

**WMRC Reports**  
Waste Management and Research Center

**Atmospheric Research  
and Monitoring Study of  
Hazardous Substances:**

**Second Annual Report**

**Clyde W. Sweet,  
Donald F. Gatz**

**Illinois State Water Survey**

**RR-E14  
March 1987  
Electronic Version**



## **About WMRC's Electronic Publications:**

This document was originally published in a traditional format.

It has been transferred to an electronic format to allow faster and broader access to important information and data.

While the Center makes every effort to maintain a level of quality during the transfer from print to digital format, it is possible that minor formatting and typographical inconsistencies will still exist in this document.

Additionally, due to the constraints of the electronic format chosen, page numbering will vary slightly from the original document.

The original, printed version of this document may still be available.

Please contact WMRC for more information:

**WMRC**  
**One E. Hazelwood Drive**  
**Champaign, IL 61820**  
**217-333-8940 (phone)**

**[www.wmrc.uiuc.edu](http://www.wmrc.uiuc.edu)**



WMRC is a division of the  
Illinois Department of Natural  
Resources

**HAZARDOUS WASTE RESEARCH AND INFORMATION CENTER  
Illinois State Water Survey Division**

1808 Woodfield Drive  
Savoy, Illinois 61874



**HWRIC RR 014**

**Atmospheric Research and Monitoring Study  
of Hazardous Substances: Second Annual Report**

by

**Clyde W. Sweet  
Donald F. Gatz**

**Illinois State Water Survey**

**March 1987**



**Illinois Department of Energy and Natural Resources**

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

by

Clyde W. Sweet  
Donald F. Gatz

Illinois State Water Survey

March 1987

Sponsored by

Hazardous Waste Research and Information Center  
Illinois Department of Energy and Natural Resources  
ISWS Contract STILENR-HWR-86006-017



## TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES.....	iv
LIST OF ILLUSTRATIONS.....	v
ACKNOWLEDGEMENTS.....	vi
ABSTRACT.....	vii
EXECUTIVE SUMMARY.....	viii
SAMPLING NETWORK.....	ix
TOXIC TRACE ELEMENT DATA BASE.....	x
VAPOR PHASE TRACE ELEMENTS.....	xiii
VOLATILE TOXIC ORGANICS.....	xiii
CONCLUSIONS AND RECOMMENDATIONS.....	xiv
I. INTRODUCTION.....	1
II. SAMPLING NETWORK.....	5
TOXIC TRACE ELEMENT DATA BASE.....	10
<u>Methods</u> .....	10
<u>Quality Assurance</u> .....	13
TRACE ELEMENTS.....	15
PARTICLE SIZE DATA.....	20
WIND DIRECTION DATA.....	23
III. METHODS FOR VAPOR PHASE TRACE ELEMENTS.....	27
IV. ANALYSIS OF VOLATILE TOXIC ORGANICS.....	31
V. CONCLUSIONS AND RECOMMENDATIONS.....	37
REFERENCES.....	39

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
A	Average Toxic Trace Element Concentrations in Inhalable Airborne Particles	xi
1	Analysis Methods for Toxic Trace Elements	11
2	Toxic Element Data from Co-located Samplers and Duplicate Analysis	14
3	Concentrations of Hazardous Trace Elements	16-17
4	Average Values for Toxic Trace Elements in Urban Particulate Matter	18
5	Variation of Trace Element Concentration with Wind Direction	24

## LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1.	Hazardous Air Pollutant Sampling Network	6
2.	Particle Size Data for Trace Elements.	22
3.	Analysis Systems for Trace Organics in Air.	34



## ACKNOWLEDGEMENTS

We thank Dave Kolaz and Bob Hutton of the IEPA for providing wind data and trace element data from the IEPA network. We also thank Tom Barounis and Jim Henry of the IEPA for facilitating site access and helping with equipment installation. David Stucki provided technical assistance with sampler calibration and filter processing and Jack Su helped with computer analysis of data. Finally, Jean Dennison provided expert typing of the manuscript.

## ABSTRACT

During this second year of the project, a network of three urban and one rural sampling stations has been established to monitor hazardous substances in the atmosphere of Illinois. Toxic trace elements and toxic volatile organic chemicals are the two important groups of chemicals selected for sampling. They can be released to the atmosphere as a result of the generation, treatment, or disposal of hazardous wastes and from a variety of other sources. Preliminary data show elevated concentrations of 2 out of 17 toxic trace elements analyzed in urban airborne particles in the Chicago and East St. Louis areas. The observed concentration levels are too low to have any known impact on human health, however. The toxic elements that were found probably resulted from a variety of industrial activities such as metal smelting, steel processing, and coal burning. Further data collection and analysis is under way to determine the particle size distribution of toxic trace elements, the concentration of vapor phase trace elements, and the concentration of volatile toxic organics in ambient air. Wind direction and other meteorological data will be correlated with the sampling of these chemicals to better estimate the relative contribution of various pollution sources to concentrations of hazardous substances in Illinois air.

## EXECUTIVE SUMMARY

The handling and disposal of hazardous materials can result in emissions of toxic chemicals to 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 potential for human health impacts from 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 impacts. These compounds will be collected and analyzed using recently developed techniques for handling trace organic gases in ambient air.

Compounds in both classes are important components of hazardous wastes. However, the contribution of specific activities, such as the treatment of hazardous wastes to the atmospheric load of these toxic materials, is unknown. Furthermore, the concentrations in the atmosphere and sources of toxic trace elements and toxic volatile organics in Illinois are not well documented. Neither have airborne toxic chemicals been characterized in terms of gas-solid partitioning or particle-size distribution, two parameters important to understanding potential health and environmental effects.

The overall objective of this project is to provide an in-depth chemical and physical characterization of airborne toxic trace elements and volatile toxic organic chemicals in Illinois. In addition, the data will be used to identify sources in the study areas that are important contributors to toxic chemicals in the atmosphere. During this second year of the project, the following tasks were accomplished: 1) establishment of a network of four monitoring stations; 2) collection of size-fractionated aerosol samples for a toxic trace element data base; 3) development of sampling and analytical techniques for vapor-phase trace elements; and 4) development of an analytical capability for the volatile toxic organic chemicals of specific concern.

#### SAMPLING NETWORK

After review of Illinois Environmental Protection Agency monitoring data, three urban and one rural sampling sites were chosen. The urban sites are all in areas with high levels of suspended particulate matter and trace elements in the atmosphere. Two of the urban sites, 13th and Tudor in East St. Louis and Bright Elementary School at 10740 S. Calhoun in Chicago, are close to commercial hazardous waste incineration facilities. The air around these two sites and around the third urban site at 2001 E. 20th St. in Granite City is affected by a wide variety of industrial, transportation, and commercial sources. The three urban sites were chosen because they are impacted by a wide variety of sources and because they represent the worst air quality found in residential areas in Illinois. The fourth site is located 8 km south of Bondville, Illinois near Champaign. It is normally at least 50 km downwind of any significant sources and was chosen to determine background levels in Illinois. The urban sites selected for study are air quality problem areas in Illinois. The rationale for this selection is that a wide variety of sources

contributing to poor air quality can be studied at a few sites. The in-depth characterization of problems in these areas should be applicable to other urban areas with similar sources.

Each site is equipped with an automatic dichotomous sampler capable of collecting size fractionated aerosol samples in order to provide information on particle-size distribution and vapor-particle partition. Meteorological equipment has also been installed at each site for monitoring wind speed and direction as well as other variables. A sampling schedule has been instituted to collect several types of samples to provide assessment of the temporal and directional variability of toxic trace elements. These sites will also be used to monitor volatile organics next year.

#### TOXIC TRACE ELEMENT DATA BASE

Data for 17 of 19 targeted toxic trace elements were obtained by x-ray fluorescence analysis on filters collected during late 1985 and early 1986 (Table A). In most cases, trace element concentrations were comparable to atmospheric loading of trace elements in other urban areas around the country. Although these levels are currently considered too low to have a significant impact on human health, several of the elements are known or suspected carcinogens and the long-term impact of exposure at these concentrations is uncertain.

The concentrations of certain toxic trace elements are higher than expected for a typical urban area. A mixture of trace elements including zinc, cadmium, copper, tin, and lead occurs in the fine particle aerosol collected in East St. Louis. The most likely source of this material is emissions from copper and zinc smelters located to the south and southwest of the sampling

Table A. Average Toxic Trace Element Concentrations  
in Inhalable Airborne Particles.<sup>a</sup>

<u>Element</u>	<u>Bondville</u>	<u>Chicago</u>	<u>E. St. Louis</u>	<u>Granite City</u>	<u>U.S. Average<sup>b</sup></u> <u>Urban/Rural</u>
Vanadium (V)	.003	.008	.006	.008	.021/.008
Chromium (Cr)	.002	.011	.008	.014	.011/.007
Manganese (Mn)	.009	.090	.025	.067	.038/.020
Nickel (Ni)	.001	.004	.004	.004	.010/.003
Copper (Cu)	.004	.018	.060	.036	-
Zinc (Zn)	.025	.134	.182	.146	.160/.040
Selenium (Se)	.002	.004	.003	.002	-
Molybdenum (Mo)	.001	.004	.003	.002	.002/.001
Silver (Ag)	.001	.003	.004	.002	-
Cadmium (Cd)	.002	.005	.021	.004	.002/.001
Tin (Sn)	.003	.011	.008	.006	-
Antimony (Sb)	.005	.014	.010	.010	-
Barium (Ba)	.010	.030	.030	.020	.030/.010
Mercury (Hg) <sup>c</sup>	.001	.001	.001	.001	-
Cobalt (Co)	.002	.006	.006	.006	-
Lead (Pb)	.028	.174	.175	.164	.580/.084
Arsenic (As)	.002	.005	.005	.007	-

<sup>a</sup>Particle diameter <10  $\mu\text{m}$ , concentrations are in  $\mu\text{g}/\text{M}^3$ .

<sup>b</sup>USEPA Data (1979).

<sup>c</sup>Substantial amounts of Hg are in the vapor phase.

site. In Chicago and Granite City, the levels of manganese in coarse aerosol particles are relatively high. This is probably due to the presence of large steel mills in the vicinity of these sites. Finally, the high levels of selenium (Se) at Bondville are similar to those at the urban sites. Since this site is in a rural area, the concentrations of most elements related to man-made pollution are 3-10 times lower than in urban areas. Selenium is known to be associated with coal burning and can be transported 1000 km or more in the atmosphere. In fact, Se is used as a tracer element to follow air masses originating in the Midwest due to the large number of coal burning power plants in the region.

In a preliminary experiment, the particle size distribution of several elements was also determined. More complete analysis of several size classes of airborne particles will take place next year. This information can be used to differentiate emissions from combustion sources, which produce very fine particles, from emissions of mechanically generated dust (large particles). For example, selenium and lead result from combustion and are found principally on particles with diameters less than 2  $\mu\text{m}$ . Manganese, however, is often concentrated on particles between 4 and 10  $\mu\text{m}$  in diameter. It is the fine particles that may be transported the greatest distances and are of most important health concern.

Another useful tool in estimating the contribution of various sources is wind data. By analyzing filters collected during periods of steady wind direction, emissions can often be attributed to a particular source or group of sources. This technique was used to tentatively identify smelter emissions in East St. Louis and steel mill emissions in Chicago. A larger and more complete

data set will be available for the next report which should allow identification of more sources.

#### VAPOR PHASE TRACE ELEMENTS

The vapor pressure of a few of the target trace elements is high enough that a significant fraction exists in the gas phase under normal ambient conditions. These elements (mercury, arsenic and selenium) are significantly under-sampled using conventional particle-collecting filters alone which are almost universally used for regulatory compliance monitoring. The vapors can be better collected using appropriate absorbent materials and analyzed by neutron activation or atomic absorption analysis. This will be done during the next year of this study.

To collect gas phase trace elements, cellulose filters impregnated with absorbent are placed downstream from the particle-collecting filters in the dichotomous sampler. In this way, both particle-bound and gas phase fractions of the volatile trace elements can be evaluated. After preliminary experiments with test absorbent materials, vapor phase sampling will be incorporated in the routine sampling schedule.

#### VOLATILE TOXIC ORGANICS

Work is progressing to develop sampling and analytical capabilities for ambient concentrations of volatile toxic organic chemicals. There are no generally accepted methods for this. The technique selected is to collect whole air samples in inert stainless steel canisters and then to concentrate the organics cryogenically for analysis by gas chromatography. Preliminary experiments indicate that this method should allow quantification of ambient air concentrations of benzene as low as 20 parts per trillion (ppt) and carbon



tetrachloride as low as 2 ppt. These concentrations are lower than those which have been measured in Illinois. Very little is known, however, about the ambient levels of toxic organic chemicals, so this aspect of our project will substantially increase the data base for hazardous materials in the atmosphere.

#### CONCLUSIONS AND RECOMMENDATIONS

Preliminary investigation of toxic trace element levels in urban areas in Illinois indicates that the amounts of most of the chemicals are within the range typically found in urban areas in the U.S. For a few of the elements, higher levels seem to be associated with emissions from zinc and copper smelters and manganese from steel mills.

Of the trace elements sampled in this study only lead is covered by an ambient air standard. Even the highest concentration of lead measured so far in this project ( $0.6 \mu\text{g}/\text{cubic meter}$ ) is well below this standard ( $1.5 \mu\text{g}/\text{cubic meter}$ ). Although there are no standards for the other elements at this time, the levels found are well below those now known to cause health effects. However, a number of the trace elements are carcinogenic and the long-term impact of low ambient concentrations of mixtures of these chemicals on human health is uncertain.

To fully assess ambient air concentrations of toxic elements in the urban study areas, more samples need to be collected during periods associated with a wide range of pollution levels. In addition, the particle size distribution and the vapor-particle partitioning of trace elements will help in assessing health effects and pinpointing sources.

With the development of sampling and analytical capabilities for volatile toxic organics, measurements of atmospheric concentrations of these materials will be started. Ambient levels of toxic organics have been studied very

little in Illinois even though they pose at least as large a health threat as the toxic trace elements. For this reason, it is important to include them as part of an atmospheric hazardous materials data base for Illinois.

## I. INTRODUCTION

Toxic chemicals can enter the atmosphere from a wide variety of human activities including production, handling, and disposal of hazardous materials. Many chemicals with low volatility are released or formed during high temperature processes such as incineration and are vented to the atmosphere via smokestacks. On the other hand, some organic compounds with high volatility are emitted from leaks, spills, or open sources such as landfills. These emissions are termed "fugitive" emissions.

Two groups of toxic chemicals have been selected for this study. The first consists of a number of toxic trace elements and their compounds that occur in urban air and may be present in emissions from hazardous waste incinerators. The second group consists of volatile halogenated aromatic hydrocarbons, which are normally present at levels between 0.1 and 5 parts per billion (ppb) in urban atmospheres and are important components of hazardous wastes. Chemicals in both of these groups have been implicated as major contributors to cancer risk from urban air in a nationwide study conducted by Thomson et al. (1985) for the U.S. Environmental Protection Agency (USEPA). There are, of course, many other types of toxic chemicals associated with hazardous waste facilities and urban air pollution. The two groups of specific chemicals selected in this study were chosen because there is little or no information about their occurrence or concentration levels in the atmosphere in Illinois. In fact, for some of these there is very little data about their occurrence anywhere in the world.

In a recent report, Wallace and Trenholm (1985) concluded that the trace element emissions from individual hazardous waste incinerators are equivalent to those from a typical municipal solid waste incinerator of the same capacity

and 10 to 100 times greater than those from a coal fired power plant of the same capacity. Volatile elements such as mercury (Hg), antimony (Sb), arsenic (As), cadmium (Cd) and lead (Pb) are emitted even when particulate control devices are present. Two locations near hazardous waste incinerators were chosen as sampling sites for this study along with another urban area with heavy trace element pollution and a rural control site.

The Illinois Environmental Protection Agency (IEPA) currently monitors a limited number of toxic trace elements (lead, arsenic, nickel, manganese, chromium and cadmium) in 24-hour particulate matter samples collected at urban sites every 6 days (IEPA, 1985). However, IEPA provides no monitoring data on the other toxic elements chosen for this study and no information on particle size distributions or short term (<24 hr) concentration extremes. Thus, peak concentration levels may occur at certain times of the day (e.g., traffic rush hour) that would not be determined by current monitoring systems.

There have been only a few studies of toxic volatile hydrocarbons in Illinois, and these have been short-term in scope (Brodzinsky and Singh, 1983; Singh et al., 1985). Very little information is available on ambient levels of these compounds in the atmosphere, much less on the contribution of various sources to pollution from toxic volatile hydrocarbons. Currently, the only other study under way in Illinois is a USEPA experimental project at a few locations in the Chicago area. The magnitude of releases of volatile toxic hydrocarbons from hazardous waste incinerators is unknown. However, they are a significant component of waste streams (Keitz et al., 1984) and thus could be present in hazardous stack and fugitive emissions from these facilities (U.S. EPA, 1985).

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 1985 to June 1986, the second year of this project, our objectives were to carry out the following aspects of this work:

- 1) Establish a network of 3 urban and 1 rural monitoring stations for the regular collection of air samples and meteorological data.
- 2) Begin collection and analysis of size-fractionated aerosol samples for a toxic trace element data base.
- 3) Develop techniques for the determination of selected vapor-phase trace elements.
- 4) Develop analytical capability for toxic volatile organics.

These objectives have in large part been accomplished or are well underway, and the results are presented in the remainder of this report.

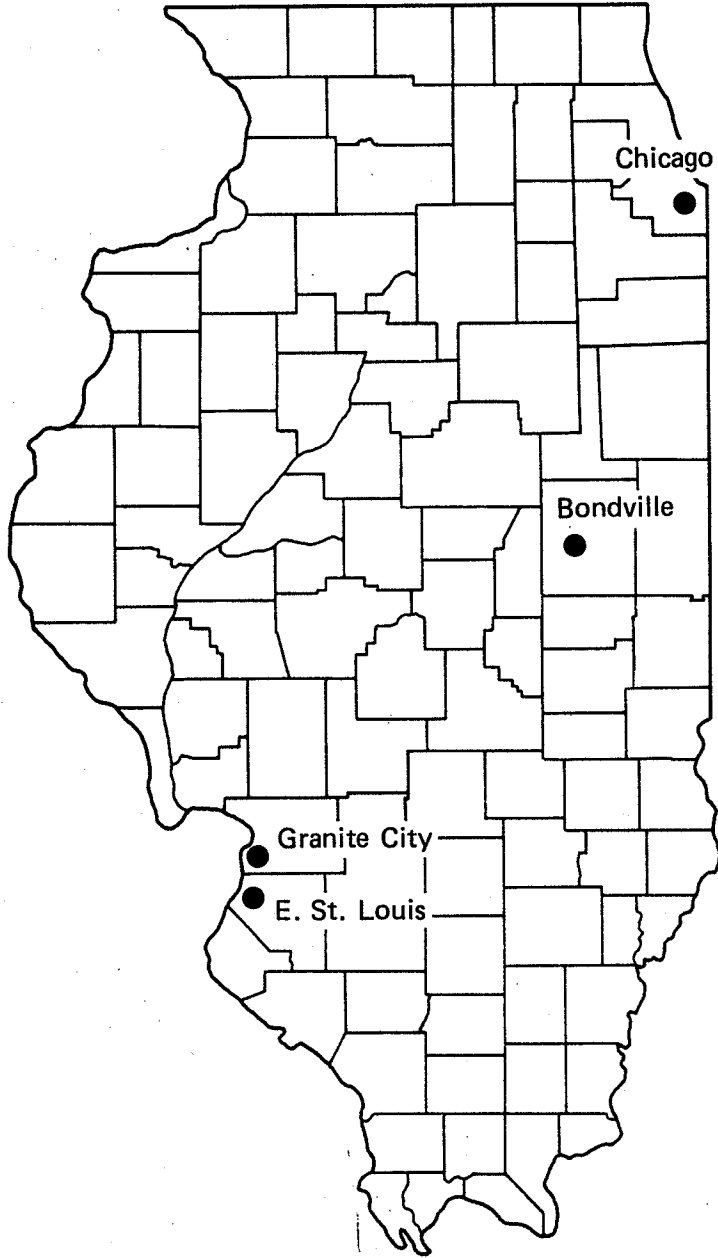


## II. SAMPLING NETWORK

One rural and three urban sampling stations were established at the locations indicated in Figure 1. Each station has an automatic dichotomous sampler (Andersen Model 245) capable of collection of aerosol particles in 2 size ranges, fine (less than  $2.5 \mu\text{m}$ ) and coarse ( $2.5$  to  $10 \mu\text{m}$ ). In addition, wind speed and direction, relative humidity, temperature and solar radiation data are collected continuously at each site. Occasional aerosol samples are also collected using a high volume cascade impactor (Andersen Model 236) which segregates samples into 7 discrete size fractions (greater than  $10 \mu\text{m}$ ,  $4-10 \mu\text{m}$ ,  $1.5-2 \mu\text{m}$ ,  $.75-1.5 \mu\text{m}$ ,  $.4-.75 \mu\text{m}$ , less than  $.4 \mu\text{m}$ ) and the Florida State University "streaker" sampler (PIXE International Corp.), which is a dichotomous sampler capable of very short (1-2 hr) time resolution. The information gained by this combination of sampling and monitoring equipment will complement the IEPA data base by adding data on additional toxic elements, particle-size distributions, short-term maximum concentrations and the relative contribution of various sources to the urban toxic element load. These are all important in assessing the health impact of trace elements in the atmosphere and the impacts of potential inputs of toxic elements from human activities including those related to hazardous wastes. The results may also be used to help determine which source controls would be most effective.

The Chicago site is located at Bright Elementary School, 10740 S. Calhoun in S.E. Chicago. It is in a residential area with nearby heavy industry (steel), landfill operations, expressways, coal-burning power plants and a variety of commercial and industrial facilities. It is also a sampling station used by EPA. A hazardous waste incinerator operated by SCA Chemical Services, Inc. is located about 2 km to the southwest. The air in this part of Chicago

Figure 1. Hazardous Air Pollutant Sampling Network.





typically has elevated levels of total suspended particulate matter (IEPA, 1985) and manganese and zinc (Gatz and Sweet, 1985) compared to other urban areas in Illinois.

The second urban site is in East St. Louis at 13th and Tudor and is also an IEPA sampling station. It is in a residential area with nearby nonferrous metals plants (copper and zinc smelting), expressways, coal-burning power plants and chemical plants. A hazardous waste incinerator operated by Trade Waste Incineration, Inc. is located about 2 km to the southwest. This site was one of 6 in the state which violated the annual average standard for total suspended particulate matter in 1984 (IEPA, 1985). Relatively high levels of cadmium, selenium, arsenic and nickel were recorded at this site during 1984 (IEPA, 1985).

Our third site, another IEPA sampling station, is at 2001 E. 20th St. in Granite City about 10 km north of the East St. Louis site. It is located in a residential/commercial area with nearby heavy industry (steel), a secondary lead smelter and a variety of other small industrial sources. Although there are no hazardous waste incineration facilities in the immediate vicinity, this site was chosen because it and other nearby sites frequently have the worst air quality in Illinois in terms of suspended particulate matter and trace elements. In 1984 (IEPA, 1985), this site had the highest mean concentration of total suspended particulate matter for any monitoring station in the state. Relatively high levels of arsenic, manganese, nickel, lead and cadmium are also regularly recorded in Granite city.

These three urban sites have the highest concentrations of airborne particulate matter for all sites in the state-wide IEPA network. They represent the worst known air quality in residential areas in Illinois. Many

sources emit toxic materials to 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 developed which should apply to many other urban areas in Illinois with similar sources.

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

Installation, calibration and preliminary check-out of all the equipment in the network were completed in January, 1986. Since then, sampling and monitoring meteorological conditions have been carried out on a regular basis.

The sampling plan at the four sites has a number of objectives. Samples are needed which will allow the determination of a wide range of toxic trace elements. To use wind trajectory analysis, the samples must be collected under conditions of relatively steady wind direction. The particle-size distribution and the importance of vapor-phase species must also be determined. Finally, the samples need to reflect the seasonal, diurnal and short-term (hourly) variations in trace element concentrations.

All of these objectives cannot be met using a single type of sampler. The basic trade-off is between a large sample size which will allow quantification of the greatest number of trace elements and short-term or divided samples which provide more information on particle-size distribution, temporal variation and wind direction. The sampling plan used in this work is designed

to answer a variety of questions concerning concentrations of the target elements.

The dichotomous samplers are used to collect 24-hour and 12-hour samples at the urban stations and 48-hour samples at the rural site. The longer sampling times provide sufficient aerosol to quantify most of the target elements and still have a reasonable possibility of steady wind direction. The shorter time, while less satisfactory in terms of element quantification, provides information on diurnal variations and has a much greater potential for constant wind direction. The dichotomous sampler is also used in some experiments with a back-up absorbent to sample vapor-phase species. For these experiments, very long sampling times are required (72-100 hours) to obtain enough material for analysis. Approximately 35 pairs of dichotomous filters and 2 back-up absorbent filters are collected each quarter. Collection of this data for a full year will allow an estimation of seasonal variation.

A second type of sampler, the cascade impactor, divides the aerosol particles into 7 size fractions for determination of particle size distributions. Due to the high analytical costs, only 1 cascade impactor sample is taken at each site per quarter.

Finally, the "streaker" sampler is used to determine changes in trace element concentrations over very short time periods (2 hours). The "streaker" sampler serves 2 functions; it allows the estimation of peak concentrations due to short-term releases; and it provides samples which were taken under very steady wind direction for more reliable identification of sources. "Streaker" samples are also very expensive to analyze; consequently, they will only be taken annually.

## TOXIC TRACE ELEMENT DATA BASE

Nineteen toxic trace elements are listed in Table 1. This list includes the elements monitored as part of the National Air Surveillance Network (NASN) study (McMullen and Faoro, 1977; Evans et al., 1984) and those used in classifying waste as hazardous (Hinners et al., 1984). Two elements (iron and titanium) mentioned in these studies, were not included because of their low toxicities. Another element, tin (Sn), was added because it occurs in the atmosphere and can be biomethylated to form highly toxic organometallic species (Byrd and Andreae, 1982).

### Methods

Analysis of aerosol filters is carried out using three multi-element instrumental techniques, x-ray fluorescence (XRF), neutron activation analysis (NAA) and proton-induced x-ray emission (PIXE). Table 1 shows the methods which may be used for each of the target elements. None of the methods can detect thallium or beryllium. Of the remaining 17 elements, XRF can be used to detect 15. Two others (arsenic and cobalt) are rarely quantified by this method.

The method chosen for analysis depends primarily on the filter matrix. Teflon filters from the dichotomous samplers were analyzed by NEA Inc., in Beaverton, Oregon, using x-ray fluorescence (XRF) analysis. This technique involves the bombardment of a thin layer of sample by high energy x-rays. Excited atoms of a particular element then emit fluorescent x-ray radiation with a characteristic wavelength. The intensity of this radiation can then be used to determine the concentration of the element. Approximately 10% of the dichotomous filters are also run using neutron activation analysis to quantify the 2 elements missed by x-ray fluorescence and for quality assurance purposes.

Table 1. Analysis Methods for Toxic Trace Elements.

<u>Element</u>	<u>NASN</u>	<u>Hazardous Waste</u>	<u>Method<sup>a</sup></u>
Vanadium (V)	*		P,X,N
Chromium (Cr)	*	*	P,X,N
Manganese (Mn)	*		P,X,N
Nickel (Ni)	*	*	P,X,N
Copper (Cu)	*	*	P,X,N
Zinc (Zn)	*	*	P,X,N
Selenium (Se)		*	P,X,(N)
Molybdenum (Mo)	*		X
Silver (Ag)		*	X
Tin (Sn)			X
Antimony (Sb)		*	X,N
Barium (Ba)	*	*	X,N
Mercury (Hg)		*	X
Cadmium (Cd)	*	*	P,X
Cobalt (Co)	*		N,(X)
Lead (Pb)	*	*	P,X
Arsenic (As)		*	N,(X)
Beryllium (Be)	*	*	-
Thallium (Tl)		*	-

<sup>a</sup>P = proton-induced x-ray emission using the "streaker" sampler.

X = x-ray diffraction

N = neutron activation

() = usually below detection limits

Because of the thickness and non-uniformity of the deposits, the cellulose cascade impactor filters are not suitable for analysis by x-ray fluorescence. They can be readily analyzed by neutron activation, however.

The streaker filters are analyzed by PIXE International, Inc. in Tallahassee, FL using proton-induced x-ray emission (PIXE). This technique is similar to x-ray fluorescence but has higher detection limits due to the small amount of aerosol analyzed. Nine of the 19 target elements can be determined using this method as shown in Table 1. Streaker data were not available for this report.

Finally, neutron activation analysis (NAA) carried out at the University of Illinois will be used with dichotomous, impactor and vapor-phase filters. This method depends on the formation of radioactive isotopes of the target elements during neutron bombardment in a nuclear reactor. For arsenic and cobalt, detection limits are lower than with XRF or PIXE. No NAA data were available for inclusion in this report; however, we expect to be able to quantitate up to 11 elements using this method (see Table 1).

From September 1985 through March 1986, approximately 550 dichotomous filters were collected. Of these, about 150 were analyzed for trace elements. Selection of filters for analysis is based on the following criteria:

- 1) low variability in wind direction over the sampling period;
- 2) representation of a wide variety of other meteorological conditions such as wind speed, temperature, and solar radiation; and
- 3) inclusion of filters anticipated to have maximal and minimal loadings.

The idea behind these criteria is to include the most directional data possible in the data base to assist in source identification. Maximum and minimum

concentration ranges can also be determined. Although the initial data may not represent average conditions well, the collection of more data throughout the third year of the project will provide a more reliable estimation of average annual trace element concentrations and seasonal variation.

#### Quality Assurance

The quality assurance program in this project involves both sampler calibration and analytical quality control. Since sampler flow rates must be known to determine the volume of air sampled, all samplers are calibrated on a monthly basis. A Sierra-Andersen mass flow meter is used for the dichotomous samplers. The cascade impactor is run using a flow-controlled General Metal Works high-volume sampler calibrated with General Metal Works manometer. The streaker is calibrated using a Singer flow meter.

For the analytical methods, the instruments are calibrated using National Bureau of Standards (NBS) aerosol standards. Field blanks are run and the results subtracted from the samples in calculating the final results.

Co-located dichotomous samplers are run to determine the variability in the sampling method and occasionally samples are resubmitted for analysis to determine analytical variability. The results of two experiments are shown in Table 2. Most analyses agree quite closely for each set. The exceptions are a few of the heavier elements where the values are near detection limits.

In the future, some samples will be analyzed with both x-ray fluorescence and neutron activation. These data were not available for inclusion in this report, however.

Table 2. Toxic Element Data from Co-located Samplers and Duplicate Analysis ( $\mu\text{g}/\text{filter}$ )<sup>a</sup>.

		<u>Co-located Samplers</u>		<u>Duplicate Analysis</u>	
		<u>A</u>	<u>A'</u>	<u>B</u>	<u>B'</u>
Vanadium	F <sup>b</sup>	.053	.058	ND <sup>b</sup>	ND
	C	.125	.129	ND	ND
Chromium	F	.053	.044	.038	.032
	C	.106	.111	.061	.063
Manganese	F	.164	.168	.080	.076
	C	.585	.557	.197	.218
Nickel	F	.022	.024	.018	.018
	C	.042	.053	.019	.022
Copper	F	.055	.065	.042	.050
	C	.040	.158	.043	.038
Zinc	F	.769	.777	.287	.298
	C	.368	.467	.159	.142
Selenium	F	.092	.084	.041	.027
	C	.041	.034	.015	.013
Silver	F	.060	.065	.032	.026
	C	ND	ND	ND	ND
Cadmium	F	.116	.046	.058	ND
	C	.096	.046	ND	ND
Tin	F	.041	.068	ND	ND
	C	.137	.125	ND	ND
Barium	F	.488	.546	ND	ND
	C	ND	ND	ND	ND
Mercury	F	.018	.021	.003	.012
	C	.020	.018	.013	.012
Lead	F	1.355	1.307	.732	.632
	C	.489	.492	.323	.266

<sup>a</sup>Antimony, molybdenum, cobalt and arsenic were not detected in any of these samples.

<sup>b</sup>F = fine filter    C = coarse filter    ND = not detected.



## TRACE ELEMENTS

Statistical information on the XRF data from dichotomous samples collected thus far is shown in Table 3. Of the 19 target elements, 17 could be detected in at least some of the samples. Arsenic (As) was below detection limits at all the stations except Granite City. Antimony (Sb), tin (Sn), silver (Ag), molybdenum (Mo) and barium (Ba) were at or below detection limit for most of the samples at all four sites.

For averaging purposes, values which are below detection limits are assigned a value of one half the detection limit. The rationale for this is that we know the true value is somewhere between zero and the detection limit; so one half the detection limit is a reasonable estimate of the true value. Obviously, when all or most of the points are below detection limits, the only quantitative information we have is that the true average value is somewhere below the detection limit. The values calculated in this way are comparable with recent IEPA Hi-vol data (IEPA, 1985) for most elements which were analyzed in both networks (Table 4). The concentration of manganese (Mn) is higher in the IEPA data because their collection method, high volume sampling, collects particles larger than the inhalable range sampled in this work. In contrast to the other elements measured in both networks, Mn is enriched on these larger particles. The concentrations of most of the elements listed in Table 4 are also well within national norms determined by the NASN (McMullen and Faoro, 1977; Evans et al., 1984) for comparable urban and rural areas with the following exceptions. Cadmium (Cd) levels are relatively high at the East St. Louis monitoring site. Average concentrations there are higher than 95% of the urban samples taken nationwide in the NASN (Evans et al., 1984). Dzubay (1980) found similar Cd levels in the same area during the 1976 Regional Air Pollution

Table 3. Concentrations of Hazardous Trace Elements.<sup>a</sup>

Element <sup>b</sup>	SAMPLING STATION							
	Bondville		Chicago		East St. Louis		Granite City	
	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
Vanadium (0.1)	<.1-2.7 (1.2)	<.1-1.4 (1.1)	<.1-32 (4.8)	<.1-8.5 (2.7)	1.1-7.5 (3.1)	<1-7.0 (2.6)	2-4 (6.0)	<1-4.2 (2.4)
Chromium (0.2)	<.2-2.5 (1.2)	<.2-1.5 (0.7)	<1-35 (7.4)	<1-18 (3.8)	<1-15 (4.2)	<1-12 (2.6)	2.3-25 (9.6)	<1-24 (4.0)
Manganese (0.2)	1-12 (5.8)	1-6.0 (3.0)	1.8-520 (60)	2.8-191 (30)	4.3-64 (17)	2.3-22 (7.7)	15-150 (53)	3.8-41 (14)
Nickel (1.0)	<1-1.6 (0.6)	<1-1.1 (0.5)	<1-11 (2.0)	<.1-6.6 (2.2)	<1-4.9 (2.0)	<1-3.7 (1.9)	<1-5.8 (2.0)	<1-102 (1.9)
Copper (1.0)	1.1-5.0 (1.5)	2-8.8 (2.1)	1.6-43 (6.2)	1.4-108 (12)	1.0-99 (14)	1.0-438 (46)	1.0-39 (14)	<1-76 (22)
Zinc (1.0)	3-17 (8.3)	6-34 (17)	9-126 (43)	12-267 (91)	12-566 (97)	13-447 (85)	9.3-189 (69)	11-217 (77)
Selenium (0.5)	<.2-.9 (0.4)	.7-2.8 (1.5)	<5-2.5 (0.9)	<.5-8.3 (2.7)	<.5-1.3 (0.8)	<.5-23 (2.1)	<.5-.9 (0.5)	.5-2.7 (1.5)
Molybdenum (2.0)	<1-2.3 (0.9)	ND (0.5)	<2-17 (1.8)	<2-18 (2.0)	<2 (1.7)	ND (1)	ND (1)	ND (1)
Silver (2.0)	ND (0.5)	<1-1.4 (0.9)	<2-2.7 (1.6)	<2-2.9 (1.6)	<2-4 (1.8)	<2-4 (1.8)	ND (1)	ND (1)
Cadmium (2.0)	ND (1)	<2-2.5 (1.3)	<3-4.1 (2.3)	<3-6.3 (2.5)	<3-100 (10)	<3-82 (11)	ND (1.5)	<3-55 (2.3)
Tin (3.0)	<3-3 (1.8)	<3-3 (1.5)	<5-21 (4.3)	<5-48 (6.3)	<5-9.4 (4)	<5-37 (4)	ND (2.5)	<5-5.5 (3.0)
Antimony (10)	ND (2.5)	ND (2.5)	<10-18 (6.8)	<10-15 (7.2)	<10-10 (4)	<10-13 (6)	ND (5)	ND (5)
Barium (20)	ND (5)	<10-14 (6.8)	<20-33 (14)	<20-31 (14)	<20-36 (17)	<20-3 (16)	ND (10)	ND (10)
Mercury (0.5)	<.2-5 (0.2)	<.2-.6 (0.3)	<.5-1.5 (0.4)	<.5-1.7 (0.9)	<.5-2 (0.6)	<.5-1.7 (0.6)	<.5-1.7 (0.5)	<.5-1.9 (0.7)
Cobalt (6.0)	<2-5 (1.2)	ND (1)	<6-7.4 (3)	ND (3)	<6-1.1 (3)	ND (3)	ND (3)	ND (3)

Table 3 (cont.)

Lead (1.0)	3-14 (7.9)	6-33 (20)	3.3-306 (44)	8.9-830 (130)	12-240 (58)	28-502 (117)	11-360 (78)	25-234 (76)
Arsenic (5)	ND (1)	ND (1)	ND (2)	ND (3)	ND (4)	ND (6)	ND (1.5)	<3-45 (6.3)
TOTAL MASS ( $\mu\text{g}/\text{M}^3$ )	3-18 (10)	6-22 (13)	6-80 (20)	9-41 (23)	10-51 (21)	6-85 (20)	11-41 (21)	9-97 (34)

<sup>a</sup>Minimum-Maximum (Mean) in nanograms ( $10^{-9}$  g) per cubic meter; "<" = at or below detection limit; ND = All samples below detection limit. To calculate the mean, all samples below detection limit were assigned a value of one-half the detection limit.

<sup>b</sup>Detection limits are given beneath each element in nanograms ( $10^{-9}$  g) per cubic meter. The listed values are for the urban sites. Detection limits at the Bondville site are lower because of higher volumes sampled.

Table 4. Average Values for Toxic Trace Elements  
in Urban Particulate Matter ( $\mu\text{g}/\text{cubic meter}$ ).

	ISWS (1986)		IEPA (1985)		RAPS (1976)	NASN (1979)
	<u>ESL<sup>a</sup></u>	<u>CHI<sup>a</sup></u>	<u>ESL</u>	<u>CHI</u>	<u>East St. Louis</u>	<u>U.S. Urban Avg.</u>
Arsenic	<.020	<.010	.006	.001	-	-
Cadmium	.021	<.006	.016	.000	.027	.002
Chromium	.007	.011	.001	.004	.037	.011
Copper	.060	.018	-	-	.095	.259 <sup>b</sup>
Manganese	.025	.090	.050	.193	.048	.038
Nickel	.004	.004	.001	.003	.014	.010
Selenium	.003	.004	.002	.002	.004	-
Lead	.175	.174	.330	.120	.585	.584
Vandium	.006	.008	-	-	.018	.021
Zinc	.182	.134	-	-	.096	.163

<sup>a</sup>ESL = East St. Louis

CHI = Chicago

<sup>b</sup>Artifact due to sample contamination by Hi-Vol motors.

Study (RAPS) using similar sampling and analysis methods. Copper (Cu) levels were also elevated in the RAPS study and in our study. However, in the case of Cu, the NASN data cannot be used for comparison because the hi-vol samplers used in that study contaminate the filters with copper (Moyers et al., 1974). Dzubay concluded that nonferrous metals plants located to the southwest of our site were the probable sources of the excess Cd and Cu.

Another element showing higher concentrations than national norms is manganese (Mn) at the Chicago site. This site is within a few kilometers of large steel mills which are recognized as sources of airborne Mn (National Research Council, 1973).

Arsenic (As) is not included in the NASN database, so concentrations of this element cannot be compared to national norms. However, relatively high concentrations of As have been measured by IEPA (1985) in the Granite City and E. St. Louis areas. This study also found higher levels in the atmosphere in Granite City (Table 3).

Finally, although selenium (Se) in the atmosphere is not thought to be a human health hazard, Se concentrations are known to be elevated in air in the Midwest (Rahn and Lowenthal, 1985). Since about 60% of the Se found in the atmosphere comes from the combustion of coal (National Research Council, 1976), this element is considered to be a good atmospheric tracer for emissions from coal-fired power plants in the region. An unusual aspect of Se concentrations in the atmosphere is that the rural levels are about the same as the urban levels, even though Se is derived almost exclusively from man-made sources (Shaw and Paur, 1983). This will be discussed further in the section on vapor-phase trace elements.

## PARTICLE SIZE DATA

It has long been recognized that many industrial processes emit vapors and very fine particles which are not efficiently controlled and which carry toxic elements into the atmosphere (Lee and von Lehmden, 1973). Toxic elements on particles with diameters less than 10 micrometers ( $\mu\text{m}$ ) are especially significant in terms of impact on human health due to their deposition in the respiratory system where toxins can be absorbed into the blood (Milford and Davidson, 1985). Respirable particles usually have a bimodal distribution in the atmosphere. Larger particles (2-10  $\mu\text{m}$ ) are produced by mechanical processes such as soil erosion, agricultural and construction activities, material handling and certain combustion processes. Small particles ( $<2 \mu\text{m}$ ), on the other hand, are commonly associated with high temperature processes such as welding, smelting of metals, and combustion of fossil fuels (Lee and von Lehmden, 1973). The dichotomous sampler is designed to sample these 2 particle size fractions. At our sites, a special inlet excludes non-inhalable particles, (diameters greater than 10  $\mu\text{m}$ ). The inhalable particles are then separated into fine (0.1-2.5  $\mu\text{m}$ ) and coarse (2.5-10  $\mu\text{m}$ ) components.

In Table 3, the concentrations of toxic elements in the fine and coarse fractions are listed for each sampling station. Two of the elements, Pb and Se, are found primarily in the fine fraction at most of the sampling sites. The principal sources of these two elements are auto emissions for Pb and coal burning for Se (Shaw and Paur, 1983). Both of these high temperature processes produce fine particles which are widely dispersed in the environment.

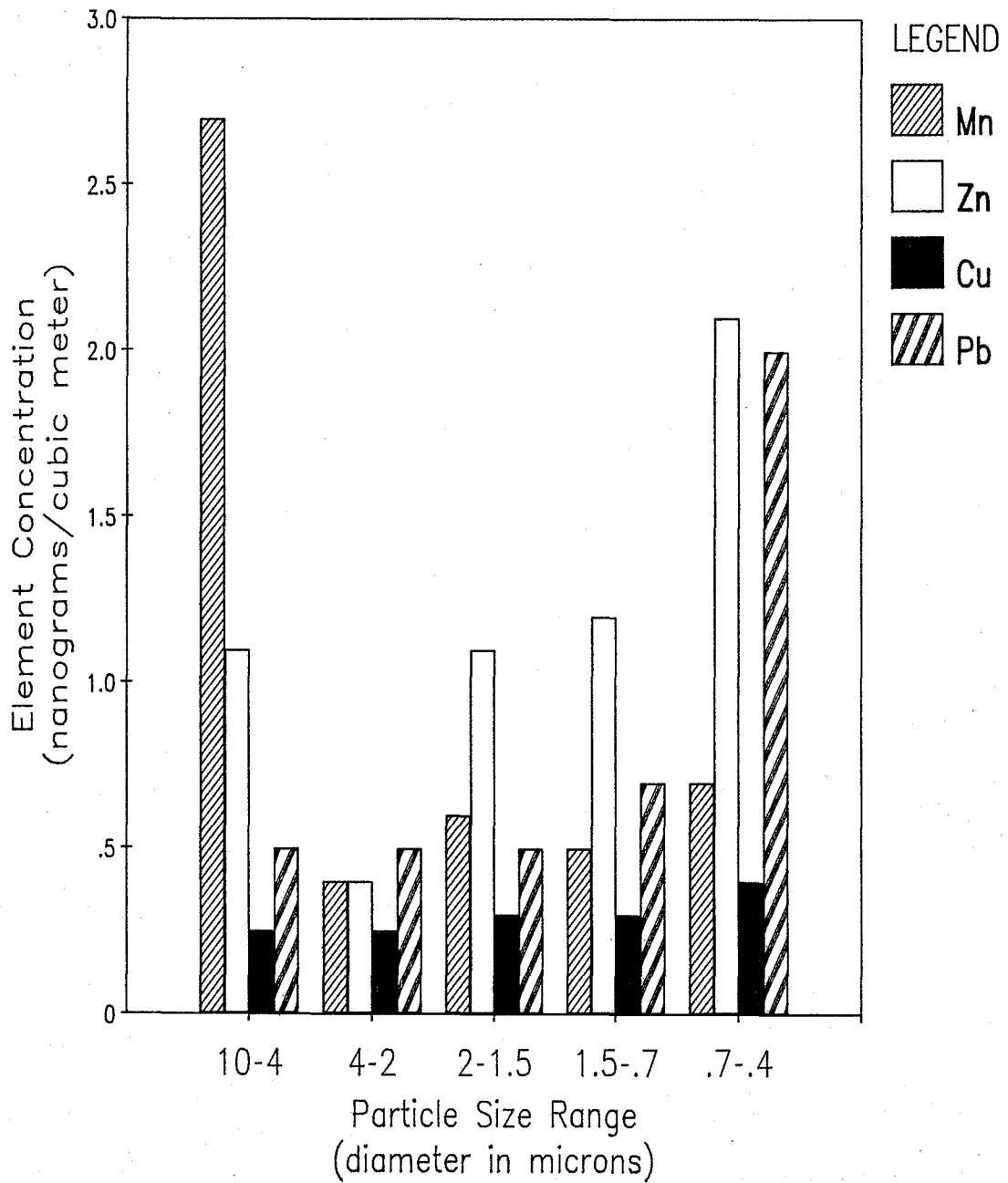
When winds are out of the southwest, high amounts of a group of elements (Zn, Cd, Cu, Sn) appear in the fine particulate matter collected in East St.

Louis. Dzubay (1980) noted the same elements during the 1976 RAPS study. He attributed them to the copper and zinc smelters in the area.

The elevated levels of manganese (Mn) that occur at the Chicago and Granite City sites are mostly associated with the coarse particle fraction. The fact that high levels of iron are also found in these samples suggests a steel industry source for these elements. It has been shown that the steel industry is an important source of Mn to the atmosphere in Chicago (Scheff et al., 1984) and that most of the Mn emitted to the air during steel processing is in the coarse respirable fraction (Dzubay, 1980).

The cascade impactor provides a more detailed look at the size distribution of atmospheric particles in the respirable range. Figure 2 shows cascade impactor data from a sample collected at the Bondville field site. These samples were analyzed by proton-induced x-ray emission (PIXE) due to problems with the neutron activation analysis. Although this method is not ideal for the cellulose substrate, it does give an indication of the type of data which can be obtained. Due to the limitations of the method, only 5 of the 7 fractions could be analyzed. In this sample, Mn, Zn, Cu and Pb were detected. The particle-size distributions of these elements is similar to that found in urban air. Manganese is associated with the coarsest particles, and lead is attached to the finest particles. Zinc and copper are abundant in both fine and coarse particles. Since all of these elements are primarily associated with urban pollution rather than soil erosion, it seems likely that the sources of these elements are mostly in distant urban areas. Indeed, Elestad (1980) has detected urban air pollution plumes in Illinois up to 350 km from the urban source area.

Figure 2. Particle Size Data for Trace Elements  
Bondville Site





Additional cascade impactor samples from both urban and rural sites will be analyzed during the coming year. This technique is a useful tool in helping to assess health impacts and identifying sources of individual elements.

#### WIND DIRECTION DATA

For preparation of this report, sufficient monitoring data for wind direction analysis was only available for the East St. Louis and Chicago sites. Only those toxic elements whose concentrations were above detection limits in at least 75% of the samples were selected for this analysis. In addition to the toxic elements, two non-toxic elements are also included, iron (Fe) and sulfur (S) along with total mass. These elements are tracers for steel plants and coal-fired boilers, respectively. The concentration data for all trace elements were sorted according to wind direction, and the mean concentrations and standard deviations are listed in Table 5. For both monitoring sites, there is considerable variation in element concentration for different wind directions.

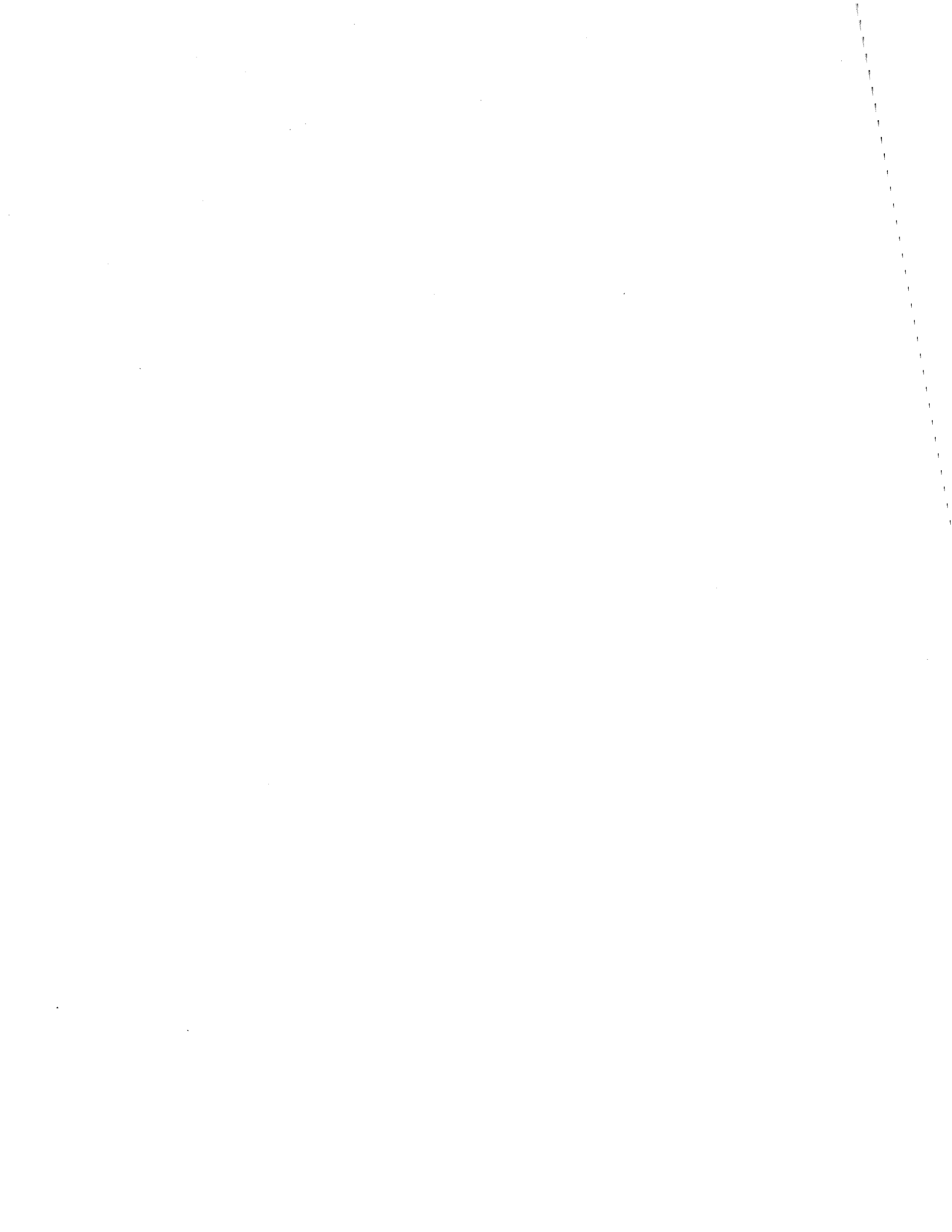
In East St. Louis, southwesterly winds result in high concentrations of Cu, Zn, Se and Pb. As discussed earlier, Dzubay (1980) found similar high concentrations of the same elements in a 1976 study in East St. Louis. He attributed these to emissions from copper and zinc smelters located to the southwest of our site. The predominance of southwesterly winds at this site means that the high concentrations associated with that direction make a large contribution to the average ambient levels listed in Table 3. Neither the total mass of respirable particulate matter nor the concentrations of other elements varied as much with wind direction at this site. Highest concentrations of Cr, Mn, Fe, S and total mass were obtained with winds from the southeast.

Table 5. Variation of Trace Element Concentration<sup>a</sup> with Wind Direction.

<u>Element</u>		<u>NE (0-90°)</u>	<u>SE (90-180°)</u>	<u>SW (180-270°)</u>	<u>NW (270-360°)</u>
East St. Louis	V	8 ± 1.5	6 ± 1.5	3 ± 1	6 ± 3.2
	Cr	7 ± 3	9 ± 4	5 ± 3	9 ± 3.5
	Mn	24 ± 7	30 ± 14	21 ± 7	14 ± 4
	Ni	4 ± 1	4 ± 1.4	5 ± 1	4 ± .7
	Cu	12 ± 4.5	51 ± 50	200 ± 140	11 ± 4
	Zn	120 ± 37	105 ± 66	525 ± 195	72 ± 13
	Se	3 ± 1	3 ± 1	5 ± 2	3 ± .6
	Pb	125 ± 40	170 ± 85	300 ± 140	135 ± 40
	Fe	665 ± 250	900 ± 530	620 ± 310	320 ± 140
	S	1475 ± 500	2700 ± 1250	1640 ± 560	1650 ± 530
Total Mass		40 ± 6	48 ± 17	32 ± 8	26 ± 10
Chicago	V	12 ± 6	13 ± 4	4 ± 1	3 ± 2
	Cr	15 ± 7	33 ± 11	7 ± 2	4 ± 2
	Mn	138 ± 106	281 ± 91	40 ± 21	19 ± 10
	Ni	5 ± 1.5	11 ± 3	4 ± 1	2 ± .6
	Cu	26 ± 21	34 ± 16	17 ± 6	5 ± 2
	Zn	162 ± 56	316 ± 35	100 ± 30	82 ± 37
	Se	4 ± 2	5 ± 1	4 ± 2	1 ± 3
	Pb	129 ± 75	505 ± 200	245 ± 208	76 ± 42
	Fe	1858 ± 1112	3316 ± 1250	641 ± 260	468 ± 290
	S	2273 ± 854	3392 ± 750	2308 ± 860	1150 ± 380
Total Mass		44 ± 11	84 ± 24	48 ± 7	29 ± 7

<sup>a</sup>Concentrations in ng/M<sup>3</sup> except for mass which is µg/M<sup>3</sup>. These are the sums of coarse and fine fractions from dichotomous samples.

At the Chicago site, high concentrations of Mn, Cr, Ni, Cu, Zn and Pb were associated with winds from the northeast and southeast. Highest average concentrations for all elements and total mass were obtained from the southeast. The lowest concentrations were obtained from the northwest quadrant. Except for Mn, none of the average ambient levels for these elements (Table 3) is elevated above normal levels for urban areas. This may be due to the fact that northeasterly and southeasterly winds are relatively uncommon at this site and so polluted air coming from these directions makes a relatively small contribution to the average ambient concentration. Samples taken when winds are out of the southeast have particularly high levels of these elements as well as high total particulate mass, iron (Fe) and sulfur (S). Harrison et al., (1971) in a study of trace elements in northwest Indiana, measured high concentrations of Fe and many of the same toxic trace elements. They attributed them to several large steel mills in East Chicago, Indiana, about 10 km to the southeast of our site. Smaller steel mills are also located to the east and northeast of this site in Illinois.



### III. METHODS FOR VAPOR PHASE TRACE ELEMENTS

Among the toxic trace elements studied in this project, there are 3 that have a significant vapor-phase component under ambient conditions. Airborne mercury (Hg) occurs as a number of volatile chemical species, including elemental Hg, HgCl<sub>2</sub> and alkylated mercury compounds. As a consequence of this, the particle-bound fraction of Hg in the atmosphere is often less than 10% 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 this may lead to a significant undersampling of As using particle filtration techniques alone. Finally, selenium (Se) can exist in a variety of vapor forms including elemental Se, SeO<sub>2</sub> and organoselenides (Ross, 1984). Indeed, Pillay et al. (1971) found that about 60% of atmospheric selenium passes through aerosol filters.

Two of these elements, As and Hg, have been specifically designated as hazardous air pollutants by the USEPA and are undergoing review to set emission standards (Cannon, 1986). Only 6 other toxic air pollutants are currently considered hazardous enough to warrant such 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. The levels of particle-bound Se are relatively high in Illinois and do not vary much between urban and rural sites (Table 3). This may mean that the air near urban source areas is enriched in vapor-phase Se, which is not detected by aerosol sampling. This Se is likely to be converted to particulate Se as the air mass ages and moves into rural areas. Therefore, Se levels in urban areas may be higher than expected from measurements of particle-bound Se alone. Because of

the potential health effects of these three elements, it is important to include vapor phase measurements in this project. The exposure to these elements may be greater than that estimated from particle measurements alone.

Volatile forms of trace elements are generally collected by passing filtered air through a series of absorbents or impingers that chemically or physically bind the species of interest. The absorbent can be enclosed in a tube or impregnated into a standard filter medium. Walsh et al., (1977) used cellulose filters soaked in a non-volatile base to collect acidic vapors of arsenic trioxide. This absorbent should also work with other acidic species such as  $\text{SeO}_2$ . Activated charcoal is a very useful absorbent that has been used for collection of atmospheric Hg (Schroeder, 1982). This absorbent also collects Se and the organometallic forms of a variety of trace elements.

Two types of impregnated filters are being evaluated for trace element sampling in this work. The first is a cellulose filter (Whatman 41) soaked in a 10% solution of tetrabutylammonium hydroxide (TBAH) for collection of As and some forms of Se. The second is a commercial filter consisting of Whatman 41 cellulose impregnated with activated charcoal. This should be useful in collecting Hg, Se, and the organometallics. 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 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 back-up filter is used to detect breakthrough.

Analysis can be by neutron activation analysis (NAA) or by atomic absorption. Neutron activation analysis is a multi-element method suitable for both As and Se; however, Hg often escapes by volatilization during the

irradiation procedure, so the results for Hg are somewhat unreliable. Atomic absorption requires solubilization of the sample and analysis of each element individually. However, detection limits are adequate for all three target elements using vapor generation techniques.

Preliminary screening of the two impregnated filter materials is being carried out by INAA. Subsequent regular analyses will be done using atomic absorption after vapor generation instrumentation is installed. The analytical results from the preliminary experiments are not yet available.





#### IV. ANALYSIS OF VOLATILE TOXIC ORGANICS

Volatile organic compounds are those which are in the vapor phase at normal ambient concentrations and conditions. This corresponds to a vapor pressure of about  $10^{-5}$  mm Hg or greater (Eisenreich et al., 1980). Compounds less volatile than this that occur in the atmosphere are mostly bound to particles in urban air. Two classes of volatile compounds are targets in this study: 1) halogenated hydrocarbons containing 1-3 carbon atoms and 2 or more chlorine or bromine atoms; and 2) lower molecular-weight aromatic hydrocarbons (e.g., benzene, toluene, xylenes, and ethylbenzene). Many of the halogenated hydrocarbons are widely used as solvents and are recognized carcinogens (Thomson et al., 1985). This combination of widespread use and toxicity give rise to a high potential for health impacts. The volatile aromatics are also widely used as solvents and at least one, benzene, is a known carcinogen. In addition, many of these compounds are abundant in motor fuels resulting in exhaust emissions of aromatics and fugitive releases during refueling.

Compounds in these two classes are also likely to be present in emissions from hazardous waste facilities. Their widespread use in commerce and industry means that these materials make up a significant fraction of the waste handled by hazardous waste incineration facilities (Keitz et al., 1984). Fugitive emissions may occur during transfer operations, via leaks and spills, or through evaporation from impoundments and landfills. Incinerator stack emission of some of the halogenated hydrocarbons are also possible due to the refractory nature of certain of these compounds. However, in a recent report, the USEPA (1985) suggested that fugitive emissions and accidental spills may release as much or more toxic material to the environment than the direct emissions from incomplete waste incineration.

Volatile organics are typically sampled by one of two methods. The first is trapping on a solid chemical absorbent. Currently, the most widely used material is Tenax-GC<sup>R</sup>, a polymeric substance with a strong affinity for many hydrocarbons (Krost et al., 1982). Air is passed over the absorbent and trapped chemicals are released for laboratory analysis by heating. For trace analysis, great care must be taken to adequately clean the absorbent and to prevent contamination or loss during transfer and storage before analysis.

There are a number of problems with the use of Tenax for this purpose. Its use is limited to compounds with a relatively narrow range of volatilities. Highly volatile compounds are not trapped efficiently and compounds with low volatility are difficult to remove quantitatively. More importantly, Tenax reacts with ozone and other pollutants to form low molecular weight compounds that are subsequently desorbed and analyzed. These artifacts greatly complicate interpretation of the analytical results (Walling, 1984).

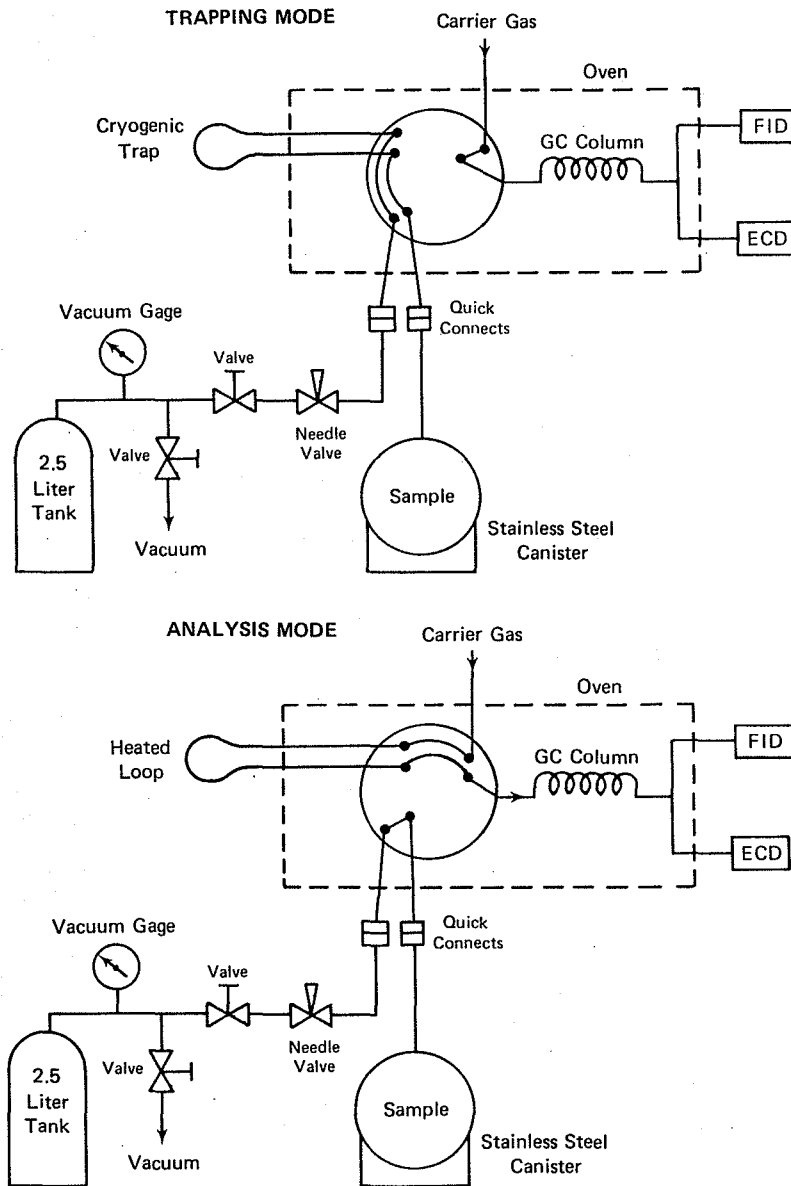
The second method is cryogenic concentration. Typically, whole air samples are collected in the field and brought back to the laboratory for concentration and analysis. The air is dried and then passed through a tube packed with glass beads in contact with liquid oxygen or argon at about -180°C. This temperature results in efficient trapping of the trace organics in the sample without condensing the oxygen in the air (McClenny et al., 1984). Upon heating, the trapped compounds are released for analysis.

Analysis of volatile organics is best accomplished by gas chromatography (GC) which separates complex mixtures into individual chemical components. There are a variety of detectors which can be used with the GC. The mass spectrometer (MS) allows detection, quantification and identification of target compounds, which makes the GC-MS combination a very versatile tool in the

analysis of organics. Its major disadvantage is the high cost of instrumentation. Compounds can also be detected and quantified using the flame-ionization detector (FID), which is sensitive to any organic compound, or selective detectors like the electron capture detector (ECD) for halogenated compounds and the photoionization detector (PID) for aromatic compounds. Although identification is not as reliable with these detectors as compared to MS, detection limits can be much lower.

The organic chemical analytical system being developed for this project is illustrated by the schematic diagram in Figure 3. Samples will be collected and stored in stainless steel canisters supplied by Scientific Instrumentation Specialists of Moscow, Idaho. These containers are capable of storing a wide variety of trace organics for 14 days with no change in concentration (Oliver et al., 1986). In the trapping mode, air from the canister will be drawn through a cryogenic trap into an evacuated 2.5 L cylinder. The change in pressure, measured by a precision vacuum gage, can be expressed in terms of the volume sampled. After sampling between 0.5 and 2 L of air, the trap will be heated to 80°C by immersion in a hot water bath and the sampling valve switched to the analysis mode. In this configuration, carrier gas sweeps the concentrated organic onto the GC column for analysis. The column effluent is split into 2 streams, one entering an FID and the other entering an ECD. This arrangement will allow detection of nonhalogenated target compounds like benzene, toluene and xylene using the FID and halogenated components of interest using the ECD which is more selective and sensitive. A similar simultaneous analysis system was used effectively by Cox and Earp (1982) to analyze a wide variety of organic compounds in ambient air. Using our system, it is possible to detect benzene concentrations as low as 20 ppt and carbon

Figure 3. Analysis Systems for Trace Organics in Air.



tetrachloride concentrations as low as 2 ppt. For these compounds, concentrations well below those of health concern will be measurable.

Standards will be prepared using static dilution bottles as described by Morris et al. (1983). These standards will be used to prepare calibration curves for each target compound and for internal standards added to collected samples. Other quality assurance procedures will include running blank samples, duplicate samples and outside audit samples. In addition, about 10% of the samples will be run using GC-MS to verify compound identifications and to detect compounds which elute simultaneously from the GC.

During the coming year, we plan to collect preliminary air samples at the four sites in our network to evaluate this method and then establish a schedule for regular organics monitoring at these sites. Some monitoring of fugitive emission will also be conducted near a hazardous waste landfill in Danville, IL which is scheduled for excavation and capping later this year. This work will begin the first long-term attempt to characterize the occurrence of volatile toxic organics in the atmosphere in Illinois.



## V. CONCLUSIONS AND RECOMMENDATIONS

The results reported here are preliminary in nature. The complete sampling network has been in place since February of 1986 and the earliest samples analyzed from any of the stations were collected in the fall of 1985. Therefore the current data base reflects conditions during late fall and winter when pollutant levels are typically at their lowest. Samples selected for analysis represent as many different wind directions as possible, however many wind directions were sparsely sampled because of their infrequent occurrence. Finally, the data from neutron activation were not available for this report so several toxic trace elements whose detection limits are high with x-ray fluorescence could not be quantified in most of the samples.

With this in mind, the ambient levels of toxic trace elements measured can be compared to reported levels in other urban areas. The element concentrations which are higher than these norms, magnesium in Chicago, cadmium in East St. Louis and selenium throughout the region, appear to be due to known sources which have been documented in other work. At this time, there is no evidence that hazardous waste incineration is significantly affecting air quality at these monitoring stations in terms of toxic trace elements. In Chicago, the incinerator is located to the southwest of the sampling site. As shown in Table 5, trace element levels associated with winds out of the southwest at the Chicago site are relatively low. The incinerator at the East St. Louis site is also to the southwest of the site as are several nonferrous metal smelters. Winds from this direction correspond to elevated trace element concentrations. However, the trace elements found, their relative concentrations, and their particle size distribution are all similar to those determined in the RAPS study in 1976 before the incinerator was in operation.

The impact on human health of the trace element levels measured here is unknown. Currently, lead is the only trace element studied in this project that is covered by an ambient air standard. Even the highest concentration of lead measured so far in this project ( $0.6 \mu\text{g}/\text{M}^3$ ) is well below this standard ( $1.5 \mu\text{g}/\text{M}^3$ ). Although there are no standards for the other elements at this time, the levels reported here are well below those known to cause health effects. However, several of the trace elements are known (Cr, As, Cd) or possible (Hg, Ni) carcinogens. The long-term impact of low ambient concentrations or exposure to mixtures of these elements on human health is uncertain.

To fully assess ambient air concentrations of toxic elements in Illinois, more samples need to be collected during periods associated with a wide range of pollution levels. In addition, the particle size distribution and the vapor-particle partitioning of trace elements will help in assessing health effects and pinpointing sources.

With the development of sampling and analytical capabilities for volatile toxic organics, concentrations of these additional materials will be determined. Ambient levels of toxic organics have been studied very little in Illinois even though they pose at least as large a health threat as the toxic trace elements. For this reason, it is important to include them as part of an atmospheric hazardous materials data base for Illinois.



## REFERENCES

- Appel, B.R., Tokima, Y., Hoffer, E.M. 1984. "Efficiency of Filter Sampling for Arsenic in the Atmosphere." Atmospheric Environment, 18:1, 219-222.
- 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.
- Byrd, J.T. and Andreae, M.O., 1982. "Tin and Methyl-tin Species in Seawater: Concentrations and Fluxes." Science, 218:565-569.
- Cannon, J.A. 1986. "The Regulation of Toxic Air Pollutants: A Critical Review." Journal of the Air Pollution Control Association, 36(5):562-573.
- Cox, R.D. and Earp, R.F., 1982. "Determination of Trace Level Organics in Ambient Air by High Resolution Gas Chromatography with Simultaneous Photoionization and Flame Ionization Detection." Analytical Chemistry, 54:2265-2270.
- Dzubay, T.B. 1980. "Chemical Element Balance Method Applied to Dichotomous Sampler Data." Annals of the New York Academy of Science, 338:126-144.
- 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.
- 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.

- Harrison, P.R., Rahn, K.A., Dams, R., Robbins, J.A., Winchester, J.W., Brar, S.S. and Nelson, D.M. 1971. "Area Wide Trace Metal Concentrations Measured by Multi Element Neutron Activation Analysis: A One Day Study in Northwest Indiana." Journal of the Air Pollution Control Association, 21(9):563-570.
- Hinners, T.A., Oppenheimer, J.A., Eaton, A.D., and Leong, L.Y.C., 1984. "Multi-element Analytical Techniques for Hazardous Waste Analysis: The State-of-the-Art." Report EPA-600/S4-84-028. U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, NV 89114.
- Keitz, E., Vogel, G., Holberger, R., and Boberschmidt, L. 1984. "A profile of existing hazardous waste incineration facilities and manufacturers in the United States." Report EPA-600/2-84-052, Contract No. 68-03-3021, Mitre Corp., Metrek Division, McLean, VA 22102, Industrial Environmental Research Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, OH 45268.
- Krost, K.J., Pellizzari, E.D., Walburn, S.G., and Hubbard, S.A. 1982. "Collection and Analysis of Hazardous Organic Emissions," Analytical Chemistry, 54:810-817.
- Lee, R.L. and von Lehmden, D.J. 1973. "Trace Metal Pollution in the Environment." Journal of the Air Pollution Control Association, 23(10): 853-857.
- McClenny, W.A., Pleil, J.D., Holdren, M.W., and Smith, R.N. 1984. "Automated Cryogenic Preconcentration and Gas Chromatographic Determination of Volatile Organic Compounds in Air." Analytical Chemistry, 56(14):2947-2951.
- McMullen, T.B. and Faoro, R.B. 1977. "Occurrence of Eleven Metals in Airborne Particulate and in Surficial Materials," Journal of the Air Pollution Control Association, 27(12):1198-1202.
- 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., Bertley, R., and Bumgarner, J. 1983. "Preparation of Multicomponent Volatile Organic Standards Using Dilution Bottles," Analytical Letters, 16:1585-1593.
- Moyers, J.L., Duce, R.A., and Hoffman, G.L. 1972. "A Note on the Contamination of Atmospheric Particulate Samples Collected from Ships." Atmospheric Environment, 6:551-552.
- 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.
- 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. Atmos. Environ., 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.
- Rahn, K.A. and Lowenthal, D.H. 1985. "Pollution Aerosol in the Northeast: Northeastern-Midwestern Contributions," Science, 228:275-284.
- Ross, H.B. 1984. "Atmospheric Selenium." Report CM-66, Dept. of Meteorology, University of Stockholm, Stockholm, Sweden.
- Scheff, P.A., Wadden, R.A., and Allen, R.J. 1984. "Development and Validation of a Chemical Element Mass Balance for Chicago." Environmental Science and Technology, 18(12):924-931.
- Schroeder, W.R. 1982. "Sampling and Analysis of Mercury and its Compounds in the Atmosphere," Environmental Science and Technology, 16:7.
- Schaw, R.W. and Paur, R.J. 1983. "Composition of Aerosol Particles Collected at Rural Sites in the Ohio River Valley," Atmospheric Environment, 17(10):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.
- Thomson, V.E., Jones, A., Hoemisegger, E., and Stergerwald, 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.
- Walling, J.F. 1984. "The Utility of Distributed Air Volume Sets When Sampling Ambient Air Using Solid Adsorbents," Atmospheric Environment, 18(4):855-859.

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.