

**Toxic Volatile Organic  
Chemicals in Urban Air  
in Illinois**

**Clyde W. Sweet  
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Illinois State Water Survey**

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**Printed October 1991**



*Illinois Department of Energy and Natural Resources*

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## CONTENTS

	<u>Page</u>
TABLES .....	iii
FIGURES .....	iv
ABSTRACT .....	v
EXECUTIVE SUMMARY .....	vi
CHAPTER 1. INTRODUCTION .....	1
CHAPTER 2. SAMPLING LOCATIONS AND STUDY AREAS .....	5
CHAPTER 3. METHODS AND QUALITY ASSURANCE .....	15
CHAPTER 4. DATA ANALYSIS .....	21
REFERENCES CITED .....	49
APPENDIX A - Quality Assurance Data .....	53
APPENDIX B - CMB Profiles .....	61

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## TABLES

	<u>Page</u>
Table 1.	Toxic VOCs in ambient air in Illinois . . . . . vii
Table 2.	Toxic VOCs found in urban air. . . . . 2
Table 3.	Point source inventory -- southeast Chicago. . . . . 8
Table 4.	Point source inventory -- Granite City/Madison/Venice. . . . . 11
Table 5.	Point source inventory--East St. Louis/Cahokia/Sauget. . . . . 13
Table 6.	Average concentrations of airborne toxic VOCs . . . . . 22
Table 7.	Statistical summary of data base samples. . . . . 23
Table 8.	Wind trajectory analysis of Sauget VOC data . . . . . 26
Table 9.	Wind trajectory analysis of Washington School (Chicago) VOC data . 26
Table 10.	Contribution of sources to average ambient VOC concentrations . . . . 31
Table 11.	Factor loadings for Chicago . . . . . 33
Table 12.	Factor loadings for East St. Louis . . . . . 34
Table 13.	Chicago CMB Results . . . . . 41
Table 14.	East St. Louis CMB Results . . . . . 46
Table A-1.	Average blank values for precleaned canisters . . . . . 53
Table A-2.	Analytical variability of target VOCs. . . . . 54
Table A-3.	Analytical recovery of target compounds . . . . . 55
Table A-4.	Recovery of target compounds using the automatic sampler. . . . . 56
Table A-5.	Analysis of USEPA working standard . . . . . 57
Table A-6.	ISWS-Radian Intercomparison, SAIL Site 11/10/88 . . . . . 58



## FIGURES

	<u>Page</u>
Figure 1. Air toxics monitoring sites. ....	6
Figure 2. Southeast Chicago study area. ....	7
Figure 3. Granite city study area. ....	10
Figure 4. East St. Louis study area. ....	12
Figure 5. Automatic sampler for stainless steel canisters. ....	16
Figure 6. Analytical system for VOCs. ....	19
Figure 7. The influence of wind direction on VOC concentrations at Sauget. ...	25
Figure 8. Seasonal variations in VOC concentrations at Chicago. ....	28
Figure 9. Diurnal variations in VOC concentrations at Sauget. ....	29
Figure 10. VOC sources in Chicago under average conditions. ....	38
Figure 11. VOC sources in Chicago during pollution episodes. ....	39
Figure 12. VOC sources in Chicago for individual samples. ....	40
Figure 13. VOC sources in East St. Louis under average conditions. ....	43
Figure 14. VOC sources in East St. Louis during pollution episodes. ....	44
Figure 15. VOC sources in East St. Louis/Sauget for individual samples. ....	45

## ABSTRACT

The airborne concentrations and sources of 13 toxic volatile organic chemicals (VOCs) were evaluated in three urban areas in Illinois: southeast Chicago, East St. Louis and Granite City. VOC concentrations and meteorology were monitored between May 1986 and April 1990. Using emissions inventories and source signatures developed for the study areas, we applied wind trajectory analysis, factor analysis and chemical mass balance to the data. This statistical analysis indicates that most of the toxic VOCs in the study areas come from urban area sources such as vehicle exhaust, evaporation of petroleum products, and solvent emissions by commercial and industrial sources. Emissions of benzene from coke ovens in Chicago and several aromatic and chlorinated hydrocarbons from a chemical complex in Sauget produce high concentrations of these chemicals in ambient air within 1 km of these sources. However, these emissions do not have a large impact on the overall air quality in the study areas. We conclude that to reduce average concentrations of the target VOCs in the study areas, controls on area sources would be most effective. Additional controls on large industrial point sources would help reduce ambient levels of toxic VOCs within 1 km of these sources.

## EXECUTIVE SUMMARY

This report provides a comprehensive evaluation of the concentrations and sources of a group of 13 toxic volatile organic chemicals (VOCs) in ambient air in three urban areas in Illinois. It follows a companion report (Sweet, Vermette and Gatz, 1990) on airborne toxic trace elements in the same areas. The urban study areas were southeast Chicago, East St. Louis, and Granite City. These areas were chosen because they have poor air quality in terms of the criteria pollutants and because they contain a large number of area and point sources of toxic VOCs. Area sources are those involving many small sources over a wide area such as vehicle emissions or dry cleaning. Point sources are single large emitters restricted to a small area; industrial sources like coke ovens and chemical plants are in this category. Finally, a rural site near Champaign (Bondville) was used to evaluate regional background levels of airborne VOCs.

At each study site, air samples and meteorological data were collected between May 1986 and April 1990. Over 200 individual air samples were analyzed using gas chromatography with cryogenic preconcentration of the VOCs from the sample. The VOCs selected for analysis are associated with a large proportion of the health risk from breathing urban air. Due to analytical limitations, we were not able to analyze all toxic VOCs. For this reason, the information reported here is only a start toward understanding VOC concentrations in urban air.

The overall objectives of this study were to characterize concentrations of selected toxic VOCs in ambient air and to identify important sources of these pollutants in the study areas. We used the toxic VOC database developed in this work along with existing emissions inventories and VOC source signatures to carry out the receptor modeling. Using these statistical methods, we quantified the contributions of individual sources to the concentrations of specific VOCs found in urban air.

### Toxic VOC Database

Data for the 13 toxic VOCs that could be measured in this study are summarized in Table 1. For most of the compounds, average concentrations in urban air are 2 to 10 times higher than those measured at our rural background site. In general, the urban VOC levels are more variable than rural levels, approaching background when ventilation rates (high wind speed and mixing height) are high and major point sources are downwind and reaching maximum values when ventilation rates are low and major sources are upwind.

Table 1. Toxic VOCs in ambient air in Illinois<sup>a</sup>

Compound	Southeast Chicago	East St. Louis	Granite City	Rural Background	U.S. Average Urban/Rural
benzene	4.6	10.6	1.3	1.3	8.8/4.5 <sup>b</sup>
toluene	8.9	8.5	6.0	3.0	22/2.5 <sup>c</sup>
m,p-xylene	3.9	16	4.2	1.2	13/0.4 <sup>b</sup>
ethylbenzene	1.4	6.9	1.6	0.4	4.1/- <sup>c</sup>
o-xylene/styrene	2.9	3.3	3.3	1.1	5.2/0.4 <sup>b</sup>
chloroform	0.3	0.5	0.3	0.3	0.3/0.2 <sup>b</sup>
1,1,1-trichloroethane	3.3	3.9	1.5	1.1	2.8/0.6 <sup>b</sup>
carbon tetrachloride	0.7	0.9	0.7	0.8	1.2/0.8 <sup>b</sup>
trichloroethylene	1.0	2.1	0.6	0.6	0.8/0.1 <sup>b</sup>
tetrachloroethylene	1.8	1.4	0.6	0.4	2.3/1.4 <sup>b</sup>
chlorobenzene	0.3	3.0	0.4	0.2	1.5/- <sup>b</sup>

<sup>a</sup> Average concentrations in  $\mu\text{g}/\text{m}^3$

<sup>b</sup> Brozinsky and Singh, 1983

<sup>c</sup> Edgerton et al, 1989

The average concentrations of the toxic VOCs measured here are similar to those in other urban and rural areas in the United States (see Table 1). The health risk attributable to these compounds in our urban study areas is therefore no higher than expected for a typical urban environment without major industrial point sources. This indicates that emissions from area sources contribute most of these VOCs to the atmosphere. The additional industrial point sources unique to our urban study areas contribute some specific toxic VOCs but in general they do not result in average concentrations greater than those found in urban areas without such sources.

#### Seasonal and Diurnal Variations

In addition to variations due to wind direction, there are regular fluctuations in toxic VOC concentrations associated with seasonal and diurnal (day-night) changes. In general, higher VOC concentrations in ambient air occur during the warmer months when evaporation potential is high. Diurnal variations are probably related to changes in atmospheric mixing. Low mixing heights and low wind speeds at night correspond to relatively high concentrations of airborne VOCs. During the day, higher wind speeds and mixing heights result in more dilution of toxic emissions and lower VOC concentrations.

## Source Identification and Apportionment

Wind trajectory analysis and simultaneous upwind and downwind sampling of suspected sources were two techniques used to identify and characterize major industrial point sources in the study areas. Important sources identified in this way are a large chemical manufacturing complex in Sauget and steel mill coking ovens in southeast Chicago. High concentrations of benzene and several chlorinated hydrocarbons were measured directly downwind of these industrial sources. However, the impact of these emissions at monitoring sites beyond 1 km from the plant boundaries was small.

Application of receptor modeling to the data identified other important sources. These statistical methods analyze the pattern of individual VOCs in the database compared with known patterns of the same VOCs in suspected sources. Once sources have been identified, the relative importance of emissions from several sources can be related to the ambient concentration of each toxic compound. Vehicle exhaust and gasoline vapors were identified as primary area sources of benzene in all of the study areas. Coke ovens in Chicago and the chemical manufacturing complex in the East St. Louis area were also identified as important point sources of benzene. No other VOCs in southeast Chicago could be specifically attributed to industrial point sources. Indeed, the concentrations of other toxic VOCs in southeast Chicago are similar to those found outside of the industrial area or in other urban areas without major industrial sources. In East St. Louis, the chemical complex was a significant source of several aromatic and chlorinated toxic VOCs at our Sauget monitoring site 0.5 km southeast of the source. At our other East St. Louis site, 2 km northeast of the chemical complex, these emissions had very little impact on average air quality.

## Conclusions

Toxic VOCs in the urban areas studied are largely attributable to area sources common to all metropolitan areas. These sources include vehicle exhaust, evaporation of petroleum products, and use of commercial solvents by dry cleaners and small industrial sources. The ambient concentrations of the VOCs studied in this project are no higher than those in urban areas without major industrial sources. The effects of emissions from large industrial sources in our study areas are quite localized, increasing maximum concentrations of toxic VOCs within a kilometer of the source but having little impact on overall air quality farther away.

Reduction of toxic VOCs in the study areas will require controls on area sources. Controls on industrial sources could reduce high concentrations of toxic VOCs in localized areas but would not have a large impact on overall concentrations of these compounds in ambient urban air.

## CHAPTER 1. INTRODUCTION

During the past few years, increased awareness of air pollutants and new potential sources of airborne toxic chemicals have brought a concern that the release of toxic pollutants to air may be a health hazard. Many toxic chemicals are not routinely monitored in ambient air in Illinois, and little is known about ambient concentrations or the relative importance of various sources of these chemicals. The study described in this report was intended to provide this information for two selected groups of toxic air pollutants in three industrialized urban areas in Illinois. In a companion report (Sweet et al., 1990), we presented data on concentrations and source attribution for the toxic trace metals in the urban study areas. In this report, concentrations and source attribution for the toxic volatile organic chemicals (VOCs) will be discussed.

Toxic air pollutants in urban air are recognized as important carcinogenic risk factors. In a U.S. Environmental Protection Agency study (Thomson et al., 1985), most of the cancer risk from urban air was attributed to 15 toxic chemicals. The majority of these chemicals are either trace metals or VOCs. In fact, the three pollutants with the highest risk factors were two VOCs and a trace metal (benzene, carbon tetrachloride and chromium). The additive lifetime risk from breathing ambient urban air containing average amounts of all 15 toxic chemicals is  $10^{-3}$ . This means that one person in one thousand gets cancer from breathing urban air in areas with "normal" concentrations of toxic air pollutants. Table 2 lists some of the most important toxic VOCs commonly found in urban air and their health effects.

Illinois has several urban areas where people live in close proximity to a variety of industrial sources (smelters, steel mills, incinerators, etc.). Such industrial sources usually are composed of a few large emission sources confined to a small area and are termed "point" sources. These sources add to the toxic chemical burden already entering the air from normal urban sources such as vehicle exhaust (sources that involve many small emitters spread over a wide area are termed "area" sources). In fact, state-wide monitoring (IEPA, 1990) shows that three of these urban areas, southeast Chicago, the metro East St. Louis area and Granite City have higher levels of some of the "criteria" pollutants (total suspended particles, sulfur dioxide) and toxic trace metals (arsenic, cadmium, chromium) than other urban areas in the state. Our data show that the average concentrations of airborne trace metals in these areas are five to ten times higher than the concentrations in background ambient air (Sweet et al., 1990). Most of this increase is attributable to industrial sources and to fugitive emissions of urban dust contaminated by industrial fallout.

Table 2. Toxic VOCs found in urban air.

Compound	Major Source	IEPA Priority toxic chemicals (air emissions)	Health Hazard <sup>a,b</sup>	Analysis Method
benzene	auto exhaust, chemical and steel industry	YES	KHC	GC/FID
toluene	auto exhaust, petroleum products, paint, graphic arts	YES	RT & FT	GC/FID
m,p-xylene	auto exhaust, petroleum products, graphic arts	NO	OE	GC/FID
ethyl benzene	petroleum products	NO	OE	GC/FID
o-xylene	petroleum products	NO	OE	GC/FID
chloroform	water treatment plants	NO	PHC	GC/ECD
1,1,1-trichloroethane	industrial solvent	NO	BM	GC/ECD
carbon tetrachloride	landfills, chemical industry	NO	PHC	GC/ECD
trichloroethylene	industrial solvent	YES	PHC	GC/ECD
tetrachloroethylene	dry cleaning	YES	PHC	GC/ECD
chlorobenzene	chemical industry	NO	BM	GC/FID
methylene chloride	solvent	NO	BM	GC/FID
p-dichlorobenzene	chemical industry	YES	BM	GC/ECD
ethylene dibromide	gasoline	NO	PHC	GC/ECD

<sup>a</sup> KHC = known human carcinogen, PHC = probable human carcinogen, RT = reproductive toxicant, FT = fetal toxicant, OE = other effects (IEPA, 1989)

<sup>b</sup> BM = bacterial mutagen (Brodzinsky and Singh, 1983)

The atmosphere is the largest receptor of toxic chemicals exceeding water, underground injection, and land releases. The rationale for a "toxic" designation for particular chemicals is not discussed in this report, but is based on an IEPA designation (IEPA, 1989). The toxic VOCs studied in this report, their health effects, and sources, are shown in Table 2. There are, of course, many other toxic VOC compounds in urban air that were not covered in this study. However, the VOCs measured are thought to be some of the most important toxic VOCs in urban air (Brodzinsky and Singh, 1983) and/or are listed on IEPA's Air Emission "Tier 1" and "Tier 2" Priority Toxic Chemical ranking. The first tier receives priority attention, and the second tier receives further intense scrutiny (IEPA, 1989).

The overall objectives of this project were to measure concentrations of selected toxic VOCs in ambient air and to identify important sources of these pollutants in three urban areas in Illinois. Preliminary results were discussed in three previous interim reports (Gatz and Sweet, 1985; Sweet and Gatz, 1986, 1988). This report contains the findings, conclusions and recommendations of the project on the toxic VOCs. The ambient concentrations, the effects of meteorological variables and the most important sources of the target organic compounds are discussed. This work is based on monitoring data collected between May 1986 and April 1990.





## CHAPTER 2. SAMPLING LOCATIONS AND STUDY AREAS

Four study areas and seven sampling locations were used in this work. The three urban study areas were chosen because they have the worst known air quality in Illinois in terms of criteria pollutants such as total suspended particles (TSP) and sulfur dioxide (SO<sub>2</sub>) and because they contain a wide variety of industrial point sources including many known to emit toxic air pollutants. These areas have the potential for levels of airborne toxic materials higher than other locations in Illinois. The IEPA Toxic Air Pollutant (TAP) emission inventory ranks the counties of the three urban study areas first, third and fifth in the state for toxic VOC emissions. This constitutes 40% of Illinois total toxic VOC emissions (IENR, 1990). For comparison, the fourth study area is in a rural location near Champaign. This site was chosen to be representative of regional air quality and provides an estimate of background concentrations of toxic air pollutants in Illinois. VOC emissions in Champaign County (7181 ton/yr) approach the county average for the state (8,000 tons/yr) (IEPA, 1989). The locations of the four study areas are shown in Figure 1. In this section, site maps and point source emissions inventories are described for each of the urban study areas.

The Chicago study area is a 64 square kilometer area in southeast Chicago bounded by 95th Street to the north, the Indiana state line to the east, the Chicago city limits to the south and State Street to the west. Iron and steel and related industries dominate the study area's manufacturing base and inventoried emissions. These industries are largely confined to a north-south strip running either side of the Calumet River. Associated with the iron/steel industries are large tracts of land that serve as storage locations for coal, slag, scrap steel, limestone and other raw materials. Other significant facilities include an auto assembly plant, a municipal sewage treatment works, hazardous waste incinerator and numerous landfills. There are oil refineries west of the study area and east of the study area in Indiana. There are also numerous industrial sources northeast of the site around Gary, Indiana; however this area is generally downwind of our study area. Air quality was measured at three sites. Bright Elementary School at 10740 S. Calhoun, from May 1986 to August 1986, Washington Elementary School at 3611 E. 114 Street, from December 1987 to April 1990, and Carver High School at 13100 S. Doty during August 1989. The locations of these sites along with the locations of major point sources are shown on the map in Figure 2. A list of these sources and an emissions inventory is given in Table 3.

The Granite City study area is bounded by the Mississippi River to the west and northwest, and Horseshoe Lake to the southeast and includes the municipalities of Granite City, Madison, and Venice. The city of East St. Louis is located to the south and the city of St. Louis, Missouri to the southwest. Like southeast Chicago, iron/steel industries dominate the manufacturing base of Granite City. In addition to iron and steel, lead smelting and lead recycling facilities are located within the study area. Air quality was

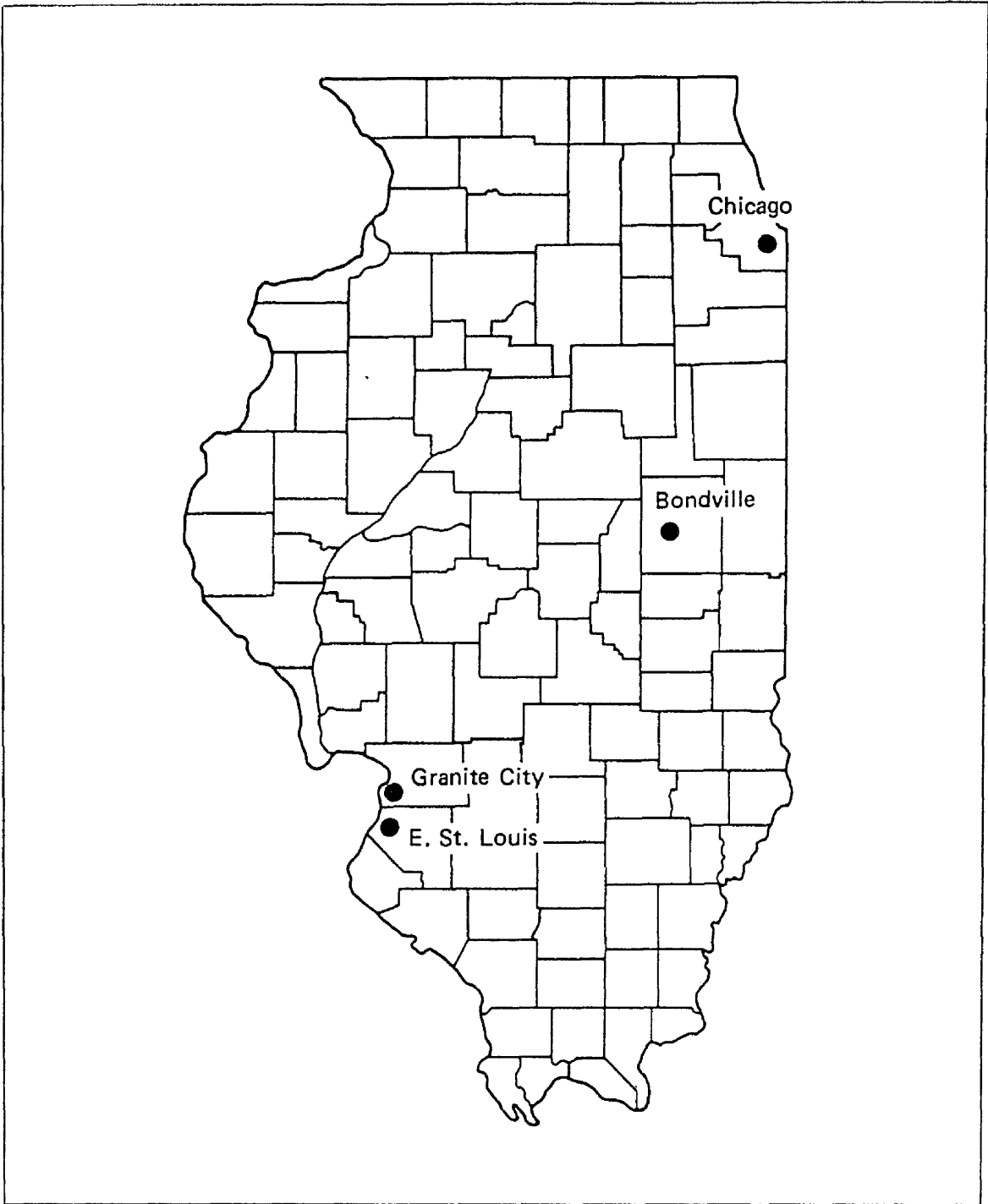


Figure 1. Air toxics monitoring sites.

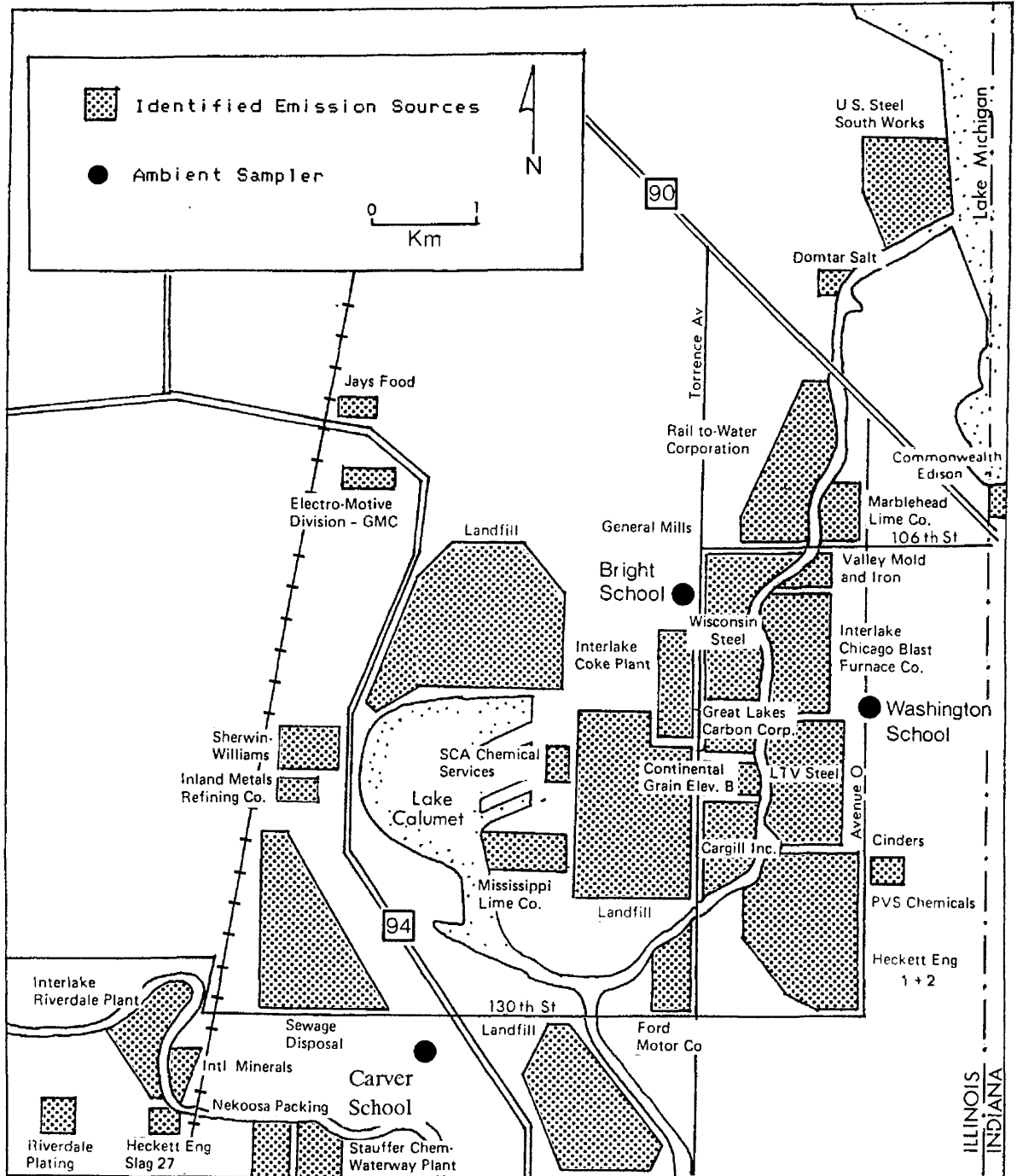


Figure 2. Southeast Chicago study area.

Table 3. Point source inventory -- southeast Chicago<sup>a</sup>.

## Emissions (tons/year)

Industry Name	Particulate Matter	Emissions (tons/year)		SIC <sup>b</sup>	Description
		SO <sub>2</sub>	Significant Others		
Interlake-Riverdale	373.6	639.8	695.1 (NOX)	3312	Steel manufacturing
US Steel-Southworks	110.0	0.1	37.5 (NOX)	3312	Steel manufacturing
Chicago Blast Furn	324.2	818.9	2170.0 (NOX)	3312	Steel manufacturing
LTV Steel	515.0	680.3	420.0 (NOX) 1713.0 (CO)	3312	Steel manufacturing
Chicago Coke Plant	151.6	437.4	401.6 (HC)	3312	Steel manufacturing
Heckett-Plant 27	36.5	0	-	3295	Slag processing
Heckett Eng.	76.8	0	-	3295	Slag processing
Heckett En. Harsco	110.9	0	-	3295	Slag processing
Cinders	142.5	0	-	3295	Slag processing
Inland Metals	1.2	0	-	3341	Refining nonferrous
Marblehead Lime	129.7	532.8	-	3274	Lime manufacturing
Domtar Ind.	12.9	0	-	2899	Refining Na Cl
Great Lakes Carbon	6.9	376.8	-	2999	Petro & coal prod
PVS Chemicals	129.7	532.8	26.5 (NOX)	2819	Inorganic chemicals
SCA Chemical	16.3	0	17.3 (NOX)	4953	Refuse disposal
Ford Motor Co.	9.0	1.9	869.0 (HC)	3711	Auto manufacturing
Rail-to-water	11.7	0	-	4463	Marine cargo hand.
Mississippi Line	12.4	0	-	4463	Marine cargo hand.
Int. Minerals	16.9	0	-	4463	Marine cargo hand.
Stolt Terminals	7	0.9	9.8 (NOX) 89.4 (HC)	4226	Warehouse & storage
Sherwin-Williams	2.4	0	-	2851	Paint manufacturing
Stauffer Chemical	20.6	0	-	2874	Fertilizer mfg.
Continental-Elv B	121.3	1.6	-	5153	Marketing grain
Cargill, Inc.	54.0	0	-	5153	Marketing grain
General Mills, Inc.	154.0	0	-	2041	Milling grain
Jay's Foods	11.6	0	-	2099	Food preparation
CID Landfill	4.4	0	-	N/A	Landfill site
Con-Ed Peaking Units	6.5	69.5	121.1 (NOX)	4912	Electric power
Riverdale Plating	19.4	0	-	3471	Plating

<sup>a</sup> Source: Illinois Environmental Protection Agency, Emissions Inventory, unpublished data<sup>b</sup> Standard Industrial Code

measured at 20th and Adams Streets in Granite City between November 1986 and November 1989. The site map and emissions inventory for the Granite City study area are in Figure 3 and Table 4.

The East St. Louis study area is bounded by the Mississippi River on the west and includes the municipalities of East St. Louis, Sauget, and Cahokia. The city of St. Louis is located to the west of the study area, across the Mississippi River. The dominant manufacturing activities in the study area are copper and zinc smelting and organic chemical production. Air quality was measured at two sites in this area: the Illinois Environmental Protection Agency (IEPA) trailer at 13th and Tudor streets from November 1986 to April 1990 and the Kerr-McGee lot at Little Avenue and 19th Street in Sauget from September 1987 to November 1989. A map with these sites shown and a table of major point sources and emissions inventories are given in Figure 4 and Table 5.

The fourth site in this network is in a rural area near Champaign 8 km south of Bondville, IL. This site was chosen to be representative of regional air quality and is also used in several national air and precipitation monitoring programs. There are no point sources within 10 km and the site is at least 50 km downwind of urban areas during times of prevailing northwest and southwest winds. In this location, concentrations of airborne toxic air pollutants should be representative of conditions in most of rural Illinois and should provide an estimate of the contribution of the regional background to urban pollution. Samples were collected between February 1987 and April 1990.

It is important to recognize that for all three urban study areas the existing emissions inventories are only a starting point for identifying important sources of toxic VOCs. The many sources that are not inventoried here include area sources such as vehicle emissions, service stations, dry cleaners and small industrial sources. Major point sources outside the study areas in Missouri and northwest Indiana can affect the study areas when the wind is from the right direction. Finally, there may be point sources within the study area that are not included in the official emissions inventory. The data in Tables 3-5 are based on the 1987 IEPA emissions inventory. Since we collected samples until 1990, this inventory does not include newer sources in the study areas.

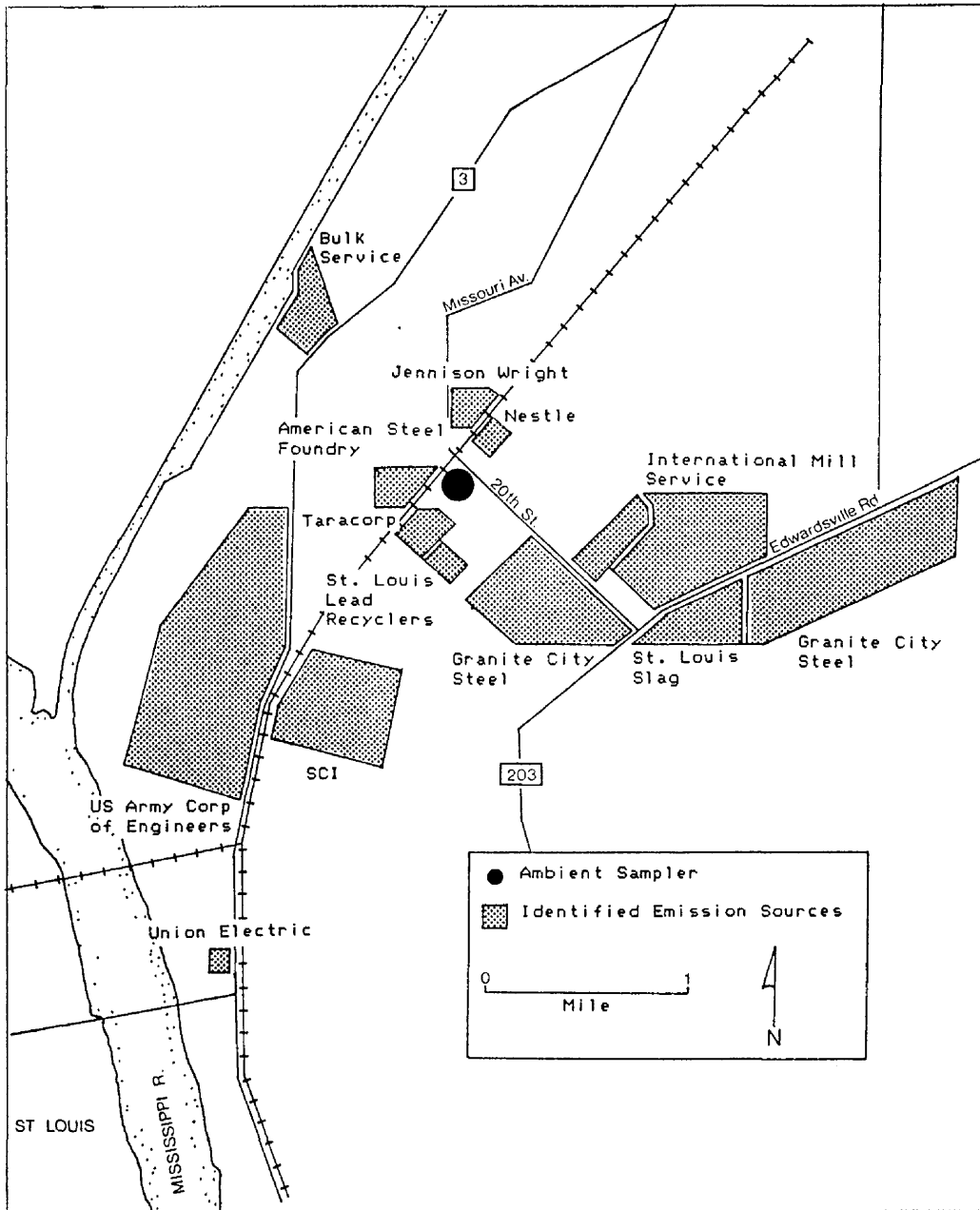


Figure 3. Granite City study area.

Table 4. Point source inventory -- Granite City/Madison/Venice<sup>a</sup>.

Emissions (tons/year)

Industry Name	Particulate Matter	SO <sub>2</sub>	Significant Others	SIC <sup>b</sup>	Description
Granite City Steel	2282.0	8641.0	3473.0(NOX) 172.0(HC)	3312	Steel manufacturer
St. Louis Slag Products	242.0	-	-	3295	Slag processing
Bulk Service	104.0	-	-	4463	Marine cargo hand
Archer Daniels Midland	107.0	14.0	52.4(NOX) 33.5(HC)	2075	Soybean processing
U.S. Army	9.6	110.0	47.5(NOX)	9711	Construction
Nestle Co.	35.9	28.7	51.2(NOX)	3341	Food manufacturer
Tara Corp.	74.4	-	17.3(NOX)	3341	Secondary lead smelter
Corn Sweeteners, Inc.	2.4	10.5	11.6(HC)	2087	Grain processing
International Mill Service	48.8	-	-	3295	Ground minerals
St. Louis Lead Recyclers	5.4	-	-	5093	Lead recycling
SCI	51.5	0.2	48.7(NOX)	3341	Secondary A1 smelter
Kerr-McGee	8.4	-	61.6(HC)	2491	Wood preserving
Union Electric	7.7	8.2	113.0(NOX) 8.4(HC)	4911	Coal fired power plant
American Steel Foundry	0.3	-	-	3325	Steel foundry
Jennison Wright Corp.	12.7	-	4.1(HC)	2491	Wood preserving

<sup>a</sup> Source: Illinois Environmental Protection Agency, Emissions Inventory, unpublished data

<sup>b</sup> Standard Industrial Code



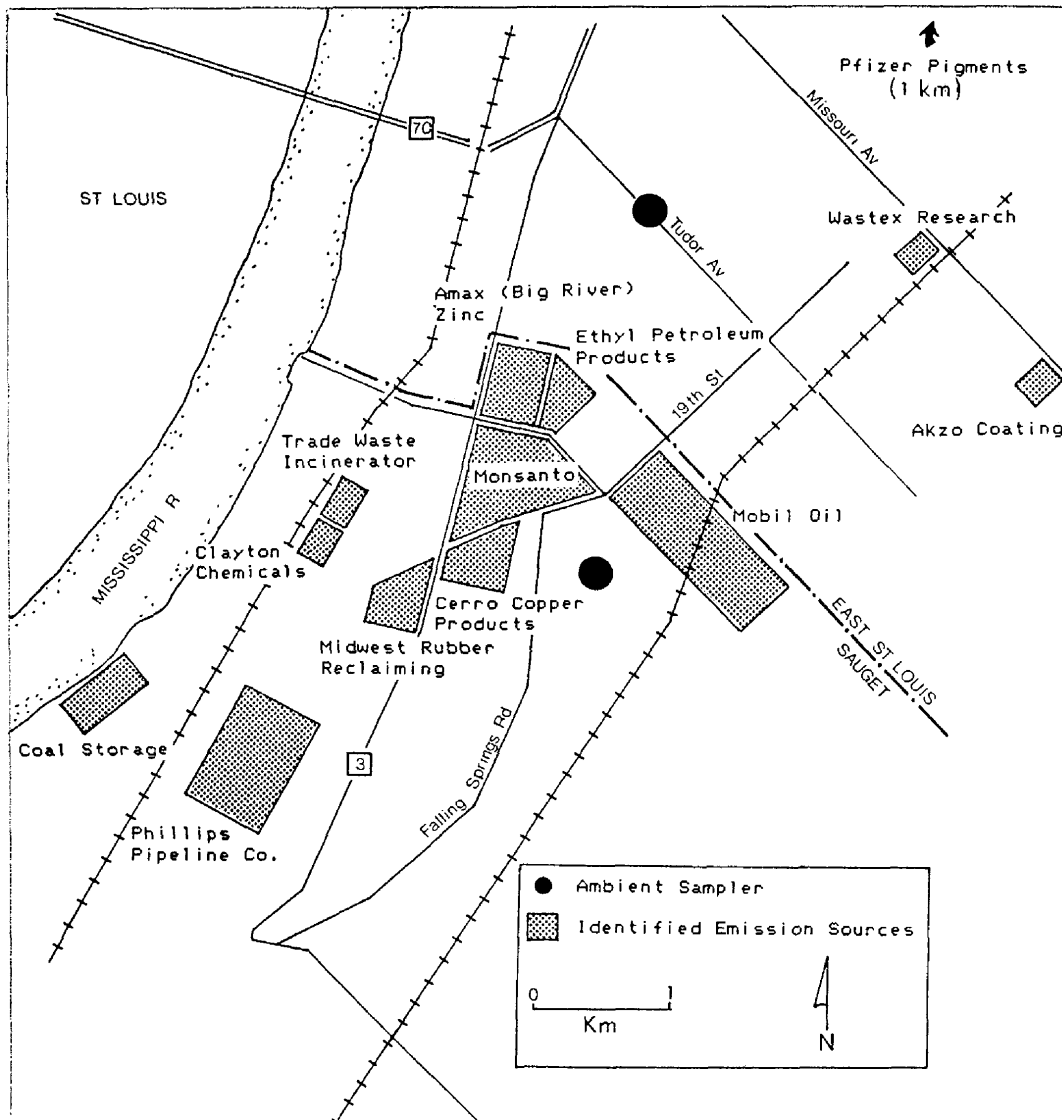


Figure 4. East St. Louis study area.

Table 5. Point source inventory--East St. Louis/Cahokia/Sauget<sup>a</sup>.

Emissions (tons/year)					
Industry Name	Particulate Matter	SO <sub>2</sub>	Significant Others	SIC <sup>b</sup>	Description
Cerro Copper Products	49.1	-	3.2 (NOX)	3341	Secondary Copper Smelter
Amax (Big River) Zinc	120.1	3.2	7.2 (NOX)	3333	Zinc Smelter
Monsanto	168.3	5112.0	185.0 (HC) 1011.0 (NOX)	2869	Organic Chemicals
Midwest Rubber Reclaiming	376.0	110.0	5.5 (HC)	3031	Reclaimed Rubber
Trade Waste Incinerator	71.1	-	8.9 (HC)	4953	HW Incineration
Pillsbury	132.0	-		4463	Grain Handling
Mobil Oil	-	-	328.0 (HC)	5171	Petroleum Products
Clayton Chemicals	0.2	6.6	62.4 (HC)	2869	Organic Chemicals
Ethyl Petroleum Products	3.3	1129.0	327.9 (HC)	1869	Organic Chemicals
Wastex Research	-	-	20.4 (HC)	2869	Organic Chemicals
Atro Coating	-	-	31.9 (HC)	2899	Chemicals Preparation
Central Soya	45.0	-		5151	
Phillips Pipeline Co.	1.3	.4	1350.0 (HC)	5171	Petroleum Terminal
Pfizer Pigments	156.7	108.0	246.5 (NOX)	2816	Inorganic Pigments

<sup>a</sup> Source: Illinois Environmental Protection Agency, Emissions Inventory, unpublished data

<sup>b</sup> Standard Industrial Code



## CHAPTER 3. METHODS AND QUALITY ASSURANCE

In this section methods for the sampling and analysis of volatile organic chemicals (VOCs) will be discussed in detail along with quality assurance procedures. Additional quality assurance data are included in Appendix A.

### Sampling Methods

Samples were collected in Summa-polished, stainless steel, 6-liter canisters (SIS, Inc., Moscow, ID). These canisters are capable of holding air samples for up to 30 days with no significant change in the concentrations of target VOCs (Oliver et al., 1986). The canisters were cleaned by flushing three to five times with humidified "zero air" (Linde Specialty Gases, Zero Grade) and evacuated with a high vacuum pump. During evacuation, the canisters were isolated from the pump by a liquid nitrogen trap. After evacuation, the canisters were pressurized with zero air, allowed to equilibrate and analyzed for the target compounds. The concentrations of VOCs in cleaned canisters were usually less than 20% of those found in background air. Canisters with higher concentrations of target VOCs were recleaned and reanalyzed until acceptable chromatograms were obtained. For a few of the chlorinated VOCs, blank values after repeated cleanings remained higher than the 20% goal, but were still well below the concentrations of these compounds in rural air (see Table A-1, p.53). Canisters were checked one to seven days before sample collection, and the samples were analyzed within 30 days of canister cleaning. To verify that the canisters were leak-free, the pressurized canisters were submerged in water and checked for leaks.

Samples of ambient air were taken using three techniques. In all cases, the canister was evacuated before sampling. Grab samples were collected by opening the canister valve and allowing ambient air to flow in. The canisters reach atmospheric pressure in less than one minute. A second technique is to use a 30-gage needle as a critical orifice (Overcamp, 1985). A needle is carefully inserted through a septum that seals the opening to the evacuated canister. This arrangement provides a constant flow of 30 ml per minute for at least two hours. Critical orifice sampling was used for quality assurance checks of the automatic samplers. Finally, most of the ambient samples were taken using computer-controlled, commercial automatic samplers (SIS, Inc., Moscow, ID) capable of taking up to six independent air samples in separate canisters. A schematic diagram of these samplers is shown in Figure 5. The samplers feature a stainless steel pump with a Viton diaphragm (Model N 05 SV, Newberger Corp, Princeton, NH), a flow controller (Millaflow, Model SC423BFT, Veriflow Corp., Richmond, CA) and latching stainless steel solenoid valves (Datron-EEMCO, Inc., Los Angeles, CA). All transfer lines are stainless steel. Upon receipt, the samplers were purged for several hours with clean moist air while heat was applied to all valves and lines with a heat gun to drive off VOCs adsorbed to sample lines and other surfaces. Sampler flow rates were set at 6 to 12 ml/min using a bubble flow meter for the beginning of each run. Flow rates varied by less than 10% when rechecked at the end of the sampling period. Between seven and ten liters of ambient air were collected in a typical sample.

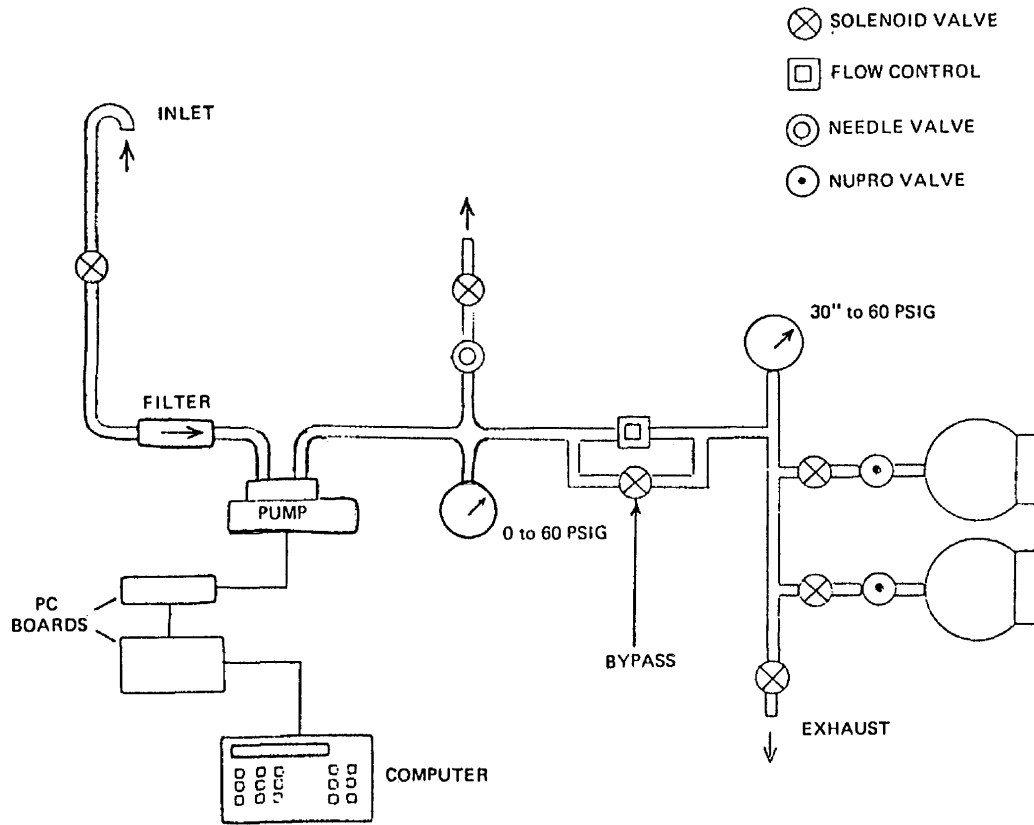


Figure 5. Automatic sampler for stainless steel canisters.

As a quality assurance check, the recovery of the target compounds and contamination of the automatic SIS samplers were evaluated by simultaneous manual sampling with a canister equipped with the needle critical orifice. The sampler flow rate in this experiment was set at 30 ml/min to correspond to the flow through the needle and the collection period was two hours. The rationale for this experiment is that the only difference between the two samples will be sampler effects attributable to the SIS samplers. Additional compounds in the samples resulting from contamination from the sampler and low recoveries due to wall losses in the sampling train can both be evaluated at the same sub-ppb concentrations found in actual ambient samples. The SIS sampler has a complex sampling train with several meters of tubing, valves, and a pump while in the manual system the sample only passes over a few centimeters of inlet needle. This system is essentially identical to taking a grab sample. The results of these experiments are summarized in Tables A-3 and A-4 (p 53 and 54). In general, differences in concentrations of target compounds were within analytical error ( $\pm 20\%$ ). This indicates that no significant contamination was present and recoveries of target compounds were acceptable. One sampler did exhibit styrene/o-xylene contamination after one field sampling period. The styrene/o-xylene concentrations were discarded in this case and the sampler recleaned. One of the samplers also exhibited contamination due to an unidentified compound which interfered with the determination of methylene chloride. Concentrations of this target compound could not be determined using this sampler. Recoveries were also poor (25% or less) for a number of unidentified compounds that elute from the gas chromatograph after the xylenes. This is presumably due to wall losses and indicates that this sampler may not be appropriate for compounds less volatile than the xylenes.

### Analytical Methods

The following analytical procedures were adapted from methods developed by USEPA researchers (Pleil et al., 1988). Upon receipt at the laboratory, the overpressure was measured and then the canisters were pressurized to 2.0 atmospheres with dry zero air. After adjusting for sample dilution, the equivalent of 0.5 liter of sampled air was passed over a liquid nitrogen-cooled U-trap consisting of a 10 cm length of eighth-inch nickel tubing packed with 60/80 mesh glass beads into a calibrated receiving flask fitted with a precision vacuum gauge. Trapped oxygen was released by removing the liquid nitrogen Dewar until the vacuum gauge reading stabilized (a few seconds). The trapped sample was then released by heating the trap to 80° C in a water bath and back-flushed onto the chromatographic column through a six port gas sampling valve. The valve and connections to the column were heated to 150° C. A schematic diagram of the analytical system is provided in Figure 6. Recoveries of the analytes from this system were evaluated by comparing the analytical results from direct injection onto the chromatographic column with cryogenic preconcentration from a canister. This process included dilution of the analytes with moist clean air, storage in a stainless steel canister, trapping with liquid nitrogen, and flushing the sample onto the chromatographic column by heating the trap. The results of these recovery experiments are given in Table A-3, p.55.

A Hewlett Packard 5890A gas chromatograph equipped with flame ionization (FID) and electron capture (ECD) detectors was used. The chromatographic column was a 30 meter, 0.325 mm ID fused silica capillary column with a 1.0  $\mu\text{m}$  thick film of DB-5 bonded liquid phase (J&W Scientific, Folsom, CA). The column effluent was split 10:1 between the FID and ECD using a FSOS capillary outlet splitter (SGE, Inc., Austin, TX). The temperature program was from  $-35^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  at  $8^{\circ}\text{C}/\text{minute}$ . Compound identification was by retention time and quantification by peak height. Injector temperature was  $200^{\circ}\text{C}$ , detector temperatures were  $275^{\circ}\text{C}$ , and helium was the carrier gas. The GC was checked for internal leaks and helium gas purity by disabling the gas sampling valve and running the temperature program. External plumbing leaks and zero air purity were evaluated by concentrating and injecting 0.5 liters of zero air.

The gas chromatograph was calibrated using an eight compound standard (Scott Specialty Gases, Plumsteadville, PA) containing benzene ( $300\ \mu\text{g}/\text{m}^3$ ), toluene ( $360\ \mu\text{g}/\text{m}^3$ ), m-xylene ( $470\ \mu\text{g}/\text{m}^3$ ), chloroform ( $47\ \mu\text{g}/\text{m}^3$ ), 1,1,1-trichloroethane ( $59\ \mu\text{g}/\text{m}^3$ ), carbon tetrachloride ( $59\ \mu\text{g}/\text{m}^3$ ), trichloroethylene ( $61\ \mu\text{g}/\text{m}^3$ ), and tetrachloroethylene ( $79\ \mu\text{g}/\text{m}^3$ ). This standard mixture was diluted with clean humidified air to give a working standard with final concentrations of one half that of the commercial standard. The concentrations of the halocarbons were the lowest available from the manufacturer and the diluted aromatic compounds were in the range of the maximum concentrations encountered in ambient samples. The commercial standard was diluted to introduce a small amount of water which is necessary to prevent adsorption of analytes onto the walls of the canisters. The diluted standard was analyzed daily in the same way as a typical air sample. Recovery of compounds in the standard from the canisters was 80% to 120% (Table A-3, p.50). Dilution experiments showed that the responses of the detectors are linear throughout the analytical ranges of all the compounds except carbon tetrachloride and tetrachloroethylene. The response of the ECD to these two compounds decreased markedly at concentrations below  $7\ \mu\text{g}/\text{m}^3$ . Since ambient concentrations of these two compounds were often in this range, the values were corrected using a calibration curve.

Several compounds were analyzed that were not in the calibration standard. Standards for methylene chloride, ethylene dibromide, styrene, chlorobenzene, and m,p-dichlorobenzene were prepared using the static dilution bottle technique (Morris et al., 1983). The working standard for these compounds had concentrations of about  $10\ \mu\text{g}/\text{m}^3$ . Response factors and retention times for these compounds were also verified using a 41-compound working standard provided by the USEPA (see Appendix A, p.57).

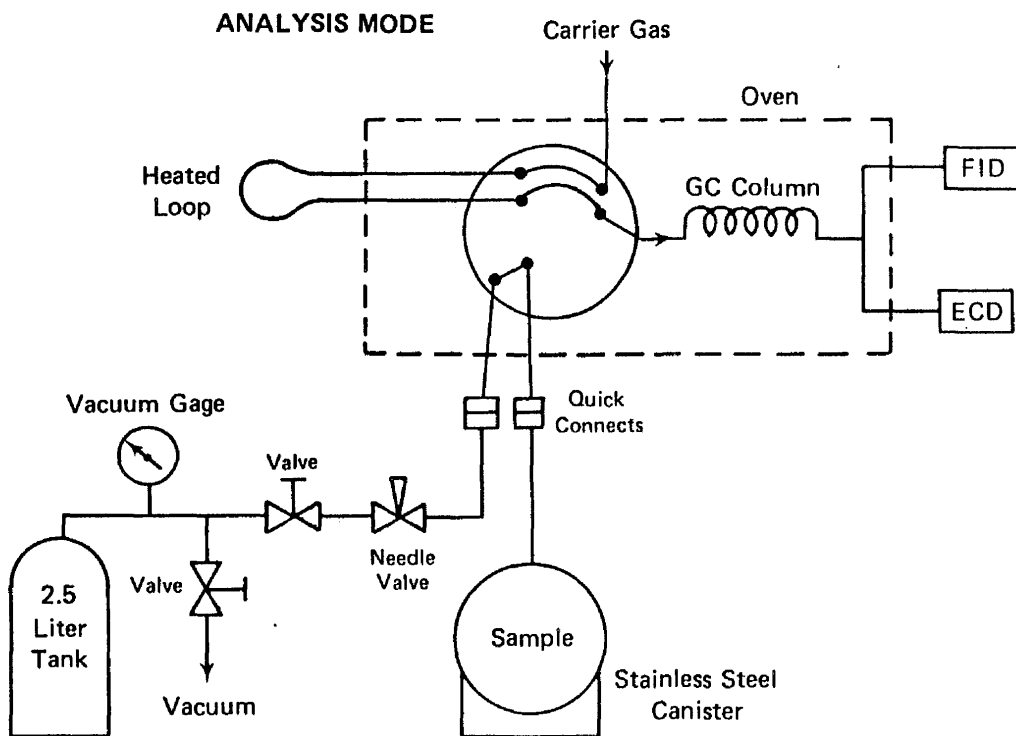
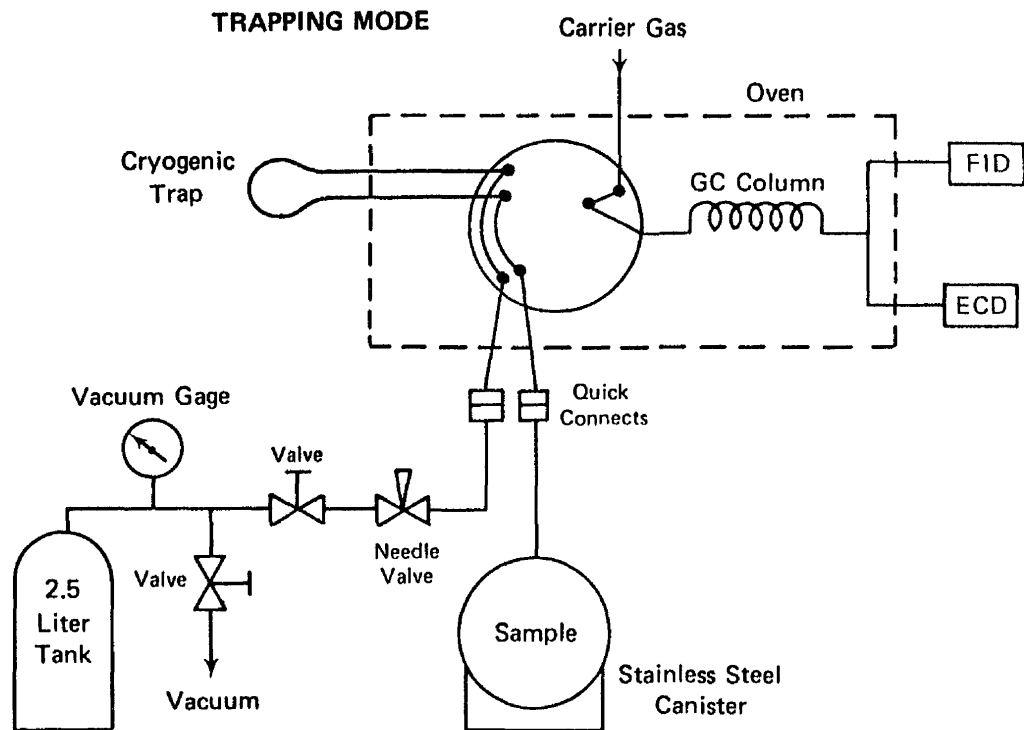


Figure 6. Analytical system for VOCs.





## CHAPTER 4. DATA ANALYSIS

### A. Data Summary

Between 1986 and 1990, over 200 air samples were collected in the three urban study areas and at our rural background site. Twelve toxic VOCs could be quantified in over 95% of the samples. The concentrations found for these compounds are shown in Table 6. In the case of the meta- and para- isomers of xylene, only the sum is given because these two compounds are not separated by the particular column used in the gas chromatograph. Likewise, styrene and ortho-xylene could not be reliably separated and are reported together. In addition to the VOCs in Table 6, a few other toxic VOCs were occasionally detected at the urban sites when the wind was coming from nearby sources. These include p-dichlorobenzene, methylene chloride and ethylene dibromide at the Sauget site and methylene chloride and ethylene dibromide at the Washington School site in Chicago. Since these compounds were only detected in a few samples, they have not been included in the compilation of average values in Table 6.

A summary breakdown of the collected samples, by sample type, seasonality and wind direction, are presented in Table 7. For Chicago and East St. Louis, grab samples, day samples, night samples and 24 hr samples were collected, while Granite City and our rural site for the most part were limited to grab samples. For each of the monitoring sites, samples were collected representing each season and wind direction. Overall, this breakdown is useful to evaluate possible bias in the data attributed to sample collection.

Average airborne VOC concentrations in the study areas are similar to those outside the industrial zones (O'Shea and Scheff, 1988) and to those in other urban areas without major industrial sources (Edgerton et. al., 1989; Levaggi et. al., 1988). This indicates that emissions from industrial sources are relatively unimportant for these compounds. O'Shea and Scheff (1988) reported that in the central Chicago area emissions from vehicles and evaporation of gasoline account for 72% of total VOCs and 96% of the benzene in ambient air. Since overall benzene levels are no higher in southeast Chicago, it seems likely that these sources are also predominant here.

For most of the compounds in Table 6, average urban concentrations are 2 to 10 times higher than the regional background levels measured at our rural site in central Illinois. The urban concentrations are much more variable than those found at the rural site as indicated by the higher standard deviations and maximum values found for most compounds in the urban areas. The average concentrations of a few compounds are not significantly different than those measured at the background site. The best example is carbon tetrachloride ( $\text{CCl}_4$ ). This material was mostly removed from commercial use 20 years ago so current releases are very small. However,  $\text{CCl}_4$  has a very long atmospheric residence

Table 6. Average concentrations of airborne toxic VOCs<sup>a</sup>

Compound	Chicago <sup>b</sup> (n = 103)	E. St. Louis <sup>b</sup> (n = 83)	Granite City (n = 24)	Rural Site (n = 23)
benzene	4.6 ± 6.6 (54)	10.6 ± 17.2 (102)	1.3 ± 1.8 (7.5)	1.3 ± .5 (2.4)
toluene	8.9 ± 8.9 (56)	8.5 ± 9.3 (45)	6.0 ± 7.7 (40)	3.0 ± 2.3 (9.5)
m,p-xylene	3.9 ± 8.3 (22)	16 ± 42 (312)	4.2 ± 4.8 (24)	1.2 ± 0.8 (3.9)
ethylbenzene	1.4 ± 1.2 (7.6)	6.9 ± 17 (110)	1.6 ± 1.8 (7.4)	0.4 ± 0.3 (1.6)
o-xylene/styrene	2.9 ± 5.5 (44)	3.3 ± 8.6 (55)	3.3 ± 3.8 (13)	1.1 ± 0.9 (4.3)
chloroform	0.3 ± 0.2 (1.6)	0.5 ± 0.9 (6.6)	0.3 ± 0.1 (0.5)	0.3 ± 0.1 (0.4)
1,1,1-trichloroethane	3.3 ± 3.5 (25)	3.9 ± 6.1 (31)	1.5 ± 1.6 (7.5)	1.1 ± 0.6 (1.9)
carbon tetrachloride	0.7 ± 0.2 (1.7)	0.9 ± 0.3 (1.7)	0.7 ± 0.4 (1.8)	0.8 ± 0.2 (1.2)
trichloroethylene	1.0 ± 1.0 (5.9)	2.1 ± 5.8 (43)	0.6 ± 0.5 (2.1)	0.6 ± 0.5 (1.5)
tetrachloroethylene	1.8 ± 1.6 (9.1)	1.4 ± 1.3 (6.1)	0.6 ± 0.7 (3.3)	0.4 ± 0.3 (1.2)
chlorobenzene	0.3 ± 0.2 (1.6)	3.0 ± 6.3 (36)	0.4 ± 0.2 (0.7)	0.2 ± 0.1 (0.5)

<sup>a</sup> Concentrations in  $\mu\text{g}/\text{m}^3 \pm$  standard deviation, maximum value in parenthesis, n = number of samples

<sup>b</sup> Samples collected at multiple sites in the study area

Table 7. Statistical summary of data base samples.

	Chicago	East St. Louis	Granite City	Rural Site
<b>Total # of Samples</b>	103	83	24	23
<b>Sample Period</b>	May 86 - April 90	Nov 86 - April 90	Nov 86 - Nov 88	Feb 87 - April 90
<b>Sample Type</b>				
Grab	27%	34%	100%	88%
Day (0600-1800)	19%	22%	0%	0%
Night (1800-0600)	17%	20%	0%	0%
24 hr.	36%	24%	0%	22%
<b>Season<sup>a</sup></b>				
Spring	16%	25%	38%	35%
Summer	33%	8%	13%	9%
Autumn	20%	31%	13%	30%
Winter	30%	35%	38%	26%
<b>Wind Direction</b>				
NE (0°-90°)	18%	5%	8%	13%
SE (91°-180°)	27%	29%	21%	17%
SW (181°-270°)	36%	28%	38%	22%
NW (271°-0°)	13%	34%	33%	22%

<sup>a</sup>Spring (March, April, May)  
 Summer (June, July, August)  
 Autumn (September, October, November)  
 Winter (December, January, February)

time and has become well mixed in the global atmospheric environment at about  $0.75 \mu\text{g}/\text{m}^3$  (Singh et al., 1979). The average concentrations of chloroform and chlorobenzene were also not significantly different from rural background levels in samples collected at the Chicago and Granite City study sites. However, in Chicago maximum concentrations of these two VOCs were higher than those found at the rural site indicating at least a small contribution from sources in the study area.

The pattern of urban/rural differences for toxic VOCs is similar to that found for toxic trace elements in the same study areas (Sweet et al., 1990). In both cases, pollutant concentrations tend to approach rural background levels when the wind is from a direction away from nearby industrial sources and ventilation rates (wind speed times mixing height) are high. Maximum concentrations are associated with periods of low ventilation rates when nearby industrial sources are directly upwind.

#### B. Wind Trajectory Analysis

The dependence of ambient VOC concentrations on wind direction can be demonstrated using wind trajectory analysis (WTA). With this technique, samples that correspond to periods of steady wind direction (standard deviation of wind direction  $< 20^\circ$ ) are selected for analysis (Rheingrover and Gordon, 1980). The data in Table 8 illustrate WTA results at the Sauget site in the East St. Louis study area. This site is about 0.5 km southeast of a large chemical complex (see map on p 11). Samples taken during periods of northwesterly winds are compared to samples taken when the wind was coming from other directions. These data clearly indicate that there is a major source of aromatic and chlorinated hydrocarbons northwest of the site. This source has a significant impact on the average concentrations of these compounds at this site compared to our other East St. Louis area site which is about 2 km away from the source. Plotting these compounds for individual samples reinforces these conclusions (Fig. 7). We confirmed that the chemical plant is the source of these compounds by collecting samples directly upwind during periods of northwesterly wind flow. Analysis of these samples yielded results identical to the "other winds" category in Table 8.

Data from the Washington School site in Chicago were also evaluated by WTA (Table 9). This site is about 1 km due east of a large coke oven complex (see map on p.6). The concentration of benzene, an important air pollutant from coking operations, was significantly higher when winds were out of the west. However, the difference here is not large enough to have a significant impact on the overall average benzene concentration at the site.

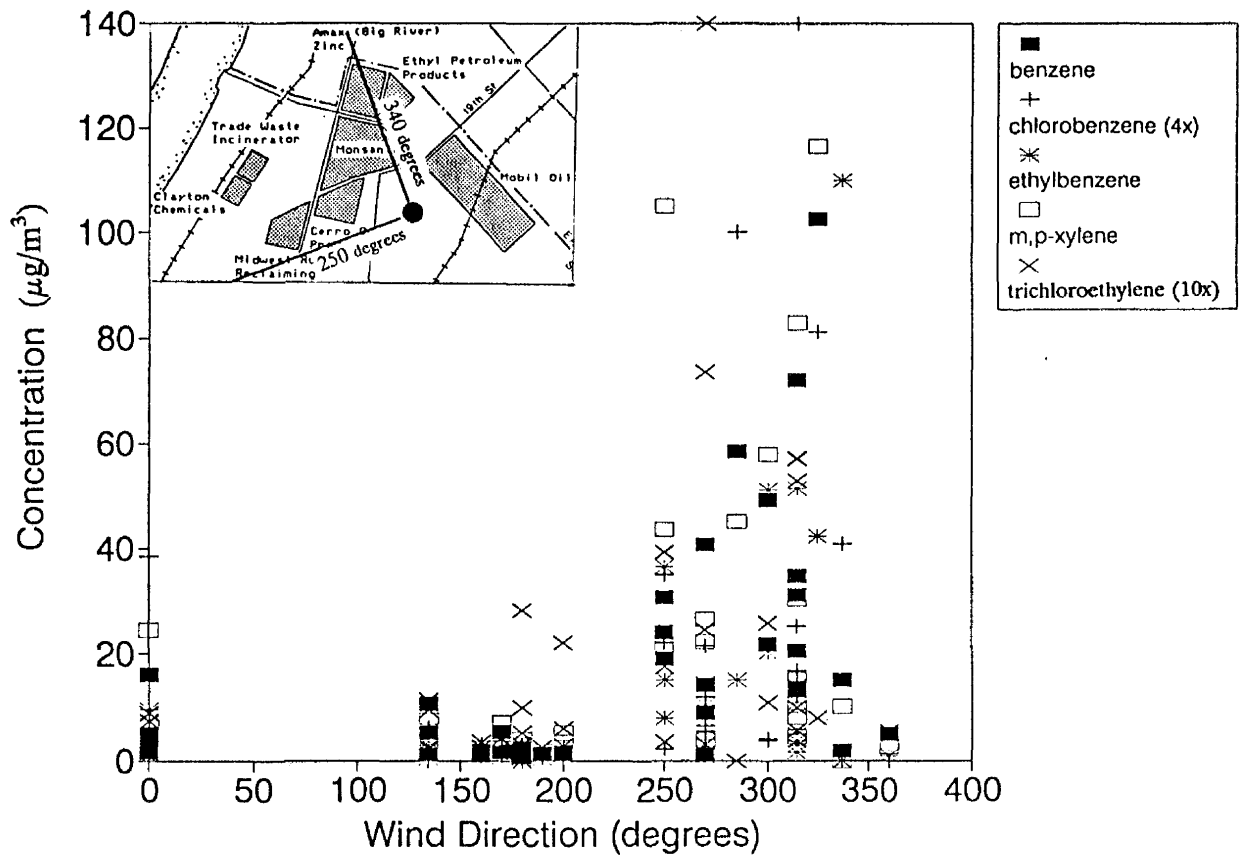


Figure 7. The influence of wind direction on VOC concentrations at Sauget.

Table 8. Wind trajectory analysis of Sauget VOC data<sup>a</sup>

Compound	Northwest Winds	Other Winds	Overall Average
benzene	30 ± 8.0	2.2 ± 2.2*	14 ± 21
toluene	6 ± 6	9 ± 9	8 ± 9
m, p-xylene	52 ± 73	0.5 ± 0.5*	2.5 ± 53
trichloroethylene	5.9 ± 10	0.5 ± 0.5*	2.7 ± 7.0
chlorobenzene	5.9 ± 6.8	0.5 ± 0.4*	4.0 ± 7.3
p-dichlorobenzene	58 ± 61	3.0 ± 1.8*	38 ± 54

<sup>a</sup> Concentrations are in  $\mu\text{g}/\text{m}^3 \pm$  standard deviation, n=10 for each wind sector, \* indicates values that are significantly lower ( $p > .95$ ) than other values in the same row. "Overall average" is the average of all samples collected the site.

Table 9. Wind trajectory analysis of Washington School (Chicago) VOC data<sup>a</sup>

Compound	West Winds	Other Winds	Overall Average
benzene	8.9 ± 8.0	3.2 ± 1.6*	4.4 ± 4.4*
toluene	10.4 ± 13.1	9.0 ± 4.5	9.0 ± 4.7
m, p-xylene	3.5 ± 1.7	4.3 ± 2.6	3.9 ± 3.0

<sup>a</sup> Concentrations in  $\mu\text{g}/\text{m}^3$ , n=10 for each wind sector, \* indicates values are significantly lower ( $p > .95$ ) than other values in the same row. "Overall average" is the average of all samples collected at the site.

### C. Seasonal Time Series

The data were examined for possible seasonal trends. For our rural site, East St. Louis and Granite City there is no clear trend for any of the toxic VOCs studied. For Chicago, there is a hint of higher summer concentrations (e.g., toluene - Fig. 8). Higher concentrations during the summer are reasonable given the relationship of volatilization to increased temperatures. The fact that not all summer measurements show higher concentrations indicates that other controlling factors are important. For 1,1,1-trichloroethane, the higher summer concentrations are attributed to a single site (Carver School) located near a sewage disposal facility; however, neither WTA nor upwind-downwind sampling give any indication that the sewage facility is an emission source.

### D. Diurnal Time Series

Concentrations of toxic VOCs can also be affected by meteorological conditions. Figure 9 illustrates the data from a time series of samples taken at the Sauget site in the East St. Louis study area. Six consecutive 12-hr. samples were taken, alternating between day (6AM to 6PM) and night (6PM to 6AM) collection periods. Wind speeds were 4 to 7 mph during the day and 1 to 3 mph during the night. Wind direction was from the south (160° to 200 °) throughout the period. All of the aromatic hydrocarbons showed a cyclical variation. Concentrations during the night were about double those measured during the day. The chlorinated hydrocarbons, in contrast, showed less diurnal fluctuations, but changed gradually during the period. These differences are probably due to differences in the sources. The aromatic hydrocarbons are locally emitted in auto exhaust and emissions from petroleum product transfer and storage facilities in the area that were upwind during the sampling period. The concentrations of these chemicals decline when ventilation rates (the product of wind speed and mixing height) are high during the day and locally generated pollutants are diluted with cleaner regional air masses or are depleted by photochemical reactions. Conversely, concentrations rise when ventilation rates and photochemical activity are low at night. Similar diurnal cycles have been measured in other urban areas (Singh et al., 1983). In contrast, there were no major local sources of chlorinated hydrocarbons during this period because the chemical plant and other major urban commercial and industrial facilities were downwind of the sampling site. The concentrations of chlorinated materials, therefore, were affected by gradual changes in regional air quality due to changes in the source regions of large scale air masses and not dependent on local changes in air mixing.



# Toluene

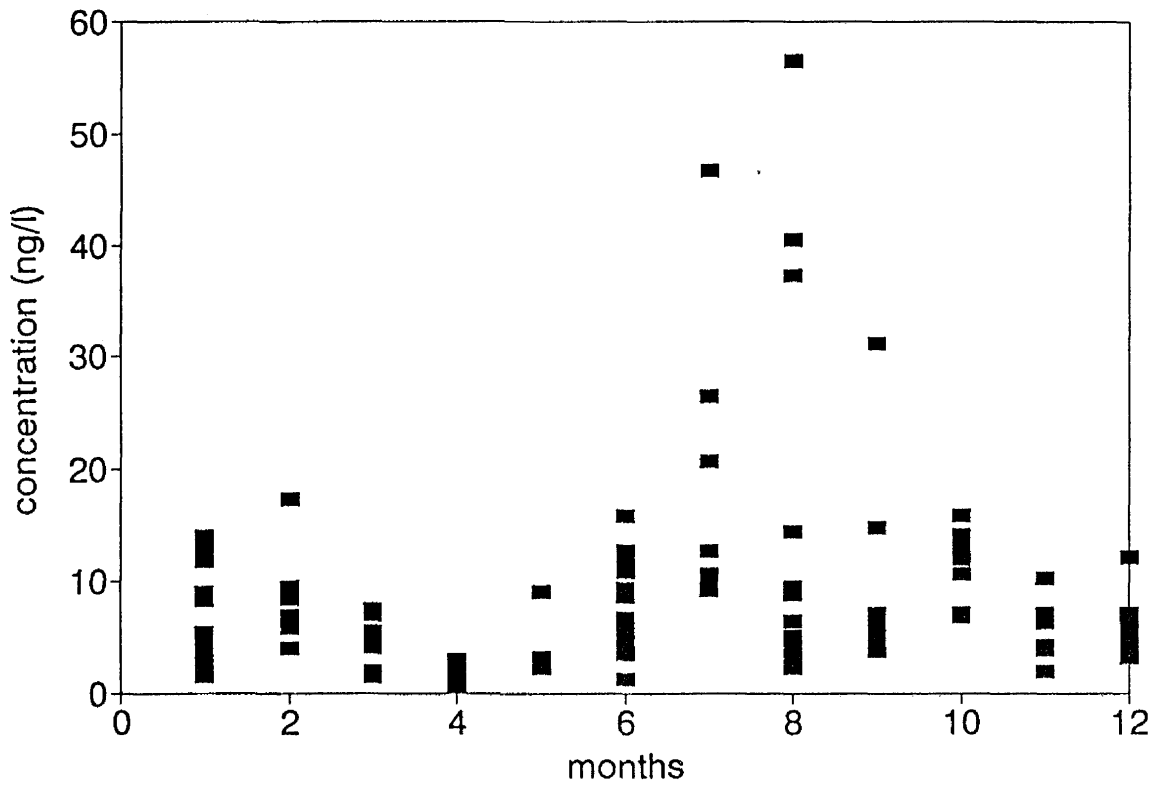


Figure 8. Seasonal variations in VOC concentrations at Chicago.

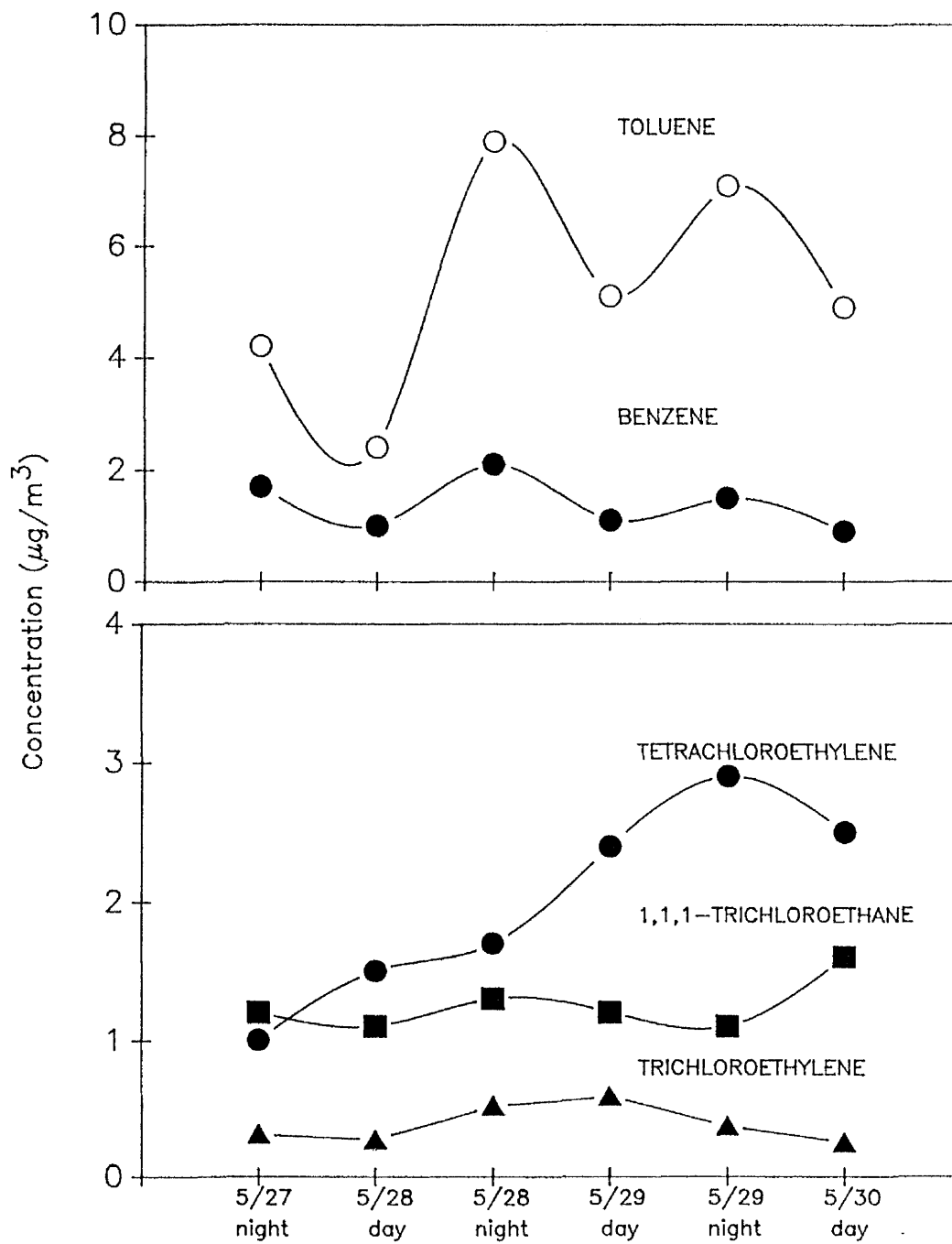


Figure 9. Diurnal variations in VOC concentrations at Sauget.

## E. Emissions Inventory Data

The State of Illinois, including the cities of Chicago, East St. Louis and Granite City, are the focus of an IENR project to develop a complete and accurate emission inventory for toxic air pollutants (IENR, 1990). Four source types are defined within the inventory; process; combustion; incineration and fugitive emissions. This inventory builds on the Total Air System (TAS) file maintained by the IEPA which includes only emissions from point sources reported by the industries. The IENR inventory contains emissions from all industrial point sources as well as area sources such as vehicles. This approach is a conservative one: to develop the best possible estimates for directing resources and activities to reduce air toxic emissions. Using this approach, total VOC emissions estimated for all potential sources are 6.6 times the VOC emissions estimated for permitted sources that have reported emissions in the TAS file. The IENR emission inventory is the most up-to-date and the higher estimates of VOC emissions are more in line with ambient measurements.

We applied a simple box model (Vermette et al., 1988) to these emission factors to estimate the average contribution of various sources to the overall ambient VOC concentrations. In this model the airspace 800 m above the study area (the average of winter and summer mixing heights) is ventilated at the average wind speed (12 km/hr) or the equivalent of 38 air changes per day. The local emissions diluted by this volume of air give an estimate of the contribution of local sources to average ambient levels of VOCs. In Table 10, the results of these calculations are shown for twelve VOCs for which reported ambient values and inventories were available. Except for benzene, chlorobenzene and toluene inventoried sources account for no more than 25%, and most often less than 10%, of the average concentrations of these compounds in ambient air. The additional VOCs most probably come from a combination of uninventoried or underestimated sources within the study areas as well as VOCs already present in the air coming into the study area. In the case of benzene, the inventoried emissions account for most of the measured ambient concentrations. The better accounting for benzene may be due to well characterized emission sources, such as a chemical complex in Sauget, coke ovens in southeast Chicago and Granite City, and vehicle emissions within all three study areas.

Table 10. Contribution of sources to average ambient VOC concentrations

Compound	S.E. Chicago		E. St. Louis <sup>a</sup>		Granite City <sup>b</sup>	
	Tons/Yr <sup>c</sup>	(%) <sup>d</sup>	Tons/Yr <sup>c</sup>	(%) <sup>d</sup>	Tons/Yr <sup>c</sup>	(%) <sup>d</sup>
benzene	3328	(92)	2753	(33)	1242	(122)
toluene	2693	(39)	546	(8)	598	(13)
ethylbenzene	60	(5)	127	(2)	49	(4)
o-xylene/styrene	479	(21)	1650	(21)	328	(10)
m,p-xylene	310	(10)	42	(0.3)	95	(3)
chlorobenzene	654	(278)	800	(34)	107	(34)
chloroform	12	(5)	9	(2)	19	(8)
1,1,1-trichloroethane	94	(4)	18	(0.6)	15	(1)
trichloroethylene	197	(25)	18	(1)	15	(3)
carbon tetrachloride	20	(4)	56	(8)	28	(5)
tetrachloroethylene	173	(12)	28	(3)	25	(5)

<sup>a</sup> East St. Louis/Sauget/Cahokia

<sup>b</sup> Granite City/Madison/Venice

<sup>c</sup> Source: ILENR (1990)

<sup>d</sup> Percent of average ambient concentration explained by inventoried emissions

#### F. Receptor Modeling

In characterizing toxic VOCs and in identifying and apportioning sources, a receptor modeling approach can also be used. Receptor modeling is a method in which sources contributing to air quality are identified and apportioned using data collected at a receptor (air sampling) site. Unlike dispersion models, receptor modeling techniques do not require a detailed inventory of emissions, meteorology, etc. Rather, receptor modeling techniques build on the chemical analysis of the collected samples. The strategy used in this report is to compare the information from simple receptor relationships (i.e., wind trajectory analysis) to the more statistical receptor models (i.e., factor analysis and chemical mass balance). The following section contains statistical receptor modeling results for the southeast Chicago and East St. Louis/Sauget databases. We did not have enough Granite City data to apply receptor modeling.

## Factor Analysis

Factor analysis is a multivariate analysis method for characterizing complex data sets and is commonly used in atmospheric chemistry for pollution source identification (Gaarenstroom, et al, 1977; Gatz, 1975; Hopke, 1985; Gordon, 1988; Liou, et al, 1989). It takes a number of measured variables and finds fewer linear combinations (factors) of those variables that explain most of the variance. These factors represent underlying causal parameters that can be interpreted as identifying possible emission source categories within the study area (Hopke, 1985). Factor loadings may be loosely considered as correlation coefficients of the original variable (VOC concentration) with that of a new combination of variables or factors. The closer the factor loading is to 1.0 the more significant the relationship between the individual variable and factor or between the concentration and a possible source. A factor loading less than 0.4 is not significant. Factor analysis requires no a priori knowledge of emission source categories and thus is useful as an independent method for confirming the importance of known emission sources or for suggesting emission sources not inventoried or previously considered. While factor analysis provides a ranking on the importance of a source, identifying and labeling these sources is based on previous findings, knowledge of the study area, and known emission source characteristics taken from the scientific literature.

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

For Chicago, FA statistics indicate the presence of four sources, ranked in order of significance: Chicago area emissions, unknown, regional and coke oven sources (Table 11). The Chicago area emission factor associated with toluene, ethylbenzene, m,p-xylene, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene is attributed to vehicle emissions, gasoline evaporation and solvent emissions. Individual sources within these categories covaried and could not be separated by FA. Numerous iterations with FA were unable to separate these compounds into their respective sources. In general, numerous small emitters acting collectively account for most of the sample variance (45.3%). Our inability to separate these sources is, in itself, indicative of the numerous sources and of the thorough mixing of VOCs in the urban airshed. Aside from industry, consumer use likely contributes to this area source. For example, 1,1,1-trichloroethane is found in numerous products -- adhesive, cleaning fluids, hair products -- and consumer use accounts for one-third of the emissions to the air. Benzene is associated with coke ovens, which were previously implicated by WTA. Separation of a coke oven source from the more inclusive area sources

(Factor 1) is attributed to the nature of the source (point source) and to its proximity to one of the sampling sites. The third factor, associated with CCl<sub>4</sub>, can be attributed to a source from outside the city, likely a regional source. CCl<sub>4</sub> has been removed from commercial use and has become well mixed in the atmosphere. The unknown factor, (Factor 2) characterized by chlorobenzene and o-xylene, cannot be attributed to a specific source at this time.

Table 11. Factor loadings for Chicago<sup>a</sup>

Compounds	Identified Source	Factor Loadings <sup>b</sup>	Percent Variance <sup>c</sup>
FACTOR 1			45.3
toluene	vehicle exhaust, solvents	.89	
ethylbenzene	vehicle exhaust, solvents	.85	
m,p-xylene	vehicle exhaust, solvents	.84	
1,1,1-trichloroethane	chlorinated solvents	.87	
tetrachloroethylene	chlorinated solvents	.80	
trichloroethylene	chlorinated solvents	.73	
FACTOR 2	unknown		13.4
o-xylene		.90	
chlorobenzene		.86	
FACTOR 3	regional		11.4
carbon tetrachloride		.93	
chloroform		.43	
FACTOR 4	coke ovens		8.3
benzene	coke ovens	.95	

<sup>a</sup> Varimax rotation (percent of variance explained by FA) = 78.4%

<sup>b</sup> Only factor loadings  $\geq 0.4$  are included

<sup>c</sup> Percent of variance explained by the factor

For East St. Louis, FA statistics indicate the presence of four sources, ranked in order of significance: local chemical plant, regional/St. Louis area, chlorinated solvents, and petroleum product evaporation (Table 12). The local chemical plant factor (Factor 1) includes compounds (benzene, m,p-xylene, trichloroethylene, and chlorobenzene) previously allocated, by WTA (see Table 8) to the chemical plant in Sauget. The second factor associated with carbon tetrachloride and chloroform, suggests a regional source because

Table 12. Factor loadings for East St. Louis<sup>a</sup>

Compounds	Identified Sources	Factor Loadings <sup>b</sup>	Percent Variance <sup>c</sup>
FACTOR 1	local chemical plant		46.2
m,p,-xylene		0.97	
ethylbenzene		0.96	
benzene		0.89	
chlorobenzene		0.86	
trichloroethylene		0.60	
1,1,1-trichloroethane		0.52	
FACTOR 2	regional/St. Louis area		18.7
carbon tetrachloride		0.85	
o-xylene		0.83	
chloroform		0.72	
trichloroethylene		0.54	
trichloroethylene		0.52	
FACTOR 3	chlorinated solvents		11.0
tetrachloroethylene		0.94	
trichloroethylene		0.52	
1,1,1-trichloroethylene		0.47	
FACTOR 4	petroleum evaporation		10.3
toluene		0.97	

<sup>a</sup> Varimax rotation (percent of variance explained by FA) = 86.3%

<sup>b</sup> Only factor loadings  $\geq 0.4$  are included

<sup>c</sup> Percent of the variance explained by the factor

these two compounds are relatively high in regional background samples. Inclusion of a number of other compounds in this factor suggests further influence from St. Louis. The third factor is associated with chlorinated solvents. Recognized sources of these solvents include wastewater treatment and vapor degreasing; however, no large sources of these compound have been identified in the study area. The single loading of toluene may indicate vehicle emissions if ethylbenzene and m,p-xylene are being masked by Factor 1. Alternatively, Factor 4 may indicate other petroleum uses (e.g. evaporation of toluene from petroleum transfer stations) located in the study area.

### Chemical Mass Balance

The final output in our receptor modeling approach is the source apportionment of the toxic VOCs. Apportionment statistics were determined from chemical mass balance (CMB) statistics (Axetell and Watson, 1987). The CMB model, using a calculation known as least square estimates "sorts out" the contributions of emission source categories to the ambient air sample. Mass balance equations are written for each compound and source contribution estimates are calculated for the period represented a particular sample. This period ranges from a grab sample (2-3 minutes) to a 24 hour sample. This approach has the advantage that the number of sources that need to be considered are minimized. If the wind direction is constant during the sampling period, only upwind sources affect the sampling site. The major disadvantage is that CMB from a single collection period represents only the time period sampled, not average conditions. In order to reflect average conditions, CMB would have to be done on a very large number of samples representing all meteorological conditions in proportion to their actual occurrence throughout the year. Even then, some samples representing calm or variable wind conditions with high VOC concentrations would not be represented. In addition, CMB analysis of single samples can be easily distorted by analytical errors.

Our approach to CMB modeling is to use the average results reported earlier (Table 6, p. 22). These results generally reflect average conditions at the site and include proportional contributions from sources located in different locations around the receptor. Analytical errors in a few individual samples will not be as significant when averaged into a large database. Although all sources affecting the site need to be considered, we have already narrowed the list considerably by using emission inventories, wind trajectory analysis and factor analysis. Most of the chemical profiles for various emission sources were obtained from the literature (Scheff et al., 1989). Specific source profiles for the major industrial sources, coke ovens in Chicago and the chemical complex in Sauget, were developed from fence-line air monitoring data upwind and downwind of the source (Scheff, 1990) for the coke ovens; and Table 8 for the chemical plant). All profiles are listed in Appendix B. In addition, CMB was carried out on a few individual samples representing both pollution episodes when a particular site was directly downwind of a major source and other wind conditions when no major point sources were upwind of the receptor.

CMB was carried out using the target compounds listed earlier (Table 6) as fitting



species. Three additional non-toxic VOCs, propane, n-butane and isopentane, were also used as fitting species in order to help differentiate vehicle exhaust, gasoline vapor and refinery emissions. The CMB results are presented in two formats: (1) emission sources as a percent of total toxic VOC concentrations (Figures 10 to 15), and (2) emission sources as a percent of individual toxic VOC compounds (Tables 13 and 14). For both formats, the data are reported as the percent of toxic VOCs attributed to a particular source category by the CMB model. It should be recognized that the model may over- or under-predict a particular VOC species and that there may be sources that are not attributable using this model. The results given are the best fit of the ambient data to available source profiles using CMB statistics. They should be considered approximations rather than absolute values and considered along with the emissions inventory, wind trajectory and factor analysis results presented earlier.

The specific toxic VOCs used are those in Table 6 except for chloroform, carbon tetrachloride and chlorobenzene. These were not included because their concentrations were generally the same in both urban and background samples. To evaluate the CMB results, two statistics are given that can be used to evaluate the "fit" of the model. The first " $r^2$ " should be as close to one as possible but always greater than 0.8. The second,  $X^2$  (chi squared) should be less than 4 and as close to one as possible (Axetell and Watson, 1987).

### Southeast Chicago

Under average conditions in southeast Chicago, it is apparent that most of the studied toxic VOCs can be attributed to vehicle exhaust (Fig. 10). Other sources include degreasing solvents and a tetrachloroethylene source (dry cleaning). The coke ovens appear not to be a significant source of VOCs. This is in agreement with wind trajectory analysis findings for benzene, an important air pollutant from coking operations (Table 9). When nearby sites like Washington School are downwind of the coke ovens, (Fig. 11), they account for between 10 percent to 25 percent of the toxic VOCs found in ambient air. These results are from CMB analysis of individual samples rather than average results. Other sources present in the same direction as the coke ovens include a paint plant and gasoline vapor sources. It is interesting to note that samples taken during the day (0600 to 1800) show a larger vehicle and a lower coke oven share of VOCs than samples taken at night (1800 to 0600). This is reasonable considering the higher number of active vehicles during daylight hours as opposed to at night. Under conditions with winds from other directions (Fig. 12) apportionments are similar to those for average conditions.

In Table 13, CMB results for individual VOC species are given for a sample at Washington School when it was downwind of the coke ovens and for average data in the Chicago study area. In the "high pollution" sample, coke ovens account for most of the benzene and a small amount of other aromatic hydrocarbons. The rest of the toxic VOCs are mostly due to vehicle exhaust and solvent evaporation. For the average data, all of the

toxic VOCs can be explained by vehicle emissions and solvent evaporation. These results are very similar to those obtained from individual samples taken when the receptor was not downwind of the coke ovens. Neither CMB nor factor analysis indicate a significant influence from refinery emissions. Although there are no refineries in the Chicago study area, there are several located a few miles to the west and east. Other CMB studies in Chicago have indicated that refinery emissions constitute a significant source of VOCs in Chicago (O'Shea and Scheff, 1988). The fact that we were not able to attribute any VOCs to refineries may be due to the fact that we are using a more limited group of fitting species and are unable to differentiate refinery emissions from similar profiles such as gasoline vapors and vehicle exhaust. On the other hand, we have found that major industrial sources in this study do not seem to have a large impact on average VOC concentrations at receptors more than a kilometer away. The highly localized influence of industrial point sources is also predicted from meteorological dispersion modeling of inventoried emissions in the southeast Chicago area (Crowder et al., 1989).

# Chicago (Average)

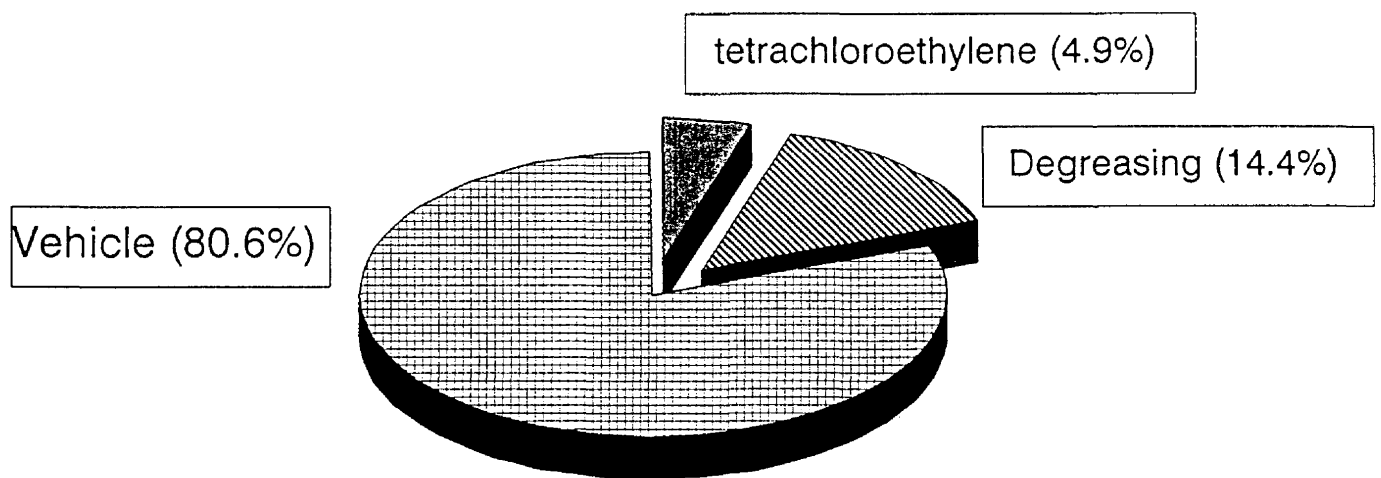
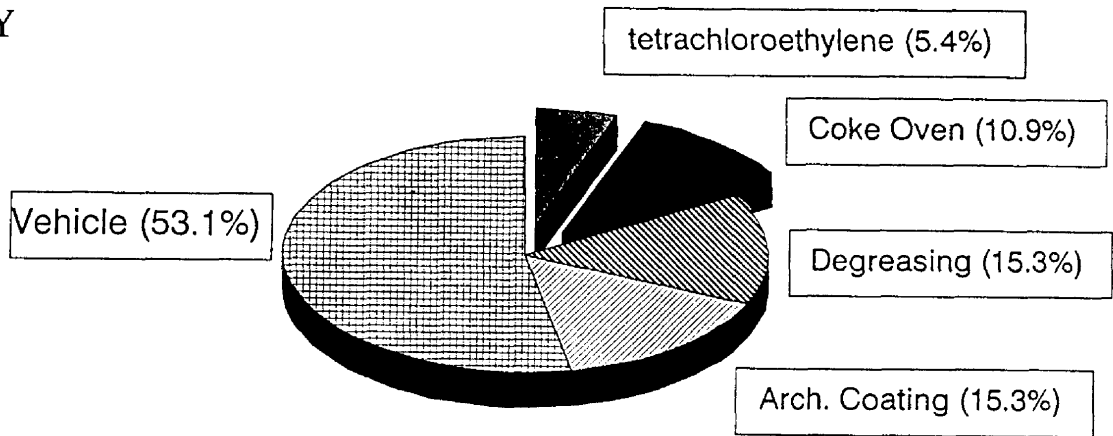


Figure 10. VOC sources in Chicago under average conditions.

# Chicago (West Winds)

DAY



# Chicago (West Winds)

NIGHT

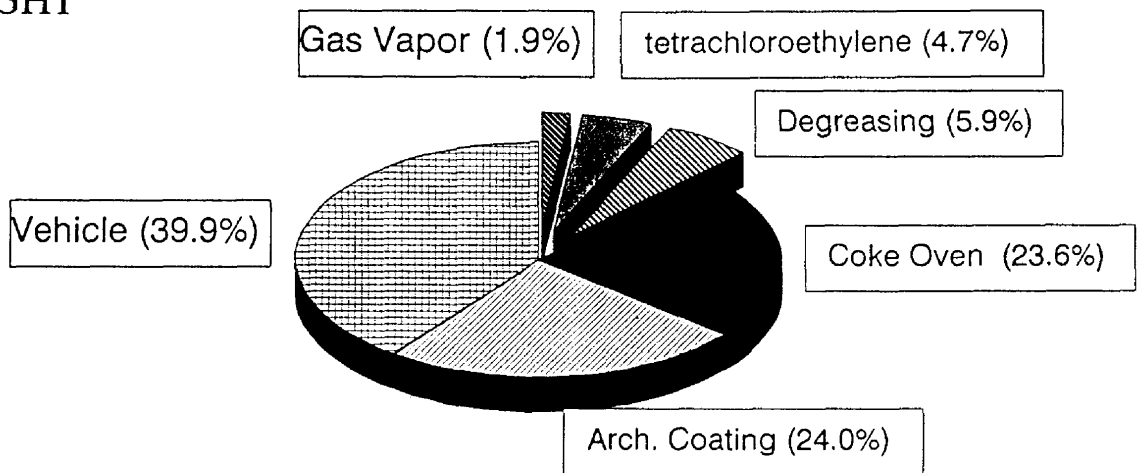
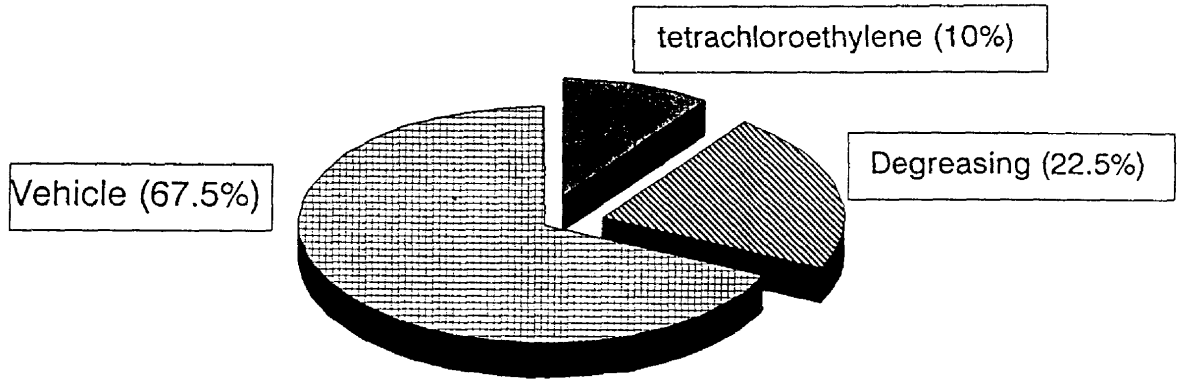


Figure 11. VOC sources in Chicago during pollution episodes.

# Chicago (Other Winds)



# Chicago (Other Winds)

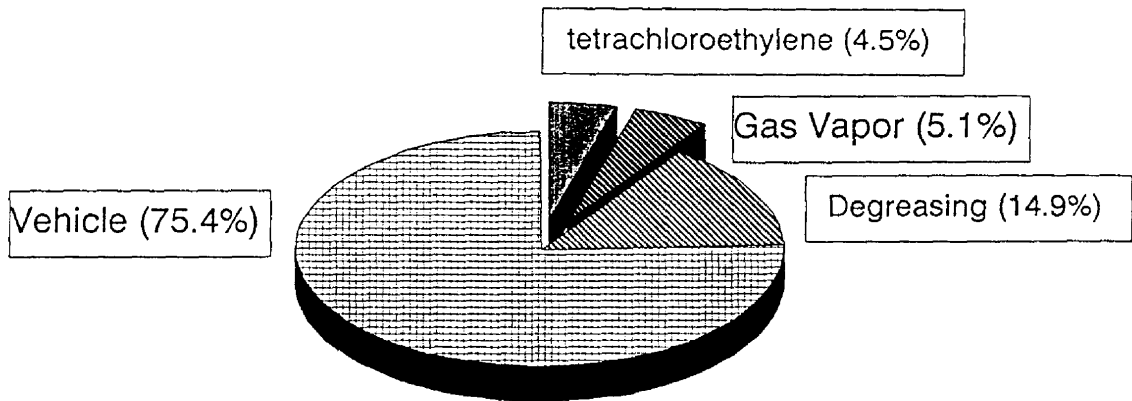


Figure 12. VOC sources in Chicago for individual samples.

Table 13. Chicago CMB Results

CMB Results for a Chicago Sample  
(Washington School) during a Pollution Episode

$R^2 = .97$   
 $X^2 = 4.31$

D.F. = 5

VOC	Calculated Measured	Coke Ovens	Vehicle Exhaust	Paint	Gasoline Vapor	Degrease Solvent	Dry Cleaning
Benzene	0.79	71.6%	26.3%	0.6%	2.3%	0%	0%
Toluene	0.98	0.8%	45.6%	52.0%	1.8%	0%	0%
Ethyl benzene	1.03	17.0%	68.3%	9.4%	5.3%	0%	0%
m,p-Xylene	1.06	8.3%	71.8%	18.4%	1.8%	0%	0%
o-Xylene	1.01	1.4%	66.6%	30.3%	1.4%	0%	0%
1,1,1-Trichloroethane	0.65	0%	0%	0%	0%	100%	0%
Trichloroethylene	1.33	0%	0%	0%	0%	100%	0%
Tetrachloroethylene	1.00	0%	0%	0%	0%	12.9%	87.1%

Average CMB Results for the Southeast Chicago Study Area

$R^2 = .97$   
 $X^2 = 2.72$

D.F. = 5

VOC	Calculated Measured	Vehicle Exhaust	Degreasing Solvent	Dry Cleaners
Benzene	1.04	100%	0%	0%
Toluene	1.03	100%	0%	0%
Ethylbenzene	0.95	100%	0%	0%
m,p-Xylene	1.10	100%	0%	0%
o-Xylene	0.87	100%	0%	0%
1,1,1-Trichloroethylene	0.66	0%	100%	0%
Trichloroethylene	1.31	0%	100%	0%
Tetrachloroethylene	1.00	0%	25.3%	74.7%

## East St. Louis

Under average conditions in East St. Louis, it is apparent that, like Chicago, vehicle exhaust accounts for most of the toxic VOCs studied (Fig. 13). The chemical plant in Sauget accounts for the second largest share of toxic VOCs (16.9%). This is consistent with WTA findings (Table 8). Other sources include degreasing solvents and tetrachloroethylene (dry cleaning). Under conditions with winds blowing from the Sauget chemical plant, this source accounts for most of the toxic VOCs, in individual samples (Fig. 14). This is reasonable given that the Sauget site is less than 0.5 km from the chemical plant fence line. Other sources include degreasing solvents, vehicle exhaust and gas vapors. Under conditions with winds from other directions (Fig. 15), vehicle exhaust dominates as a source of VOCs. Other sources include evaporation of degreasing solvents and dry cleaning (tetrachloroethylene). For the East St. Louis site, a toluene source appears independent of wind direction (Figures 14 and 15). This is consistent with factor analysis results showing toluene as a separate factor or source (Table 12). The identity of this source is not clear, but it is probably related to the petroleum product transfer and storage stations in the area that produce most of the inventoried VOC emissions.

For the East St. Louis study area, individual species data at the Tudor Street site are analyzed in Table 14. Data from the Sauget site are not included because this site tends to be dominated by the chemical complex 0.5 km to the northwest. When the Tudor Street site is downwind from this source, it is responsible for most of the aromatic and chlorinated toxic VOCs. Vehicle exhaust and petroleum related emissions account for most of the rest. Under average conditions, most of the toxic VOCs come from vehicle exhaust and solvent evaporation. The results from individual samples taken when the receptor was not downwind from the chemical complex are very similar to the average results. The CMB statistics for both the average data and individual "low pollution" samples from East St. Louis are not very good. Several of the aromatic hydrocarbons are poorly predicted. This is probably due to the fact that we do not have specific source profiles for the petroleum transfer stations that make up a major component of inventoried VOC emissions in this area. Our profiles for the chemical complex are based on a small number of samples so they too may not reflect the actual emissions very accurately. In spite of these deficiencies, it seems clear that a large proportion of the toxic VOCs we measured in East St. Louis are attributable to area sources rather than industrial point sources.

## East St. Louis (Average)

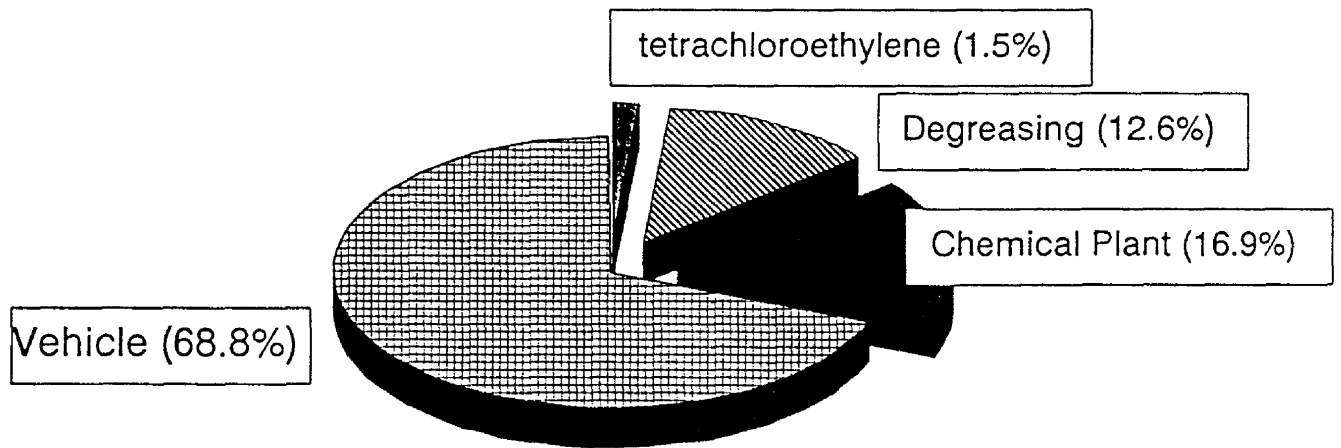
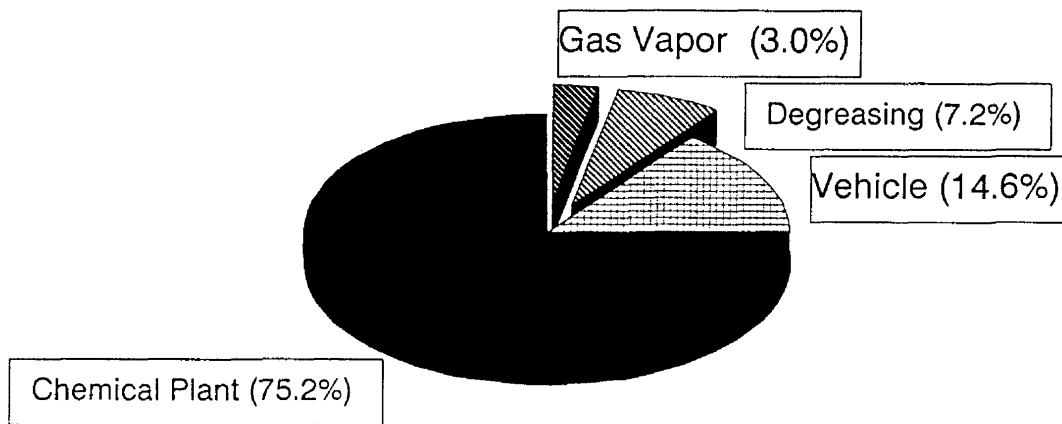


Figure 13. VOC sources in East St. Louis under average conditions.



## Sauget (Northwest Winds)



## East St. Louis (South Winds)

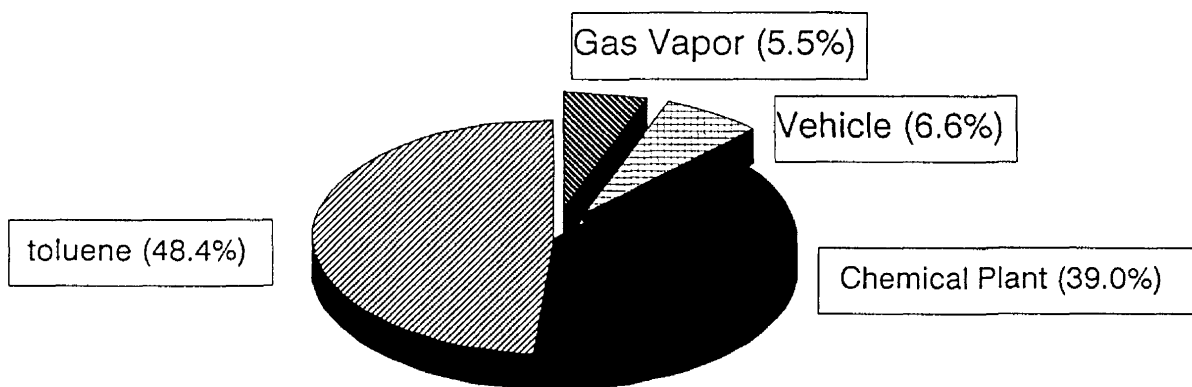
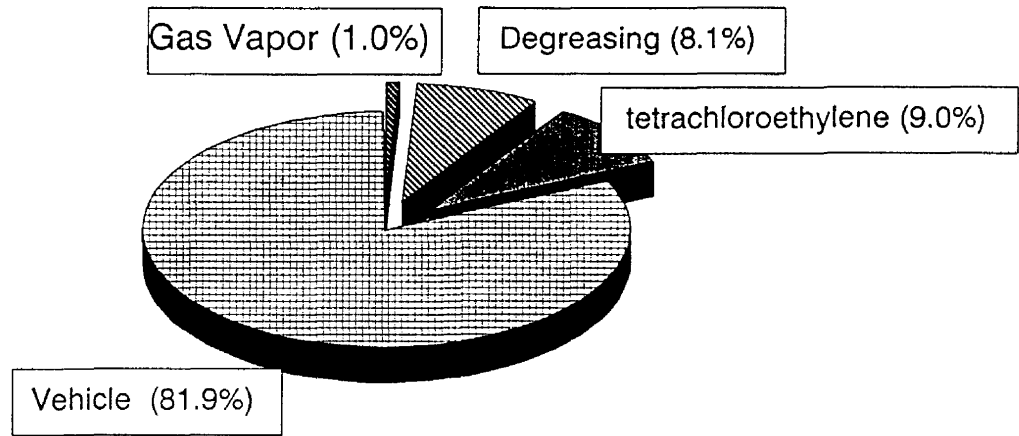


Figure 14. VOC sources in East St. Louis during pollution episodes.

## Sauget (Other Winds)



## East St. Louis (Other Winds)

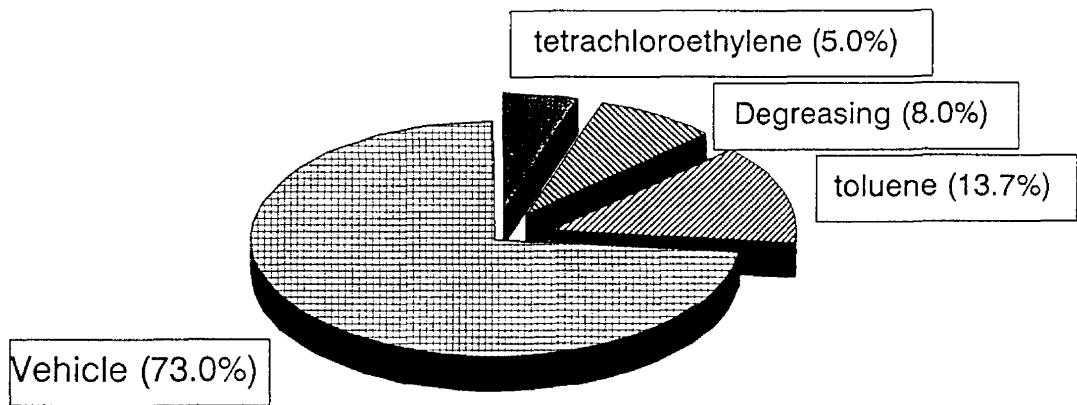


Figure 15. VOC sources in East St. Louis/Sauget for individual samples.

Table 14. East St. Louis CMB Results

CMB results for an East St. Louis sample during a pollution episode.

$R^2 = .96$   
 $X^2 = 4.75$

D.F. = 5

VOC	Calculated Measured	Chemical Plant	Vehicle Exhaust	Toluene Source	Dry Cleaning	Gas Vapor/ Refinery
Benzene	0.98	93 %	4 %	0 %	0 %	4 %
Toluene	1.14	<1 %	6 %	89 %	0 %	5 %
Ethylbenzene	0.47	60 %	20 %	0 %	0 %	20 %
m,p-Xylene	0.67	39 %	15 %	38 %	0 %	9 %
o-Xylene	1.05	0 %	63 %	0 %	0 %	36 %
1,1,1-Trichloroethane	0.95	100 %	0 %	0 %	0 %	0 %
Trichloroethylene	1.46	100 %	0 %	0 %	0 %	0 %
Tetrachloroethylene	1.00	56 %	0 %	0 %	44 %	0 %

CMB results for average data at East St. Louis (Tudor St. site)

$R^2 = .83$   
 $X^2 = 21.6$

D.F. = 4

VOC	Calculated measured	Chemical Plant	Vehicle Exhaust	Dry Cleaning	Degreasing Solvent
Benzene	1.13	48.6 %	51.4 %	0 %	0 %
Toluene	1.59	0.3 %	99.7 %	0 %	0 %
Ethylbenzene	0.30	11.7 %	89.3 %	0 %	0 %
m,p-Xylene	0.42	10.0 %	90.0 %	0 %	0 %
o-Xylene	1.10	0 %	100 %	0 %	0 %
1,1,1-Trichloroethane	0.99	18.3 %	0 %	0 %	81.7 %
Trichloroethylene	1.01	7.5 %	0 %	0 %	92.5 %
Tetrachloroethylene	1.00	0 %	0 %	51.3 %	48.7 %

## CHAPTER 5. CONCLUSIONS

In our companion report on airborne trace metals in these study areas, we used a variety of sampling and analytical tools to generate a database for toxic trace elements. This database includes information on the concentration and particle size distribution of about 30 trace elements from about 600 individual samples. We also discussed source characteristics for most of the significant sources in the study areas. By applying the statistical techniques of factor analysis and chemical mass balance to the data we were able to quantitatively attribute individual toxic metals to their major sources. The success of this analysis was due, in large part, to a stepwise or redundant approach where a variety of sampling and analytical methods provide supporting evidence toward the overall conclusions.

A similar approach was used for the toxic volatile organic chemicals (VOCs). There are, however, a number of limitations of the VOC data: 1) only 12 or 13 individual toxic VOCs could be measured in each sample compared to 20 to 30 trace elements (up to 50 additional non-toxic hydrocarbons could also be measured in the samples); 2) the VOCs are all in the vapor phase at ambient conditions so particle size distributions could not be used to provide insights on sources of target compounds; 3) only about 200 air samples were analyzed versus 300 for the trace metals; and 4) the high resolution time series data obtained for trace elements using the "streaker" sampler have no VOC counterpart. Because of these limitations, source attribution for VOCs is somewhat less certain and complete than was the case for trace metals. However, receptor modeling did identify a number of major sources of VOCs and provided a comprehensive overview of target VOC concentrations in the study areas.

In general, the average concentrations of toxic VOCs in the three urban study areas are similar to those measured in other urban areas in the United States without major industrial sources. This finding is somewhat unexpected because these study areas are affected by industrial emissions as well as general urban emissions. The air quality in these areas is among the worst in Illinois as measured by criteria pollutants such as inhalable particles and sulfur dioxide. The relatively good air quality in terms of toxic VOCs indicates that industrial emissions have less of an impact for these pollutants. This conclusion is supported by the chemical mass balance analysis. For most of the sites, average concentrations of toxic VOCs are largely attributable to area sources such as vehicle exhaust, evaporation of petroleum products, solvent evaporation and other sources common to all urban areas. Under some circumstances, specific industrial sources can have a significant impact on the concentrations of specific toxic VOCs in the air. This is the case at our Sauget site, southeast of a major chemical complex and at the Washington School site in Chicago, east of a coke oven area. At each of these sites, prevailing westerly winds carried VOC emissions to a nearby sampler. The local nature of these effects is shown by the small impact of industrial point sources on the average VOC concentrations at other sites only 1 or 2 km away in the same study areas. Meteorological dispersion modeling of emissions also predicts very localized areas of high VOC concentrations within the Chicago

study area.

As with the toxic trace elements, the regional background concentrations make a major contribution to VOC concentrations in urban air. Because of its central location, air coming into Illinois from any direction carries air pollutants from other urban areas. These pollutants are responsible for the VOC concentrations measured at our rural background site. Similar concentrations occur at the urban sites when the ventilation rate (wind speed times mixing height) is high and major nearby sources are downwind. Maximum concentrations occur at the urban sites when ventilation is low (usually at night) and when nearby point sources are upwind.

Improvements in airborne toxic VOC levels in the urban study areas can be most efficiently achieved by attacking the sources responsible for most of the emissions. In the case of benzene, in southeast Chicago, these are coke ovens, vehicle exhaust and petroleum product evaporation. Better control of these point and area VOC sources would have the additional benefit of reducing ozone precursors. Similarly, in East St. Louis, both point and area sources are responsible for toxic VOCs in the atmosphere. As in southeast Chicago, point source emissions have more localized effects on air quality. Control of industrial sources is most important for reducing very high ambient concentrations of toxic VOCs near plant boundaries but will have less effect on overall air quality in the region.

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## APPENDIX A - Quality Assurance Data

In this section, quality assurance data and the results of several quality control experiments are presented.

### A. Blanks

Before sampling each can was cleaned and checked chromatographically. Any residual amount of target compound present is subtracted from the final concentration determined for the sample. For urban samples the blank was less than 10% of the total, in most cases. For rural samples, the blank was typically 10 to 50% of the sample. Table A-1 shows average blank values and standard deviations for the target organics in this study.

Table A-1. Average blank values for precleaned canisters<sup>a</sup>

Compound	Concentration
benzene	0.19 ± 0.15
toluene	0.48 ± 0.79
chlorobenzene	0.19 ± 0.14
ethylbenzene	0.18 ± 0.16
m, p-xylene	0.18 ± 0.16
o-xylene	0.17 ± 0.13
dichlorobenzene	1.3 ± 1.5
chloroform	0.11 ± 0.12
1,1,1-trichloroethane	0.22 ± 0.19
carbon tetrachloride	0.016 ± 0.014
trichloroethylene	0.258 ± 0.132
perchloroethylene	0.05 ± 0.05

<sup>a</sup> average concentrations and standard deviations for 10 randomly selected blank analyses,  $\mu\text{g}/\text{m}^3$

### B. Analytical Variability

Normally all samples were run in duplicate where two successive aliquots of a diluted

air sample were injected onto the GC. Table A-2 shows the percent difference between such runs for each of the target compounds contained in our working standard. The average variation is between 10 and 20%. The variation for trichloroethylene is slightly higher (29%) due to the fact that sample concentrations of this compound were usually quite low.

Table A-2. Analytical variability of target VOCs.

Compound	Average Difference (%) <sup>a</sup>
benzene	12 ± 9
toluene	9 ± 7
m,p-xylene	13 ± 10
chloroform	18 ± 14
1,1,1-trichloroethane	17 ± 21
carbon tetrachloride	11 ± 11
trichloroethylene	29 ± 25
tetrachloroethylene	12 ± 9

<sup>a</sup> The average of the absolute values of the percent differences for 25 duplicate analyses ± the standard deviation.

### C. Analytical and Sampler Recoveries

Recoveries from analytical and sampling manipulations were determined experimentally. The analytical system was tested by transferring the eight-compound standard to a canister using a gas-tight syringe and diluting with humidified zero air. Analysis was by cryoconcentration and injection onto the GC column. These analytical results were compared with injection of the standard onto the GC column directly from the syringe. As shown in Table A-3, recoveries range from 83% to 120%. This range is similar to the analytical error of the system (± 20%). Sampler recoveries were determined by simultaneous sampling by the automatic samplers and by a canister fitted with a critical orifice consisting of a 30-gage needle. This device provides a constant flow into an evacuated canister of 30 ml/min for at least two hours. By setting the flow to the automatic samplers at the same rate, identical samples are collected differing only by additions to or deletions from the sample due to the automatic sampler. Contamination is identified when compounds are present in the sample collected by the auto sampler and not in the needle sample. Analyte

removal by the auto sampler is shown by higher concentrations in sample collected using the needle orifice. Table A-4 shows results from these experiments. For the target compounds, recoveries generally indicated that the auto sampler did not contaminate the sample nor did it adsorb an appreciable amount of analyte. Minor contamination was seen for two analytes, toluene and tetrachloroethylene, at "rural" concentrations. This contamination is negligible in most urban air samples. The concentrations of a number of unidentified compounds that are less volatile than the target compounds in this study were significantly lower in the samples taken using the auto sampler compared to samples taken with the needle orifice. This indicates that the automatic system used here may not be reliable for compounds less volatile than the xylenes due to wall losses in the sampler.

Table A-3. Analytical recovery of target compounds

Compound	% Recovery <sup>a</sup>
benzene	83
toluene	91
m,p-xylene	95
chloroform	108
1,1,1-trichloroethane	118
carbon tetrachloride	120
trichloroethylene	94
tetrachloroethylene	83

<sup>a</sup> GC Response from canister sample/GC Response from direct injection X 100

Table A-4. Recovery of target compounds using the automatic sampler.

Compound	% Recovery <sup>a</sup>
benzene	107
toluene	144
m,p-xylene	114
chloroform	110
1,1,1-trichloroethane	102
carbon tetrachloride	93
trichloroethylene	110
tetrachloroethylene	150

<sup>a</sup> GC Response from auto sampler sample/GC Response from needle orifice sample X 100.

#### D. Comparability of Results

Analytical and sampling methods were evaluated by interlaboratory comparisons with two outside laboratories. The Environmental Monitoring Systems Lab of USEPA at Research Triangle Park, NC provided us with samples of a 41-compound standard in a canister. They use this working standard in routine calibrations of their analytical system. The results for compounds we could quantify is shown in Table A-5. In most cases, agreement was within  $\pm 20\%$ , our average analytical error.

The second experiment involved both sampling and analytical procedures. As part of a separate project, Radian Corp. collected and analyzed several collocated samples at our Saugnet site. They used a similar canister based sampling system. Analysis was by cryogenic preconcentration and gas chromatography using a 3-detector (flame ionization, photoionization and electron capture) system. Canisters were exchanged so that both labs ran all the samples. This allows comparison of both sampling and analytical methods. The results of this intercomparison are shown in Table A-6. Generally, agreement was within the  $\pm 20\%$  analytical precision. Our xylene results were uniformly lower than Radian's indicating a calibration problem at one or both labs for this compound. The sample we collected had lower concentrations of some of the hydrocarbons (toluene, xylene, ethylbenzene) according to analysis by both labs. These are all petroleum related materials. Since our sampling system does not remove these compounds from the sample at normal ambient concentrations (see Table A-4), a contamination problem in the Radian samples is indicated. Finally, our sampling system does not efficiently collect compounds less volatile than the

xylenes. For this reason, there is a large discrepancy in the dichlorobenzene results between samples for these compounds. The fact that we could not recover most of the dichlorobenzene in the canisters sent from Radian indicates that there may be problems with the storage stability of these compounds in canisters as well.

Table A-5. Analysis of USEPA working standard

Compound	USEPA	ISWS
benzene	10.6	9.9
toluene	9.6	4.5
m,p-xylene	25.6	17
chloroform	7.9	6.6
1,1,1-trichloroethane	8.2	9.6
carbon tetrachloride	8.5	7.5
trichloroethylene	8.3	9.4
tetra chloroethylene	7.9	8.6
ethylbenzene	12.7	11.2
chlorobenzene	7.1	7.4
ethylene dibromide	6.8	6.4
o-xylene	10.8	9.8

Table A-6. ISWS-Radian Intercomparison, SAIL Site 11/10/88<sup>a</sup>

Compound	ISWS SAMPLE		RADIAN SAMPLE	
	SG8315		0661D	
	ISWS	Radian <sup>b</sup>	ISWS <sup>b</sup>	Radian <sup>b</sup>
chloroform	0.12	-	0.2	-
1,1,1-trichloroethane	3.3	3.7	3.7	3.7
carbon tetrachloride	0.16	0.19	0.14	0.17
trichloroethylene	1.0	1.3	0.8	0.7
tetrachloroethylene	0.7	0.7	0.7	0.7
benzene	6.4	8.6	7.0	7.8
toluene	1.4	1.5	2.1	2.5
m/p-xylene	2.5	4.9	5.6	10.0
ethylbenzene	0.9	0.8	1.9	1.6
styrene/o-xylene	1.1	0.9	2.3	1.8
chlorobenzene	0.7	0.9	0.9	1.0
p-dichlorobenzene	ND	ND	0.13	4.1
o-dichlorobenzene	ND	ND	ND	.3

<sup>a</sup> units = ppbv, ND=not detected

<sup>b</sup> laboratory that performed the analysis

#### E. Summary of Quality Assurance Data

The methods used to determine VOC concentrations in ambient air in this work provide many challenges. This is due to the facts that in many cases the ambient VOC concentrations measured are near the limit of detection and laboratory air often has VOC concentrations much higher than those being measured. In addition to this contamination potential, trace amounts of hydrocarbons can be lost by absorption to sampling lines and containers. A number of experiments were conducted to show that the target VOCs could be recovered in the analytical system and that contamination from the sampling and analytical procedures was minimal.

For these reasons, blank levels and analytical variability are somewhat higher than might be considered ideal. However, blank concentrations were always well below even the

lowest concentrations in the ambient samples and usually less than 10% of the ambient concentrations in urban samples. Analytical variability was relatively high ( $\pm 20\%$ ), but this value is in line with published results from the U.S. Environmental Protection Agency lab that developed this method (Pleil et al., 1988).

Finally, both the sampling and analytical methods were compared with those used in "state-of-the-art" laboratories. In most cases, our results agree within the analytical error ( $\pm 20\%$ ). In a few instances where differences were greater, values still agree to within a factor of 2. This sets some bounds on the uncertainty of our data. Most of the data should be within 20% of the true value with occasional data points up to twice or one-half the true value.





APPENDIX B - CMB Profiles

VOC*	Wt %	Error	
2	.048000	.004800	COKE OVEN (Chicago)
3	.002000	.000200	
4	.005000	.000500	
5	.217000	.021700	
6	.003000	.000300	
7	.006000	.000600	
8	.009000	.000900	
9	.001000	.000100	
10	.000000	.000000	
11	.000000	.000000	
12	.000000	.000000	
13	.000000	.000000	
2	.009100	.000910	VEHICLE EXHAUST (Chicago)
3	.048100	.004810	
4	.038800	.003880	
5	.035800	.003580	
6	.076500	.007650	
7	.010900	.001090	
8	.035100	.003510	
9	.021200	.002120	
10	.000000	.000000	
11	.000000	.000000	
12	.000000	.000000	
13	.000000	.000000	
2	.171300	.017130	REFINERY (Chicago)
3	.141600	.014160	
4	.135600	.013560	
5	.011200	.001120	
6	.037700	.003770	
7	.004700	.000470	
8	.011600	.001160	
9	.006800	.000680	
10	.000000	.000000	
11	.000000	.000000	
12	.000000	.000000	
13	.000000	.000000	
2	.000000	.000000	REFINERY (Chicago)
3	.029000	.002900	
4	.106000	.010600	
5	.022500	.002250	
6	.046000	.004600	
7	.008000	.000800	
8	.020000	.002000	
9	.011500	.001150	
10	.000000	.000000	
11	.000000	.000000	
12	.000000	.000000	
13	.000000	.000000	

2	.000000	.000000
3	.000000	.000000
4	.000000	.000000
5	.002700	.000270
6	.783400	.078340
7	.013600	.001360
8	.080800	.080800
9	.086500	.008650
10	.000000	.000000
11	.000000	.000000
12	.000000	.000000
13	.000000	.000000

ARCHITECTURAL COATINGS

2	.000000	.000000
3	.000000	.000000
4	.000000	.000000
5	.023300	.002330
6	.061700	.006170
7	.012600	.001260
8	.000000	.000000
9	.000000	.000000
10	.012980	.001298
11	.284300	.028430
12	.163500	.016350
13	.196900	.019690

WASTE WATER

2	.000000	.000000
3	.000000	.000000
4	.000000	.000000
5	.000000	.000000
6	.930900	.093090
7	.000000	.000000
8	.069100	.006910
9	.000000	.000000
10	.000000	.000000
11	.000000	.000000
12	.000000	.000000
13	.000000	.000000

TOLUENE  
(Graphic Arts)

2	.000000	.000000
3	.000000	.000000
4	.000000	.000000
5	.000000	.000000
6	.674200	.067420
7	.062400	.006240
8	.171000	.017000
9	.055400	.005540
10	.000000	.000000
11	.000000	.000000
12	.000000	.000000
13	.000000	.000000

AUTO PAINT

2	.000000	.000000
3	.000000	.000000
4	.000000	.000000
5	.000000	.000000
6	.000000	.000000
7	.000000	.000000
8	.000000	.000000
9	.000000	.000000
10	.000000	.000000
11	.550600	.055060
12	.333500	.033350
13	.115900	.011590

DEGREASING SOLVENTS

2	.000000	.000000
3	.000000	.000000
4	.000000	.000000
5	.000000	.000000
6	.000000	.000000
7	.000000	.000000
8	.000000	.000000
9	.000000	.000000
10	.000000	.000000
11	.000000	.000000
12	.000000	.000000
13	1.000000	.100000

TETRACHLOROETHYLENE  
(Dry Cleaning)

2	.000000	.000000
3	.000000	.000000
4	.000000	.000000
5	.682000	.068200
6	.005000	.000500
7	.029000	.002900
8	.081000	.008100
9	.000000	.000000
10	.006000	.000600
11	.081000	.008100
12	.019000	.001900
13	.000000	.000000

CHEMICAL PLANT

2	.067200	.006720
3	.090200	.009020
4	.071900	.007190
5	.066400	.006640
6	.141600	.014160
7	.020100	.002010
8	.066400	.006640
9	.039000	.003900
10	.000000	.000000
11	.000000	.000000
12	.000000	.000000
13	.000000	.000000

VEHICLE EXHAUST

2	.212900	.021290	REFINERY
3	.176000	.017600	
4	.168500	.016850	
5	.013900	.001390	
6	.046800	.004680	
7	.005800	.000580	
8	.014400	.001440	
9	.008400	.000840	
10	.000000	.000000	
11	.000000	.000000	
12	.000000	.000000	
13	.000000	.000000	

2	.016600	.001660	GAS VAPOR
3	.416800	.041680	
4	.202200	.020220	
5	.012800	.001280	
6	.013200	.001320	
7	.003600	.000360	
8	.003700	.000370	
9	.001900	.000190	
10	.000000	.000000	
11	.000000	.000000	
12	.000000	.000000	
13	.000000	.000000	

*	2	propane
	3	n-butane
	4	i-pentane
	5	benzene
	6	toluene
	7	ethylbenzene
	8	m,p-xylene
	9	o-xylene
	10	chloroform
	11	1,1,1-trichloroethane
	12	trichloroethylene
	13	tetrachloroethylene