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Atmospheric Research and Monitoring Study of Hazardous Substances:

Third Annual Report

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Illinois State Water Survey

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Atmospheric Research and Monitoring Study of Hazardous Substances: Third Annual Report

by

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ABSTRACT

During this third project year, a network of three urban and one rural sampling stations was operated to monitor hazardous chemicals in the atmosphere of Illinois. Seventeen toxic trace elements were measured on airborne inhalable particles or as vapor. Stack and fugitive emissions from major industrial sources account for most of the increase in airborne trace element concentrations above regional background levels. Resuspended surface soil and dust were identified as important components of these emissions. Finally, a preliminary data base of toxic volatile organic concentrations at the sampling sites is presented.

EXECUTIVE SUMMARY

The handling and disposal of hazardous materials can result in emissions of toxic chemicals into the atmosphere. Volatile chemicals can evaporate during transfer operations, from spills and leaks, or directly from disposal impoundments and landfills. Nonvolatile materials and poorly combustible materials can be emitted from incinerator stacks, generally in particulate form. In addition, some toxic materials can be formed and released during incineration.

Two classes of toxic chemicals have been selected for examination in this study. One class consists of a group of 17 toxic trace elements and their compounds that have the potential to affect human health by airborne exposure. The elements chosen can be readily analyzed in aerosol particles using commercially available multi-element instrumental techniques. The second class, volatile toxic organic chemicals, includes both aromatic and halogenated hydrocarbons that also have potential human health effects. These compounds were collected and analyzed using recently developed techniques for handling trace organic gases in ambient air.

To date, there has been very little comprehensive monitoring of either of these groups of chemicals in Illinois and almost no work on source attribution. More information on their physical and chemical characteristics is needed to model transport and deposition of trace elements and organics and to make better decisions about pollution abatement.

The overall objective of this project is to provide an in-depth chemical and physical characterization of airborne toxic trace elements and toxic volatile organics in Illinois. From July 1986 to June 1987, the period covered in this report, the following aspects of this work were carried out:

1. A data base for particulate toxic trace elements was developed and preliminary source apportionment analysis undertaken.
2. Particle size distributions of toxic elements were determined under a variety of conditions.
3. Source determination was also carried out using the streaker sampler.
4. Vapor phase species of the volatile toxic trace elements (arsenic, mercury and selenium) were collected and analyzed.
5. A preliminary data base for volatile organics was begun.

Trace Element Data Base

Data for 17 toxic trace elements were obtained using a combination of x-ray fluorescence and instrumental neutron activation analysis. These data are summarized in Table 1. In most cases, the concentrations found at the Bondville site are similar to national rural values and are representative of regional background. The major exception is lead. Both urban and rural airborne levels of this element have declined markedly during the last 10 years with the introduction of unleaded gasoline. At the urban sites, airborne trace elements often approach regional background levels. Occasionally, these "normal" concentrations increase dramatically. Such pollution episodes coincide with wind directions from nearby industrial point sources. The average concentrations are then a composite of regional background values and elevated values due to the influence of nearby sources. At a particular sampling point, the concentration is a function of prevailing wind direction during the sampling period.

In terms of human health risk, two elements in this data base are of particular concern. Cadmium concentrations are quite high at the East St. Louis site due to the presence of a zinc smelter nearby. Airborne cadmium is an important carcinogen even at "normal" urban concentrations, which are 10 times lower than those found in East St. Louis. Airborne chromium is also an important carcinogen; however, the concentrations found near steel mills in southeast Chicago are only slightly higher than those associated with "normal" urban air.

Particle Size Distributions

Airborne particulate matter was separated into six particle size fractions using a cascade impactor with a high-volume sampler. By analysis of wind direction during the sampling period, samples that are strongly influenced by major sources can be identified. In air affected by these sources, the particle size distribution for many trace elements differs markedly from the regional background distributions. For these trace elements there is a larger proportion on the coarse inhalable particles (10-4 μm). These particles are thought to originate from mechanical processes and wind erosion. Although particles in the coarse size range do not penetrate deeply into the lungs, they settle rapidly out of the atmosphere and contaminate nearby urban soil and dust.

Source Determination

The streaker sampler was used to determine sources and peak concentrations. With this method, sampling intervals as short as two hours can be used. This high time resolution makes it possible to measure peak concentrations. It is also easier to identify sources with this data because wind direction tends to be constant during such short sampling periods.

Table 1. Average Toxic Trace Element Concentrations in Inhalable Airborne Particles.[a]

Element	Bondville	Chicago	E. St. Louis	Granite City	U.S. Average[b] Urban/Rural
Vanadium (V)	.002	.007	.006	.006	.021/.008
Chromium (Cr)	.002	.013	.006	.010	.011/.007
Manganese (Mn)	.010	.100	.025	.047	.038/.020
Nickel (Ni)	.001	.006	.004	.003	.010/.003
Copper (Cu)	.005	.019	.004	.026	-
Zinc (Zn)	.034	.175	.164	.104	.160/.040
Selenium (Se)	.002	.004	.003	.003	-
Molybdenum (Mo)	<.001	.003	.001	.001	.002/.001
Silver (Ag)	.001	.002	.003	.002	-
Cadmium (Cd)	.001	.003	.019	.005	.002/.001
Tin (Sn)	.001	.009	.010	.008	-
Antimony (Sb)	.003	.011	.010	.011	-
Barium (Ba)	.004	.010	.013	.011	.030/.010
Mercury (Hg)[c]	.001	.001	.001	.001	-
Cobalt (Co)	<.001	.001	.001	<.001	-
Lead (Pb)	.027	.184	.181	.114	.580/.084
Arsenic (As)	.001	.003	.004	.002	-
Total PM10	27	46	39	46	-

[a] Particle diameter <10 μm, concentrations are in $\mu g/M^3$.
[b] USEPA Data (1979).
[c] Substantial amounts of Hg are in the vapor phase.

The data on individual elements indicate that steel mills are a major source of manganese, chromium, lead and zinc in Chicago. Smelters are major emitters of zinc, copper and lead in East St. Louis and Granite City. Also identified as trace element sources were an incinerator in St. Louis and a paint plant in Chicago.

In several cases, trace element emissions seemed to be due to fugitive emissions of resuspended urban soil and dust. For example, the coarse Pb emissions from the secondary lead smelter in Granite City strongly correlated with wind speed suggesting wind erosion of deposited surface material.

Vapor Phase Trace Elements

Using special vapor traps, the vapor phases of mercury, arsenic and selenium were collected in filtered air. In regional background samples, only mercury was detected in the vapor phase. In urban samples, from 20 to 80 percent of the mercury and 15 to 30 percent of the selenium were present in the vapor phase. No vapor phase arsenic was detected.

Volatile Organics Data Base

Volatile toxic organics were analyzed in grab samples taken at all four sampling locations. Up to 12 individual toxic compounds were determined. These data are summarized in Table 2. In general, concentrations were similar to those found in other urban areas in the U.S. Occasionally, high concentrations were detected. In these cases, analysis of the wind direction suggests these emissions originated from nearby industrial sources. However, too few samples were collected to accurately assess the frequency or effect of such events on overall air quality.

Table 2. Average Concentrations of Toxic Organics (ppbv)[a].

Compound	Bondville	Chicago	E. St. Louis	Granite City	U.S. Average Urban/Rural
benzene	0.2	1.6	1.0	0.8	2.8/1.4
toluene	0.5	1.7	1.1	2.0	11/0.7
ethylbenzene	0.1	0.2	0.2	0.3	1.2/0.5
o-xylene	0.4	2.2	0.4	2.1	1.2/0.1
m,p- xylene	0.1	0.6	0.6	1.0	2.8/0.1
chlorobenzene	ND[b]	0.3	ND	ND	1.5/0
styrene	ND	0.1	0.7	0.2	0.5/0
chloroform	0.3	0.4	2.5	0.1	0.1/0.04
methylchloroform	0.2	0.5	0.3	0.3	0.5/0.1
carbon tetrachloride	0.07	0.07	0.1	0.05	0.2/0.1
tetrachloroethylene	0.03	0.2	0.1	0.05	0.3/0.2

[a] parts per billion on a volume:volume basis
[b] ND = not detected

Conclusions and Recommendations

The overall picture of airborne trace elements at the urban sites studied is one in which the concentrations of these elements normally approach regional background levels. This situation is often interrupted by pollution episodes during which trace element concentrations may rise by a factor of 10 or more. Such episodes occur when the wind blows from the direction of major industrial point sources or during periods of low wind speed when mixing is reduced. Thus the average concentrations are made up of a combination of regional and local inputs and depend on the prevailing wind direction.

Two elements were identified that are of particular concern: cadmium in East St. Louis and chromium in southeast Chicago. Both of these elements are carcinogens and pose a significant health risk even at "normal" urban levels. The concentrations measured in this study are significantly higher than those found at other urban locations in the U.S.

Particle size determinations and source identification indicate that resuspension of urban soil and dust makes a significant contribution to the amounts of trace elements in inhalable particles in urban air. This is especially true when winds are from the direction of major industrial sources. The fact that such resuspended material may have been deposited during earlier pollution episodes means that the concentration of airborne trace elements may not always reflect current industrial activity or stack emissions.

Vapor phase mercury and selenium are significant components of urban air. This means that these elements are under-sampled if only airborne particles are analyzed.

Finally, concentrations of airborne volatile toxic organics were generally similar to those expected for urban areas. Better assessment of average values and better identification of the sources of these compounds will be made using time-integrated sampling over several hours coupled with wind direction data.

CHAPTER I. INTRODUCTION

Toxic materials can enter the atmosphere via a wide variety of human activities including the handling and disposal of hazardous wastes. Chemicals with low volatility can be released during high temperature processes such as incineration (Wallace and Trenholm, 1985) or emitted as mechanically generated or wind-blown dust. Many highly volatile materials are readily destroyed at high temperatures but can vaporize as fugitive emissions from leaks, spills, impoundments or land disposal sites (U.S. EPA, 1985).

This study focuses on two classes of toxic chemicals that have been associated with most of the health risk due to ambient urban air (Thomson et al., 1985). One group is the toxic trace elements, 17 elements (see Table 3) and their compounds that can occur in urban air at levels that may be harmful to human health. The second group consists of toxic volatile hydrocarbons, a variety of chlorinated and aromatic organic chemicals (see Table 7) emitted into urban air from a large number of different sources.

To date, there has been very little comprehensive monitoring of either of these groups of chemicals in Illinois and even less work on source attribution. The Illinois Environmental Protection Agency (IEPA, 1987) currently monitors 8 of the toxic trace elements, (Mn, Cr, Se, As, Pb, Ni, Be and Cd) but does not determine particle size distributions or sources. This information is needed to model transport and deposition of trace elements and to make better decisions about pollution abatement. Toxic organics are not routinely monitored in Illinois so little information exists on ambient levels or major sources. The few previous studies done in Illinois on these chemicals have been very short-term and limited in scope (Brodzinsky and Singh, 1983; Singh et al., 1985).

This report covers the third year of a project designed to evaluate the amounts and sources of selected toxic air pollutants in two urban airsheds in Illinois. In the first year's report (Gatz and Sweet, 1985), background on previous monitoring in Illinois, on sampling and analysis methods, and on the potential effects of hazardous waste incineration in Illinois were reviewed. The second annual report (Sweet and Gatz, 1987) discussed the sampling network, sampling and analysis protocols and included a preliminary data base for toxic trace elements. In this, the third report, additional data on toxic trace elements will be discussed together with the most likely sources of these materials in the study areas. Preliminary data on the volatile organics will also be presented; however, this data base is not currently complete enough to fully attribute sources. Finally, quality assurance measures and results will be discussed.

The overall objective of this project is to provide an in-depth chemical and physical characterization of airborne toxic trace elements and toxic volatile organic chemicals in Illinois. From July 1986 to June 1987, the period covered in this report, our objectives were to carry out the following aspects of the work:

1. To continue monitoring particulate toxic trace elements for incorporation into a data base that can be used for source apportionment analysis.
2. To collect and analyze size-fractionated aerosol samples for determination of the particle size distribution of toxic elements under a variety of conditions.
3. To make preliminary estimates of source attribution for the toxic trace elements.
4. To collect and analyze samples of vapor-phase toxic trace elements (arsenic, mercury and selenium).
5. To begin collection and analysis of volatile toxic organics.

The results are presented in the remainder of this report.

CHAPTER II. SAMPLING LOCATIONS

One rural and three urban sampling stations have been established for this project at the locations indicated in Figure 1. Each station is equipped to continuously monitor wind speed, wind direction, temperature, relative humidity and solar radiation. Aerosol samples are taken using an automatic dichotomous sampler capable of collecting both fine (<2.5 μm) and coarse (2.5-10 μm) inhalable particles. Quarterly cascade impactor samples (24 hour) are taken at each site with an instrument capable of dividing inhalable aerosol particles into six size fractions. Volatile toxic trace elements are measured quarterly using back-up vapor traps on the dichotomous samplers. Finally, 1-week "streaker" samples are taken once a year at each site. This combination of sampling methods allows a very complete analysis of the variation in concentration and particle size distribution of several airborne toxic trace elements. The information generated by this analysis is useful in evaluating human exposure to airborne toxic pollutants, in predicting their movements and deposition, and in determining their most significant sources.

The precise locations of the three urban sampling sites are shown in Figures 2, 3, and 4. The Chicago site is located at Bright Elementary School (10740 S. Calhoun). This site is affected by a wide variety of urban pollutant sources including transportation, fuel handling, resuspended dust, coal burning, materials handling, and manufacturing. In addition, this site is strongly affected by a large steel making complex to the southeast. There is also a hazardous waste incinerator 2 kilometers to the southwest of the site.

The East St. Louis site (13th and Tudor) is also surrounded by many urban pollutant sources similar to those found at the Chicago site and is near a hazardous waste incinerator as well. The most important trace element sources at this site are the nonferrous metals smelters located to the southwest of the site. The Granite City site (20th and Adams) is near a secondary lead smelter and a number of steel-making complexes.

The fourth site in our network is located in a rural area outside of Champaign, 8 kilometers south of Bondville, IL. This site is 13 kilometers from the nearest urban area and about 50 kilometers downwind from all urban areas during times of prevailing SW and NW winds. Because the trace element levels in this location are probably typical of rural areas in most of Illinois, this site will provide background levels of toxic pollutants to compare with the urban levels.

The three urban sites have the highest concentrations of total suspended particulate matter (TSP) for all sites in the statewide IEPA network. They represent the worst known air quality in residential areas in Illinois. Many sources emit toxic materials into the air in these areas. For this reason, they provide an opportunity to study a wide variety of sources at a small number of sites. By fully characterizing the air quality at these three sites, information will be gathered that may apply to many other urban areas in Illinois with similar sources.

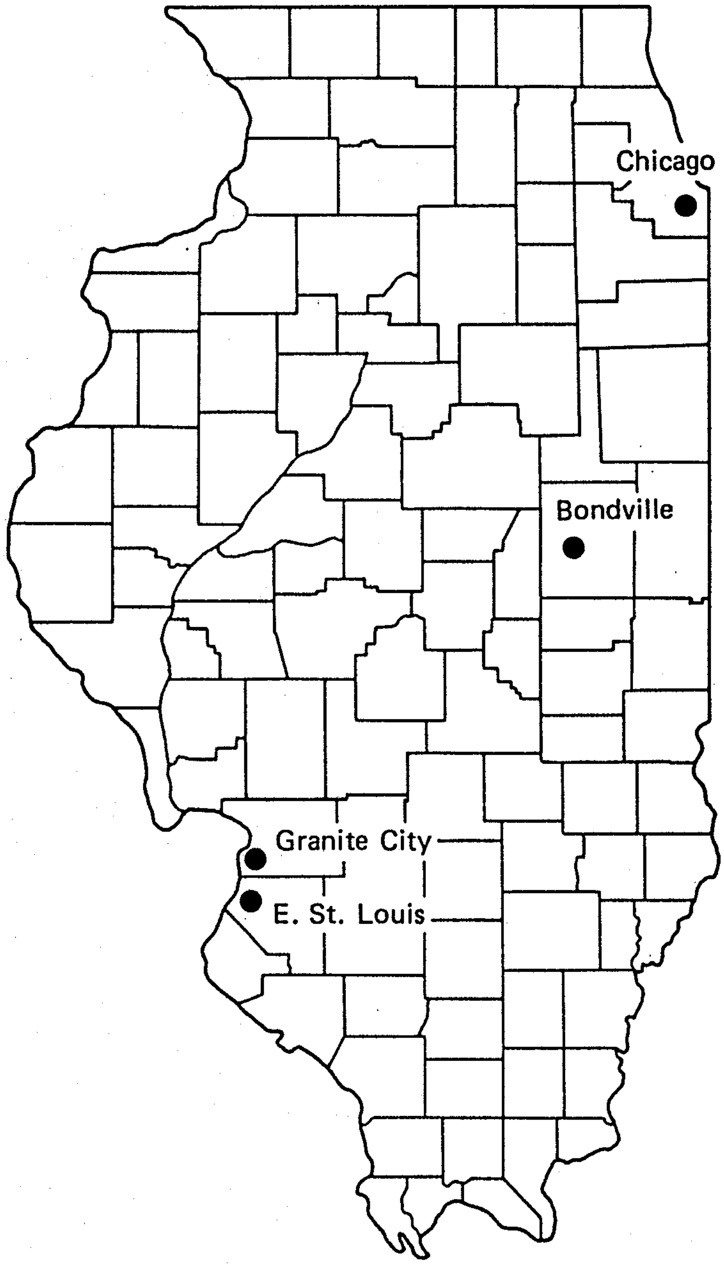


Figure 1. Toxic air pollutant sampling sites.

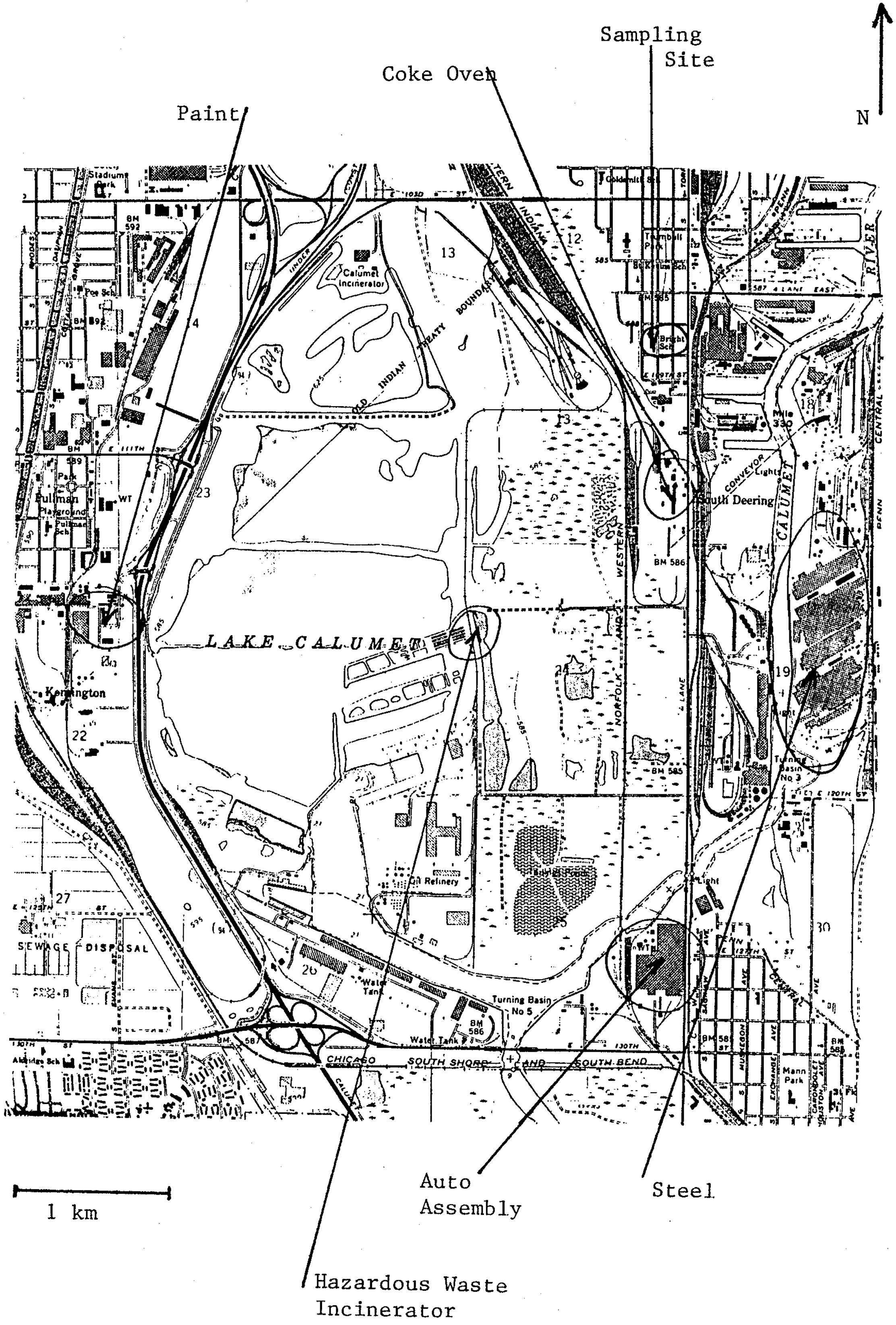


Figure 2. Chicago Site Map .

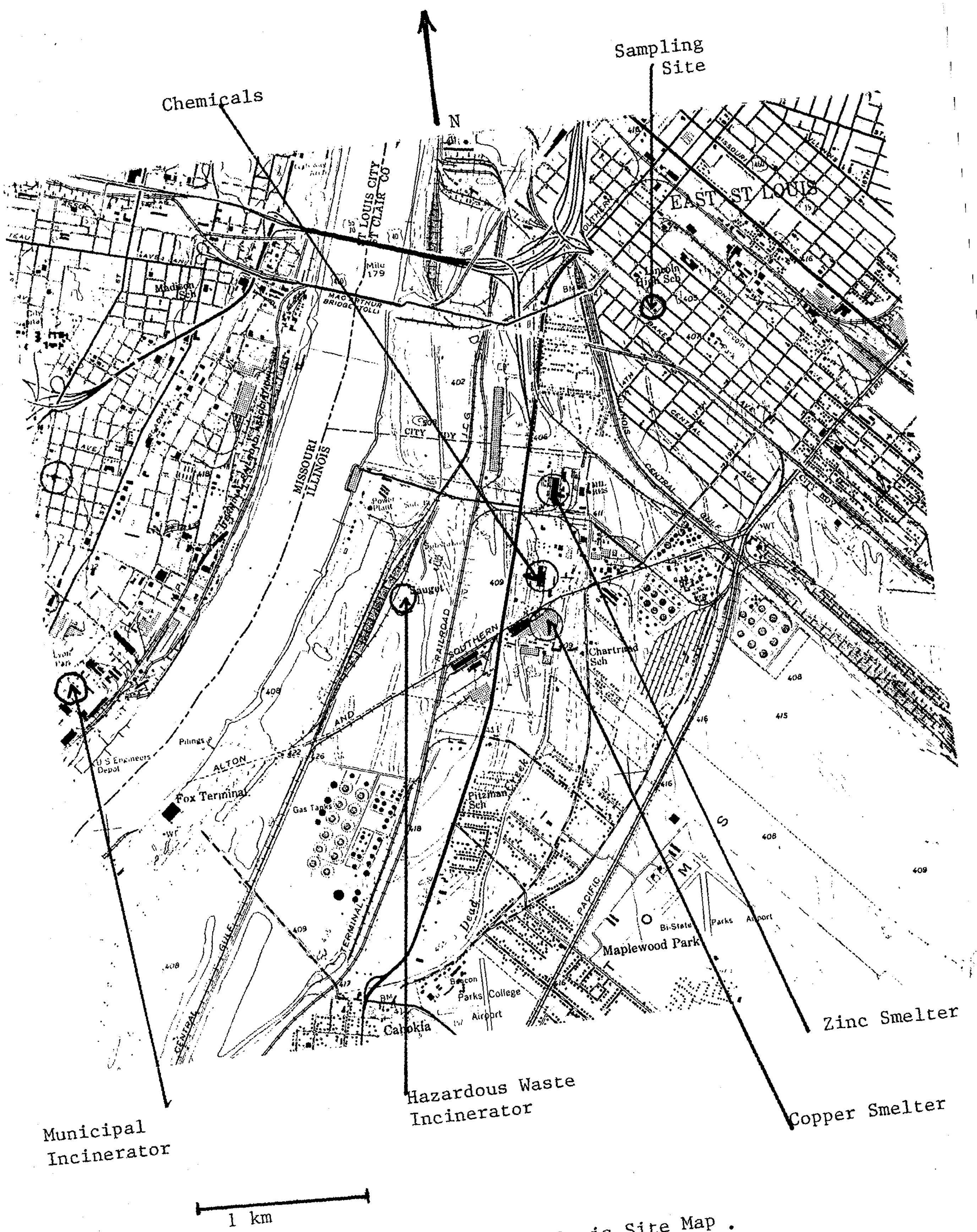


Figure 3. East St. Louis Site Map .

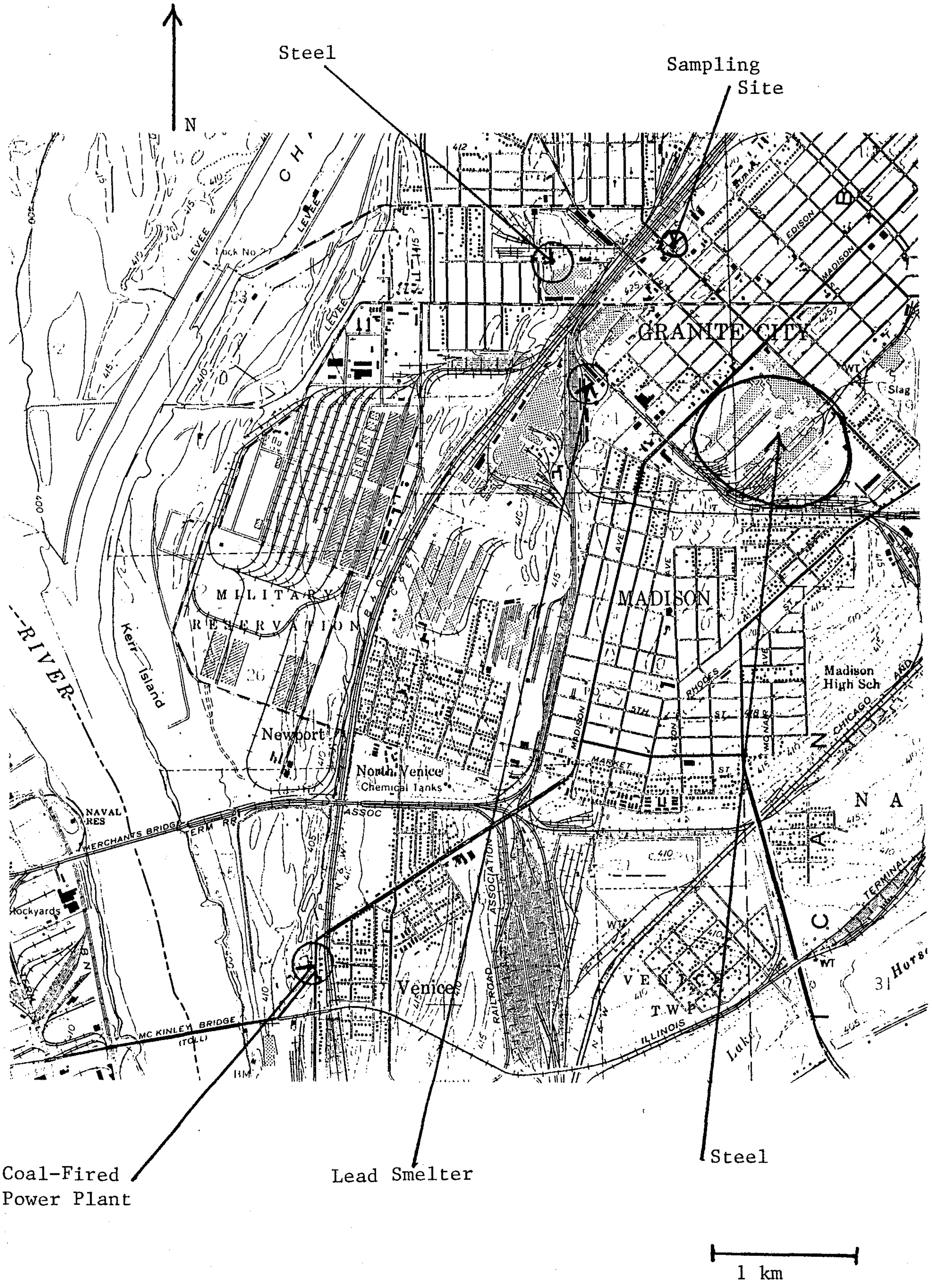


Figure 4. Granite City Site Map.

CHAPTER III. TOXIC TRACE ELEMENTS

Nineteen toxic trace elements have been selected as target chemicals for this study. Their presence in the atmosphere is due to human activities and their concentrations in urban areas have increased greatly during the last few decades (Galloway et al., 1982). All of these elements have acute toxic effects at levels much higher than the levels found in ambient urban air; however, the potential health effects of chronic exposure to low levels of these chemicals, especially those with mutagenic or carcinogenic properties, are of concern. Table 3 lists these 19 elements, their most important urban sources, and their health effects. Although the toxic effects of elements and their individual compounds can vary considerably, no attempt was made in this work to analyze elements and their compounds separately. All the concentrations given are total amounts. Of the 19 elements, 17 could be determined in ambient aerosol particles using either instrumental neutron activation analysis (INAA) or x-ray fluorescence (XRF).

Results from 21 months of monitoring at the sampling sites (September 1985 to June 1987) are given in Table 4. Data collection and analysis were discussed in an earlier report (Sweet and Gatz, 1987). Values for PM-10 were determined by direct weighing. All of the elements except As and Co were determined by x-ray fluorescence (XRF). As and Co were determined by instrumental neutron activation analysis (INAA). Averages were calculated from all measured values. A value of one-half the detection limit was used in this calculation for all measured values below detection limit.

The data from the Bondville site represent background concentrations for Illinois. This is a rural site reflecting regional air quality. As such, it is influenced to some degree by long-range transport of pollutants from urban areas and other sources up to several hundred kilometers away. Indeed, when higher levels of fine Pb, for example, have been found at Bondville, back-trajectory calculations indicate movement of air masses from urban source areas during the sampling periods.

The average concentrations of most of the trace elements are roughly 5 times higher in the urban samples than in the rural samples. This indicates that regional pollution sources account for about 20 percent of the average toxic trace element levels in urban air. The remaining 80 percent is derived from local sources. This local contribution is quite variable. Airborne trace elements in the urban areas can vary from near regional background levels to an order of magnitude higher. Episodes of high concentrations usually occur in conjunction with steady winds from the direction of major pollutant sources or light winds combined with local temperature inversion conditions that prevent the dispersal of pollutants.

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
Chromium (Cr)[a]	Coal, Steel	Carcinogen	XRF/INAA
Manganese (Mn)	Steel	Neurotoxin, Mutagen	XRF/INAA
Nickel (Ni)	Coal, Oil, Metallurgy	Carcinogen	XRF
Zinc (Zn)	Metallurgy, Incineration	-	XRF/INAA
Arsenic (As)[a]	Coal, Metallurgy	Carcinogen	INAA
Selenium (Se)	Coal, Metallurgy	Metabolic Toxin	XRF
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
Barium (Ba)	Coal	-	XRF
Mercury (Hg)	Coal	Neurotoxin	XRF
Lead (Pb)	Gasoline, Metallurgy	Neurotoxin, Mutagen	XRF
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

Table 4. Average and Maximum Concentrations of Trace Elements in Illinois.[a]

Parameter		Bondville		Chicago		E. St. Louis		Granite City	
		Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
PM10	Avg	17±8	10±8	27±11	19±12	22±15	17±9	25±18	21±19
	Max	32	47	50	81	95	44	99	97
V	Avg	0.8±0.5	0.9±0.7	3.5±3.3	3.8 ± 3.1	2.8±2.5	3.0±2.0	2.8±2.3	3.6±3.1
	Max	2.3	2.6	14	13	12	10	8	14
Cr	Avg	0.8±1.0	1.1±0.9	5.3±5.5	7.6±6.7	1.8±2.3	3.9±2.9	3.1±4.7	7.4±7.0
	Max	5.9	3.6	28	35	14	17	27	32
Mn	Avg	3.7±2.3	5.8±4.1	43±54	56±82	8.5±5.2	15±10	13±11	34±30
	Max	12	18	259	563	24	62	48	152
Ni	Avg	0.5±0.3	0.6±0.5	3.3±3.1	2.3±2.0	2.0±1.4	1.7±1.4	1.6±1.3	1.5±1.2
	Max	1.5	2.1	13	11	5.7	6.0	7.2	5.7
Cu	Avg	2.9±2.6	2.3±5.5	14±19	5.2±6.5	78±176	9.4±11	20±22	6.0±8.1
	Max	12	24	129	44	775	50	87	42
Zn	Avg	26±35	8.4±9.2	136±127	39±36	87±98	85±116	65±55	39±38
	Max	210	46	577	216	497	514	250	174
As	Avg	0.8±0.4	0.5±0.3	1.6±1.7	1.0±10.9	1.9±2.6	1.6±1.8	1.2±0.6	1.0±0.6
	Max	1.2	0.9	4.8	2.7	8	5	2.3	2.0
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±0.9	0.3±0.2	3.1±2.2	0.4±0.4	2.4±1.9	0.4±0.4	2.3±1.6	0.3±0.4
	Max	4.0	1.1	9.8	2.2	11	2.1	8.7	1.5
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	0.8±0.9	0.6±1.1	1.5±2.1	1.0±1.4	12±21	7.0±15	2.9±3.3	1.8±2.1
	Max	2.7	4.5	9.8	4.9	90	88	13	7.5
Sn	Avg	0.6±0.8	0.7±0.9	6.9±11	2.2±3.2	7.3±13	2.9±5.5	5.1±11	2.5±2.9
	Max	2.8	2.8	57	16	67	39	67	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	1.1±1.3	0.3±0.3	0.7±0.5	0.4±0.4	0.8±0.9	0.3±0.4
	Max	.8	.5	7.1	1.2	2.0	1.9	4.1	1.6
Pb	Avg	22±12	5±3	156±235	28±42	136±127	45±45	74±64	40±74
	Max	54	13	1392	229	565	206	304	358

[a] PM-10 in $\mu g/m^3$, Elements in ng/m^3.

In comparing these data to information available from other networks, it is important to recognize that only inhalable particles (PM-10) were collected in this study. Until recently, only total suspended particles (TSP) were analyzed in most other sampling networks. Inhalable particles generally comprise about 60 percent of TSP (Kolaz, Sweitzer, and Bomke, 1986). The Illinois Environmental Protection Agency (IEPA) collects and analyzes aerosol particles at the urban sites used in this work. For many of the elements analyzed in both networks (Pb, Se, Cd, Ni and As), average concentrations are generally similar (IEPA, 1986, 1987). The concentrations of Mn and Cr found by IEPA in TSP are somewhat higher than those reported here because these two elements are found on large particles not sampled in PM-10 (see Chapter IV, Particle Size Distribution). Concentrations measured in a national network of urban sites (Evans et al., 1984) also comparable with or slightly higher than the results reported for this study. The major exceptions are the concentration of Cd, which is 10 times higher in East St. Louis than in other urban areas and Mn, which is twice as high in southeast Chicago. The concentration of inhalable airborne Cr is also high in southeast Chicago relative to other urban areas in Illinois and appears to be high relative to total airborne Cr in other major cities (Saltzman et al., 1985). The concentrations of Pb reported here are considerably lower than those reported for urban areas from their late 1970s. This is due to the reduced use of leaded gasoline in recent years. Finally, Se and Hg are notable in that the rural concentrations are almost as high as the urban concentrations. Shaw and Paur (1983) reported similar Se levels in aerosol samples collected at rural locations in the Midwest. These elements are much more volatile than the other toxic trace elements and their gaseous forms need to be considered as well as their particulate forms. More information on vapor phase trace elements can be found in Chapter VI, Vapor Phase Trace Elements.

CHAPTER IV. PARTICLE-SIZE DISTRIBUTIONS

As part of the sampling plan (Sweet and Gatz, 1987), inhalable aerosols are collected and fractionated using a high-volume sampler fitted with a six-stage cascade impactor (Andersen, Model 236). Size-fractionated samples are collected quarterly at each sampling site. The sampler filters about 1000 m^3 of air during a 24-hour period and is capable of separating the collected particles into six discrete size classes with diameters ranging from several microns to submicron particles. Since several milligrams of material are recovered in each fraction, a large number of toxic elements can be determined. Neutron activation analysis was used to analyze these filters. This method gives good results with 11 of the toxic elements listed earlier. Concentrations of Ag and Mo were near detection limits in the urban samples and below detection limits in the rural samples. Neutron activation is not suitable for determination of Pb, Cd, Hg and Sn. These elements were not determined in these samples.

Cascade impactor samples were taken at all four sampling sites. The urban samples could be divided into two categories on the basis of wind direction during the sampling period: 1) those which were heavily influenced by steel mills (Chicago and Granite City) or non-ferrous metal smelters (East St. Louis), and 2) those which were not influenced by these sources and which reflected typical ambient conditions for an urban area.

The particle size data are presented in Figures 5 to 15. In these graphs, particle size is plotted against the concentration for a particular size class. The total concentration is the sum of the concentrations for each size class. These concentrations vary widely depending on the element and the sources influencing a particular sample. Most of the elements show a bimodal distribution with the highest concentrations in the largest and smallest size classes. These maxima result from two different mechanisms for particle formation (Milford and Davidson, 1985). Larger particles are formed via mechanical processes such as wind erosion of materials contaminated with trace elements. On the other hand, trace elements become attached to small particles when they condense from the vapor state as hot stack or exhaust gases cool in the atmosphere. Since most of the available surface area for condensation is on submicron particles, these particles become enriched in trace elements. Enrichment of submicron particles in urban air is generally correlated to the volatility of individual elements. Se, Sb, Zn and As are more volatile and are concentrated on submicron particles (Figs. 5, 6, 7 and 9) while Cr, Mn, V, Co and Ba are nonvolatile and have more uniform particle size distributions (Figs. 10, 11, 13, 14, and 15).

The concentrations of several elements were much higher when the wind was blowing from the direction of a nearby industrial source. Smelters are important emitters of Se, Zn, Cu and As (Figs. 5, 7, 8 and 9) and steel mill emissions have relatively large amounts of Cr, Mn, Ni, V and Co (Figs. 10, 11, 12, 13, and 14). In many cases, these trace element concentrations are 10 or more times higher than those normally found in urban air. Since winds from the directions (SW and SE) of these industrial sources are relatively common throughout the year, they have a major effect on the average trace element concentrations seen at the urban sampling sites.

For most of the trace elements, the particle size distributions of urban and rural samples are similar. However, in those samples that are heavily affected by industrial sources the distribution is often shifted toward larger particle sizes. For example, in normal urban air the concentration of Zn in the 10-4μm fraction is considerably less than that found on submicron particles (Fig. 7). In air samples influenced by smelters, on the other hand, the large particles have more Zn than the small particles. A similar situation is found for Cr in samples affected by steel mill emissions (Fig. 10). Although large particles are less likely to be deposited in the lungs, the rapid dry deposition of larger particles from the atmosphere will result in more local contamination of urban soil and dust where toxic substances can pose an ingestion hazard for young children (Boeckx, 1986). A substantial amount of airborne particulate matter is larger than 10 μm in diameter (Kolaz, Sweitzer, and Bomke, 1986). Although trace element concentrations were not measured for particles larger than 10 μm, it seems likely that they would also be high, especially under conditions where coarse PM-10 particles are heavily loaded.

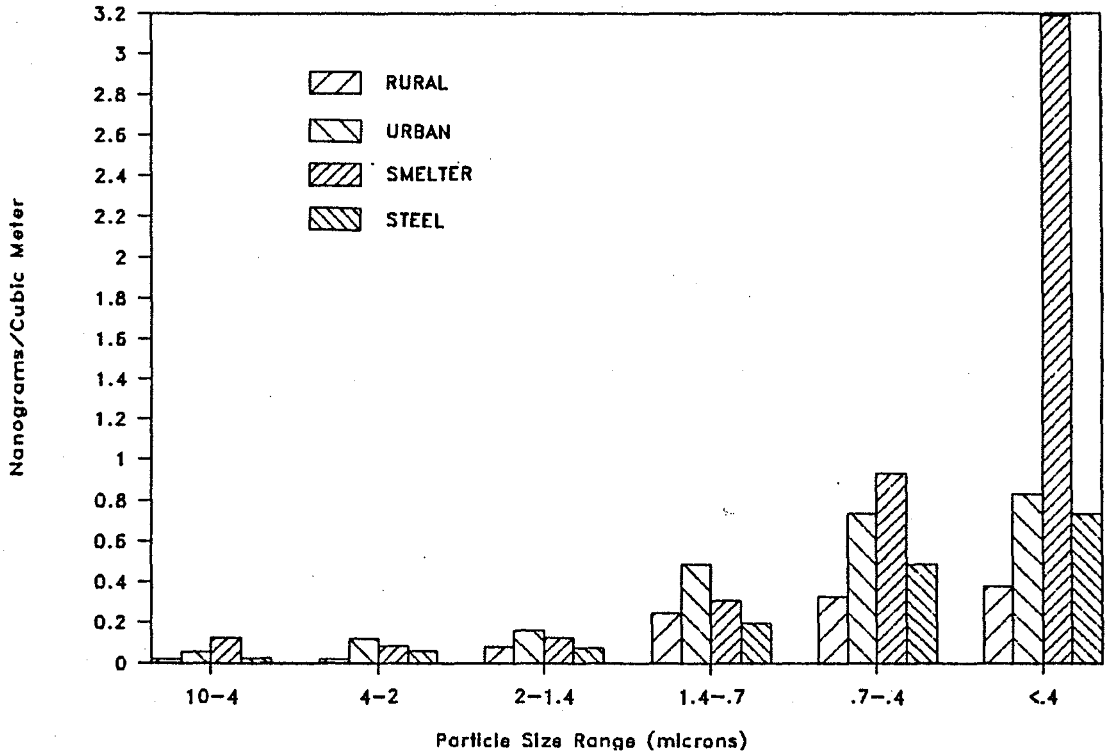


Figure 5. Particle size distributions of toxic trace elements in Illinois: selenium.

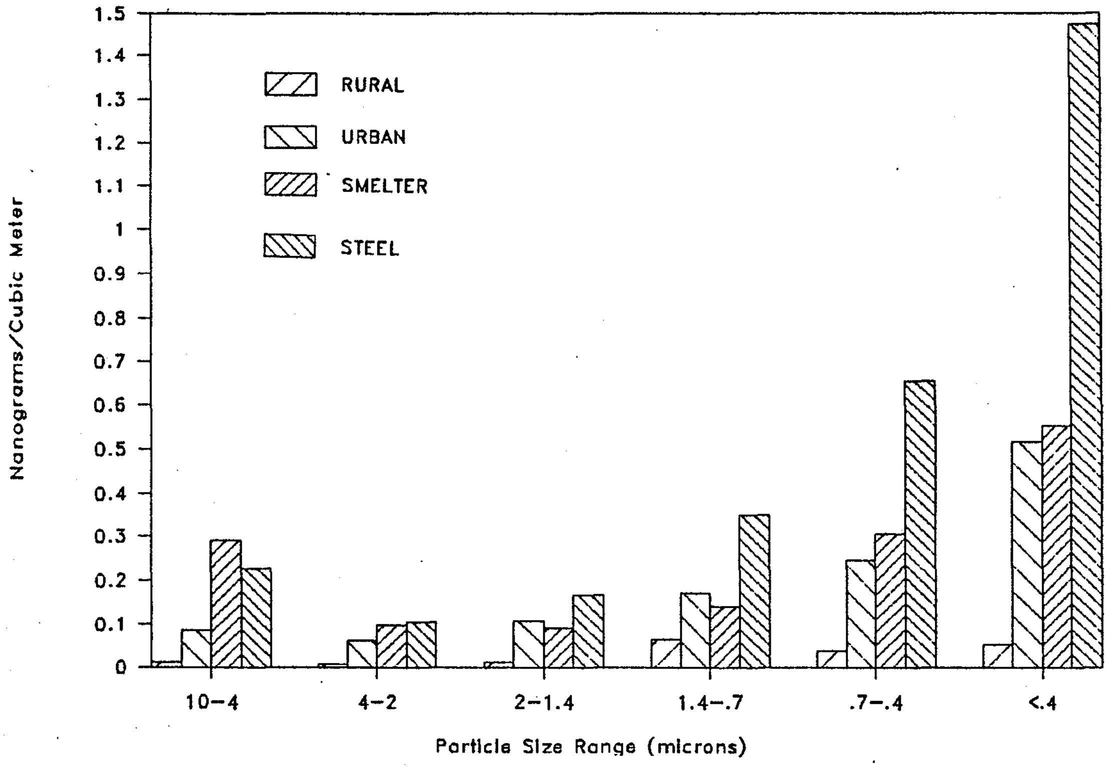


Figure 6. Particle size distributions of toxic trace elements in Illinois: antimony .

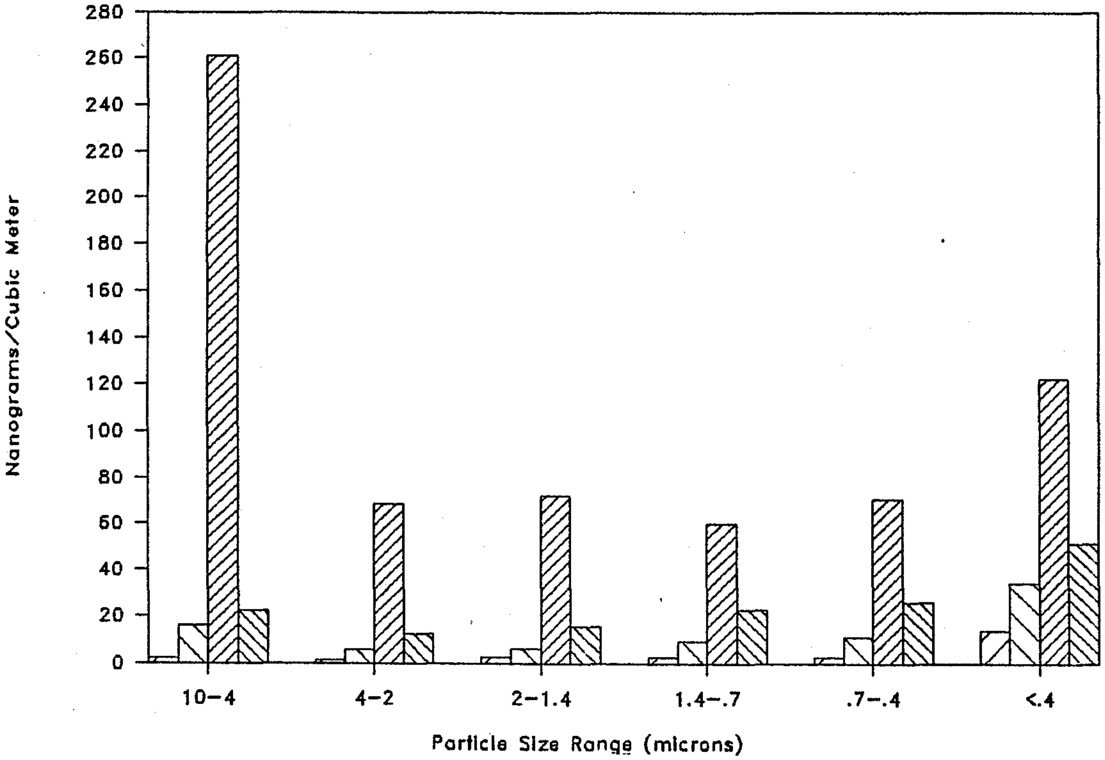


Figure 7. Particle size distributions of toxic trace elements in Illinois: zinc .

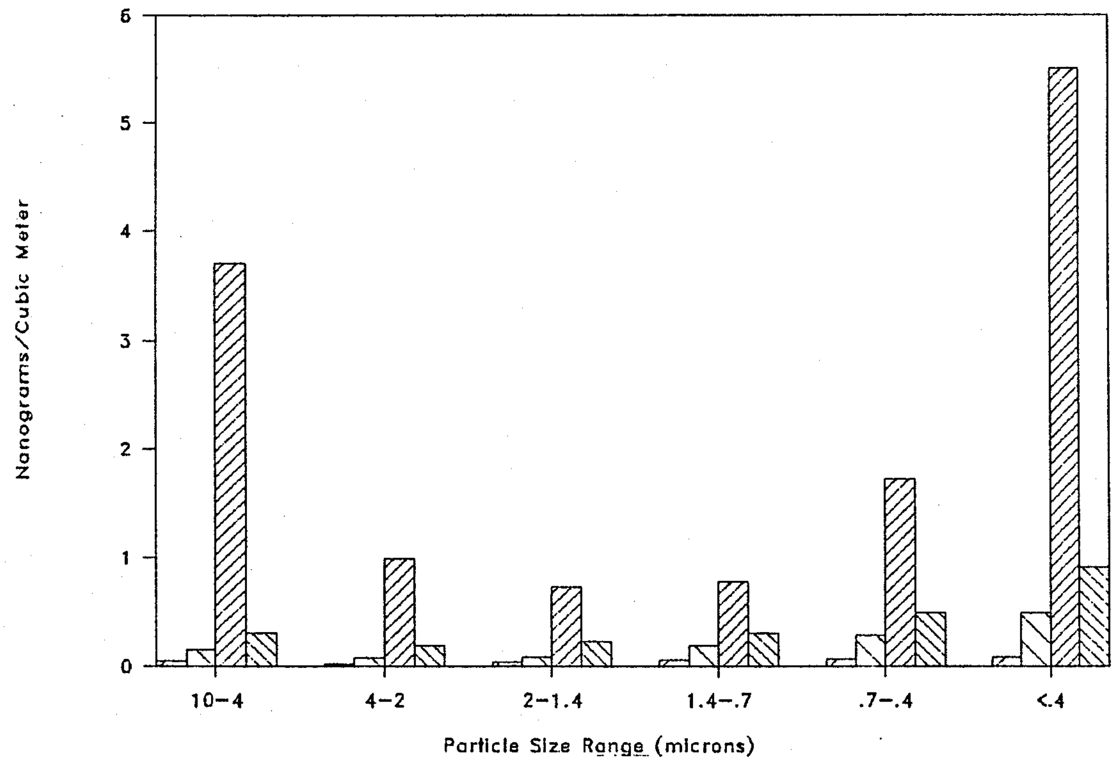


Figure 8. Particle size distributions of toxic trace elements in Illinois: copper .

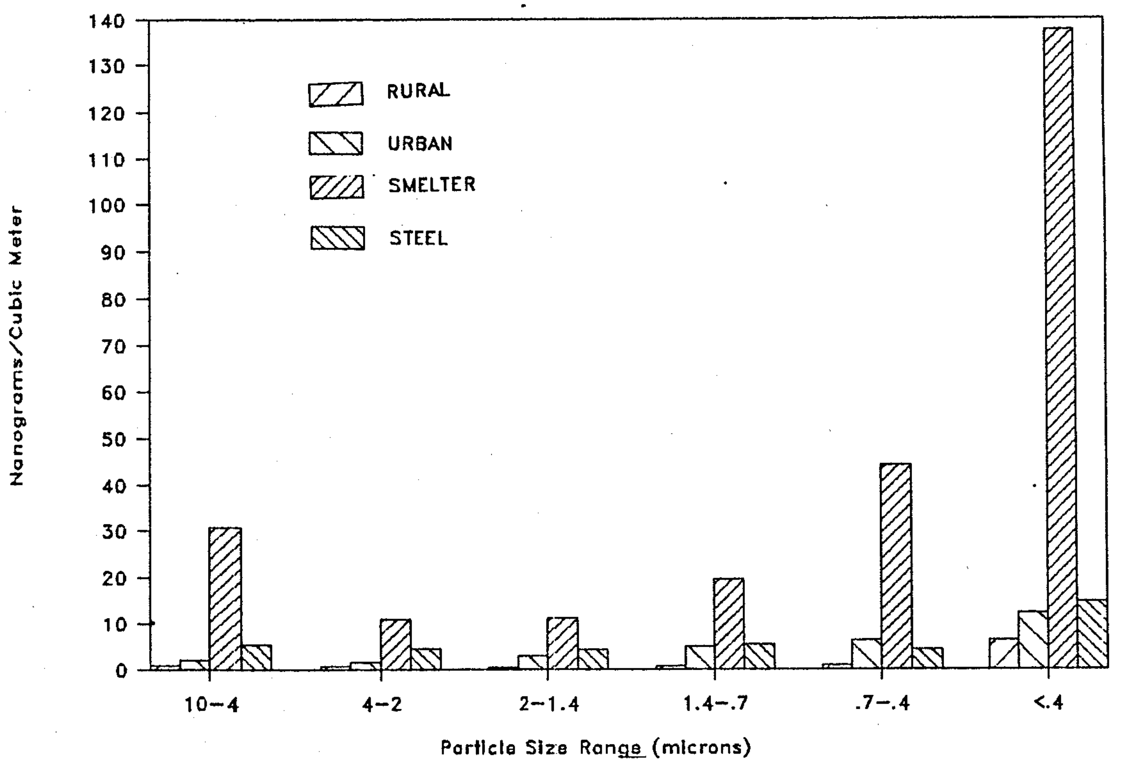


Figure 9. Particle size distributions of toxic trace elements in Illinois: arsenic.

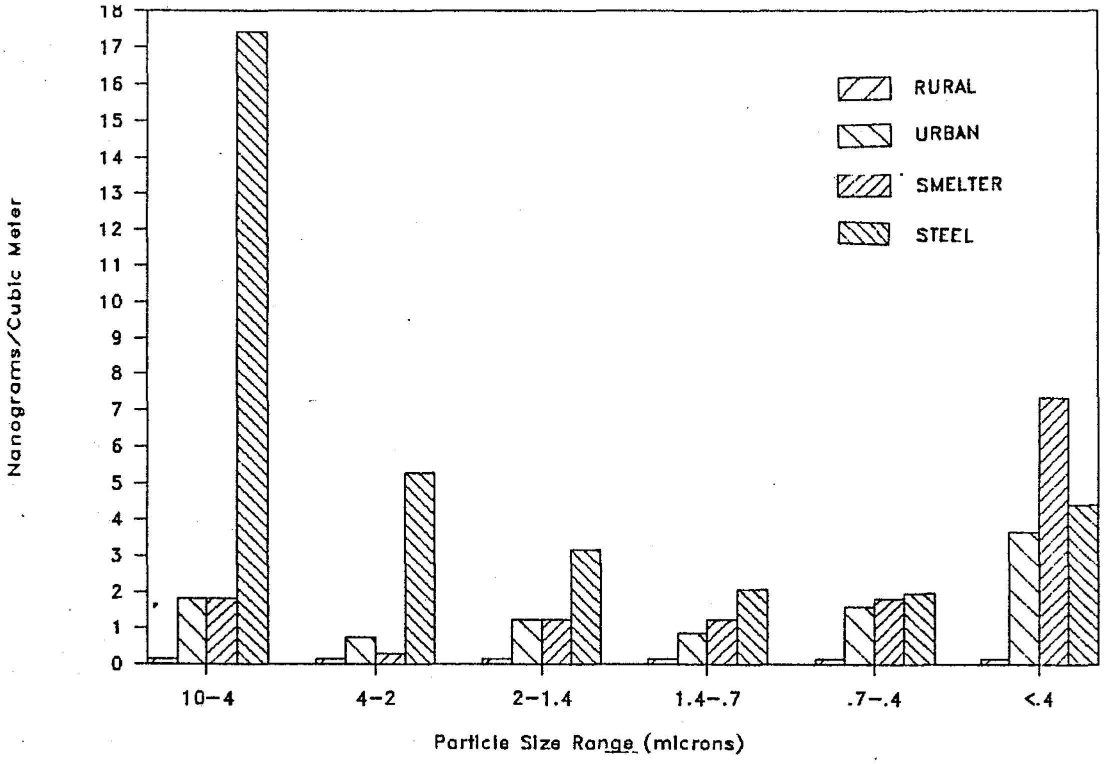


Figure 10. Particle size distributions of toxic trace elements in Illinois: chromium.

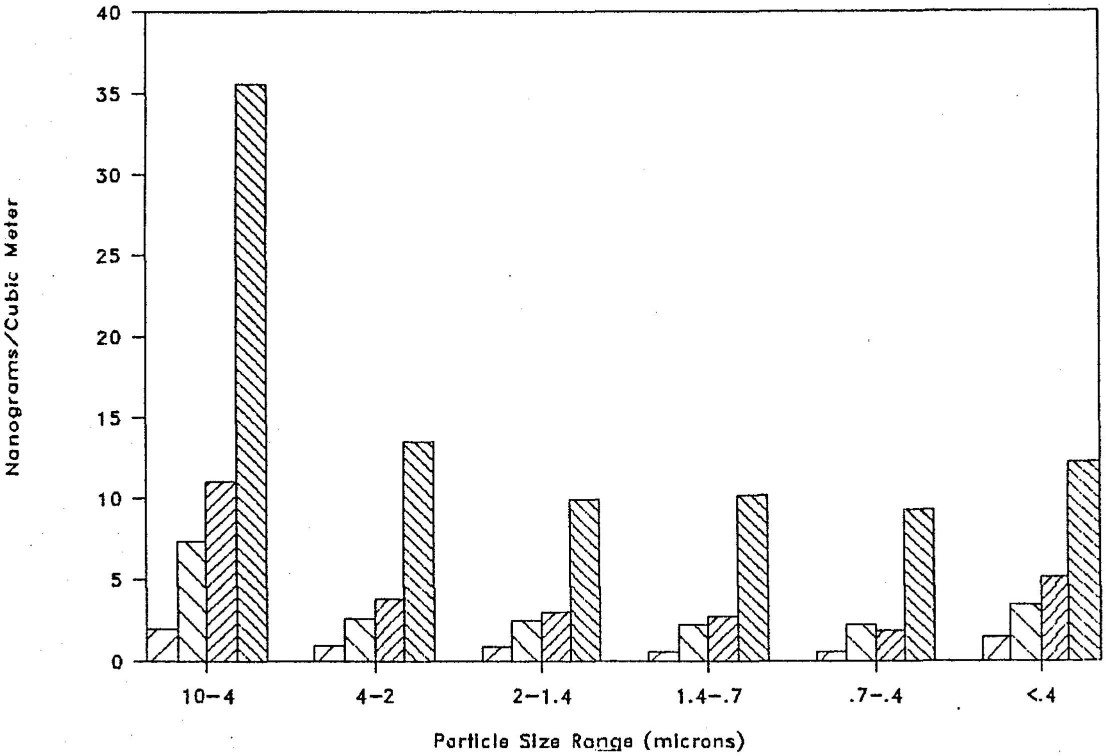


Figure 11. Particle size distributions of toxic trace elements in Illinois: manganese.

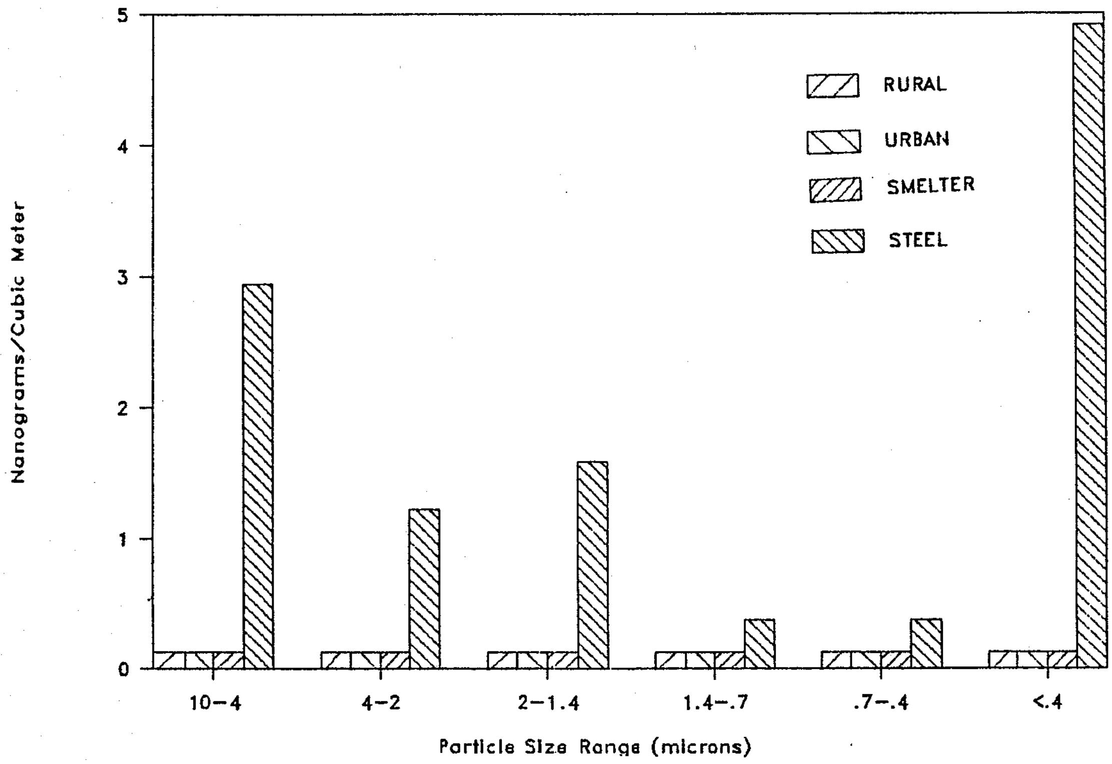


Figure 12. Particle size distributions of toxic trace elements in Illinois: nickel.

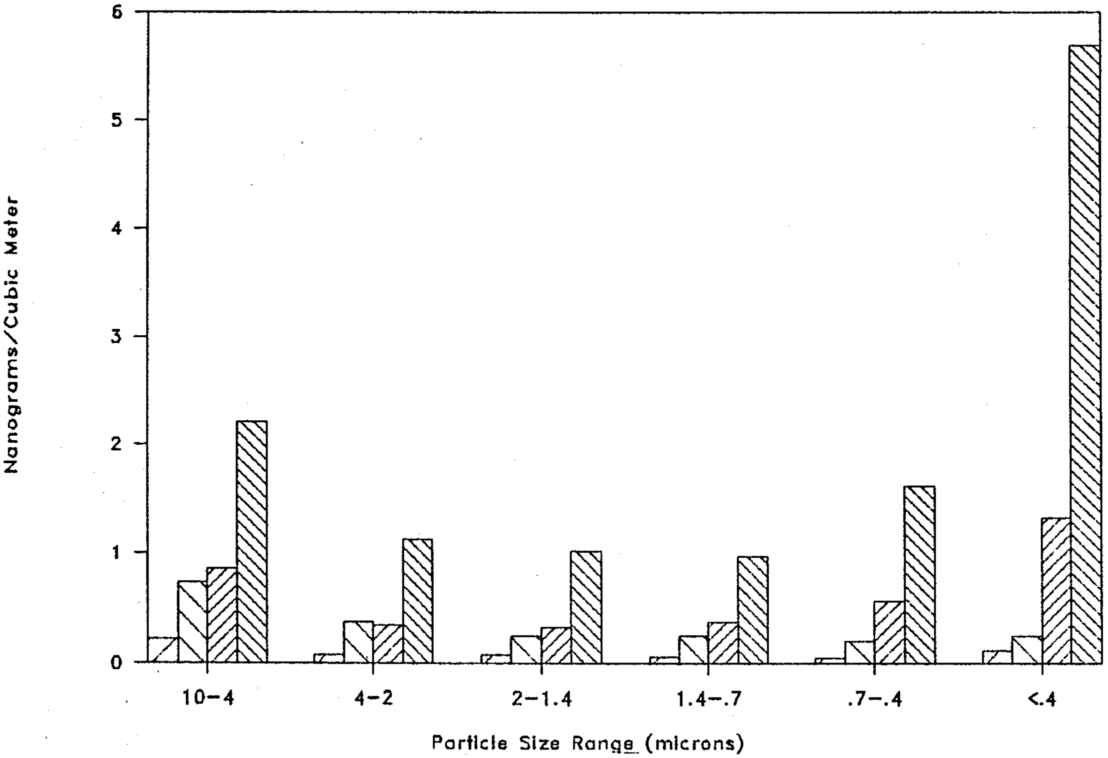


Figure 13. Particle size distributions of toxic trace elements in Illinois: vanadium.

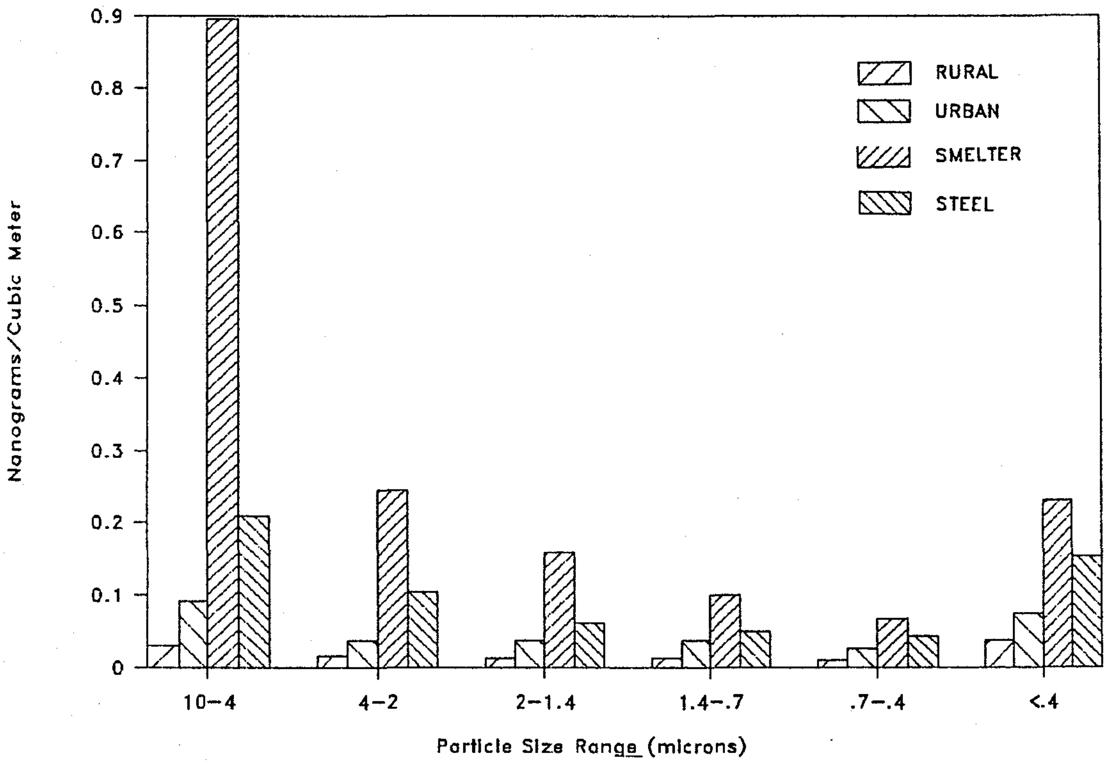


Figure 14. Particle size distributions of toxic trace elements in Illinois: cobalt.

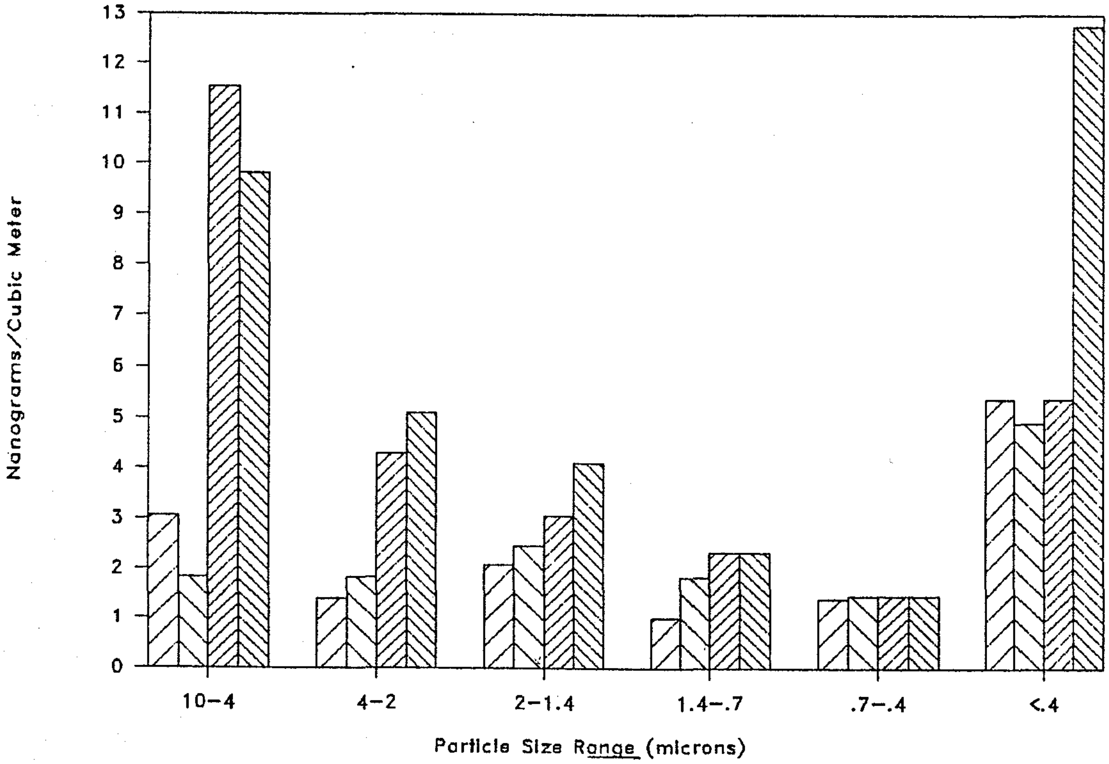


Figure 15. Particle size distributions of toxic trace elements in Illinois: barium.

CHAPTER V. MAXIMUM CONCENTRATION AND SOURCE DETERMINATION

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 10μm 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.

Due to its high time resolution, the streaker sampler provides data that can not be obtained from dichotomous samplers. Concentrations can be obtained for much shorter time periods than by other methods, so the streaker sampler can record short-term peaks that would be lost by dilution during a longer sampling period. This is illustrated in Figure 16. Here the concentrations of airborne coarse and fine Pb in Granite City are plotted against time during a one-week sampling period. Two peaks can be seen corresponding to elevated coarse Pb concentrations. The wind direction during both of these events was between 180 and 210 degrees, the direction of a secondary Pb smelter about 1 kilometer away. During the period corresponding to the maximum Pb concentration, wind speeds were 12 to 17 mph. This fact coupled with the absence of a simultaneous fine Pb peak indicates that the source of this Pb is resuspended wind-blown dust rather than stack or exhaust emissions.

Maximum concentrations of six elements are listed in Table 5 for each of the urban sites. One disadvantage of the streaker method is that only a few trace elements can be measured because of the small size of the sample being collected. For those elements which can be detected, two-hour peak concentrations are considerably higher than those measured during 12- and 24-hour sampling periods using the dichotomous sampler (Table 4). In Chicago, maximum concentrations of elements occur with NE and SE winds, the direction of steel mills about 1 to 2 kilometers away. In East St. Louis maximum concentrations occur with SSW winds, the direction of zinc and copper smelters within 1 to 2 kilometers away.

Another way of analyzing streaker data is with pollution roses. In these, 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. In cases where all values were below detection limits, no plot is given.

In Figures 17 through 20, pollution roses are shown for selected elements in air samples taken at the Chicago site. The plots indicate that major sources of fine and coarse Mn, coarse Cr, fine and coarse Pb and fine Zn are located SSE of the site. This is the direction of the large steel mill indicated in Figure 2.

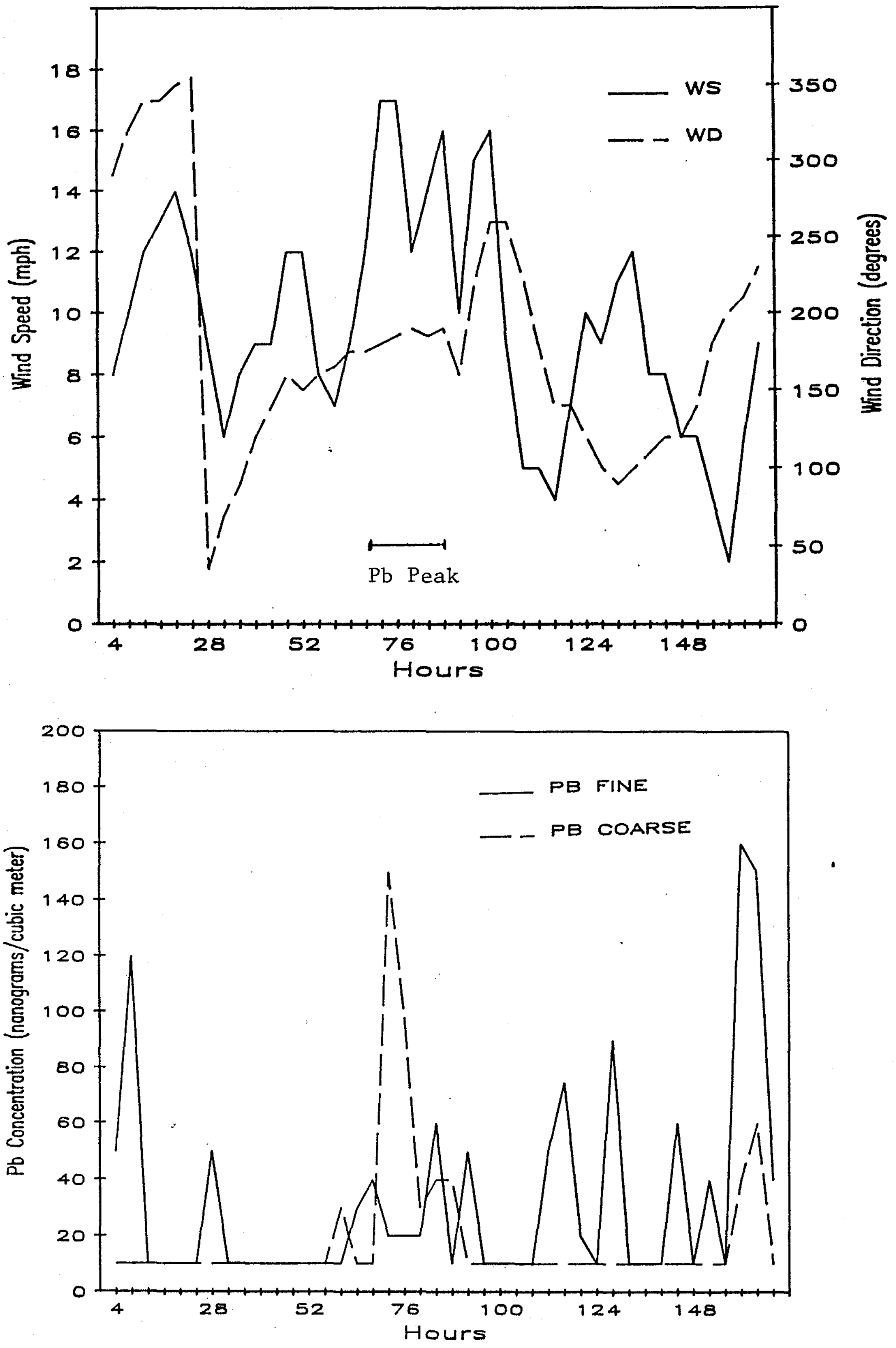


Figure 16. Variation in meteorology and lead concentration at Granite City over a one-week period.

Table 5. Maximum Concentrations (ng/m^3) of Trace Elements at Urban sites in Illinois.

	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

Other major unidentified sources of fine Cu, coarse Pb, and fine and coarse Zn are also shown by the pollution roses. For Cu, there seems to be a major source SW of the site. Although this is the direction of a hazardous waste incinerator, there is also a steel mill and plating plant a few kilometers farther in this direction. Finally, a major source of coarse particle lead is located to the WSW of the site, in the direction of a paint plant. Modern paints no longer contain Pb, but the airborne coarse lead could be generated by wind-blown fugitive surface dust contaminated by Pb in previous emissions from this site.

Fugitive Pb emissions are also evident in the Granite City pollution roses (Figure 21). There are maxima in several directions for fine particle Pb basically in the direction of urban St. Louis and the Alton-Wood River area, presumably due to automobile emissions. Coarse particle lead comes predominantly from the SSW, the direction of a secondary lead smelter. The Mn pollution roses from Granite City (Figure 22) show the influence of nearby steel operations to the SE.

The East St. Louis "streaker data" (Figures 23 to 25) is heavily affected by the Zn and Cu smelters to the SSW of the site. Zn, Cu and Pb all show maxima in this direction. The presence of a large municipal incinerator about 2 km to the WSW in St. Louis can also be detected in the fine particle Zn and Cu plots. The Mn pollution rose indicates a major source to the NE, the direction of Granite City from this site.

It should be stressed that the source identifications made here are tentative, since streaker data only indicate the directions of major sources. However, this information coupled with the chemical characteristics of the emissions and source-receptor modeling can reliably identify sources. Streaker samples taken at an additional site can also be used to help pinpoint an emission source by triangulation. Both of these approaches will be followed as additional data become available in this project.

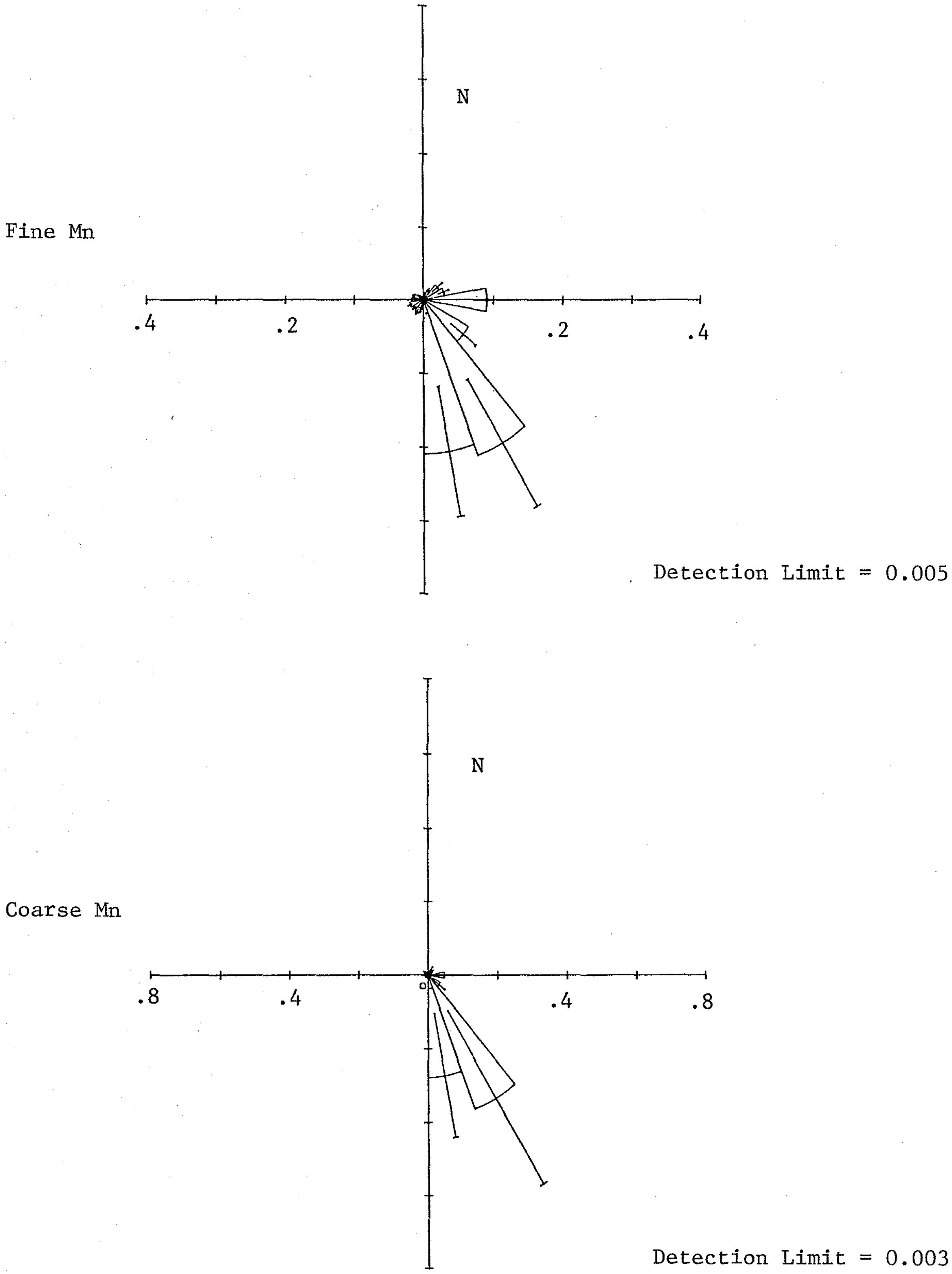


Figure 17. Variation of fine and coarse manganese concentrations ($\mu g/m^3$) with wind direction at Chicago .

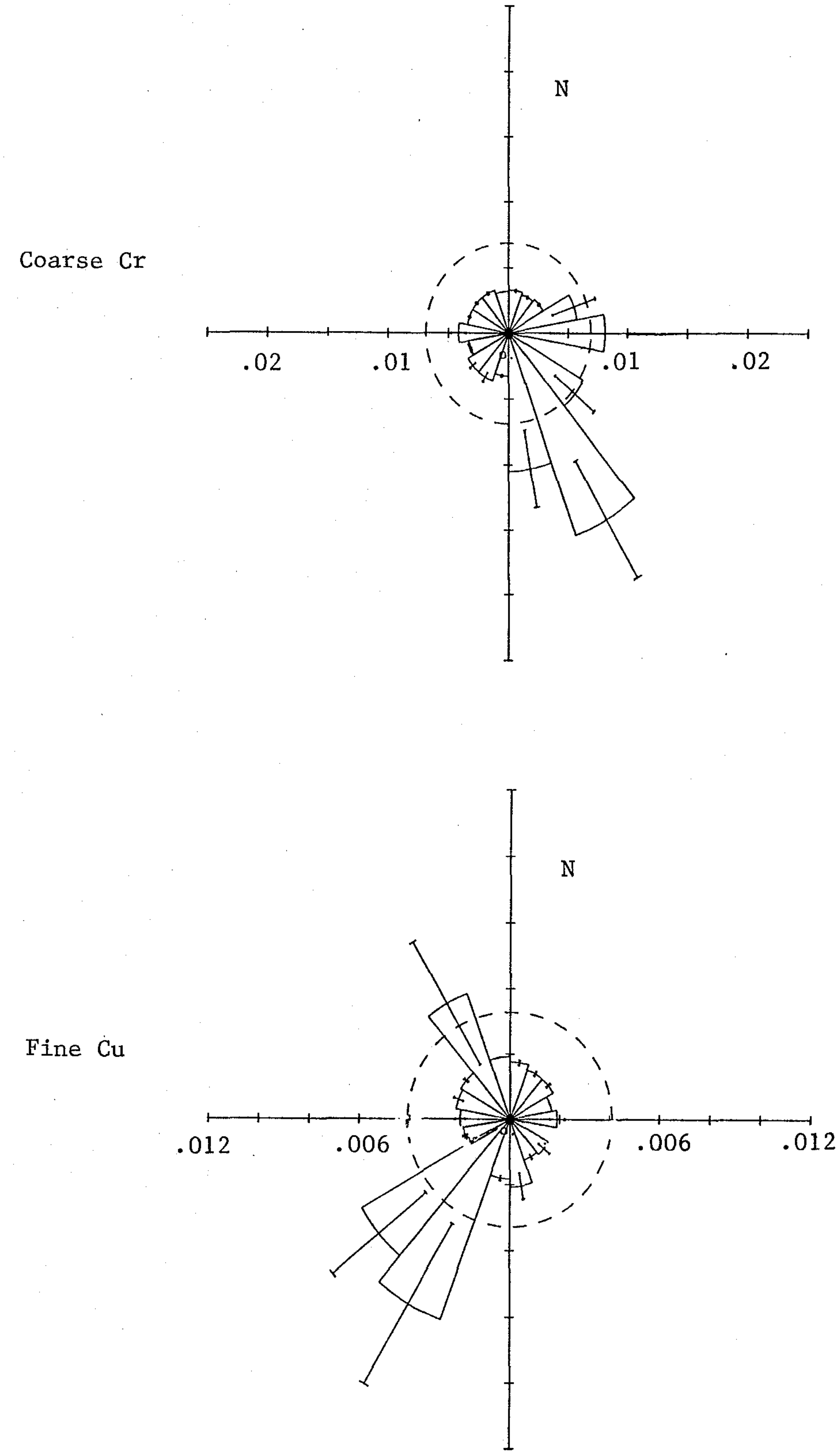


Figure 18. Variation of coarse chromium and fine copper concentrations ($\mu g/m^3$) with wind direction at Chicago.

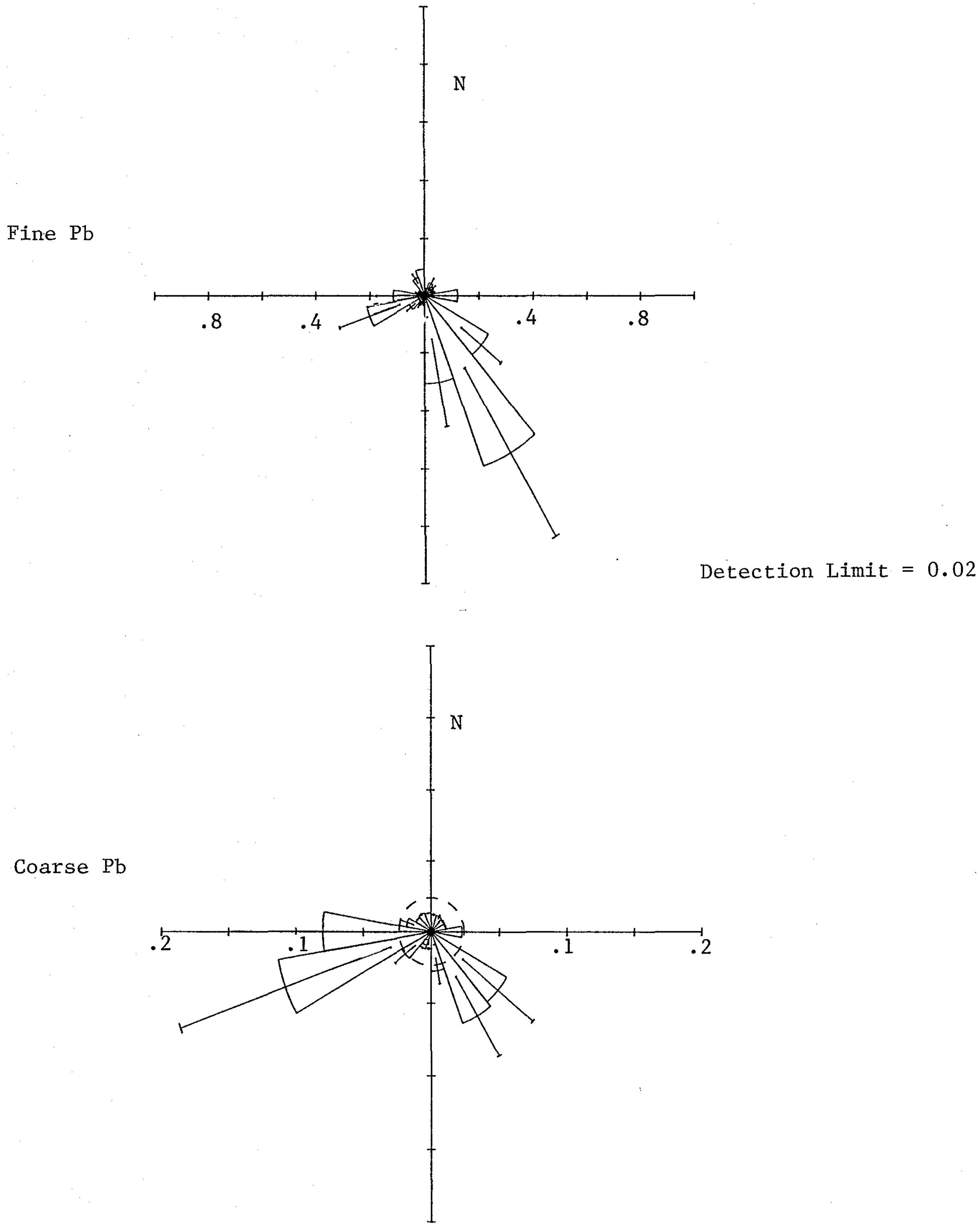
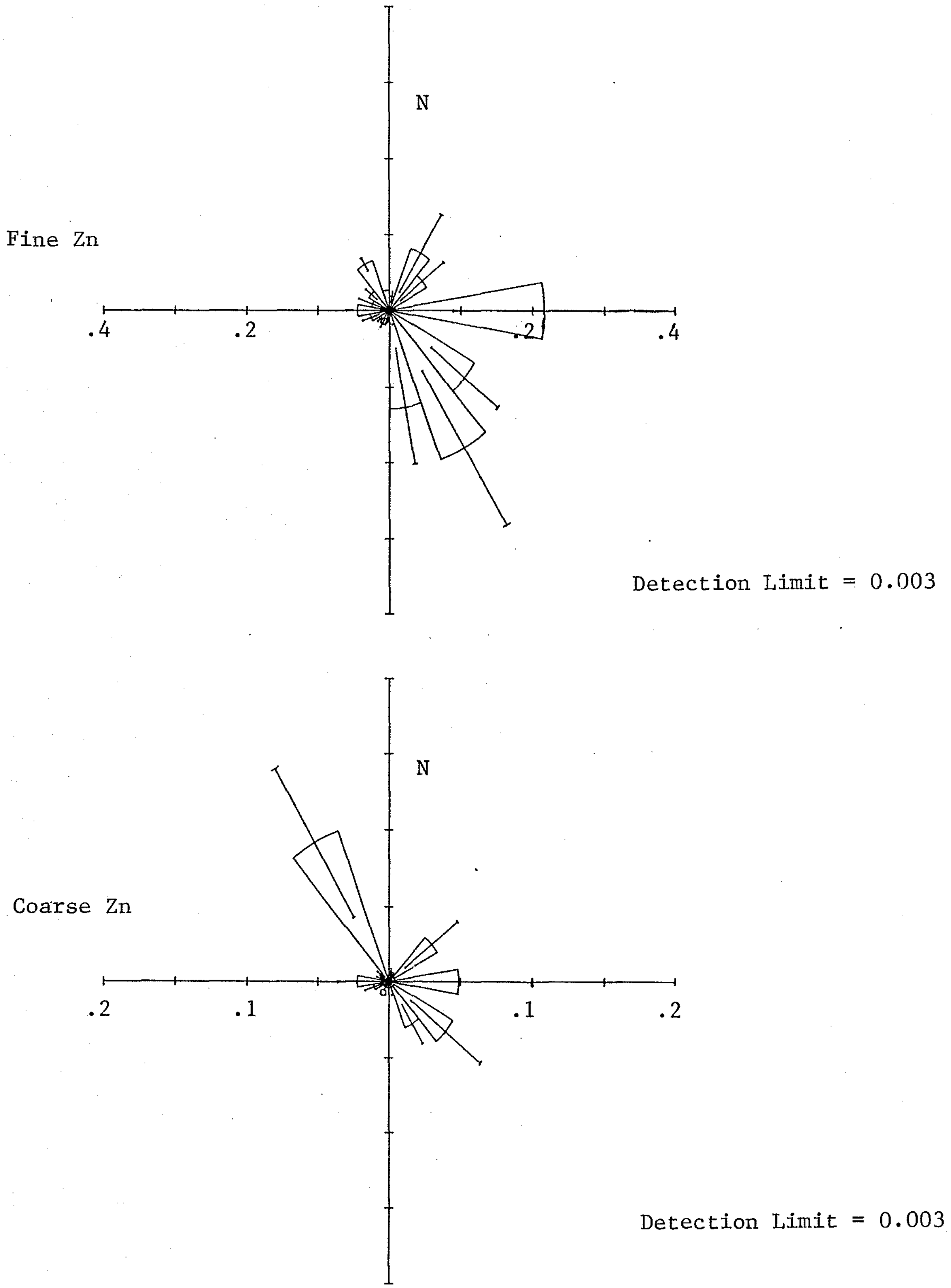


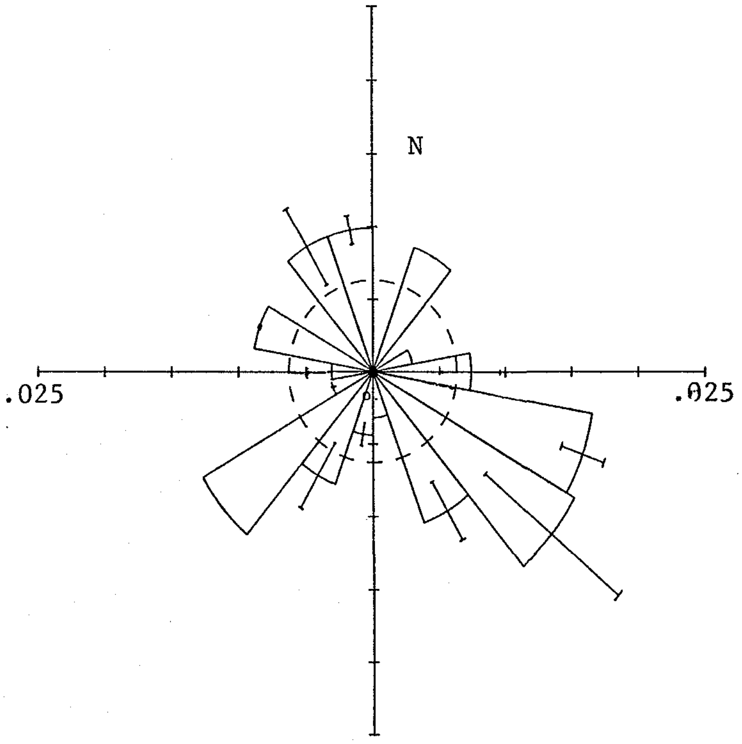
Figure 19. Variation of fine and coarse lead concentrations ($\mu g/m^3$) with wind direction at Chicago.



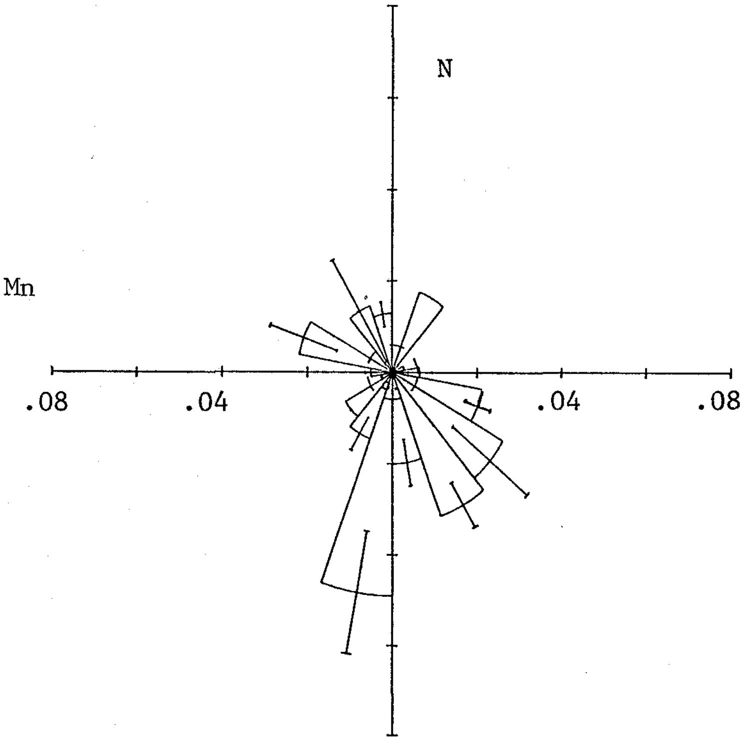
Detection Limit = 0.003

Detection Limit = 0.003

Figure 20. Variation of fine and coarse zinc concentrations ($\mu g/m^3$) with wind direction at Chicago.

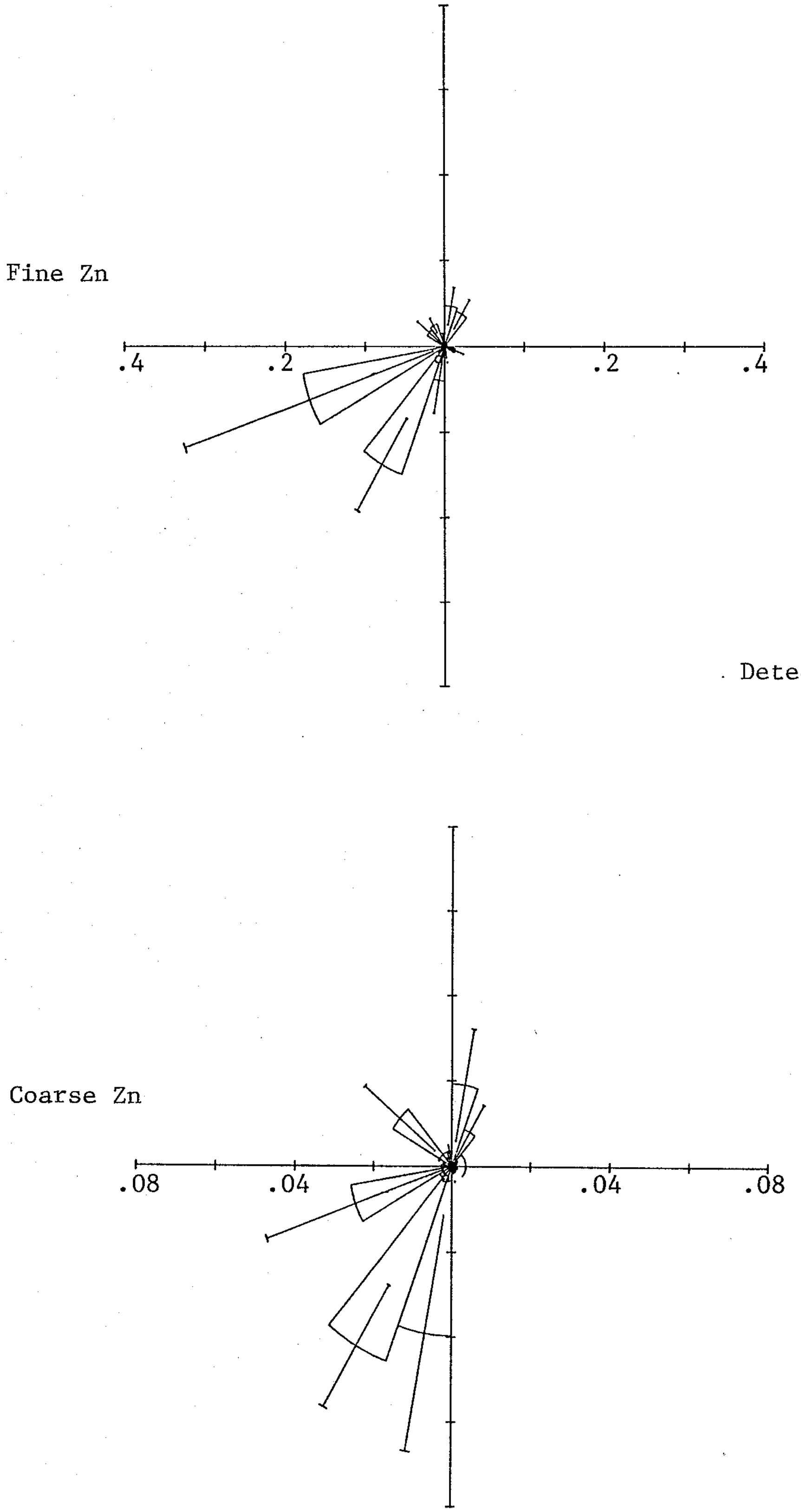


Fine Mn



Coarse Mn

Figure 22. Variation of fine and coarse manganese concentrations ($\mu g/m^3$) with wind direction at Granite City.



Detection Limit = 0.003

Figure 23. Variation of fine and coarse zinc concentrations ($\mu g/m^3$) with wind direction at East St. Louis.

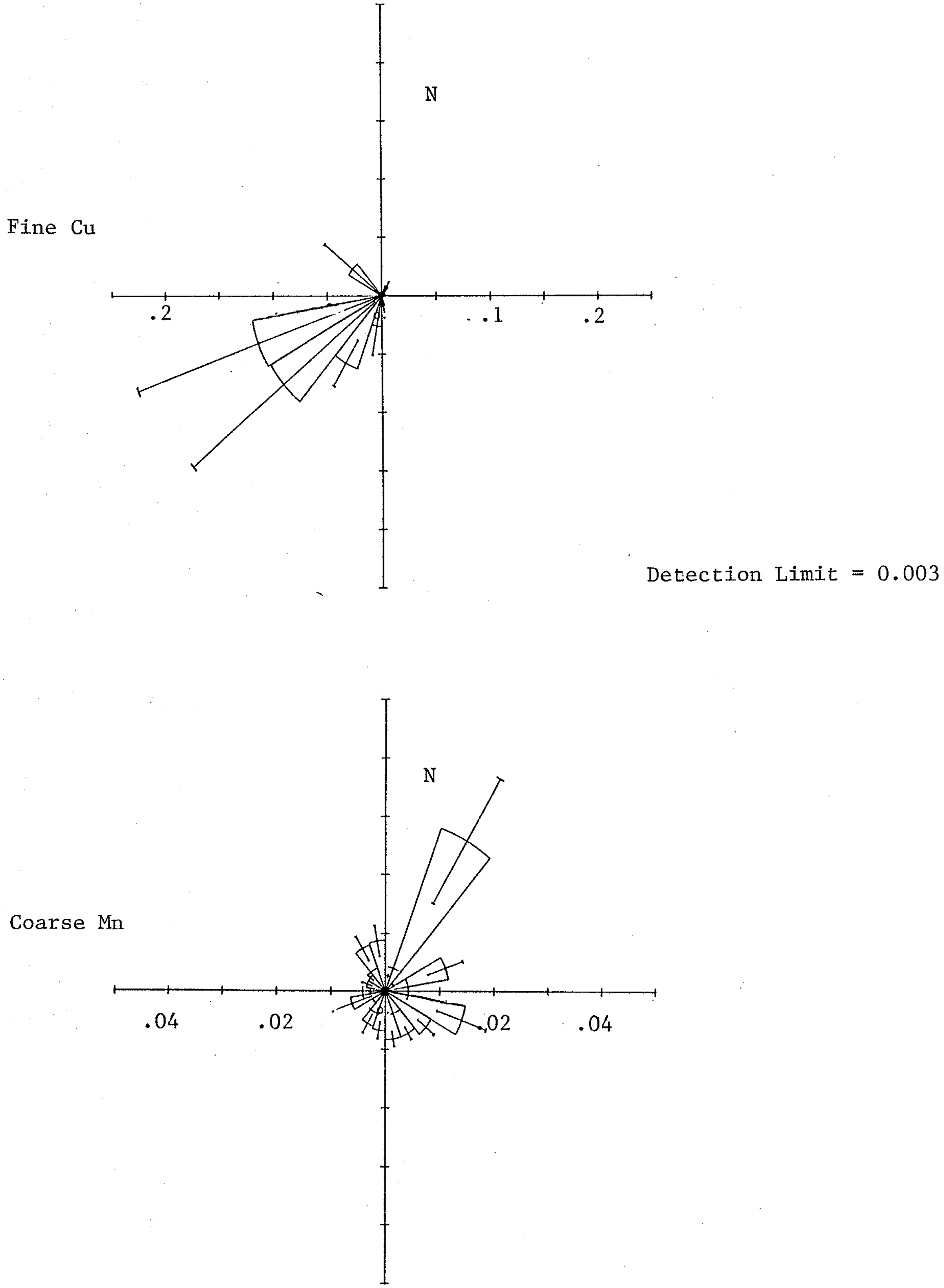


Figure 24. Variations of fine copper and coarse manganese concentrations ($\mu g/m^3$) with wind direction at East St. Louis.

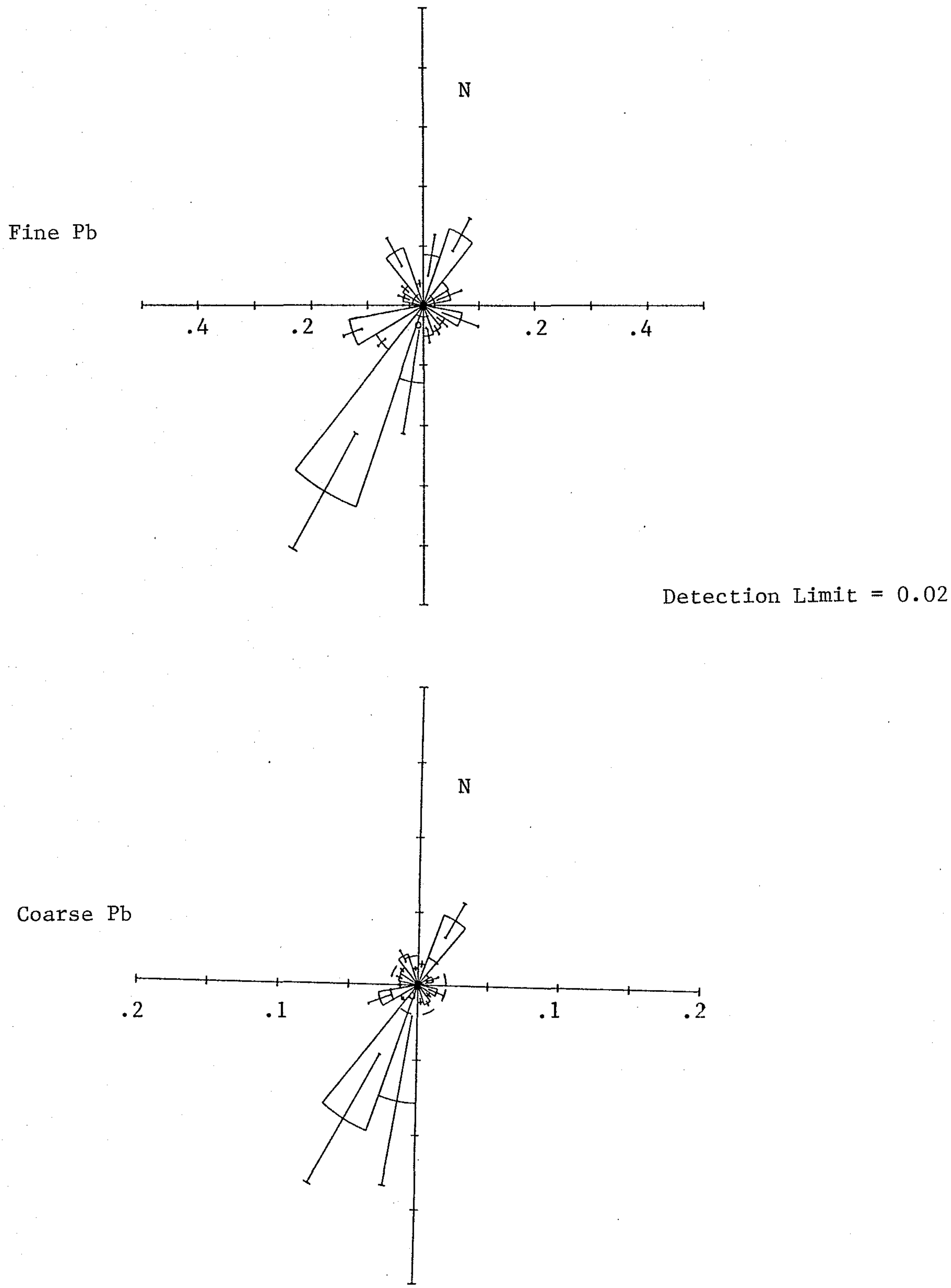


Figure 25. Variation of fine and coarse lead concentrations ($\mu g/m^3$) with wind direction at East St. Louis.

CHAPTER VI. 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, Tokima, and Hoffer (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, Thomas, and Sandel (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). Only six other toxic air pollutants are currently considered hazardous enough to warrant set emission standards. 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 do not vary much between urban and rural sites. This suggests that the air near source areas is enriched in vapor-phase Se. Because of the potential health effects of these three elements, it is important to measure their vapor phase species. 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. 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 and all chemical forms of Hg 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 6. Arsenic was only detected on one 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. On the other hand, Se was detected in the vapor traps at all the urban sites, but not at the rural site. Approximately 20 to 50 percent of the total Se was captured in the vapor trap. No Se was found on the second filter, indicating that vapor-phase Se is efficiently trapped by charcoal-impregnated filters. The levels of vapor-phase Se reported here are similar to those found in other urban samples (Pillay, Thomas, and Sandel, 1971; Mosher and Duce, 1983).

Table 6. Vapor-Phase As, Se and Hg (ng/m^3).

Sampling Site	As		Se		Hg	
	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
East St. Louis	2.5	<.1	1.8	0.3	1.3	4.6
	4.4	<.1			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 6 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, Duce and Fasching, 1977) have reported up to 20 percent of airborne As in the vapor phase in some samples, the results reported here showed no significant vapor-phase arsenic in urban samples in Illinois. 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 VII. VOLATILE TOXIC ORGANICS

Introduction

Volatile organics are those organic compounds that are predominantly in the gas phase at the conditions of temperature and particle concentration normally found in urban atmospheres. This corresponds to a vapor pressure of about 10^{-5} mm Hg or greater (Eisenreich et al., 1980). Many toxic compounds have volatilities in this range including a number of carcinogens commonly found in urban air. Sources of these materials include transportation (auto exhaust, refueling), industry (chemical plants, solvents, coke ovens) and commercial facilities (dry cleaning). Due to their high vapor pressures, fugitive emissions of many volatile toxic organics occur during the normal handling of many solvents and degreasing agents. Because of this, there are a wide variety of potential sources in most urban areas. For the purposes of this work, two categories of organics have been chosen as target compounds--aromatic hydrocarbons and polychlorinated hydrocarbons. Compounds in these two groups are common in urban air, and some of them have been implicated as important cancer risk factors (Thomson et al., 1985).

Between October 1986 and June 1987, 10 to 15 grab samples were collected at each of the sampling sites. The method used was to evacuate a clean, 6-liter stainless steel canister and open it at the site allowing it to come to atmospheric pressure over a period of 1 to 2 minutes. In the laboratory, the canisters were pressurized to 2 atmospheres with clean air. Analysis was by capillary gas chromatography after passing 1 liter of air over a liquid argon cooled trap to remove and concentrate the organics. The column effluent was split and channeled to both a flame ionization detector (FID) and an electron capture detector (ECD). In this way, both aromatic compounds (using the FID) and polychlorinated compounds (using the ECD) can be measured with a high degree of sensitivity. Working quantification limits are approximately 0.1 ppbv for benzene and 0.02 ppbv for trichloroethylene. Further details of this method are contained in an earlier report (Sweet and Gatz, 1987) and in the quality assurance section of this report. The results from the first year's monitoring are summarized in Table 7.

As with the trace elements, the concentrations of organics are compared with average U.S. values. For the aromatic hydrocarbons, the values reported here are generally lower than those found in other U.S. urban areas. The reason for this may be that the U.S. data (Brodzinsky and Singh, 1983) are based on work done in the 1970s when the use of pollution control devices on automobiles was less widespread. Vehicle emissions are a major source of aromatic hydrocarbons (benzene, toluene and xylenes) in urban areas (Harkov et al., 1983).

Styrene is not normally found in urban air (Brodzinsky and Singh, 1983) except near industrial sources using this compound. Styrene was detected in some samples at all three urban sites. There is a large chemical complex near the East St. Louis site where the highest levels were detected. Unfortunately, the analytical system used here often does not adequately separate styrene and o-xylene, a ubiquitous urban air component. When two components are not well separated, it makes the determination of exact concentrations of either less reliable.

Concentrations of polychlorinated hydrocarbons are generally similar to those found in urban areas nationwide, with the exception of chloroform. The concentration of this compound may be influenced by industrial sources in East St. Louis and sewage treatment works in Chicago. The latter are recognized sources of airborne chloroform (Corsi et al., 1987). The average rural concentration reported here was influenced by one high value; other concentrations were all near the typical rural value.

The concentration of carbon tetrachloride is similar in both urban and rural areas. Although this compound is no longer widely used in the U.S., it has a very long residence time (50 to 100 years) in the troposphere and is now well mixed. The worldwide background of concentration is about 0.1 ppbv (Rasmussen and Khalil, 1986). Most of the values measured in this study are lower than this, indicating a slight underestimation of the concentration of carbon tetrachloride. The maximum value found in East St. Louis indicates that there may be a source near this site.

Although the concentrations of organics measured here were, in general, relatively low, they were quite variable. Maximum concentrations were up to 10 times greater than average concentrations. It is difficult to adequately estimate the overall effect of short term concentration peaks using grab samples. To determine average concentrations, samples should be collected over longer time periods. During the next project year, samples will be collected using a newly developed canister sampler capable of collecting integrated samples over time periods of several hours to several days. The results of these experiments will be included in the next annual report.

Table 7. Ambient Concentrations of Toxic Organics in Illinois (ppbv).

Compound	Bondville		Chicago		East St. Louis		Granite City		U.S. Average[b]	
	Avg	(Max)	Avg	(Max)	Avg	(Max)	Avg	(Max)	Urban	Rural
benzene	0.2 ± 0.2	(0.5)	1.6 ± 3	(11)	1.0 ± 1.1	(4.4)	0.8 ± 0.7	(2.3)	2.8	(1.4)
toluene	0.5 ± 0.5	(1.2)	1.7 ± 1.2	(4.6)	1.1 ± 0.8	(3.5)	2.0 ± 2.7	(11)	11	(0.7)
ethylbenzene	0.1 ± 0.2	(0.4)	0.2 ± 0.1	(0.8)	0.2 ± 0.1	(0.5)	0.3 ± 0.2	(0.5)	1.2	(0.5)
o-xylene[a]	0.4 ± 0.4	(1.0)	2.2 ± 3.6	(10)	0.4 ± 0.3	(1.3)	2.1 ± 3.2	(0.5)	1.2	(0.1)
m,p-xylene	0.1 ± 0.1	(0.2)	0.6 ± 0.4	(1.5)	0.6 ± 0.3	(1.3)	1.0 ± 1.4	(5.6)	2.8	(0.1)
chlorobenzene	ND		(0.3)		ND		ND		1.5	(0)
styrene[a]	ND		0.1 ± 0.2	(0.6)	0.7 ± 1.5	(5.3)	0.2 ± .4	(1.5)	0.5	(0)
chloroform	0.3 ± 0.5	(1.2)	0.4 ± 0.5	(1.2)	2.5 ± 9	(34)	0.1 ± 0.3	(0.9)	0.1	(0.04)
methylchloroform	0.2 ± 0.5	(0.3)	0.5 ± 0.4	(1.4)	0.3 ± 0.7	(2.8)	0.3 ± 0.4	(1.4)	0.5	(0.1)
carbon tetrachloride	0.07 ± 0.02	(0.09)	0.07 ± .04	(0.2)	0.1 ± 0.3	(1.2)	0.05 ± .03	(0.12)	0.2	(0.1)
tetrachloroethylene	0.03 ± 0.02	(0.06)	0.2 ± 0.2	(0.7)	0.1 ± 0.1	(0.5)	0.05 ± .05	(0.2)	0.3	(0.2)
trichloroethylene	0.04 ± 0.1	(0.3)	0.2 ± 0.2	(0.6)	0.3 ± 1	(3.4)	0.1 ± 0.1	(0.5)	0.2	(0.3)

[a] o-xylene and styrene are not well separated by this system;
[b] Source: Brozinsky and Singh, 1983 ND = not detected.

CHAPTER VIII. QUALITY ASSURANCE

Quality assurance procedures are described in detail in this section for each sampling and analysis activity.

A. Dichotomous PM-10 Samples

The dichotomous samplers used are Andersen Model 245 units with the capability of automatically collecting up to 20 independent dichotomous samples. They are equipped with flow meters and a recording timer that indicates when the sampler is operating. This allows verification of sampling rates and times.

The flow rate is checked before and after each run using a Sierra mass flow meter. These flow rates are usually within 2 percent of 1.0 m^3/hr at standard conditions (1 atm., 21^{o}C). If the deviation is more than 2 percent an average flow rate is calculated and the sample volume is corrected. Sample volumes are also corrected for the actual temperature recorded during sampling. Coarse and fine sample masses are also corrected for the small portion of fine particles trapped on the coarse particle filter.

B. Filter Handling and Weighing

The filters used are 37 mm diameter Teflon disks with an average pore size of 2.0 μm. These filters collect 99.9 percent of all particles in air passing through them (Hopke, 1986). Filters are equilibrated for 24 hours at 50 percent relative humidity before weighing. All filter handling and weighing are performed in a clean room on a laminar flow clean bench. Using the Cahn microbalance, the precision (standard deviation) of duplicate weighings under these conditions is $\pm$5 μg. Filters are shipped in special plastic holders to prevent movement during shipping to a contract laboratory (NEA, Beaverton, OR) for analysis.

C. Analysis

Filters are analyzed for trace elements by x-ray fluorescence spectroscopy (XRF). With this method, an x-ray beam is directed at a small portion of the filter. Target atoms are excited and give off fluorescent x-ray radiation at wavelengths specific for each element. The intensity of the fluorescent radiation is proportional to concentration. Filter blanks and field blanks (exposed to all handling procedures) are analyzed along with samples. Calibration is done using NBS (National Bureau of Standards) traceable standards. Table 8 lists accuracy and precision results for XRF analyses.

A few filters have also been analyzed by neutron activation analysis (NAA). This is an independent method in which filters are exposed to intense neutron bombardment in a nuclear reactor. Radioactive isotopes of many elements are produced in this way and can be measured by counting gamma rays. After calibration with NBS standards and blank subtraction, this method provides data on several elements that are usually below XRF detection limits.

Table 8. XRF Analyses of NBS Standards[a]

Element	n	Certified Value ($\mu g/cm^2$)	XRF Value ($\mu g/cm^2$)
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

[a] SRM 1832, SRM 1833

In addition, analysis of several elements by two independent methods provides a check on the accuracy of XRF determinations. Table 9 lists results from new blank filters, field blanks, and exposed filters analyzed by both methods.

Comparison of new blanks and field blanks indicates that small amounts of contamination occur during handling, but generally the levels are less than 10 percent of those found on exposed filters. Duplicate analysis using NAA and XRF showed agreement to within 10 to 25 percent except for three elements (Cr, Mn, Sb) which are present as contaminants in the support ring of the Teflon filter and show up in NAA analyses. This ring is not analyzed by the XRF procedure.

In a few cases, IEPA collected PM-10 samples at the same time samples were collected in this study. These samples are collected on glass-fiber filters using high volume samplers; then they are extracted, and analyzed by atomic absorption spectroscopy. They are compared with XRF Dichot data to provide another check on the accuracy of the data using an independent method. Table 10 lists the results of these comparisons.

For Cd and Fe, the IEPA element concentrations were consistently lower than our dichot results. This may indicate that these elements are not extracted efficiently in the IEPA procedure. For several other elements (Cr, Ni, V and As), poor agreement may be due to the low measured concentrations that are near the detection limit of the atomic absorption method, which results in large relative variations in the data. The elements present at higher concentrations (Mn, Zn, Pb, Se, Cu, total mass) can be accurately quantified, and here the two data sets agree to within 10 to 33 percent.

D. Particle Size Data

For these experiments, a Sierra-Andersen 235 cascade impactor was used. The performance characteristics of this device have been published (Willeke, 1975) showing that it effectively fractionates PM-10 particles into six stage classes. We examined particles on loaded filters using a scanning electron microscope (SEM) and found that most of the particles were within the theoretical size ranges. A potential problem with this technique is that large particles may "bounce" and fail to become lodged in the filter at the proper

Table 9. Dichotomous Filter Blanks and Duplicate Analyses (nanograms/filter).

	Blank(n=7)	Field Blank(n=6)	Fine Sample[a]		Coarse Sample[a]	
			NAA	XRF	NAA	XRF
Ca	5 ± 7	49 ± 34	1800	1757	25,000	34,000
Fe	22 ± 20	46 ± 36	-	1650	-	13,000
S	13 ± 10	300 ± 200	-	33,937	-	9,300
V	<1	2 ± 2	120	116	123	94
Cr[b]	<1	5 ± 4	3190[b]	70	1300[b]	91
Mn[b]	<1	5 ± 4	7890[b]	100	83000[b]	300
Ni	<1	4 ± 4	-	70	-	38
Cu	5 ± 1	3 ± 5	1630	1160	435	376
Zn	<1	22 ± 30	1300	1200	1600	1800
As	<2	< 2	71	-	69	-
Se	<1	< 1	-	50	-	12
Mo	<5	< 5	-	-	-	-
Ag	<5	< 5	-	-	-	-
Cd	<10	< 10	-	-	-	82
Sn	<20	< 20	-	50	-	-
Sb[b]	<50	< 50	11,300[b]	200	10,000[b]	100
Ba	<1	< 1	-	-	-	471
Hg	<1	< 1	-	15	-	13
Pb	<2	100 ± 150	–	2594	–	2393
Co	<10	-	-	-	-	-

[a] Fine = <2.5 µm Coarse = 2.5-10 µm

[b] Contamination of the polypropylene ring (not analyzed by XRF) makes NAA unreliable for these elements.

Table 10. Comparison of Co-Located Dichot and IEPA Samples (µg/cubic meter).

	Chicago		East St. Louis	
Element	IEPA PM-10	DICHOT	IEPA PM-10	DICHOT
As	0.002	ND	0.001	0.002
Se	0.005	0.005	0.002	0.002
Pb	0.110	0.097	<0.04	0.032
Cd	<0.004	0.002	0.015	0.027
Cr	0.004	0.008	0.018	0.005
Cu	0.031	0.022	0.018	0.024
Fe	0.444	0.577	0.345	0.560
V	<0.003	0.005	0.003	0.002
Ni	0.007	0.003	0.015	0.002
Mn	0.025	0.026	0.015	0.019
Zn	0.130	0.121	0.05	0.054
Total Mass	41.5	48.0	26.7	28.0

stage (Milford and Davison, 1985). This does not seem to be a major problem here, because SEM showed no large particles on the back stages of the cascade impactor.

Filters were handled using the same methods discussed earlier. The filters were analyzed using instrumental neutron activation analysis. An irradiation of $7.5\mathrm{x}10^{12}$ neutrons cm^{-2} sec^{-1} for 10 hours using a 1.7 kev detector was employed. Delay times of 2 to 3 weeks separated the short-lived isotopes from the long-lived isotopes. Field blanks and NBS traceable aerosol standards were run along with the samples. The results of the blanks and standard runs are shown in Table 11.

Table 11. INAA Analysis of NBS Standard[a] (μg/g).

Element	Blank	INAA VALUE	NBS VALUE
Antimony	0.01	0.32 ± 0.01	0.24
Arsenic	0.01	3.73 ± 0.11	3.72 ± 0.09
Barium	<0.7	76 ± 5	67.5 ± 2.1
Chromium	0.32	10.4 ± 0.39	11
Cobalt	0.01	2.26 ± 0.06	2.29 ± 0.17
Manganese	0.17	13.2 ± 0.5	12.4 ± 1.0
Molybdenum	<0.1	1.0 ± 0.13	0.9
Nickel	<0	7.35 ± 0.12	6.10 ± 0.27
Vanadium	0.2	15.8 ± 0.6	14.0
Selenium	<0.1	1.19 ± 0.07	1.29 ± 0.11

[a] NBS coal sample 1632, n = 4

E. Vapor-Phase Trace Elements

Vapor trap filters were handled in the same way as other filters discussed in this section. For vapor collection, they were mounted in Nuclepore polycarbonate filter holders rated for pressures up to 30 psi. Two-stage filters were mounted on the fine flow line of the dichot downstream from the particle filter. In this way particle free air is passed through the vapor trap. It has been pointed out that some materials can be revolatized during the collection process (Foreman and Bidleman, 1987). During a long sampling period, an increase in ambient temperature may change equilibrium conditions favoring the vapor phase. For this reason, this method gives a maximum estimate of the concentrations of vapor phase chemicals in ambient air.

Arsenic and selenium were analyzed by neutron activation using the same methods discussed earlier. Mercury was analyzed by a cold-vapor atomic absorption technique in which the filters were completely digested in acid and all the Hg was reduced to the elemental form with SnCl$_2$. Field blanks were prepared by giving filters exactly the same treatment as ordinary samples except that no air was passed over them. The results of 3 consecutive runs of blank and standard filters are given in Table 12. Standard filters were prepared by spiking blank filters with a standard Hg solution.

Table 12. Mercury Blanks and Standards.[a]

Standard	Apparent Concentration (μg/Filter)			
25.0	25.7	24.4	24.4	
62.5	60.8	58.8	62.1	
125.0	125.9	124.6	123.3	
250.0	249.8	251.9	258.4	
Field Blanks	<12	<12	<12	12

[a] Recoveries were determined to be 95% ± 5% by spiking with U.S. EPA standards (WP248, WP1183).

F. Volatile Organics

Ambient air is collected in stainless steel canisters (SIS Inc.) with surfaces treated by the Summa process to insure low adsorption of organic compounds. Organic compounds are stable in these canisters for periods of up to 30 days (Oliver, Pleil and McClenny, 1986). The samplers were cleaned by heating canisters filled with clean humid air to 90°C, then flushing three times with pure dry air. Each canister was refilled and checked chromatographically to insure that it was hydrocarbon free.

Standards were prepared using the static dilution bottle method (Morris, Berkly, and Bumgarner, 1983). A working standard containing 10 ppb of eight of the target compounds was obtained from Scott Specialty Gases Inc. In ambient air samples, the peaks were identified by retention time and quantified by peak height compared to the working standard. Standard concentrations of other compounds were run using the static dilution bottle method and the peak height ratios between these compounds and the working standard compounds were determined. These ratios were used to calculate the concentrations of compounds not present in the working standard.

As an additional check, a synthetic ambient air mixture containing 40 compounds was obtained from U.S. EPA. Results from this audit sample are given in Table 13. Only those compounds for which standards were available could be quantified.

Table 13. U.S. EPA Audit Sample

Compound	Concentration (ppbv)	
	ISWS	U.S. EPA
benzene	10.6	9.9
toluene	4.5	9.6
o-xylene[a]	9.8	10.8
m,p-xylene	17	25.6
styrene[a]	7.1	12.4
chloroform	6.6	7.9
methylchloroform	9.6	8.2
carbon tetrachloride	7.5	8.5
trichloroethylene	9.4	8.3
chlorobenzene	7.4	7.1
ethylene dibromide	6.7	6.8
tetrachloroethylene	8.6	7.9
ethylbenzene	13.3	12.7
1,1,2,2 tetrachloroethane	11.2	15.0

[a]Not well separated

CHAPTER IX. CONCLUSIONS AND RECOMMENDATIONS

The toxic trace element data base developed for this report contains information on the ambient concentrations of 17 toxic elements at 3 urban sampling sites in Illinois over an 18-month period. 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 normal ambient levels pose a significant health risk. Airborne cadmium concentrations 10 times greater than normal 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 normal 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 give 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 resuspended dust in such emissions may have been deposited during earlier pollution episodes, the levels of airborne toxic elements may not always reflect current industrial activity or stack emissions.

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. Additional data will be collected at new sampling locations to verify this information.

For the toxic elements that may have a vapor phase - mercury, arsenic and selenium - the vapor phase predominates only for mercury. Total particle loadings, therefore, do 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. This will be the subject of additional research during the next year. On the basis of a limited number of samples, arsenic does not appear to have a significant vapor phase component at these sampling locations.

A preliminary data base was assembled for the toxic volatile organics. A total of 12 compounds were analyzed in grab samples of urban air. Although the concentrations of these compounds were highly variable, average values were generally similar to those expected for urban areas. High values were often associated with wind directions from nearby industrial sources. To better assess the effect of short-term concentration peaks, time-integrated samples should be taken over periods of several hours or more. By coupling these data with wind direction, a better determination of major sources can be made.

REFERENCES

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

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 Singh, H.B. 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.

Corsi, R.L., Chang, D.P.Y., Schroeder, E.D. and Qiu, Q., 1987. "Emissions of Volatile and Potentially Toxic Organic Compounds from Municipal Wastewater Treatment Plants." Paper 87-95.7, 80th Annual Meeting, Air Pollution Control Association, June 21-26, New York, NY.

Courtney, W.J., S. Rheingrover, J. Pilotte, H.C. Kaufmann, T.A. Cahill and J.W. Nelson 1978. Journal of the Air Pollution Control Association 28:224-228.

Eisenreich, S.J., Bidleman, T.F., Murphy, T.J., Davis, A.R., Banning, D.A., Giam, C.S., Priznar, F.J., and M.O. Mullin. 1980. "Trace Organics: A Review and Assessment." In: Toxic Substances in Atmospheric Deposition: A Review and Assessment. EPA 560/5-80-001, U.S. EPA Office of Pesticide and Toxic Substances, Washington, D.C.

Evans, E.G., Evans, G.F., Ray, D.B., Risher, R., Wheeler, V.A., Cummings, S.L., Frazer, J.E., Harper, S.L., Hinners, T.A., Loseke, W.A., Pranger, L.J., and Puzak, J.C. 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.

Foreman, W.T. and Bidleman, T.F., 1987. "An Experimental System for Investigating Vapor-Particle Partitioning of Trace Organic Pollutants." Environmental Science and Technology, 21:869-875.

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

Gatz, D.F. and Sweet, C.W. 1985. "Atmospheric Research and Monitoring Study of Hazardous Substances." Report HWRIC-RR-007. Hazardous Waste Research and Information Center, Illinois State Water Survey Division, Savoy, IL 61874.

Harkov, R., Kebbekus, B., Bozzelli, J.W., and Lioy, P.J., 1985. "Measurement of Selected Volatile Organic Compounds at Three Locations in New Jersey during the Summer Season." Journal of the Air Pollution Control Association, 33:1177-1183.

Hopke, P.K. 1985. "Receptor Modeling in Environmental Chemistry." John Wiley and Sons, New York, NY p16.

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

Kolaz, D.J., Sweitzer, T.A. and Bomke, D.L., 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.

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

Morris, C., Berkley, R., and Bumgarner, J. 1983. "Preparation of Multicomponent Volatile Organic Standards Using Dilution Bottles," Analytical Letters, 16:1585-1593.

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

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.

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

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

National Research Council. 1976. Medical and Biologic Effects of Environmental Pollutants: Selenium. Washington, D.C., National Academy of Sciences.

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

Oliver, K.D., Pleil, J.D., and McClenny, W.A. 1986. Sample Integrity of Trace Level Volatile Organic Compounds in Ambient Air Stored in Summa Polished Canisters. Atmospheric Environment, 20:1403-1411.

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

Rasmussen, R.A. and Khalil, M.A.K. 1986. "Atmospheric Trace Gases: Trends and Distributions over the Last Decade." Science, 232:1623-1624.

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

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

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

Shaw, R.W. and Paur, R.J. 1983. "Composition of the Aerosol Particles Collected at Rural Sites in the Ohio River Valley." Atmospheric Environment 17:2031-2044.

Singh, H.B., Salas, L.J., Cantrell, B.K., and Redmond, R.M., 1985. "Distribution of Aromatic Hydrocarbons in the Ambient Air," Atmospheric Environment, 19(11):1911-1919.

Sweet, C.W. and Gatz, D.F., 1987. "Atmospheric Research and Monitoring Study of Hazardous Substances: Second Annual Report." HWRIC-RR-014. Hazardous Waste Research and Information Center, Illinois State Water Survey Division, Savoy, IL 61874.

Thomson, V.E., Jones, A., Haemisegger, E., and Steigerwald, B. 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.

United States Environmental Protection Agency. 1985. "Report on the Incineration of Liquid Hazardous Wastes by the Environmental Effects, Transport and Fate Committee, Science Advisory Board." U.S. EPA Office of the Administrator, Washington, D.C. 20460.

Wallace, D.D. and Trenholm, A.R. 1985. "Assessment of Metal Emissions from Hazardous Waste Incinerators." Paper presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan, June 16-21.

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

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