.0%
Ni	1.49	1.1%	12.7%	78.0%	0.9%	7.6%
Cu	1.03	0.5%	2.7%	10.1%	1.4%	85.6%
Zn	1.01	0.2%	5.0%	12.5%	0.0%	75.4%
As	0.29	0.7%	0.0%	75.2%	0.0%	22.1%
Se	0.54	0.0%	0.0%	69.4%	0.4%	29.3%
Cd	1.03	0.0%	0.0%	33.4%	0.0%	69.5%
Sn	0.74	0.0%	0.0%	56.2%	0.5%	43.6%
Pb	0.72	1.0%	21.9%	39.4%	0.1%	37.6%

Coarse Fraction

$R^2 = 0.98$
$\chi^2 = 3.91$

D.F. = 10
Predicted Mass = 116%

Element	Calculated Predicted	Steel Stack Emissions	Urban/ Industrial Dust	Lead Contaminated Urban Dust
V	1.78	22.3%	71.9%	5.7%
Cr	.93	43.2%	2.7%	54.1%
Mn	.96	15.4%	81.5%	4.1%
Ni	.89	27.9%	69.3%	2.7%
Cu	1.00	46.8%	47.8%	5.4%
Zn	1.01	3.2%	94.8%	2.0%
Pb	1.00	15.1%	35.6%	49.3%

Table 22. East St. Louis source contributions to toxic elements during pollution episodes

Fine Fraction

R^2 = 0 96
χ^2 = 1 62

D F = 10
Predicted Mass = 84 3%

Element	Calculated / Measured	Regional Background	Steel	Zinc Smelter	Copper Smelter	Motor Vehicle
V	0 87	77 6%	13 9%	8 0%	0 0%	0 0%
Cr	1 49	24 3%	50 9%	20 1%	5 0%	0 0%
Mn	0 93	24 3%	68 2%	7 2%	0 0%	0 0%
Cu	1 00	0 5%	0 0%	1 0%	97 7%	1 2%
Zn	1 04	3 5%	0 3%	90 5%	0 0%	5 2%
Se	0 79	10 0%	67 4%	0 0%	0 0%	0 0%
Cd	0 18	13 0%	0 0%	80 0%	4 4%	0 0%
Pb	1 02	3 5%	2 0%	2 2%	0 4%	95 9%

Coarse Fraction

R^2 = 0 96
χ^2 = 4 47

D F = 8
Predicted Mass = 69 4%

Element	Calculated / Measured	Urban Dust	Zinc Smelter	Copper Smelter	Motor Vehicle
Cr	0 95	89 1%	11 3%	0 3%	0 0%
Mn	1 09	96 3%	3 7%	0 0%	0 0%
Cu	1 01	3 6%	7 4%	89 6%	0 3%
Zn	0 91	1 9%	97 5%	0 0%	0 2%
Cd	0 24	0 0%	95 0%	4 5%	0 0%
Pb	1 00	58 8%	16 5%	0 4%	24 5%

CHAPTER 9. CONCLUSIONS AND RECOMMENDATIONS

Source identification of toxic trace elements in a complex urban airshed requires the use of a variety of sampling and analysis techniques The approach taken here has been to compile a data base for 17 trace elements that includes wind direction information These data coupled with particle size experiments and streaker sampling are used to identify important sources Added information from enrichment factors, factor analysis and existing emissions inventories is used to complete source identification Once the sources are known, chemical mass balance analysis apportions the airborne pollutants to the various sources

The toxic trace element data base developed for this report contains information on the ambient concentrations of 17 toxic elements at three urban study areas in Illinois over a three year period Over 600 individual filters were analyzed Most of the time, concentrations of these elements in ambient air approach regional background levels However, there are periodic episodes during which concentrations of many airborne elements reach much higher levels These episodes generally occur when the wind blows from the direction of a major point source during most of the sampling period Episodes can also occur during periods of low wind speed when mixing is reduced Since the urban sampling sites used in this study are often downwind of large point sources, such sources have a significant impact on the average air quality

Even though the urban study areas are strongly affected by industrial emissions, the average concentrations of most elements are similar to those measured in other urban areas around the country Two exceptions to this general observation were found The East St Louis site is often downwind of a large zinc smelter and the average ambient concentrations of cadmium are very high in this area Cadmium is a carcinogen, and even typical ambient urban concentrations pose a significant health risk Airborne cadmium concentrations ten times greater than typical levels, the situation in East St Louis, are a cause for concern The other exceptions are the average chromium and manganese concentrations in southeast Chicago Steel mills are important sources of chromium and manganese, and the presence of several large plants in the area of the sampling site results in elevated levels of airborne chromium and manganese The levels of chromium found in southeast Chicago are only slightly higher than those found at other urban locations; however, chromium is also a carcinogen, and even typical ambient concentrations can pose some health risk Very little is known about the health effects of manganese at these levels

The particle size distribution of the toxic elements gives an indication of the process that generates the particles Submicron particles are generated by high temperatures and found in stack emissions These particles normally carry a relatively large proportion of most trace elements in urban air Larger inhalable particles (10 to 4 μm) contaminated with toxic elements are generated by mechanical processes including the resuspension of urban soil and dust These "fugitive" emissions carry a large amount of certain toxic elements when the wind passes over major industrial sources Since the levels of airborne toxic elements in resuspended dust may not always reflect current industrial activity or stack emissions, the importance of fugitive emissions may not be apparent from current emissions inventories

Source identifications based on streaker data and the chemical composition of airborne particles indicate that steel mills and smelters are major sources of trace elements in Chicago and East St Louis, respectively

For the toxic elements that may have a vapor phase - mercury, arsenic, and selenium - the vapor phase predominates only for mercury Mercury measured only on particles, therefore, does not give a reliable estimate of total airborne mercury concentration For selenium, most of the element is carried by particles, but there is a significant vapor phase component in the urban environment In contrast, no vapor phase Se was detected in regional background samples On the basis of a limited number of samples, arsenic does not appear to have a significant vapor phase component at these sampling locations

Receptor modeling confirms that in Chicago airborne Mn and Cr come from steel-related industrial process and fugitive sources The other toxic trace elements that can be apportioned (V, Ni, Cu, Zu, As, Se, Cd, Sn, and Pb) come from a variety of sources including incinerators, oil and coal combustion, suspended soil and vehicle emissions Steel-related emissions are also major sources of Mn and Cr in Granite City Zn and Cd are related to smelter activities, and most of the excess airborne Pb found at this site comes from fugitive emissions of contaminated urban dust In East St Louis, the smelters are the primary sources of Zn, Cd, and Cu Steel emissions are the major source of Mn and Cr Pb comes primarily from auto emissions at this site; however the smelters are probably also important Pb sources although this could not be verified by the CMB model

In conclusion, the sources of the airborne toxic trace elements examined in this project are the major industries in the study areas Wind trajectory analysis and receptor modeling of their emissions agree well with observed airborne concentrations of trace elements The health risk posed by elevated levels of Cd and other trace element carcinogens has been documented and indicates that further control of these emissions is necessary Such control cannot be achieved under existing air quality regulations that only cover the total mass of airborne particles To adequately control emissions of toxic elements, individual fugitive and process sources need to be identified so that appropriate control measures can be taken This report is a first step toward that goal

REFERENCES CITED

Anon , 1983 Cancer Facts and Figures, 1982 American Cancer Society, Washington, D C

Appel, B R , Y Tokima, E M Hoffer, 1984 "Efficiency of Filter Sampling for Arsenic in the Atmosphere Atmospheric Environment 18: 219-222

Axetell, K and J G Watson, 1987 "Receptor Model Technical Series, Volume III (Revised): CMB User's Manual (Version 6 0) " EPA-450/4-83-01R Office of Air Quality Planning and Standards U S EPA , Research Triangle Park, NC

Boeckx, R L , 1986 "Lead Poisoning in Children " Analytical Chemistry 58:274A-286A

Braman, R S , 1983 "Chemical Speciation " In: Natusch, D F S and P K Hopke, Eds , Analytical Aspects of Environmental Chemistry John Wiley and Sons, New York, NY

Brodzinsky, R and H B Singh, 1983 "Volatile organic chemicals in the atmosphere: An assessment of available data " Report EPA-600/3-83-027A, Contract No 68-02-3452 SRI International, Menlo Park, CA 94025, Environmental Sciences Research Laboratory, Office of Research and Development, U S EPA, Research Triangle Park, NC 27711

Cannon, J A , 1986 "The Regulation of Toxic Air Pollutants: A Critical Review " Journal of the Air Pollution Control Association, 36(5):562-573

Chang, S N , P K Hopke, G E Gordon and S W Rheingrover, 1988 "Target-Transformation Factor Analysis of Airborne Particulate Samples Selected by Wind-Trajectory Analysis " Aerosol Science and Technology, 8: 63-80

Conley, F W and F D Buckman, 1987 Verified Performance Improvements for the Sierra Model 245 Automatic Dichotomous Air Sampler Presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, June 21-26

Cooper, J A and J G Watson, 1979 "Portland Aerosol Characterization Study - Final Report " Oregon State Department of Environmental Quality

Courtney, W J , S Rheingrover, J Pilotte, H C Kaufmann, T A Cahill, and J W Nelson, 1978 "Continuous Observation of Particulates During the General Motors Sulfate Dispersion Experiment " Journal of the Air Pollution Control Association 28:224-228

D F Gatz, 1978 "Identification of Aerosol Sources in the St Louis Area Using Factor Analysis " Journal of Applied Meteorology, 17: 600-608

Dzubay, T G , R K Stevens, G E Gordon, I Olmez, and A E Sheffield, 1988 " A Composite Receptor Method Applied to Philadelphia Aerosol " Environmental Science and Technology, 22: 46-52

Dzubay, T B , 1980 "Chemical Element Method Applied to Dichotomous Sampler Data " Annals of the New York Academy of Sciences, 338 :126-144

Elias, R W , 1986 The Relative contribution of Lead from Anthropogenic Sources to the Total Human Lead Exposure in the United States EPA/600/D-86/184 Office of Research and Development, Environmental Assessment Office U S Environmental Protection Agency Research Triangle Park, NC 27711

Evans, E G , G F Evans, D B Ray, R Risher, V A Wheeler, S L Cummings, J E Frazer, S L Harper, T A Hinners, W A Loseke, L J Pranger, and J C Puzak, 1984 "Air Quality Data for Metals 1977 through 1979 from the National Air Surveillance Network " Report EPA-600/S4-83-053 U S Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711

Gaarenstroom, P D , S P Perone, and J L Mayers, 1977 "Application of Pattern Recognition and Factor Analysis for Characterization of Atmospheric Particulate Composition in Southwest Desert Atmosphere " Environmental Science Technology, 11 795-800

Galloway, J N , J D Thornton, S A Norton, H L Volchok, and R A N McLean, 1982 "Trace Metals in Atmospheric Deposition: A Review and Assessment " Atmospheric Environment, 16:1677-1700

Gatz, D F and C W Sweet, 1985: Atmospheric Research and Monitoring Study of Hazardous Substances Report HWRIC RR007 Hazardous Waste Research and Information Center, Illinois Department of Energy and Natural Resources, Savoy, IL, 61874

Gatz, D F , 1975 "Relative Contribution of Different Sources of Urban Aerosols: Application of a New Estimation Method to Multiple Sites in Chicago " Atmospheric Environment, 9: 1-18

Gordon, G E , 1988 "Critical Review: Receptor Models " Environmental Science and Technology, 22: 1132-1142

Hopke, P K , R E Lamb, and D F S Natusch, 1980 "Multielemental Characterization of Urban Roadway Dust " Environmental Science Technology, 14 164-172

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

Illinois Environmental Protection Agency, 1987 "Illinois Annual Air Quality Report " IEPA/APC/87-008, Division of Air Pollution Monitoring IEPA, Springfield, IL 62794

Illinois Environmental Protection Agency, 1986 "Illinois Annual Air Quality Report " IEPA/APC/86-013, Division of Air Pollution Monitoring IEPA, Springfield, IL 62794

Illinois Environmental Protection Agency (IEPA), 1983 "Study of Lead Pollution in Granite City, Madison and Venice, Illinois " Springfield, Illinois 62706

Johansson, T B , R E Van Grieken, W J Nelson, and J W Winchester, 1975 Elemental Trace Analysis of Small Samples by Proton-Induced X-ray Emission Analytical Chemistry 47:855-860

Kolaz, D J , T A Sweitzer, and D L Bomke, 1986 "Illinois PM/10 Measurements: Mass and Chemical Composition " Paper 86-57 4, 79th Annual Meeting, Air Pollution Control Association, June 23-27, Minneapolis, MN

Lioy, P S , M P Zelenka, M Cheng, N M Reiss, and W E Wilson, 1989 "The Effect of Sample Duration on the Ability to Resolve Source Type Using Factor Analysis " Atmospheric Environment, 23: 239-254

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

Lyons, W A , 1970 "Mesoscale Transport of Pollutants in the Chicago Area as Affected by Land and Lake Breezes " Presented at the 2nd International Clean Air Congress of the International Union of the Air Pollution Prevention Association, Dec 6-11, 19 Washington, D C

Milford, J B and C I Davidson, 1985 "The Sizes of Particulate Trace Elements in the Atmosphere: A Review" Journal of the Air Pollution Control Association 35(12):1249-1250

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

Mosher, B W and R A Duce, 1983 "Vapor Phase and Particulate Selenium in the Marine Atmosphere" Journal of Geophysical Research, 88:6761-6768

National Academy of Sciences, 1976 "Medical and Biological Effects of Environmental Pollutants: Selenium" Nacational Academy of Sciences, Washington, D C

National Academy of Sciences, 1975 "Medical and Biological Effects of Environmental Pollutants: Nickel" National Academy of Sciences, Washington, D C

National Academy of Sciences, 1973 "Medical and Biological Effects of Environmental Pollutants: Manganese" National Academy of Sciences, Washington, D C

National Academy of Sciences, 1974a "Medical and Biological Effects of Environmental Pollutants: Chromium" National Academy of Sciences, Washington, D C

National Academy of Sciences, 1974b "Medical and Biological Effects of Environmental Pollutants: Vanadium" National Academy of Sciences, Washington, D C

Nelson, N, 1984 "Comments on the Carcinogenicity and Mutagenicity of Metals and their Compounds" Toxicological and Environmental Chemistry 9:93-107

Pillay, K K S, C C Thomas, and J A Sandel, 1971 "Activation Analysis of Airborne Selenium as a Possible Indicator of Atmospheric Sulfur Pollutants," Environmental Science and Technology 5(1): 74-77

Richman, M B, 1986 "Review Article: Rotation of Principal Components" Journal of Climatology, 6:293-335

Rodes, C F, D M Holland, L J Purdue, and K A Rehme, 1985 A Field Comparison of PM-10 Inlets at Four Locations Journal of the Air Pollution Control Association 35 345-354

Ross, H B, 1984 "Atmospheric Selenium" Report CM-66, Dept of Meteorology, University of Stockholm, Stockholm, Sweden

Saltzman, B E, J Cholak, L J Schafer, D W Yeager, B G Merners, and J Svetlik, 1985 "Concentrations of Six Metals in the Air of Eight Cities" Environmental Science and Technology, 19: 328-333

Thomson, V E, A Jones, E Haemisegger, B Steigerwald, 1985 "The Air Toxics Problems in the United States: An Analysis of Cancer Risks Posed by Selected Air Pollutants," Journal of the Air Pollution Control Association, 35: 535-540

Scheff, P A, R A Wadden, and R J Allen, 1984 "Development and Validation of a Chemical Element Mass Balance for Chicago" Environmental Science and Technology, 18(12), 923-931

Schroeder, W R, 1982 "Sampling and Analysis of Mercury and its Compounds in the Atmosphere," Environmental Science and Technology, 16:7

Seinfeld, J H , 1986 Atmospheric Chemistry and Physics of Air Pollution John Wiley and Son, New York, NY p 23-26

Sweet, C W and D F Gatz, 1986 Atmospheric Research and Monitoring Study of Hazardous Substances: Second Annual Report Report HWRIC RR014 Hazardous Waste Research and Information Center, Illinois Department of Energy and Natural Resources, Savoy, IL 61874

Sweet, C W and D F Gatz, 1988 Atmospheric Research and Monitoring Study of Hazardous Substances: Third Annual Report HWRIC RR022 Hazardous Waste Research and Information Center, Illinois State Water Survey Division, Illinois Department of Energy and Natural Resources, Savoy, IL 61874

United States Environmental Protection Agency (U S EPA), 1984 " Receptor Model Source Composition Library " EPA 450/4-85-002, Research Triangle Park, NC 27711

Vermette, S J , C W Sweet, and S Landsberger, 1988 "Airborne Fine Particulate Matter (PM-10) in Southeast Chicago: Preliminary Report II " Illinois State Water Survey, Champaign, Illinois 61820-7495

Vermette, S J and A L Williams, 1989 "Surface Dust Elemental Profiles -- Granite City " Report to Illinois Environmental Protection Agency, Illinois State Water Survey, Champaign, IL 61820

Walsh, P R , R A Duce, and J L Fasching, 1977 "Impregnated Filter Sampling System for collection of Volatile Arsenic in the Atmosphere," Environmental Science and Technology, 11(2):163-166

Watts, S F , R Yaaqub, and T Davies, 1987 The Use of Whatman 41 Filter Papers for High Volume Aerosol Sampling Atmospheric Environment 21:2731-2732

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

Willeke, K , 1975 "Performance of the Slotted Impactor " Journal of the American Industrial Hygiene Association 2:683-691

Wolff, G T , and P E Korsog, 1985 "Estimate of the Contribution of Sources to Inhalable Particle Concentrations in Detroit " Atmospheric Environment, 19(9) 1399-1409

APPENDIX A

QUALITY ASSURANCE DATA

A Sampling

To measure sampling variation, we took a series of co-located 24-hour samples using four different dichotomous samplers X-ray fluorescence (XRF) analysis for representative urban and rural sample pairs are shown in Table A-1

Table A-1. Collocated dichotomous samples[a]

	Urban				Rural			
	Sampler A		Sampler B		Sampler C		Sampler D	
Element	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
V	021	038	018	032	053	125	058	129
Cr	142	063	135	065	055	106	044	111
Mn	329	263	261	242	164	585	168	557
Ni	094	039	077	023	022	042	024	053
Cu	16 75	2 60	15 32	2 44	055	040	065	158
Zn	4 52	3 24	4 02	2 78	769	368	777	467
Se	092	007	081	010	092	041	084	034
Pb	12 22	2 51	9 39	2 38	1 355	489	1 307	492
Cd	1 58	1 28	1 36	1 03	ND	ND	ND	ND
Sn	812	ND	722	ND	ND	ND	ND	ND

[a] Values are μg/filter

The samples generally agree within ±10 percent in cases where values are well above detection limits (at least three times higher)

In a similar experiment, individual Illinois State Water Survey (ISWS) 24-hour dichotomous samples (coarse and fine combined) were compared with two individual collocated high-volume PM-10 samples collected and analyzed by the Illinois Environmental Protection Agency (IEPA) Representative results are shown in Table A-2 Precision in this interlaboratory comparison was generally within 10-20 percent

Table A-2. Co-located PM-10 and dichotomous samples[a]

	Chicago		East St. Louis	
Element	IEPA PM-10	ISWS Dichot	IEPA PM-10	ISWS Dichot
Se	0 12	0 12	0 05	0 05
Pb	2 64	2 33	< 9	0 77
Cu	0 74	0 53	0 43	0 58
Mn	0 60	0 62	0 36	0 46
Zn	3 12	2 90	1 20	1 30
Total Mass	41 5	48 0	26 7	28 0

[a] Values are μg/filter except total mass (μg/m^3)

Finally, an experiment was done to compare filter efficiencies for the Teflon filter used in the dichotomous samplers and the Whatman 41 filters used with the high-volume cascade impactor. Co-located 24-hour samples were collected at several locations The Teflon filters were analyzed by XRF and the Whatman 41 filters by nNeutron activation analysis (NAA) The elements Se and Zn were especially significant because these are both concentrated on very fine particles that may pass through the Whatman filter paper The results from three experiments in Table A-3 show that Whatman 41 filters were at least as efficient as the Teflon filters

Table A-3. Comparison of Whatman 41 and Teflon filters[a]

	A		B		C	
Element	Whatman	Teflon	Whatman	Teflon	Whatman	Teflon
Mn	11 2	10 5	100 3	85 8	21 6	18 8
Zn	25 3	18 6	257	184	120	36
Se	2 8	1 2	7 0	6 0	3 4	3 2

[a] Values in μg/filter

B Analytical Methods

The average detection limits for the three analytical methods used in this work are listed in Table A-4

Table A-4. Average detection limits (ng)[a]

	XRF	NAA	PIXE
V	25	5	0 7
Cr	25	25	0 5
Mn	25	25	0 4
Ni	25	1500	0 3
Cu	25	10	0 4
Zn	25	10	0 3
Se	10	25	1 1
Mo	50	100	13
Ag	75	25	32
Cd	100	ND	40
Su	150	ND	61
Sb	250	20	69
Ba	500	1500	3 1
Hg	10	ND	2 0
Pb	25	ND	2 5
As	250	15	1 1

[a] Detection limit = 2 5 times standard error
ND = not detectable
Sample size = 24 m^3 for XRF and NAA
Sample size = 0 1 m^3 for PIXE

Analytical precision was determined for the XRF analyses by resubmitting previously analyzed samples to the laboratory on a "blind" basis This could not be done for NAA and PIXE analyses because the sample is destroyed during analysis Results for four typical filters are shown in Table A-5 For elements that are well above detection limits, analytical precision is generally ± 10 percent

Table A-5. 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+-11	3313+-177	3379+-180	15583+-789	15123+-766	4698+-24	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	BDL	BDL	BDL	BDL
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

National Bureau of Standards standard reference materials (SRM) were analyzed using XRF, NAA and PIXE. The results and standard deviations are presented in Tables A-6, A-7 and A-8. Accuracy is generally within ±10 percent.

Table A-6. XRF analysis of NBS standard (SRM 1832)

Element	n	Certified Values (µg/cm^2)	XRF Value (µg/cm^2)
S	4	36.7 ± 2.4	36.6 ± 2.4
V	3	4.69 ± 0.49	4.55 ± 0.50
Mn	3	4.53 ± 0.49	4.82 ± 0.56
Cu	3	2.43 ± 0.16	2.51 ± 0.16
Zn	4	5.63 ± 0.34	5.84 ± 0.34
Pb	4	16.9 ± 0.9	17.9 ± 0.9

Table A-7. NAA analysis of NBS standard coal sample (1632)

Element	n	Certified Value (ppm)[a]	NAA Value (ppm)
Se	4	1.29 ± 0.11	1.19 ± 0.07
Sb	4	(0.24)	0.32 ± 0.10
As	4	3.72 ± 0.09	3.73 ± 0.11
Cr	4	(11)	10.38 ± 0.30
Co	4	2.29 ± 0.17	2.26 ± 0.06
Mn	4	12.4 ± 1.0	13.2 ± 0.5
Mo	4	(0.9)	1.03 ± 0.13
Ni	4	6.10 ± 0.27	7.35 ± 0.12
V	4	(14)	15.8 ± 0.6
Ba	4	67.5 ± 2.1	76 ± 5

a) Values in parentheses were analyzed by NBS but not certified.

Table A-8. PIXE analysis of NBS standard (SRM 1571)

Element	n	Certified Value (ppm)	PIXE Value (ppm)
Cr	3	2.6 ± 0.3	2.57 ± 0.34
Mn	3	91 ± 4	98 ± 3
Ni	3	1.3 ± 0.2	1.9 ± 3
Cu	3	12 ± 1	14.3 ± 6
Zn	3	25 ± 3	25 ± 6
Pb	3	45 ± 3	45.6 ± 7

Finally, as part of a related project, a series of 100 teflon filters were analyzed by both XRF and NAA. Five elements were selected for comparison for which values were above detection limits with both methods in at least 40 percent of the filters. The average results and standard deviations for the filters are shown in Table A-9.

Table A-9. Comparison of XRF and NAA analytical results

Element	n	Average NAA Value (μg)	Average XRF Value (μg)	XRF/NAA	R^2
Fe	83	13 7 ± 16 4	13 1 ± 17 2	0 9 ± 26	97
Mn	88	0 83 ± 1 25	0 86 ± 1 34	1 12 ± 59	98
Cr	71	0 14 ± 14	0 15 ± 19	1 10 ± 39	91
Cu	40	39 ± 26	26 ± 26	0 68 ± 26	89
Zn	91	1 90 ± 1 89	1 78 ± 1 93	0 90 ± 25	96

For four of the elements, agreement was within 10 to 15 percent between the two methods NAA gives somewhat higher values than XRF for Cu Since Cu was not analyzed by NAA in the NBS standard (Table A-7), Cu values reported in this report are from XRF analysis

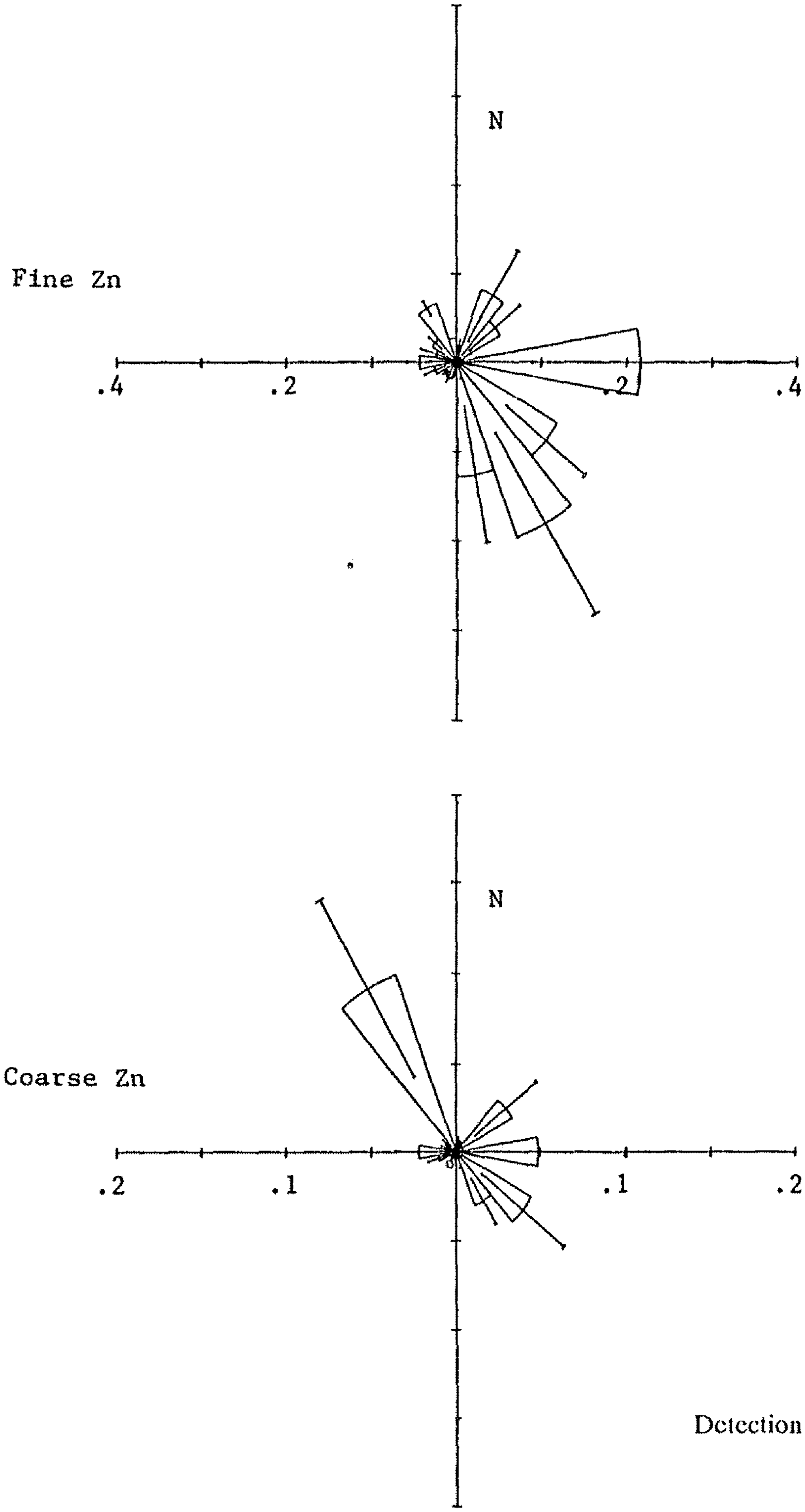
APPENDIX B

STREAKER DATA

The streaker sampler (Courtney et.al., 1978) collects airborne particles by impaction and filtration on membrane filters. The filters are continuously rotated so that the deposited particles are spread out in a "streak." Small segments of the streak, corresponding to a sampling time of one or two hours, can then be analyzed for a variety of trace elements using proton-induced x-ray emission spectroscopy (PIXE). Since the streaker sampler excludes particles above 10 μm in diameter and collects both fine (<2.5 μm) and coarse (2.5-10 μm) fractions, the results are comparable to those obtained with the dichotomous sampler.

Pollution rose plots for all streaker data collected in this project are presented in this section. In these plots, trace element concentrations are plotted against wind direction on a circular graph. The length of each bar indicates concentration in $\mu g/m^3$ and the line bisecting each concentration bar shows the standard deviation. A dashed circle indicates the detection limit. Where the detection limit is very low, the value is included on the plots. In the resultant plots, bars corresponding to high concentrations point in the direction of their sources. For elements where all values were below detection limits, no plot is given.

It should be stressed that the source identification made with these data are tentative, since streaker data only indicate the directions of major sources and represent only a one-week sample. However, this information coupled with the chemical characteristics of the emissions and source-receptor modeling can reliably identify sources. Streaker samples taken at two sites in a study area can also be used to help pinpoint an emission source by triangulation.



Detection Limit = 0 003

Figure B-1 Pollution roses for zinc - Bright School, Chicago ($\mu g/m^3$)

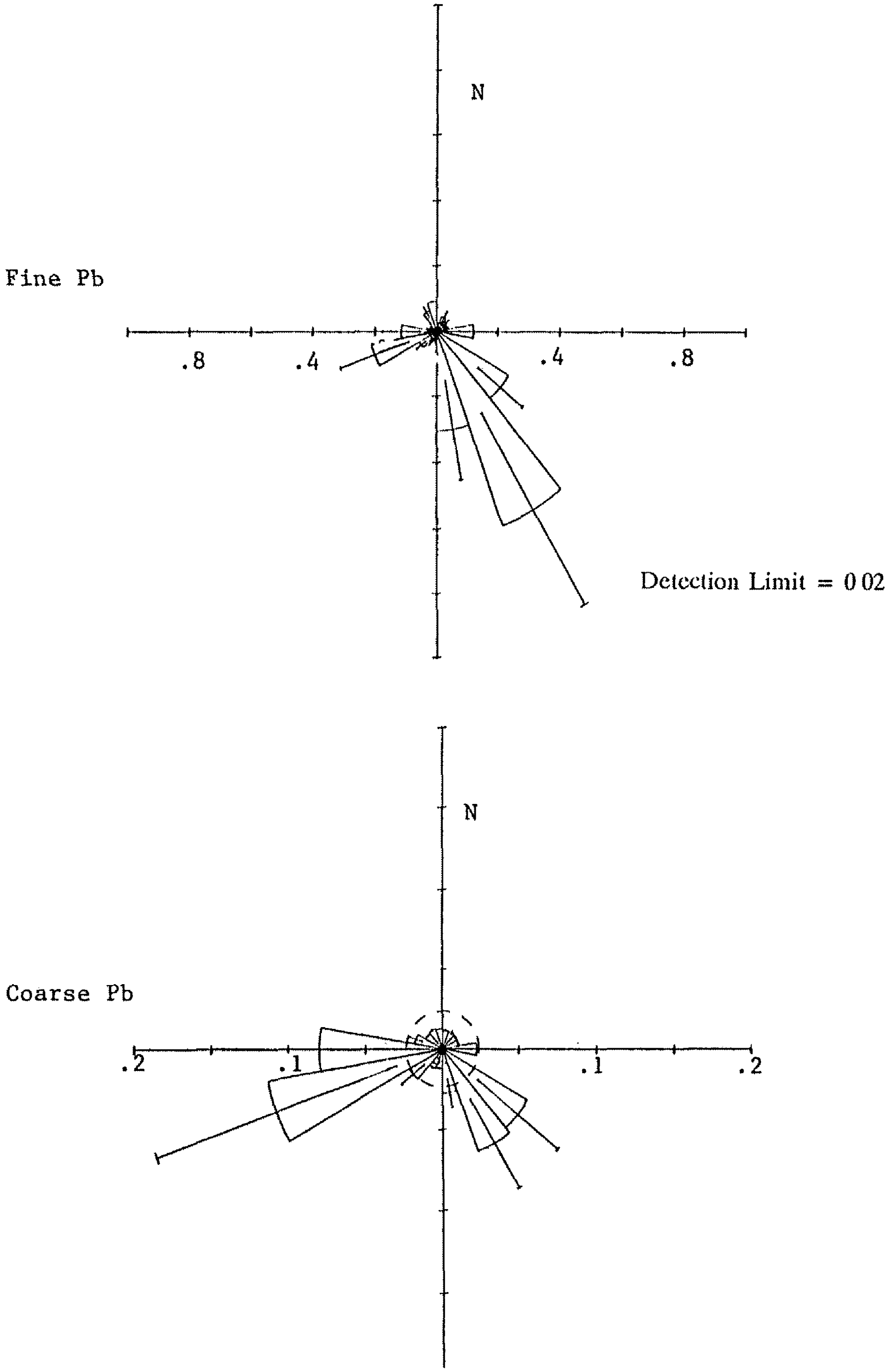
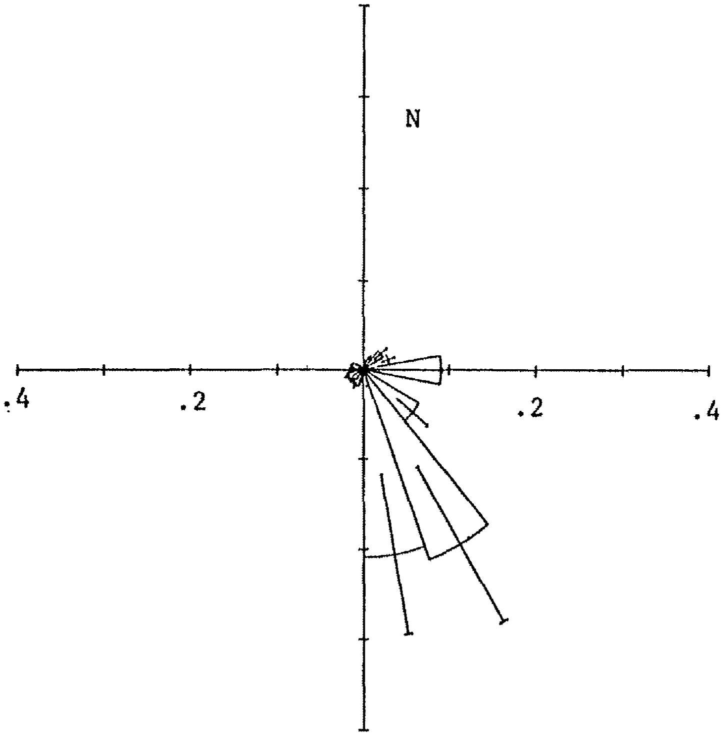
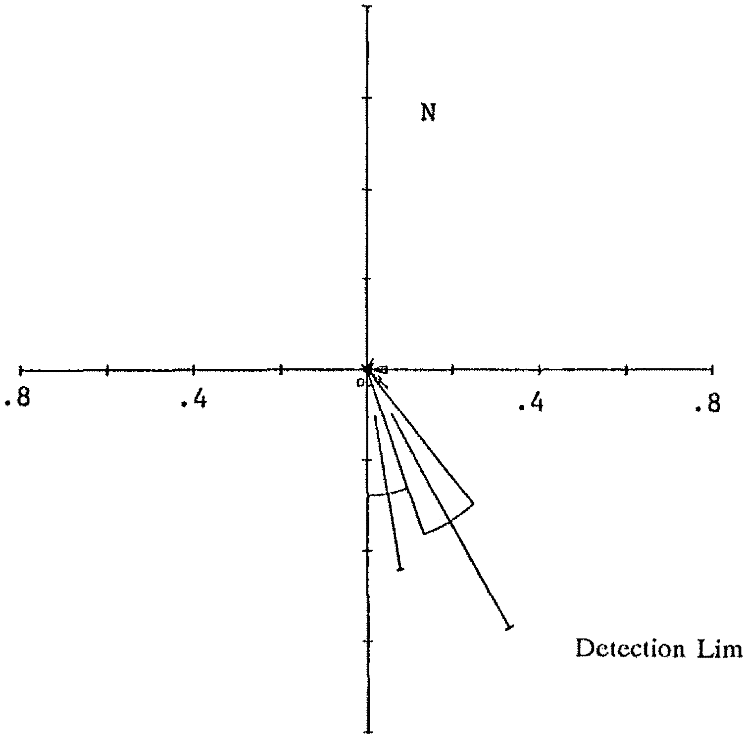


Figure B-2 Pollution roses for lead - Bright School, Chicago ($\mu g/m^3$)

Fine Mn



Coarse Mn



Detection Limit = 0 005

Figure B-3 Pollution roses for manganese - Bright School, Chicago ($\mu g/m^3$)

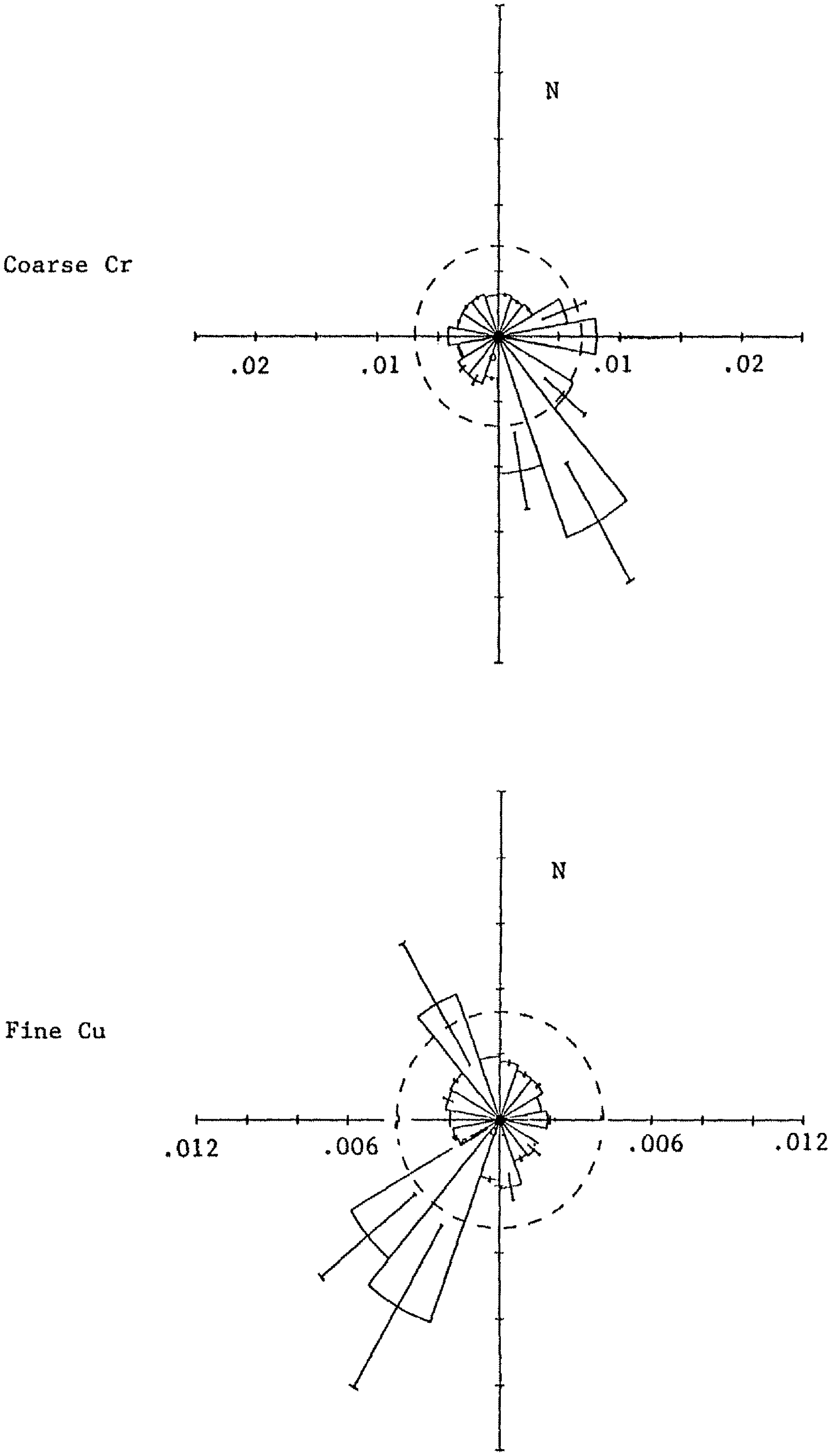


Figure B-4 Pollution roses for coarse chromium and fine copper - Bright School, Chicago ($\mu g/m^3$)

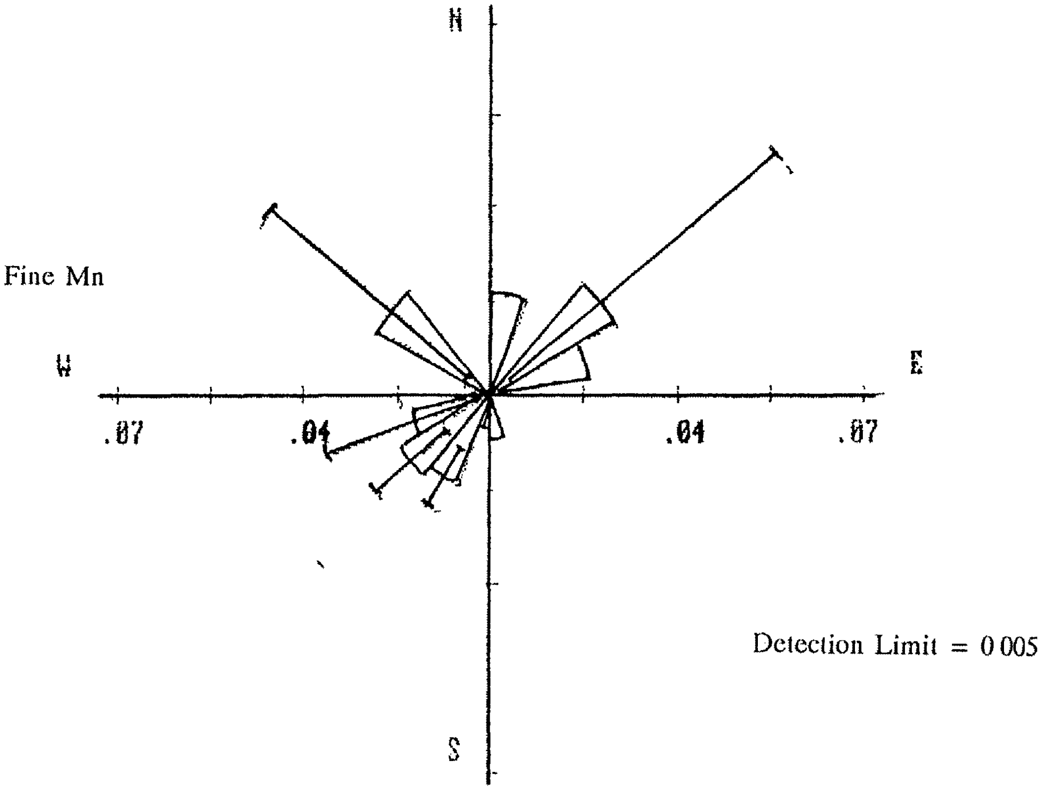


Figure B-5 Pollution roses for fine manganese - Washington School, Chicago ($\mu g/m^3$)

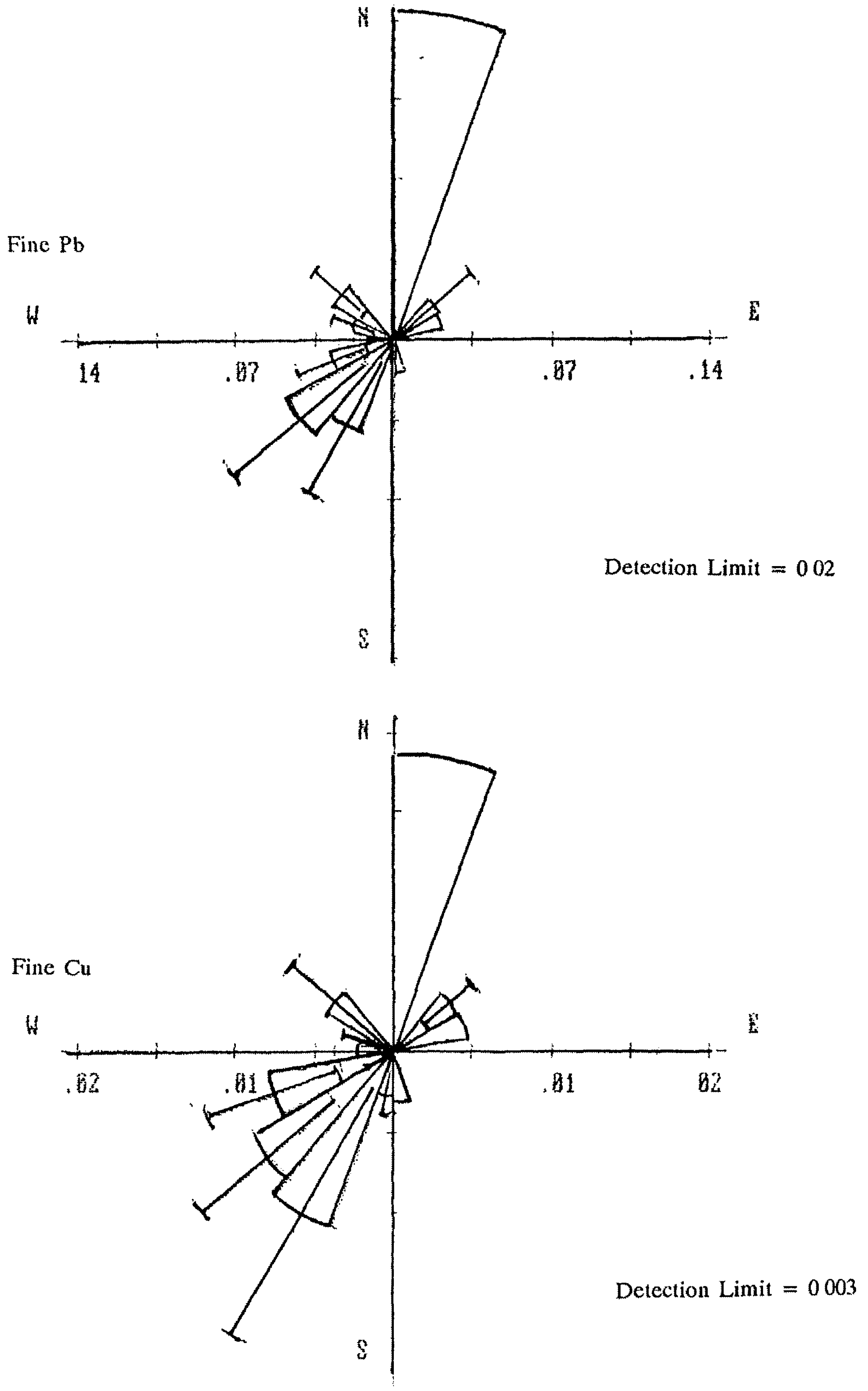


Figure B-6 Pollution roses for fine lead and fine copper - Washington School, Chicago ($\mu g/m^3$)

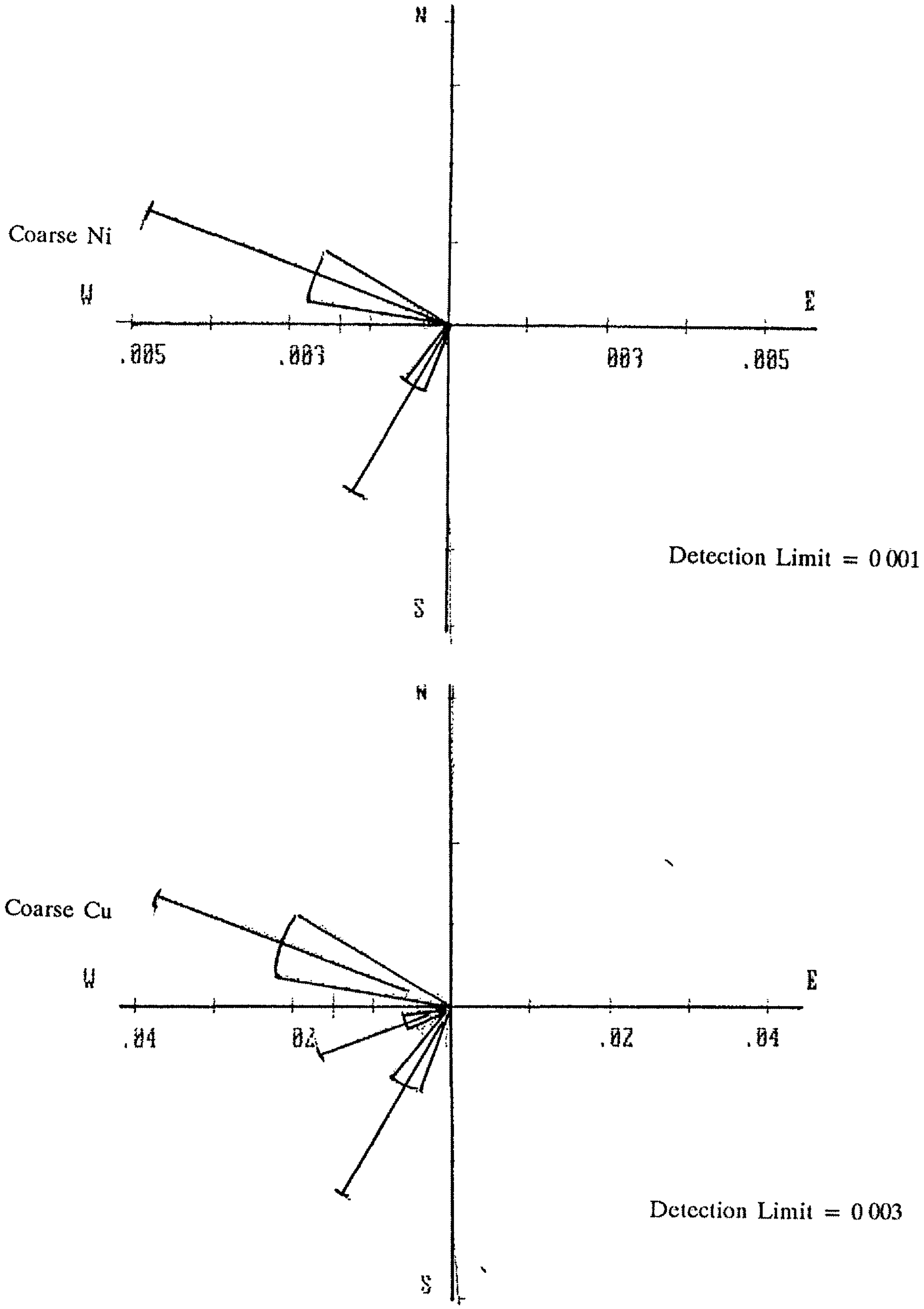


Figure B-7 Pollution roses for coarse nickel and coarse copper - Washington School, Chicago ($\mu g/m^3$)

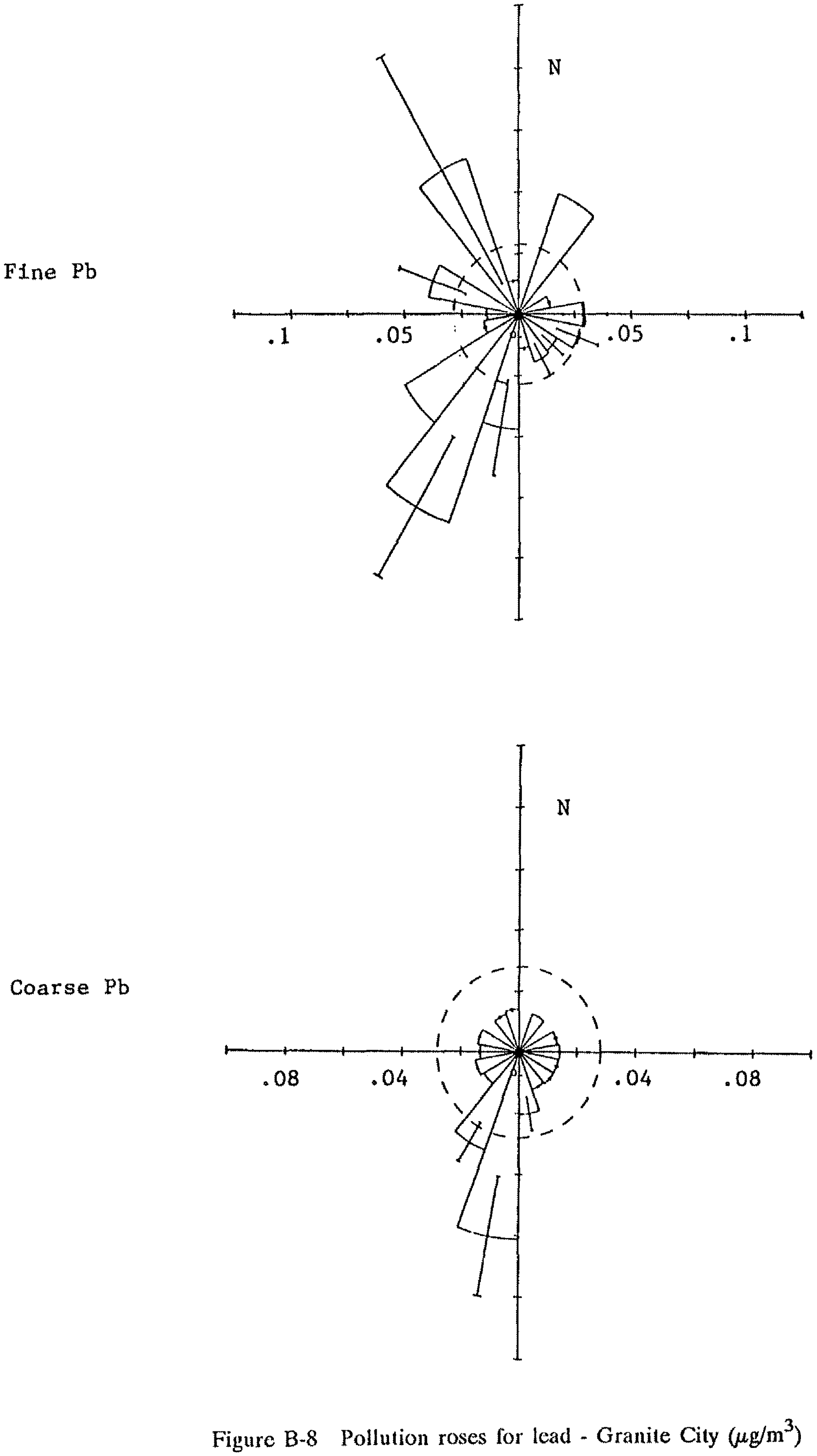


Figure B-8 Pollution roses for lead - Granite City ($\mu g/m^3$)

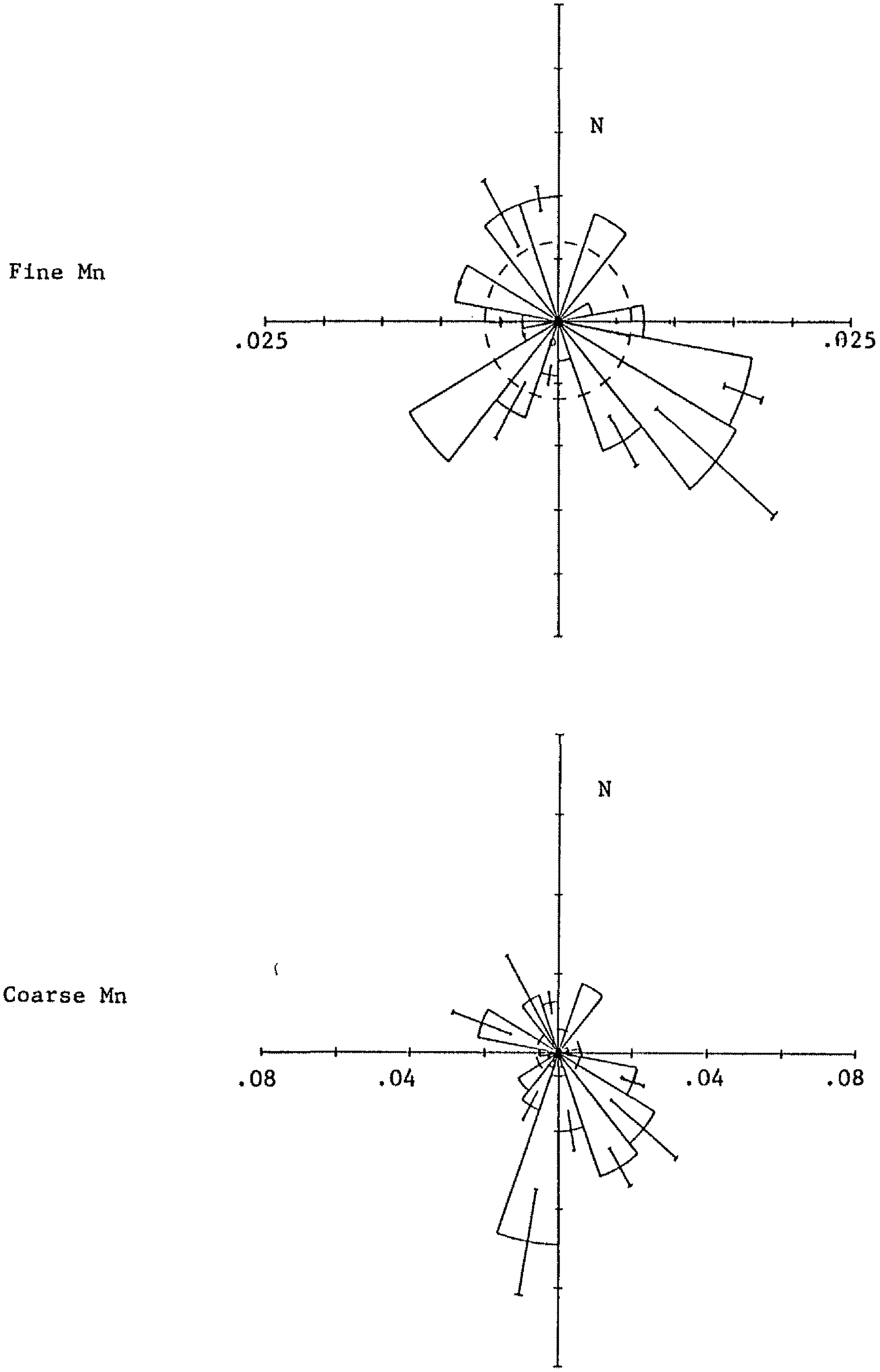
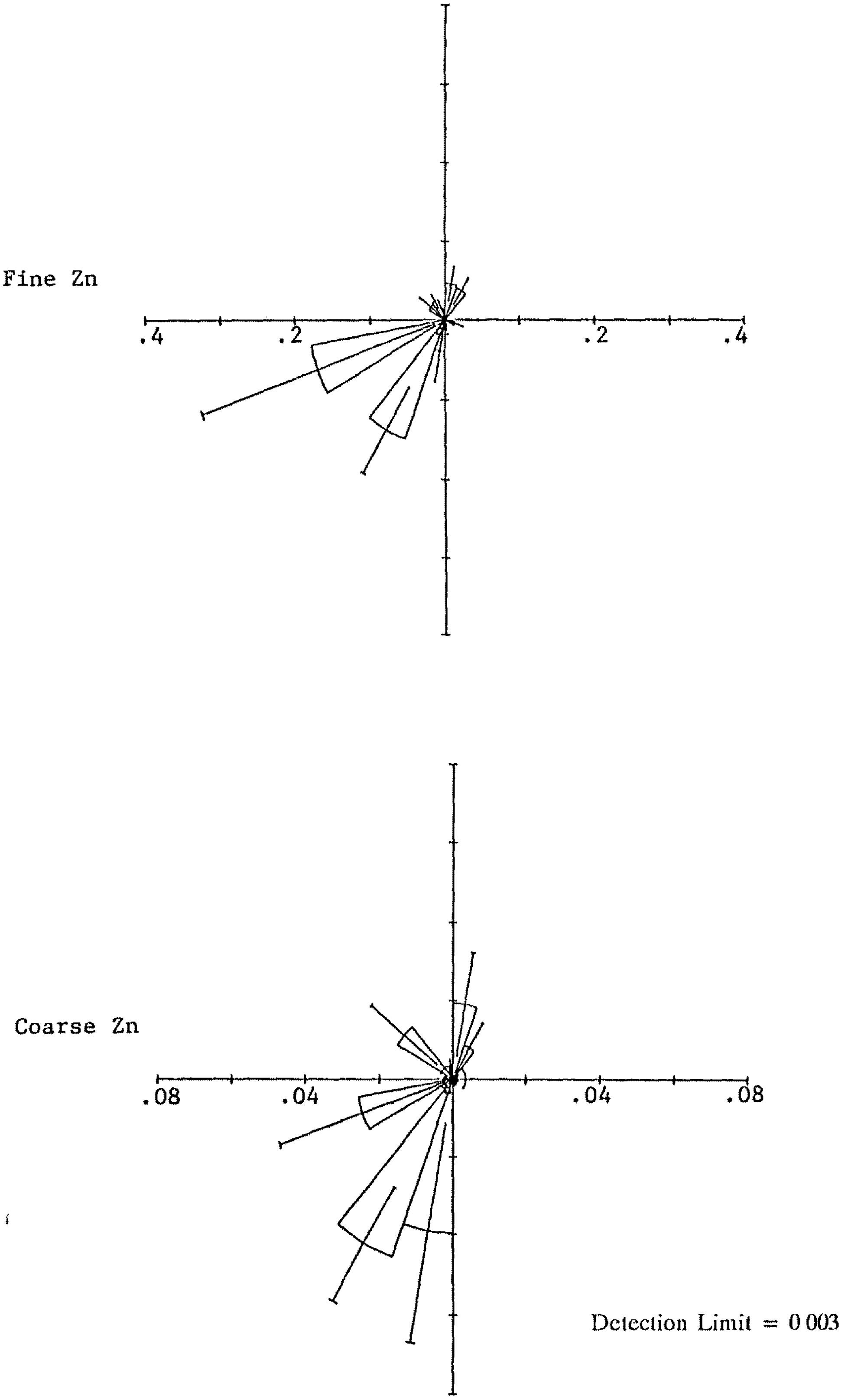


Figure B-9 Pollution roses for manganese - Granite City ($\mu g/m^3$)



Detection Limit = 0 003

Figure B-10 Pollution roses for zinc - East St Louis ($\mu g/m^3$)

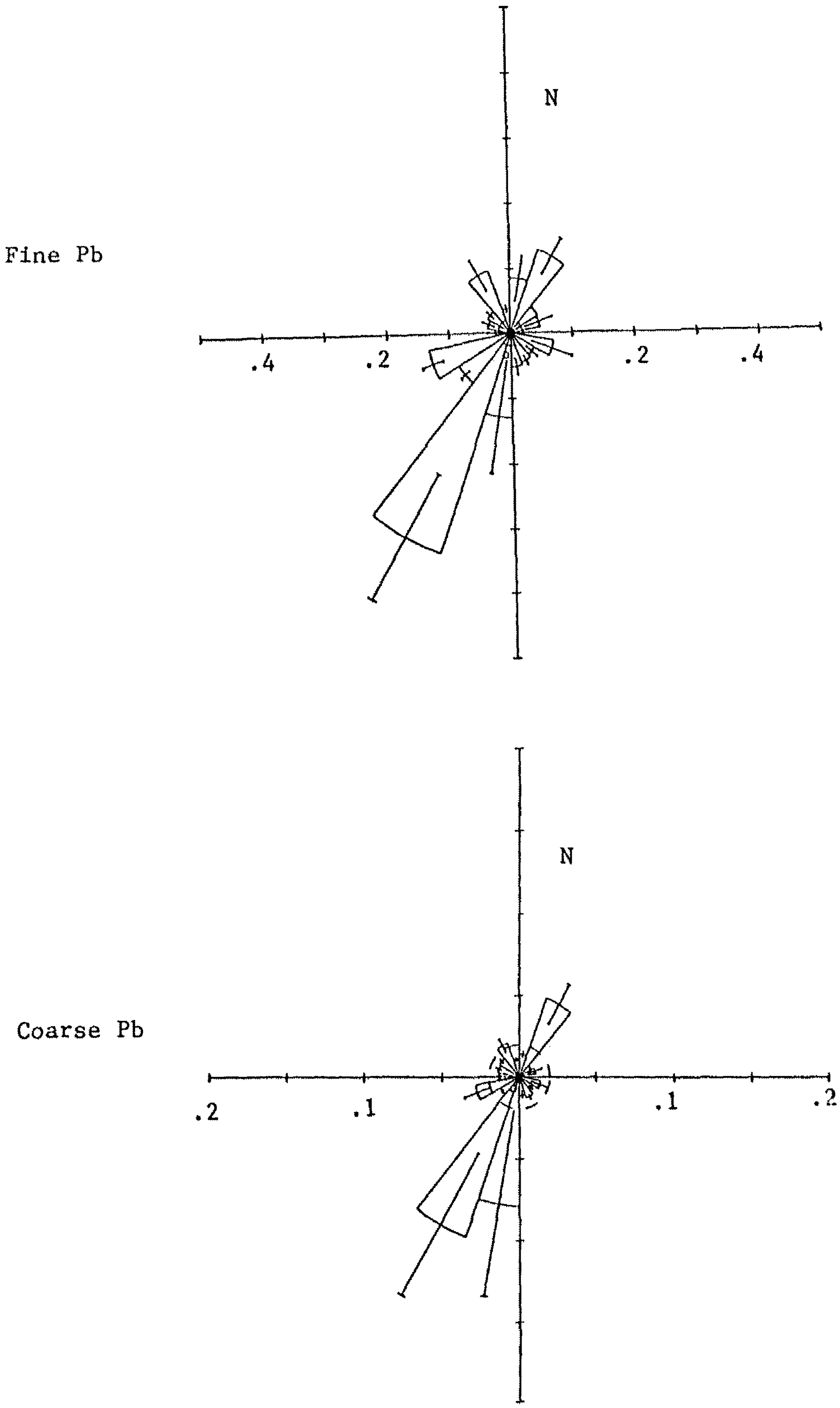


Figure B-11 Pollution roses for lead - East St Louis ($\mu g/m^3$)

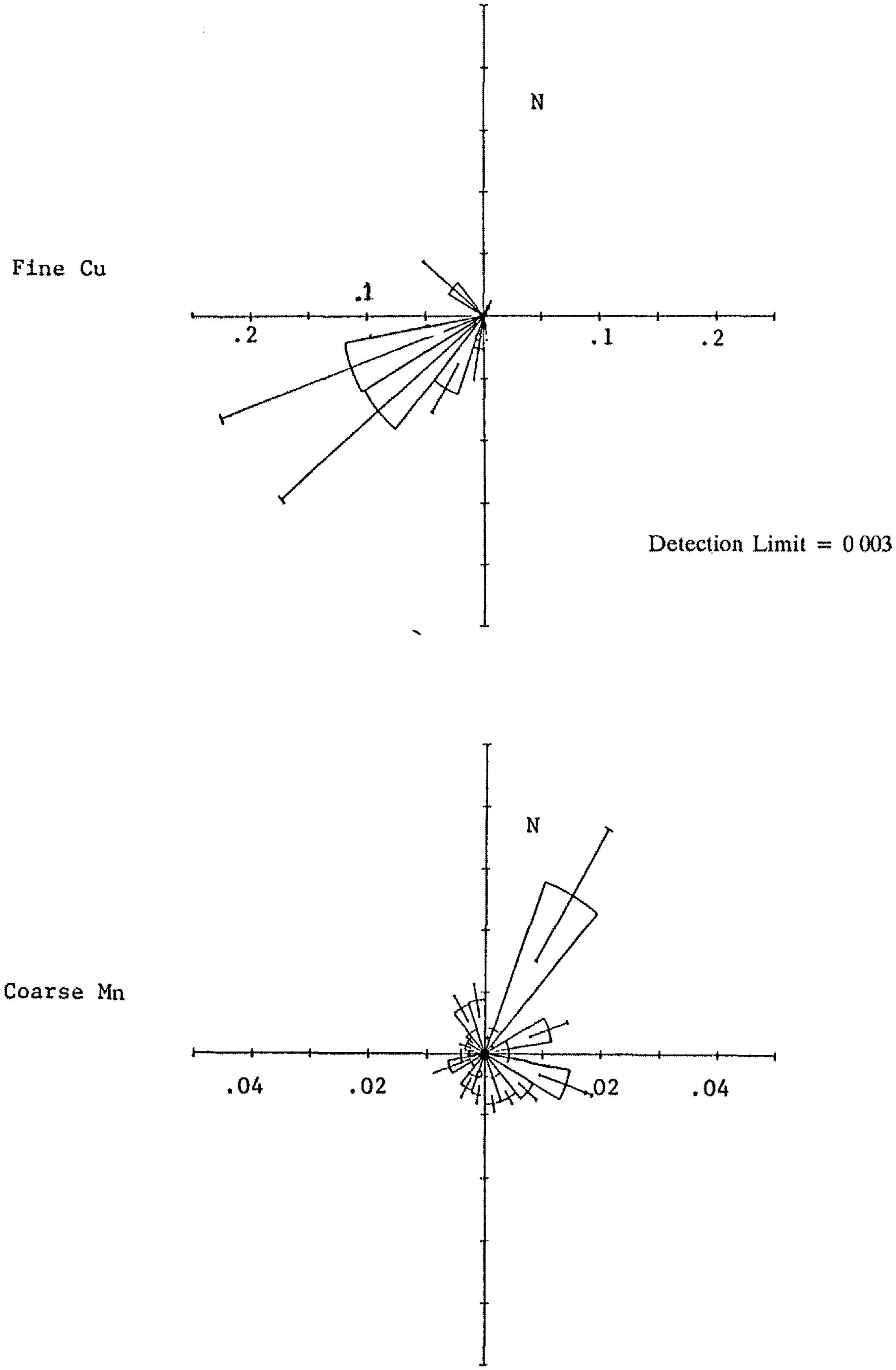
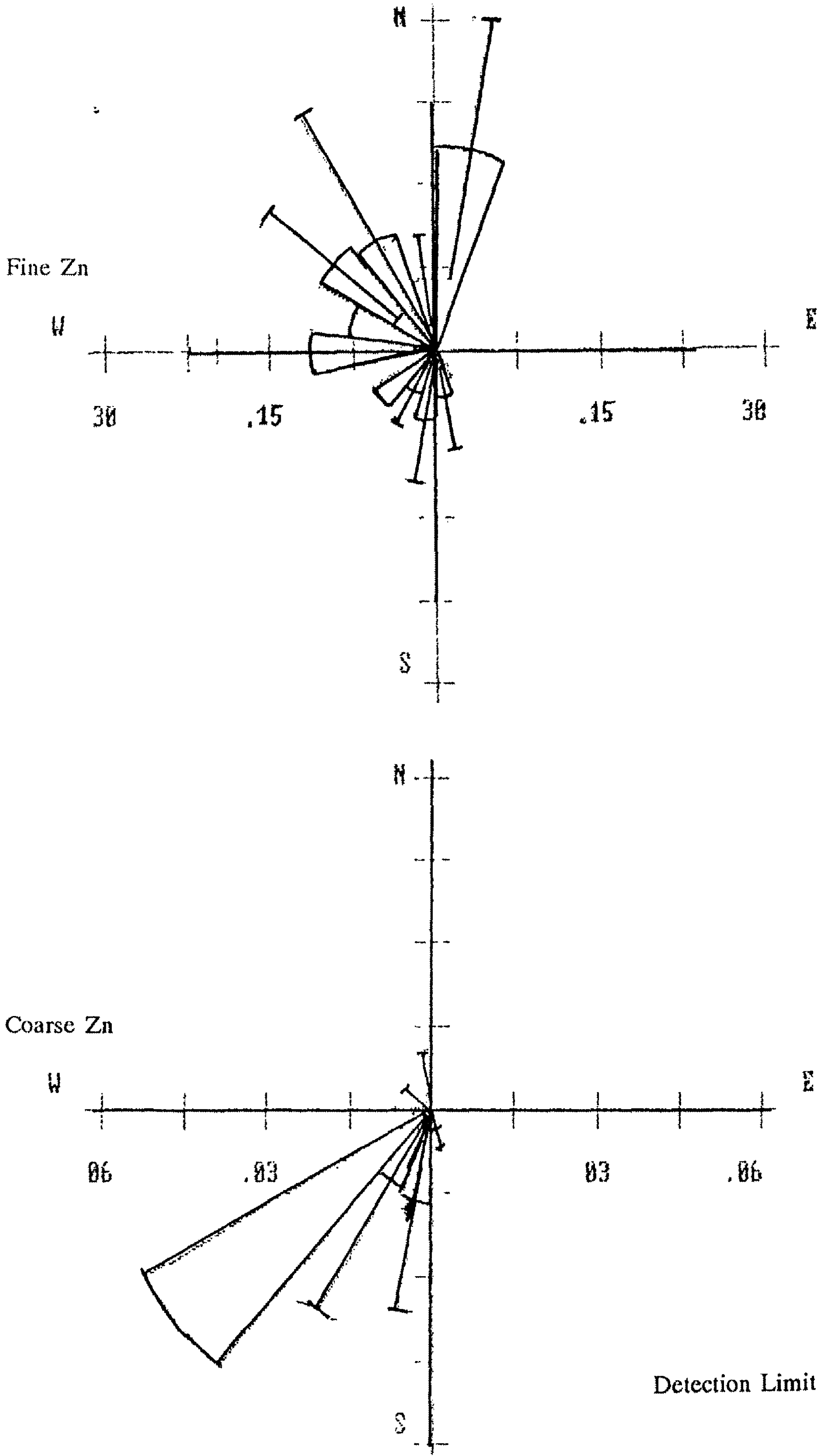
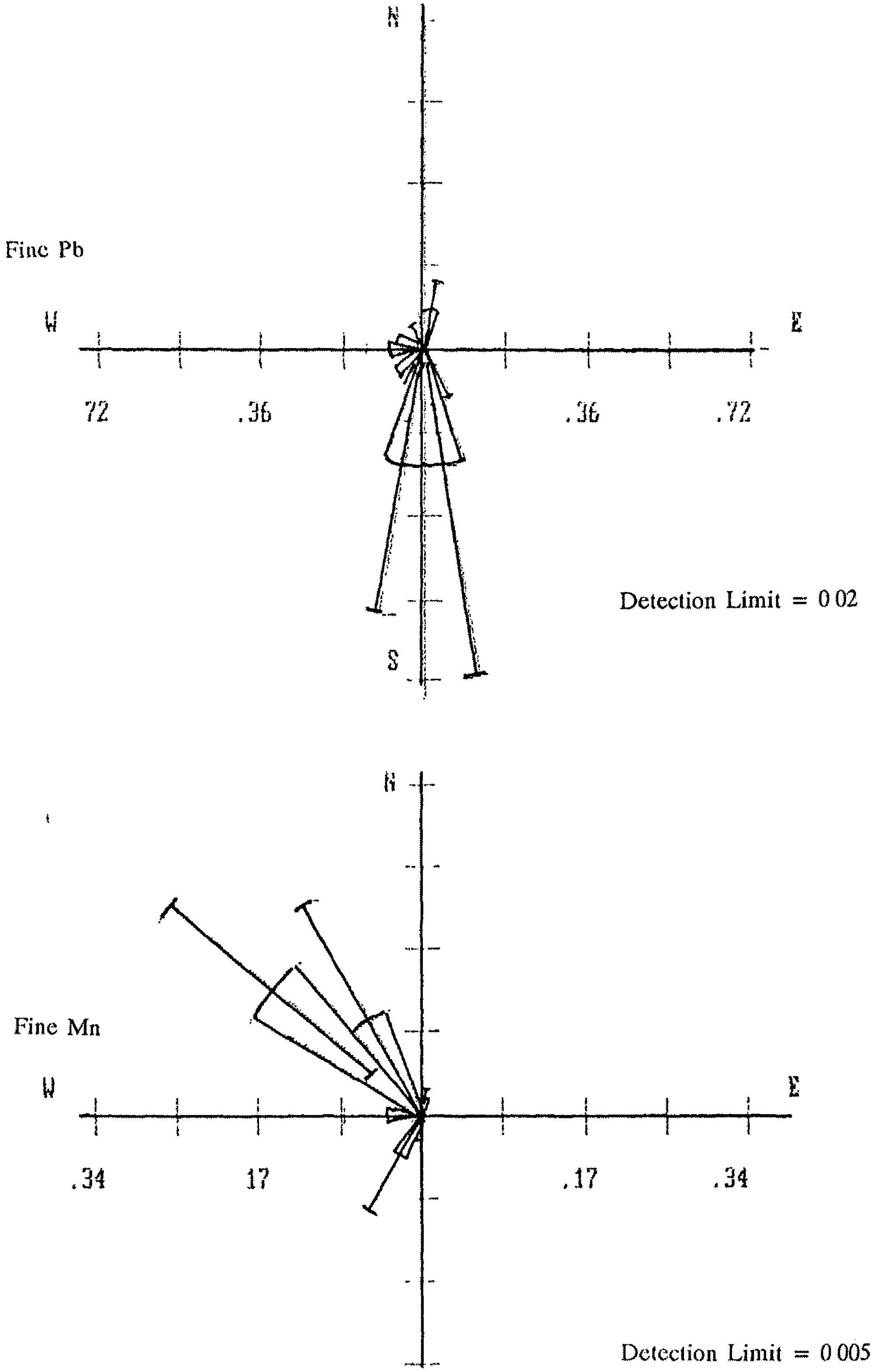


Figure B-12 Pollution roses for fine copper and coarse manganese - East St Louis ($\mu g/m^3$)



Detection Limit = 0 003

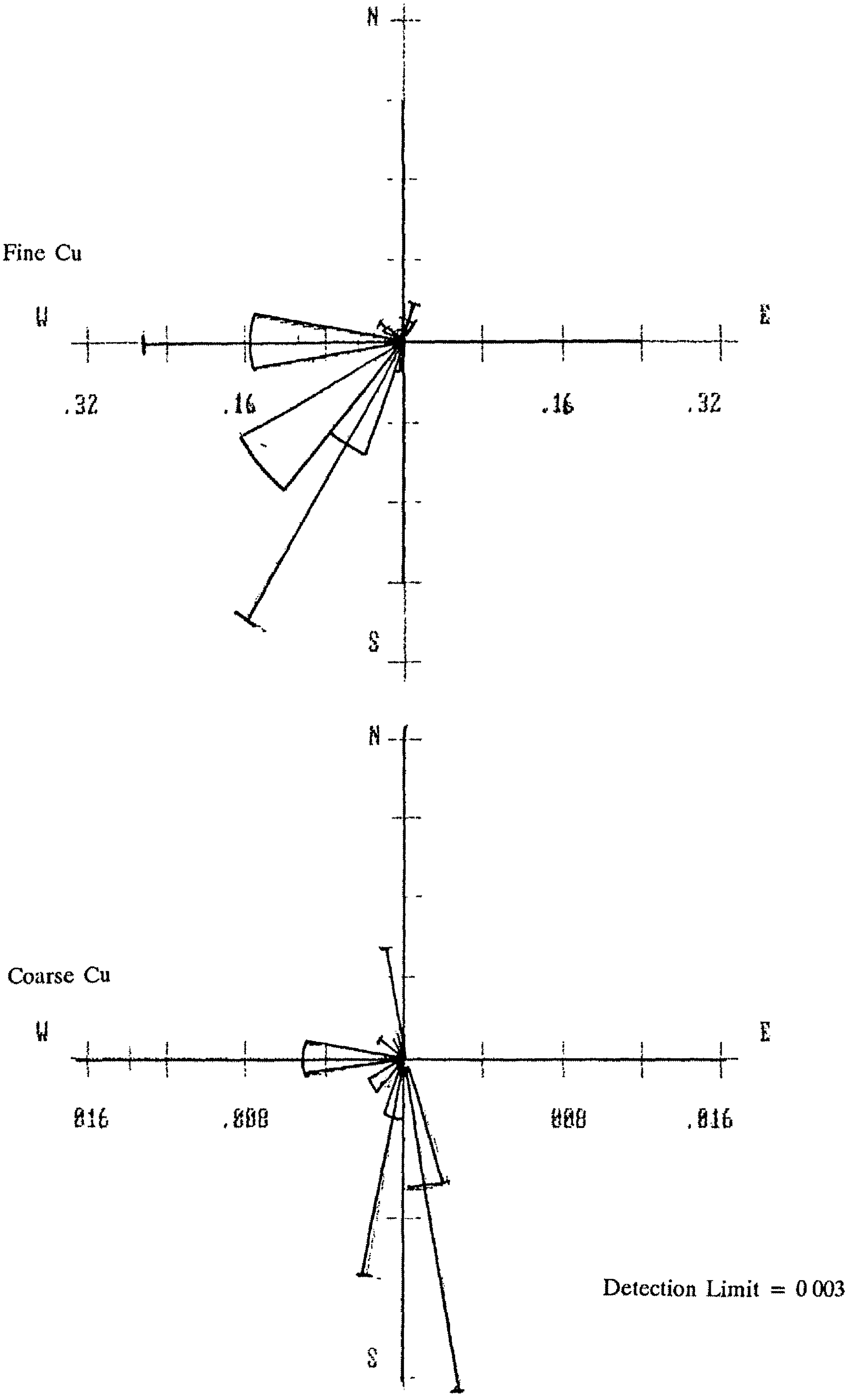
Figure B-13 Pollution roses for zinc - Sauget ($\mu g/m^3$)



Detection Limit = 0 02

Detection Limit = 0 005

Figure B-14 Pollution roses for fine lead and fine manganese - Sauget ($\mu g/m^3$)



Detection Limit = 0 003

Figure B-15 Pollution roses for copper - Sauget ($\mu g/m^3$)

APPENDIX C

CMB PROFILES

PARTICLE SOURCE PROFILES

(FRACTION OF A PARTICULAR ELEMENT IN THE TOTAL PARTICLE MASS)
(COARSE PARTICLES>2 5 um, FINE PARTICLES<2 5 um IN DIAMETER)
REFERENCES IN TABLE 16, p 76

SOURCE PROFILES 3,15,18,19,20,25,26,27,30,31,33,34 AND 35
WERE DEVELOPED IN THIS WORK

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
COAL BURNING (1)	SO4	0 015000	0 001500	0 100000	0 040000
EPA T11202	F	0 000023	0 000005	0 000000	0 000001
	NA	0 009500	0.000970	0 009500	0 000090
	MG	0 008200	0 000740	0 008200	0 000080
	AL	0 142050	0 007420	0 156790	0 007890
	SI	0 228720	0 011910	0 238370	0 011920
	S	0 006560	0 000430	0 033050	0 001800
	CL	0 001020	0 000130	0 000940	0 000410
	K	0 014360	0 000760	0 013040	0 000690
	CA	0 015140	0 000800	0 012350	0 000800
	TI	0 005080	0 000530	0 010080	0 000500
	V	0 000660	0 000060	0 000790	0 000070
	CR	0 000510	0 000030	0 000580	0 000040
	MN	0 000460	0 000030	0 000430	0 000030
	FE	0 095240	0 004960	0 084910	0 004280
	NI	0 000320	0 000020	0 000490	0 000040
	CU	0 000270	0 000020	0 000310	0 000030
	ZN	0 000450	0 000030	0 000690	0 000050
	AS			0 000810	0 000060
	SE	0 000050	0 000001	0 003600	0 000001
	BR	0 000000	0 000001	0 000000	0 000070
	CD			0 000120	0 000130
	SN			0 000000	0 000001
	PB	0 000250	0 000030	0 000360	0 000060
	C	0 670000	0 067000	0 670000	0 067000
CRUSTAL DUST (2)	SO4	0 000040	0 000010	0 000000	0 000001
EPA T41319	F	0 000023	0 000005	0 000000	0 000001
	NA	0 025000	0 005000	0 006900	0 003800
	MG	0 014000	0 003100	0 017600	0 006200
	AL	0 078000	0 017000	0 117000	0 022000
	SI	0 305000	0 015000	0 254000	0 034000
	S	0 000300	0 000001	0 000700	0 000300
	CL	0 000300	0 000001	0 000000	0 000001
	K	0 028000	0 002400	0 010000	0 002800
	CA	0 029000	0 006700	0 009300	0 003700
	TI	0 004700	0 001500	0 007600	0 002400
	V	0 000095	0 000060	0 000250	0 000060
	CR	0 000070	0 000060	0 000300	0 000080
	MN	0 000690	0 000280	0 002000	0 000900
	FE	0 035000	0 008500	0 068000	0 023000
	NI	0 000044	0 000040	0 000002	0 000040
	CU	0 000030	0 000040	0 000200	0 000040
	ZN	0 000060	0 000260	0 000410	0 000260
	AS			0 000170	0 000017
	SE	0 000000	0 000001	0 000001	0 000001
	BR	0 000003	0 000100	0 000000	0 000100
	CD			0 000015	0 000002
	SN			0 000300	0 000030
	PB	0 000015	0 000110	0 000060	0 000020
	C	0 049100	0 004900	0 200000	0 020000

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
URBAN DUST (3) SOUTHEAST CHICAGO	SO4	0 000740	0 000450	0 004200	0 003100
	F	0 000080	0 000070	0 000000	0 000100
	NA	0 017500	0.000910	0.012500	0 003400
	MG	0 015400	0 001400	0 013000	0 002700
	AL	0 018180	0 003300	0 021870	0 003370
	SI	0 057870	0 010120	0 062260	0 010120
	S	0 012170	0.001600	0 012310	0 001600
	CL	0 014110	0.000900	0 008900	0 000010
	K	0 003050	0 000600	0 003850	0 000600
	CA	0 111080	0 012760	0 117090	0 012760
	TI	0 001470	0 000150	0 001820	0 000150
	V	0 000140	0 000030	0 000170	0 000030
	CR	0 000860	0 000030	0 000450	0 000030
	MN	0 010810	0 000320	0 013600	0 000320
	FE	0 042650	0 003330	0 052810	0 003330
	NI	0 000090	0 000010	0 000150	0 000001
	CU	0 000160	0 000020	0 000210	0 000020
	ZN	0 001390	0 000150	0 002330	0 000150
	AS			0 000050	0 000050
	SE	0 000050	0 000001	0 000020	0 000001
	BR	0 000030	0 000001	0 000050	0 000050
	CD			0 000090	0 000070
	SN			0 000080	0 000100
	PB	0 000710	0 000090	0 010000	0 000090
	C	0 200000	0 020000	0 200000	0 020000
AUTO EXHAUST (4) EPA T33003 PB AND BR REDUCED	SO4	0 013000	0 004000	0 013000	0 004000
	F	0 000000	0 000100	0 000000	0 000100
	NA	0 000000	0 000500	0 000000	0 000500
	MG	0 000000	0 005000	0 000000	0 005000
	AL	0 011000	0 005000	0 011000	0 005000
	SI	0 008200	0 003000	0 008200	0 003000
	S	0 004000	0 001300	0 004000	0 001300
	CL	0 030000	0 010000	0 030000	0 010000
	K	0 000720	0 000290	0 000720	0 000290
	CA	0 012500	0 005000	0 012500	0 005000
	TI	0 000000	0 001000	0 000000	0 001000
	V	0 000000	0 000050	0 000000	0 000050
	CR	0 000000	0 000100	0 000000	0 000100
	MN	0 000000	0 000160	0 000000	0 000160
	FE	0 021000	0 008000	0 021000	0 008000
	NI	0 000180	0 000080	0 000180	0 000080
	CU	0 000730	0 000300	0 000730	0 000300
	ZN	0 003500	0 001300	0 003500	0 001300
	SE	0 000000	0 000001	0 000000	0 000001
	BR	0 020000	0 005000	0 050000	0 000100
	PB	0 060000	0 010000	0 200000	0 000100
	C	0 538000	0 053800	0 538000	0 053800
OIL BURNING (5) EPA T11501	SO4	0 481000	0 119000	0 481000	0 119000
	F	0 000530	0 000190	0 000530	0 000190
	NA	0 035000	0 017000	0 035000	0 017000
	MG	0 000000	0 030000	0 000000	0 030000
	AL	0 005300	0 002400	0 005300	0 002400
	SI	0 009600	0 004800	0 009600	0 004800
	S	0 133000	0 024000	0 133000	0.024000
	CL	0 000000	0 001000	0 000000	0 001000
	K	0 002800	0 001000	0 002800	0 001000
	CA	0 015800	0 006400	0 015800	0 006400
	TI	0 001100	0 000380	0 001100	0 000380

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
OIL BURNING (5)	V	0.034400	0.007500	0.034400	0.007500
	CR	0.000470	0.000150	0.000470	0.000150
	MN	0.000460	0.000130	0.000460	0.000130
	FE	0.029700	0.006100	0.029700	0.006100
	NI	0.053600	0.012100	0.053600	0.012100
	CU	0.000750	0.000250	0.000750	0.000250
	ZN	0.004000	0.001800	0.004000	0.001800
	AS			0.000080	0.000008
	SE	0.000000	0.000001	0.000000	0.000001
	BR	0.000130	0.000210	0.000130	0.000210
	CD			0.000020	0.000002
	SN			0.000190	0.000019
	PB	0.001100	0.000640	0.001100	0.000640
	C	0.101000	0.010100	0.101000	0.010100
COAL DUST (6)	SO4	0.000000	0.000001	0.000000	0.008800
EPA T21204	F	0.000000	0.010000	0.000000	0.010000
	NA	0.000000	0.001400	0.000000	0.001400
	MG	0.000000	0.000001	0.000000	0.000001
	AL	0.046270	0.004630	0.108650	0.010860
	SI	0.113460	0.011350	0.224660	0.022470
	S	0.004170	0.000420	0.001940	0.000190
	CL	0.000670	0.000010	0.001710	0.000200
	K	0.004890	0.000490	0.009680	0.000970
	CA	0.034220	0.003420	0.031420	0.003140
	TI	0.001610	0.000160	0.002830	0.000280
	V	0.000000	0.000001	0.000000	0.000001
	CR	0.000000	0.000001	0.000150	0.000001
	MN	0.000000	0.000001	0.000130	0.000001
	FE	0.000000	0.000001	0.014220	0.001420
	NI	0.000000	0.000001	0.000000	0.000001
	CU	0.000000	0.000001	0.000220	0.000001
	ZN	0.000000	0.000001	0.000330	0.000001
	SE	0.000000	0.000001	0.000000	0.000001
	BR	0.000000	0.000001	0.000000	0.000001
	PB	0.000180	0.000001	0.000720	0.000180
	C	0.670000	0.067000	0.670000	0.067000
COKE DUST (7)	SO4	0.000000	0.000001	0.000000	0.054000
EPA T21203	F	0.000000	0.000001	0.000000	0.001500
	NA	0.000000	0.000001	0.000000	0.003400
	MG	0.000000	0.000001	0.000000	0.010000
	AL	0.025680	0.002570	0.040390	0.005190
	SI	0.062500	0.006250	0.081310	0.010050
	S	0.005680	0.000570	0.003810	0.001320
	CL	0.000320	0.000001	0.001640	0.000550
	K	0.001670	0.000170	0.002170	0.000380
	CA	0.022850	0.002280	0.027380	0.003420
	TI	0.001570	0.000160	0.002360	0.000340
	V	0.000000	0.000001	0.000220	0.000001
	CR	0.000000	0.000001	0.000160	0.000001
	MN	0.000100	0.000001	0.000000	0.000001
	FE	0.009070	0.000910	0.014640	0.001890
	NI	0.000000	0.000001	0.000000	0.000001
	CU	0.007310	0.000730	0.005160	0.000680
	ZN	0.003130	0.000300	0.003990	0.000540
	AS			0.000410	0.000260
	SE	0.000000	0.000001	0.000000	0.000001
	BR	0.000000	0.000001	0.000140	0.000001
	CD			0.000500	0.000890

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
COKE DUST (7)	SN			0 000000	0 001190
	PB	0 001310	0 000130	0 002490	0 000490
	C	0 670000	0 067000	0 670000	0 067000
INCINERATOR (8)	SO4	0 000000	0 000001	0 000000	0 021000
EPA T17106	F	0 000000	0.000001	0 000000	0 001000
	NA	0 000000	0.000001	0.000000	0 007100
	MG	0 000000	0 000001	0 000000	0 005300
	AL	0 058270	0 004660	0 008190	0 000117
	SI	0 085700	0 005810	0 014420	0 000670
	S	0 034870	0 006010	0 019060	0 003010
	CL	0 166780	0 022180	0 212990	0 009850
	K	0 044910	0 006400	0 064640	0 003050
	CA	0 058700	0 003810	0 002230	0 000300
	TI	0 010970	0 000690	0 000120	0 000030
	V	0 000240	0 000080	0 000000	0 000010
	CR	0 001110	0 000090	0 000150	0 000010
	MN	0 000910	0 000080	0 000180	0 000010
	FE	0 018740	0 001290	0 002790	0 000130
	NI	0 000850	0 000100	0 000320	0 000020
	CU	0 000530	0 000150	0 001480	0 000070
	ZN	0 040120	0 009180	0 113030	0 005250
	AS			0 000000	0 000001
	SE	0 000030	0 000010	0 000030	0 000001
	BR	0 003750	0 000570	0 005630	0 000270
	CD			0 002840	0 002840
	SN			0 008290	0 000410
	PB	0 024280	0 006330	0 081160	0 003710
	C	0 025000	0 002500	0 025000	0 002500
BLAST FURNACE	NO3	0 005500	0 001300	0 005500	0 002300
STEEL (10)	SO4	0 400000	0 003700	0 400000	0 090000
EPA T23802	F	0 000000	0 000410	0 000000	0 000500
	NA	0 000000	0 009600	0 000000	0 029000
	MG	0 000000	0 001700	0 000000	0 010000
	AL	0 000900	0 000090	0 020000	0 001800
	SI	0 099000	0 001400	0 099000	0 003700
	S	0 130000	0 000900	0 133300	0 024000
	CL	0 000000	0 007600	0 000000	0 049000
	K	0 050000	0 002100	0 050000	0 000100
	CA	0 005500	0 000010	0 005500	0 000100
	TI	0 000000	0 000800	0 000000	0 000600
	V	0 005500	0 000035	0 005500	0 000020
	CR	0 020000	0 000015	0 020000	0 000060
	MN	0 005500	0 000400	0 005500	0 003400
	FE	0 110000	0 002200	0 110000	0 008800
	NI	0 005500	0 000050	0 005500	0 000042
	CU	0 005500	0 000038	0 005500	0 000600
	ZN	0 000000	0 000047	0 000000	0 003400
	AS			0 000500	0 000050
	SE	0 000000	0 000001	0 000000	0 000001
	BR	0 000500	0 000008	0 000500	0 000300
	CD			0 000500	0 000050
	SN			0 000500	0 000050
	PB	0 005500	0 000030	0 005500	0 002200
	C	0 200000	0 020000	0 200000	0 020000
COAL FIRED	NA	0 009700	0 000970	0 011400	0 001140
POWER PLANT (11)	MG			0 018000	0 001800
HOPKE, 1985	AL	0 026000	0 002600	0 130000	0 013000

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
POWER PLANT (11)	SI			0 230000	0 023000
	S	0 015000	0 001500	0 005000	0 000500
	CL	0 011000	0 001100	0 000265	0 000027
	K	0 010000	0 001000	0 004000	0 000400
	CA	0 023000	0 002300	0 047000	0 004700
	TI	0 002600	0.000260	0.026000	0 002600
	V	0 000130	0 000013	0 000900	0 000090
	CR	0 000400	0 000040	0 000265	0 000027
	MN	0 000310	0 000031	0 001110	0 000111
	FE	0 018000	0 001800	0 056000	0 005600
	NI	0 000180	0 000018	0 000090	0 000009
	CU	0.001300	0 000130	0 000650	0 000065
	ZN	0 003000	0 000300	0 000680	0 000068
	AS	0 000260	0 000026	0 000070	0 000007
	BR	0 000160	0 000016	0 000015	0.000001
	CD			0 000004	0 000001
	SN			0 000060	0 000006
	PB	0 002000	0 000200	0 000080	0 000008
STEEL COMPOSITE (12)	SO4	0 080000	0 013000	0 400000	0 013000
SCHEFF et al,1984	F	0 000000	0 005000	0 000000	0 005000
	NA	0 012600	0 004800	0 012600	0 004800
	MG	0 065000	0 007100	0 065000	0 007100
	AL	0 020000	0 001000	0 006500	0 000010
	SI	0 025000	0 001000	0 020000	0 002100
	S	0 009800	0 000980	0 019600	0 000700
	CL	0 009250	0 000925	0 001850	0 000100
	K	0 005000	0 000500	0 010000	0 000700
	CA	0 043000	0 002150	0 043000	0 005700
	TI	0 001000	0 000100	0 002000	0 000200
	V	0 000600	0 000300	0 000600	0 000100
	CR	0 005250	0 000263	0 005250	0 014000
	MN	0 037000	0 000370	0 037000	0 009000
	FE	0 360000	0 018000	0 110000	0 030000
	NI	0 000500	0 000025	0 000500	0 000700
	CU	0 005000	0 000250	0 000500	0 000300
	ZN	0 008100	0 000405	0 005500	0 001200
	SE	0 000500	0 000001		
	BR	0 005500	0 001000	0 008100	0 001000
	PB	0 007000	0 000350	0 007000	0 000700
	C	0 400000	0 040000	0 400000	0 040000
REGIONAL BACKGROUND (15)	SO4	0 000000	0 000001	0 000000	0 099000
	F	0 000001	0 000001	0 000000	0 000230
	NA	0 014200	0 001420	0 000000	0 010000
	MG	0 006497	0 000649	0 000000	0 010000
	AL	0 036000	0 003600	0 005540	0 000140
	SI	0 137600	0 013760	0 010320	0 000700
	S	0 021700	0 002170	0 103800	0 023000
	CL	0 004400	0 000440	0 001170	0 000060
	K	0 009200	0 000920	0 003420	0 002800
	CA	0 036300	0 003630	0 003020	0 000300
	TI	0 001600	0 000160	0 000250	0 000050
	V	0 000900	0 000090	0 000051	0 000002
	CR	0 001100	0 000110	0 000038	0 000001
	MN	0 005800	0 000580	0 000200	0 000007
	FE	0 158000	0 015800	0 003060	0 000020
	NI	0 000600	0 000060	0 000260	0 000001
	CU	0 002300	0 000230	0 000159	0 000017
	ZN	0 008400	0 000840	0 001150	0 000019

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
REGIONAL BACKGROUND (15)	AS			0.000100	0 000105
	SE			0 000110	0 000001
	BR	0 000740	0 000074	0 000250	0 000053
	CD			0 000143	0 000115
	SN			0 000194	0 000170
	PB	0 005000	0 000500	0.001060	0 000600
	C	0 200000	0 020000	0 200000	0 020000
LEADED GASOLINE EXHAUST (16) EPA T31101	NA	0 000500	0 000300	0 005000	0 000300
	MG	0 014800	0.005000	0 014800	0 005000
	AL	0 013000	0 005000	0 013000	0 005000
	SI	0 008200	0 002000	0 008200	0 002000
	S	0 005000	0 002000	0 005000	0 002000
	CL	0 030000	0 010000	0 030000	0 010000
	K	0 001500	0 000700	0 001500	0 000700
	CA	0 018000	0 005000	0 018000	0 005000
	TI	0 000050	0 000025	0 000050	0 000005
	V	0 000050	0 000025	0 000050	0 000005
	CR	0 000050	0 000025	0 000050	0 000005
	MN	0 000200	0 000200	0 000200	0 000200
	FE	0 015000	0 010000	0 015000	0 010000
	NI	0 000200	0 000100	0 000200	0 000100
	CU	0 001000	0 000500	0 001000	0 000500
	ZN	0 003500	0 002000	0 003500	0 002000
	SE	0 000020	0 000020	0 000020	0 000020
	BR	0 062500	0 020000	0 062500	0 020000
	CD	0 000600	0 000400	0 000600	0 000400
	PB	0 270000	0 020000	0 240000	0 020000
	C	0 150000	0 015000	0 520000	0 050000
SULFATE (17)	S	0 330000	0 033000	0 330000	0 033000
ZINC SMELTER (22) HOPKE, 1985	AL	0 003600	0 000360	0 003600	0 000360
	CL	0 059000	0 005900	0 059000	0 005900
	CA	0 000690	0 000069	0 000690	0 000069
	V	0 000027	0 000002	0 000027	0 000003
	CR	0 000160	0 000016	0 000160	0 000016
	MN	0 000300	0 000030	0 000300	0 000030
	FE	0 003900	0 000390	0 003900	0 000390
	CU	0 001500	0 000150	0 001500	0 000150
	ZN	0 150000	0 015000	0 150000	0 015000
	AS	0 000120	0 000012	0 000120	0 000012
	BR	0 000044	0 000004	0 000044	0 000004
	CD	0 004200	0 000042	0 004200	0 000042
	PB	0 003400	0 000340	0 003400	0 000340
ALUMINUM SMELTER (23) HOPKE, 1985	AL	0 100000	0 010000	0 100000	0 010000
	S	0 180000	0 018000	0 180000	0 018000
	CL	0 030000	0 003000	0 030000	0 003000
	K	0 042000	0 004200	0 042000	0 004200
	CA	0 003900	0 000390	0 003900	0 000390
	V	0 000320	0 000032	0 000320	0 000032
	CR	0 000510	0 000051	0 000510	0 000051
	MN	0 000150	0 000015	0 000150	0 000015
	FE	0 015000	0 001500	0 015000	0 001500
	NI	0 004600	0 000460	0 004600	0 000460
	CU	0 003600	0 000360	0 003600	0 000360
	ZN	0 007500	0 000750	0 007500	0 000750
	AS	0 000090	0 000009	0 000090	0 000009
	BR	0 000200	0 000020	0 000200	0 000020
	CD	0 002300	0 000230	0 002300	0 000230
	PB	0 006000	0 000600	0 006000	0 000600

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
COPPER	AL	0 003470	0 000350	0 003470	0 000350
SMELTER (24)	SI	0 003620	0 000360	0 003620	0 000360
EPA T29203	S	0 044880	0 004490	0 044880	0 004490
	CL	0.021160	0.002120	0 021160	0 002120
	K	0 002110	0.000210	0.002110	0 000210
	CA	0 007500	0 001000	0 007500	0 001000
	TI	0 000180	0 000018	0 000180	0 000018
	CR	0 000140	0 000014	0 000140	0 000014
	FE	0 001000	0.000100	0.001000	0 000100
	NI	0.002030	0 000200	0.002030	0 000200
	CU	0 541510	0 054150	0 541510	0 054150
	ZN	0 001270	0 000390	0 001270	0 000390
	BR	0 000180	0 000018	0 000180	0 000018
	CD	0 000880	0 000160	0 000880	0 000160
	PB	0 002340	0.000230	0.002340	0 000230
SAUGET AREA	AL	0 012000	0 000400	0 004000	0 000400
SMELTERS	SI	0 045000	0 006000	0 007000	0 000900
AMBIENT AIR (27)	S	0 030000	0 001600	0 120000	0 006200
	CL	0 008000	0 000200	0 002000	0 000500
EAST ST LOUIS	K	0 008000	0 000500	0 005000	0 000500
SITE, SW WINDS	CA	0 100000	0 003300	0 005000	0 000200
	TI	0 002000	0 000020	0 000500	0 000020
	V	0 000200	0 000010	0 000100	0 000010
	CR	0 000200	0 000010	0 000100	0 000010
	MN	0 001000	0 000020	0 000200	0 000020
	FE	0 035000	0 000400	0 003000	0 000200
	NI	0 001000	0 000010	0 000100	0 000010
	CU	0 002000	0 000300	0 006000	0 000300
	ZN	0 030000	0 000300	0 150000	0 000300
	SE	0 000050	0 000020	0 000400	0 000020
	BR	0 000200	0 000010	0 000200	0 000010
	CD	0 003000	0 000100	0 000400	0 000100
	SN	0 000200	0 000100	0 000300	0 000100
	PB	0 007000	0 000300	0 010000	0 000300
GRANITE CITY	NA	0 004670	0 000460	0 005780	0 000770
BACKGROUND	MG	0 010380	0 002080	0 050340	0 006820
ROAD DUST (30)	AL	0 049950	0 006810	0 145570	0 021860
	SI	0 164170	0 023720	0 001390	0 000670
	CL	0 002600	0 000400	0 002520	0 000430
	K	0 011700	0 001370	0 011990	0 001410
	CA	0 131660	0 015170	0 108160	0 012530
	TI	0 003560	0 000220	0 003590	0 000250
	V	0 000180	0 000001	0 000220	0 000010
	CR	0 000240	0 000020	0 000240	0 000030
	MN	0 002610	0 000150	0 002920	0 000190
	FE	0 052870	0 002790	0 059210	0 003460
	NI	0 000110	0 000010	0 000230	0 000030
	CU	0 000250	0 000020	0 000410	0 000040
	ZN	0 001170	0 000070	0 001630	0 000110
	AS	0 000010	0 000001	0 000010	0 000001
	BR	0 000020	0 000010	0 001880	0 000140
	PB	0 001560	0 000090		
	C	0 042000	0 004200	0 071000	0 007100
LEAD PLANT	NA	0 001700	0 000410	0 003620	0 000740
PARKING LOT (31)	MG	0 025330	0 002180	0 036730	0 005060
	AL	0 029440	0 004010	0 099160	0 015070
	SI	0 092690	0 013370	0 002850	0 001370
	S	0 001460	0 000900	0 001400	0 000480
	K	0 007620	0 000930	0 009490	0 001180

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
LEAD PLANT PARKING LOT (31)	CA	0 188340	0 021610	0 171420	0 020260
	TI	0 001710	0 000110	0 002520	0 000180
	V	0 000160	0 000001	0 000180	0 000001
	CR	0 000180	0 000020	0 000280	0 000040
	MN	0 002220	0 000130	0 002550	0 000170
	FE	0 037020	0 001930	0 036200	0 002290
	NI	0 000050	0 000010	0 000050	0 000020
	CU	0 000180	0 000020	0 000150	0 000040
	ZN	0 001060	0 000060	0 001350	0 000100
	AS	0 000040	0 000001	0 000060	0 000001
	SE	0 000010	0 000010	0 000030	0 000020
	BR	0 000030	0 000010	0 000040	0 000030
	SN	0 000130	0 000090		
	PB	0 006460	0 000350	0 008980	0 000590
	C	0 055000	0 005500	0 047000	0 004700
URBAN DUST GRANITE CITY (32)	NA	0 002630	0 000260	0 002740	0 000460
	MG			0 011000	0 003300
	AL	0 015390	0 002080	0 014890	0 002050
	SI	0 049060	0 007030	0 048620	0 007360
	S	0 003560	0 000890	0 010680	0 001590
	CL	0 001360	0 000320	0 001860	0 000460
	K	0 002120	0 000470	0 002120	0 000480
	CA	0 256190	0 029260	0 233200	0 027340
	TI	0 000710	0 000060	0 001130	0 000090
	V	0 000070	0 000001	0 000060	0 000001
	CR	0 000220	0 000020	0.000220	0 000030
	MN	0 000910	0 000050	0 001200	0 000090
	FE	0 022300	0 001160	0 026330	0 001630
	NI	0 000050	0 000010	0 000070	0 000020
	CU	0 000100	0 000010	0 000140	0 000030
	ZN	0 000270	0 000020	0 000360	0 000040
	AS	0 000010	0 000001	0 000020	0 000001
	BR	0 000010	0 000010		
	CD	0 000060	0 000040		
	SN	0 000070	0 000070		
	PB	0 000410	0 000030	0 000490	0 000080
	C	0 229000	0 022900	0 032000	0 003200
COKE OVEN AREA DUST GRANITE CITY (33)	NA	0 003020	0 000420	0 005170	0 000440
	MG	0 011310	0 001970		
	AL	0 016010	0 002190	0 016550	0 002310
	SI	0 036580	0 005290	0 033990	0 005210
	S	0 012500	0 001590	0 010290	0 001540
	CL	0 003800	0 000510	0 005320	0 000770
	K	0 002430	0 000300	0 003150	0 000420
	CA	0 041330	0 004790	0 039950	0 004790
	TI	0 000870	0 000070	0 001190	0 000100
	V	0 000060	0 000001	0 000060	0 000001
	CR	0 000080	0 000010	0 000170	0 000030
	MN	0 000940	0 000060	0 001480	0 000110
	FE	0 026580	0 001430	0 034200	0 002250
	NI	0 000040	0 000010	0 000070	0 000030
	CU	0 000040	0 000010		
	ZN	0 001060	0 000060	0 002330	0 000170
	AS	0 000020	0 000001	0 000030	0 000001
	BR	0 000030	0 000010		
	PB	0 000170	0 000030	0 000220	0 000100
	C	0 446000	0 044600	0 475000	0 047500

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
BLAST FURNACE AREA DUST GRANITE CITY (34)	NA	0 005220	0 000620	0 002620	0 000550
	MG	0 030720	0 001160	0 020320	0 003820
	AL	0 015130	0 002100	0 012790	0 001760
	SI	0 051340	0 007530	0 040870	0 006180
	S	0 005730	0 001130	0 004290	0 001230
	CL	0 002400	0 000470	0 004720	0 000700
	K	0 002560	0.000430	0.002160	0 000400
	CA	0 147820	0 017350	0 117540	0 013750
	TI	0 001590	0 000140	0 000820	0 000200
	V	0 000220	0 000010	0 000200	0 000010
	CR	0 000550	0 000060	0 000420	0 000080
	MN	0 005720	0 000360	0 007490	0 000520
	FE	0 202110	0 011410	0 290510	0 017540
	NI	0 000250	0.000020	0.000290	0 000040
	CU	0 000210	0 000020	0 000340	0 000040
	ZN	0 035430	0 002030	0 057540	0 003490
	AS	0 000010	0 000001	0 000020	0 000001
	SE	0 000020	0 000010	0 000020	0 000020
	BR	0 000050	0 000010	0 000030	0 000030
	CD	0 000180	0 000100	0 000250	0 000220
	SN	0 000190	0 000160		
	PB	0 001390	0 000100	0 001840	0 000160
	C	0 038000	0 003800	0 173000	0 017300
SLAG CRUSHER AREA DUST GRANITE CITY (35)	NA			0 002750	0 000580
	MG	0 050190	0 003130	0 036550	0 004080
	AL	0 032270	0 004460	0 029970	0 004080
	SI	0 105750	0 015530	0 097100	0 014610
	S	0 010240	0 001570	0 015970	0 002250
	K	0 002890	0 000500	0 003340	0 000570
	CA	0 216610	0 025600	0 228800	0 026580
	TI	0 004330	0 000260	0 003750	0 000250
	V	0 000120	0 000001	0 000100	0 000001
	CR	0 000150	0 000020	0 000180	0 000030
	MN	0 005030	0 000300	0 007280	0 000440
	FE	0 054500	0 002940	0 049330	0 002920
	NI	0 000080	0 000010	0 000110	0 000020
	CU	0 000060	0 000010	0 00012	0 00003
	ZN	0 000510	0 000030	0 00101	0 00007
	AS	0 000010	0 000001	0 00001	0 000001
	SE	0 000010	0 000010	0 00002	0 00002
	BR	0 000010	0 000010		
	CD	0 000090	0 000070		
	PB	0 000100	0 000030	0 00013	0 00007
	C	0 128000	0 012800	0 061	0 0061
PELLET STORAGE AREA DUST GRANITE CITY (18)	NA	0 001830	0 000490	0 002700	0 000500
	MG	0 020800	0 003070	0 016290	0 003930
	AL	0 008320	0 001230	0 011930	0 001670
	SI	0 037530	0 005870	0 057090	0 008710
	S			0 003290	0 001110
	K	0 000670	0 000240	0 001620	0 000360
	CA	0 079260	0 009890	0 112600	0 013390
	TI	0 000320	0 000300	0 000610	0 000220
	V	0 000300	0 000010	0 000250	0 000010
	CR	0 000520	0 000090	0 000470	0 000090
	MN	0 001860	0 000200	0 001950	0 000190
	FE	0 471690	0 026770	0 326670	0 020870
	NI	0 000170	0 000020	0 000170	0 000030
	CU	0 000120	0 000020	0 000180	0 000040
	ZN	0 000260	0 000030	0 000450	0 000050
	AS	0 000010	0 000001	0 000020	0 000001

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
PELLET STORAGE AREA DUST GRANITE CITY (18)	SE	0 000030	0 000010		
	BR	0 000030	0 000020		
	CD			0 000500	0 000270
	PB				
	C	0 083000	0 008300	0 004100	0 000410
MILLING AREA DUST GRANITE CITY (19)	NA	0 003190	0 000570	0 002400	0 000520
	MG	0 040950	0 003230	0 021490	0 003740
	AL	0 022620	0.003100	0.017570	0 002400
	SI	0 073510	0 010700	0 056800	0 008560
	S	0 002690	0 000840	0 005080	0 001130
	CL	0 000610	0 000280		
	K	0 002350	0 000430	0 001770	0 000380
	CA	0 187700	0 021910	0.157460	0 018300
	TI	0 002060	0 000140	0 001250	0 000170
	V	0 000250	0 000010	0 000200	0 000001
	CR	0 000610	0 000060	0 000540	0 000070
	MN	0 006630	0 000400	0 006660	0 000440
	FE	0 199150	0 010810	0 222930	0 013250
	NI	0 000270	0 000020	0 000280	0 000030
	CU	0 000300	0 000020	0 000390	0 000040
	ZN	0 021470	0 001190	0 029810	0 001780
	AS	0 000010	0 000001	0 000010	0 000001
	SE	0 000030	0 000010	0 000020	0 000020
	BR	0 000030	0 000010		
	SN	0 000230	0 000120		
	PB	0 000740	0 000060	0 000870	0 000100
	C	0 051000	0 005100	0 023000	0 002300
SAUGET ZINC SMELTER AMBIENT AIR (25)	AL			0 005120	0 000512
	SI			0 007180	0 000718
	S			0.064487	0.006449
	CL			0 096594	0 009659
	K			0 005092	0 000509
	CA			0 002546	0 000254
	TI			0 000224	0 000022
	V			0 000073	0 000007
	CR			0 000171	0 000017
	MN			0 002678	0 000268
	FE			0 012700	0 001270
	NI			0 000134	0 000013
	CU			0 002143	0 000214
	ZN			0 005115	0 000512
	SE			0 000068	0 000007
	BR			0 001454	0 000145
	CD			0 001972	0 000197
	SN			0 000367	0 000037
	PB			0 003325	0 000333
SAUGET COPPER SMELTER AMBIENT AIR (26)	AL			0 006550	0 000655
	SI			0 008077	0 000807
	S			0 098423	0 009842
	CL			0 002709	0 000271
	K			0 007699	0 000770
	CA			0 004898	0 000489
	TI			0 000352	0 000035
	V			0 000133	0 000013
	CR			0 000204	0 000020
	MN			0 000428	0 000043
	FE			0 004837	0 000484
	NI			0 000372	0 000037

		COARSE		FINE	
SOURCE (ID #)	ELEMENT	FRACTION	STANDARD ERROR	FRACTION	STANDARD ERROR
SAUGET COPPER SMELTER AMBIENT AIR (26)	CU			0 088811	0 008881
	ZN			0 014020	0 001402
	AS			0 003174	0 000317
	SE			0 002107	0 000211
	BR			0 000663	0.000066
	CD			0 002434	0 000243
	SN			0.009745	0 000975
	PB			0.013536	0 001354