



## Project Summary

# Volatile Organic Compounds in the Ambient Atmosphere of the New Jersey, New York Area

Barbara B. Kebbekus and Joseph W. Bozzelli

Between 1979 and 1981 the ambient atmosphere at a variety of sites in New Jersey and New York was monitored for 27 organic vapors. Included were several aromatic hydrocarbons, chlorinated aromatic compounds, halogenated one- and two-carbon compounds, and ketones. Two sites, Rutherford and Batsto, N.J. were monitored every sixth day for two years, giving the longest continuous data base for this type of analysis. Samples were also taken for a year in Elizabeth, South Amboy, Newark, and Camden, N.J. and for six months in Staten Island, N.Y., with some samples taken in Manhattan for comparison.

The desorption system was improved to allow several determinations from a single sample, and a multiple detector gas chromatographic analysis system was developed. The sample trapping methodology also was modified. Correlations were made between pollutant levels at given locations and the wind direction during sampling.

Generally, the aromatic compounds, especially benzene, toluene, and p-xylene, were the most common pollutants found and were usually the most concentrated of the species determined. Concentration levels were usually found in the low parts-per-billion range.

*This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

Epidemiological studies in recent years have shown that the occurrences of particular diseases vary with locality. One possible explanation for this is that the population is exposed to different substances in each local environment. Because the ambient atmosphere has been shown to contain measureable concentrations of volatile chemical compounds known to be toxic, mutagenic, and possibly carcinogenic, it is important to develop a data base describing the exposure of residents to these vapors. Data on the correlation between health effects and exposure to organic vapors at part-per-billion concentrations are not yet available, and the epidemiology needed to develop such data cannot be accomplished without information on the concentrations currently existing in the ambient air.

The three-year study completed in the Air Pollution Research Laboratory of the New Jersey Institute of Technology had as its major purpose the development of a long-term data base on the concentration of a selected group of volatile organic compounds in the atmosphere at several locations in the New Jersey-New York area. These compounds were monitored for two years at two sites in Rutherford, N.J., a residential neighborhood with considerable chemical industry nearby, and Batsto Village, a relatively pristine area in the Pine Barrens of southern New Jersey. With samples collected every sixth day at these locations, the data obtained in these two places are among the most extensive ever tabulated.

A secondary purpose of the project was the development and refinement of the analytical method. These included raising



the precision of the method, characterizing the properties of the sample trapping system, developing standardization procedures, improving the sampling system, and developing an overall quality assurance protocol. In addition, some correlation studies were carried out to determine the relation between the concentration of the pollutants being analyzed and the direction of the wind during the collection period.

In summary, during the course of this three-year project all samples were collected and analyzed, an analytical method was refined, a quality assurance protocol was developed, and studies on sampling systems and standardization procedures were carried out.

Rutherford, N.J. has a rather unique combination of large chemical industries surrounding long-established, quiet, tree-lined residential neighborhoods. Samples were collected at ground level in the rear yards of private houses on Pierrepont Avenue. Batsto Village is in an area little impacted by either industrial emissions or by automobile traffic. This restored colonial village is located in a state forest preserve and is about as isolated an area as exists in the state of New Jersey. Air samples were collected at Batsto Village and Rutherford continuously for approximately two years.

A shorter study of six months duration was carried out at the communities of Travis and Mariner's Harbor in Staten Island, and in the Yorkville section of Manhattan. These sites were selected to determine if sufficient differences could be detected in the concentration patterns of the pollutants to show the impact of the New Jersey industrial areas bordering the Arthur Kill on the residential areas of Staten Island. The samples were taken in the yard of a private house near the corner of Victory Blvd. and Roswell Ave. in Travis and on the grounds of St. Michael's Church in Mariner's Harbor. The Manhattan site, further north and out of the prevailing wind stream from the industrial areas in question, was chosen to give a basis of comparison. Other sites reported here were sampled for the New Jersey Department of Environmental Protection in a concurrent project in 1979. These sites included densely populated urban areas in Newark and Camden, a site in Elizabeth which was subjected both to heavy automobile traffic and to petrochemical industry, and a site at the southern end of the industrial belt of the state, in South Amboy.

The list of compounds targeted for quantitative analysis changed several times

during the project. The initial list consisted of 21 compounds, including several one- and two-carbon halogenated compounds, benzene, a group of substituted benzenes and two ketones. The compounds were selected on the basis of their toxicity, their volatility, and their widespread use in industry. Over the course of the project some compounds were dropped from the list because they were seldom detected, and others because of analytical problems. After many samples had been analyzed by GC/MS, a group of six compounds were added because they were consistently seen in samples and were well resolved in the chromatograms. In the third year of the project, the granting agency specifically requested data on two more compounds, which were added to the list. Table 1 gives the list of compounds and notes the general time that these were being determined.

Samples were collected over 24-hour periods by drawing approximately 15 liters of air through a sorbent bed in a stainless steel tube. These traps contained Tenax-GC porous polymer for trapping the majority of the compounds, or Sphero carb carbon molecular sieve for trapping the most volatile compounds, especially vinyl chloride.

Many of the previously published methods for thermal desorption of adsorbent

**Table 1.** Compounds Analyzed During the Project

	1979	1980	1981
<i>Vinyl chloride</i>			
<i>1,1-Dichloroethylene</i>	x	x	x
<i>Chloroform</i>	x	x	x
<i>1,2-Dichloroethane</i>	x		x
<i>Methylene chloride</i>			x
<i>Carbon tetrachloride</i>	x	x	x
<i>Trichloroethylene</i>	x	x	x
<i>1,1,2-Trichloroethane</i>	x	x	x
<i>1,2-Dibromoethane</i>	x	x	x
<i>Tetrachloroethylene</i>	x	x	x
<i>1,1,2,2-Tetrachloroethane</i>	x	x	x
<i>Methyl ethyl ketone</i>	x		
<i>Methyl isobutyl ketone</i>	x		
<i>Acrylonitrile</i>			x
<i>p-Dioxane</i>	x		x
<i>Benzene</i>	x	x	x
<i>Chlorobenzene</i>	x	x	x
<i>Toluene</i>	x	x	x
<i>m-Xylene</i>	x	x	x
<i>p-Xylene</i>	x	x	x
<i>o-Xylene</i>	x	x	x
<i>Nitrobenzene</i>	x	x	x
<i>Styrene</i>	x	x	x
<i>p-Dichlorobenzene</i>		x	x
<i>o-Dichlorobenzene</i>		x	x
<i>p-Chlorotoluene</i>		x	x
<i>o-Chlorotoluene</i>		x	x
<i>Ethylbenzene</i>		x	x

traps allow only a single analysis to be performed on each sample. However, more than one analysis of a particular sample are often desired, to determine the precision of the method, to analyze samples which are spiked with a known mixture for positive peak assignments, or to run samples on the GC/MS for qualitative confirmation and analysis of co-eluting species. Therefore a desorption system was developed which permits several aliquots to be taken from each sample. This system consists of a small oven, fabricated from a solid cylinder of aluminum and heated with two 400-w cartridge heaters. This oven fits closely around the traps. A 1-liter Dewar flask filled with methanol and chilled to -60°C with a refrigerated probe serves as a cold bath. A 10-ml passivated stainless steel gas cylinder fitted with a stainless steel bellows valve and an accurate gauge for measuring the pressure complete the system.

The sample trap, connected between the nitrogen inlet line and the inlet of the 10-ml sample container, is placed in the oven. The sample cylinder, previously flushed with nitrogen and evacuated to below 1-mm Hg pressure, is placed in the cold bath and the bellows valve is opened. The adsorbed sample is allowed to distill under reduced pressure into the chilled cylinder for 30 minutes. Then the nitrogen inlet valve is opened and any remaining sample is purged into the cylinder with sufficient gas to bring the final pressure to 60 psi. The bellows valve is closed and the cylinder assembly is transferred to a small heating mantle where it is warmed to 120°C before injecting the sample into the gas chromatograph. There is adequate pressure in the cylinder to allow the injection of at least three samples. Samples are recovered from Tenax traps by desorption at 250°C while Sphero carb traps are desorbed at 350°C.

The samples are analyzed on a Varian 3700 gas chromatograph. The injection system was replaced with a manifold consisting of a gas sampling valve with a 2-ml volume sample loop, a pressure gauge, and a vacuum line to evacuate the sample loop. The gas sampling valve is held at 120°C and all the exposed lines through which sample or standard mixture pass are heated with flexible tape to 60°C. The column is connected directly to the gas sampling valve with a graphite ferrule. A fused silica SP2100 column, 50 m in length, is used for the separation. Samples are run with helium carrier gas at a flow-rate of 1.0 ml/min. Because the 2-ml sample volume is large for a capillary column, the organic fraction is focused at

-90°C into a sharp plug at the head of the column. The temperature is raised to -4°C in 1 minute, held for 1 minute, raised at 3°C per minute to 90°C and then at 7°C per minute to 140°C. The entire run takes 42 minutes. An alternate program, suitable for use on a GC which does not have subambient temperature programming capability, involves trapping the sample in a loop of fused silica tubing cooled with liquid nitrogen before the column, removing the cold trap, and heating the column from 40 to 140°C at 3°C per minute.

At the end of the column, nitrogen make-up gas is added to the sample at the rate of 30 ml/min to prevent peak broadening in the detectors. The column effluent is split between a flame ionization detector, which is used for most of the quantitation, and an electron capture detector, which is used to identify the chlorinated target compounds and to quantitate those which occur at levels below the sensitivity of the FID. The detector signals are integrated and the sample concentrations are calculated with a Spectra-Physics Model 4000 multichannel integrator.

A spiking method was developed to aid in the identification of peaks in the complex chromatograms obtained from the air samples. After the sample concentrate is analyzed, the sample remaining in the 10-ml cylinder is spiked with a small quantity of gaseous mixture containing pure compounds at the ppm level in helium and then rechromatographed. The increase in peak height or the appearance of new peaks locates the compounds of interest. Spiked samples are run at regular intervals, especially when the sampling location is changed. Compound peaks vary in size from day to day within a geographic area, but the general pattern of substances present changes very little.

Co-eluting peaks are uncommon given the high resolution of the chromatography, but they can be distinguished by mass spectrometry, and GC/MS analysis is performed on samples at regular intervals. The GC and GC/MS have shown very good agreement on the qualitative analysis, and no species was observed to interfere at concentrations above 10% of the target compounds in field samples.

Analysis to confirm the identities of the peaks as assigned from the GC system are performed on a Varian MAT 44 quadrupole mass spectrometer. Approximately 5% of the total number of samples were analyzed by GC/MS. This analysis provided qualitative verification of the target pollutants and identified other volatile organic species present in the atmosphere of the sampling sites at levels above 0.1 ppb.

GC/MS analysis can verify all target compounds adsorbed on Tenax, including vinyl chloride. Mass spectral analysis of Sphercarb samples qualitatively identifies vinyl chloride, vinylidene chloride (1,1-dichloroethylene), methylene chloride, chloroform, 1,2-dichloroethane, trichloroethylene, and benzene.

GC/MS analysis is accomplished by use of a column identical to that used in the routine GC analysis, and the temperature program is similar, except for the subambient section of the program. The sample is focused into a sharp plug by use of a liquid nitrogen cold trap, which is removed 10 minutes after the injection. The column is held at 32°C for six minutes, then heated at 4°C per minute to a final temperature of 145°C. The final temperature is held for 10 minutes, allowing elution of trichlorobenzenes and naphthalene, before the end of analysis.

## Results

Geometric averages of the analytical data, which are less sensitive to the effect of a few high outlying points, were calculated to provide a measure of the typical compound concentrations. Arithmetic averages are also reported.

The benzene level at Elizabeth, NJ (geometric average = 2.3 ppb) was the highest average level found in the project, as high as the toluene level at this site. The data obtained at the Rutherford and Batsto, NJ sites confirm the large difference in overall pollution levels between them. Both sites showed average toluene levels higher than any other compound, with benzene about two-thirds as high as the toluene. Rutherford showed levels of the most concentrated compounds at least three times higher than those at Batsto, except for chlorobenzene, which was comparable at the two sites. This relatively elevated concentration of chlorobenzene was noted at Batsto in both years of the project, but its source remains unexplained. It is apparent from the data that the atmosphere in Batsto Village had much lower concentrations of the target compounds. In several mass spectrometric analyses naturally occurring organic vapors— $\alpha$ -pinene and camphene—have been found, but vapors from both industrial and automotive sources are low in comparison to other sites. The arithmetic average concentrations of the seven compounds most commonly detected at these sites during 1979 and 1980 are displayed in Figures 1 and 2. The mass spectral analysis indicated that many other pollutants are commonly present in the air. Table 2 lists those routinely detected.

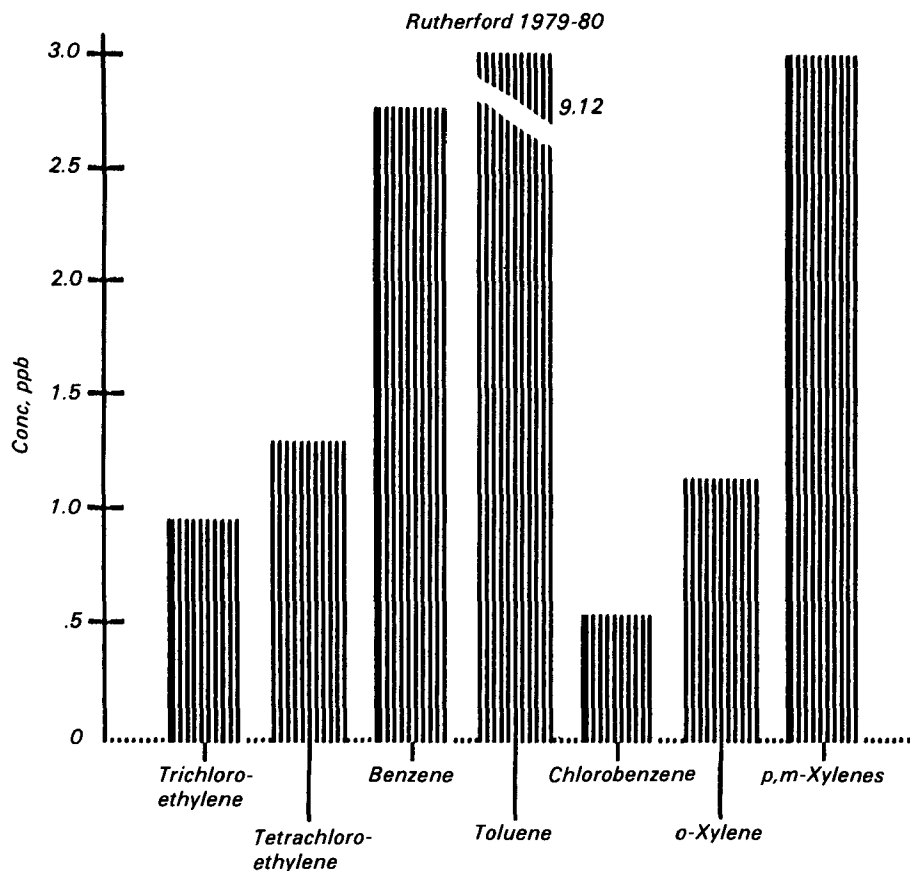
The overall levels of organic vapors found in the two Staten Island sites were significantly lower than those detected in northern Manhattan. All the compounds detected at levels above 0.1 ppb at Travis were at higher levels in Manhattan, frequently substantially higher. Mariner's Harbor showed higher levels than did Travis, but lower than Yorkville in Manhattan, except for tetrachloroethylene, which averaged 2 ppb at both sites.

Several methods of correlating the concentrations of the target compounds with the prevalent wind direction at the sampling site were applied to the data generated in this project. In one grouping, samples were selected such that the wind only originated from a single 90° quadrant during the sampling. The average concentrations were then plotted for each compound, each site, and each quadrant. In another method, for samples taken on days when the wind shifted out of a single quadrant, a concentration factor was calculated for each of eight wind rose segments, consisting of the concentration of pollutant and the fraction of the sampling period during which the wind was in that segment. The data for specific pollutants were summed for each site and each quadrant, resulting in "pollution rose" graphs. These are shown for South Amboy in Figure 3. The location of this site, at the southern end of the industrial complex of the New Jersey-New York area, explains the elevated concentrations seen when the wind is blowing from the north or northeast.

The results from the monitoring carried out in this project show that there are a large number of organic vapors present in the ambient atmosphere, especially in the urban areas sampled. Many samples showed two hundred compounds at levels above 0.05 ppb. Of these, the known carcinogen benzene proved to be ubiquitous, although at low levels. The benzene levels ranged from a low average of 0.9 ppb over 1.5 years at the Pineland site to a high annual average of 6.2 ppb in Elizabeth. Other toxic and/or suspected carcinogenic compounds frequently detected were toluene, trichloroethylene, and tetrachloroethylene.

The differences in overall contamination of the atmosphere by these compounds at urban and rural sites is evident, with many fewer compounds detected at much lower levels at Batsto.

The monitoring of these compounds over a substantial period of time generates important data for future studies on the transport of pollutants, on the epidemiological impact of the organic fraction of



**Figure 1.** Average concentration of seven target compounds in the atmosphere of Rutherford, NJ in 1979 and 1980.

air pollution, and on the longer range trends in these levels brought about by changes in industrial, domestic, and transportation patterns in the country.

Batsto 1979-80

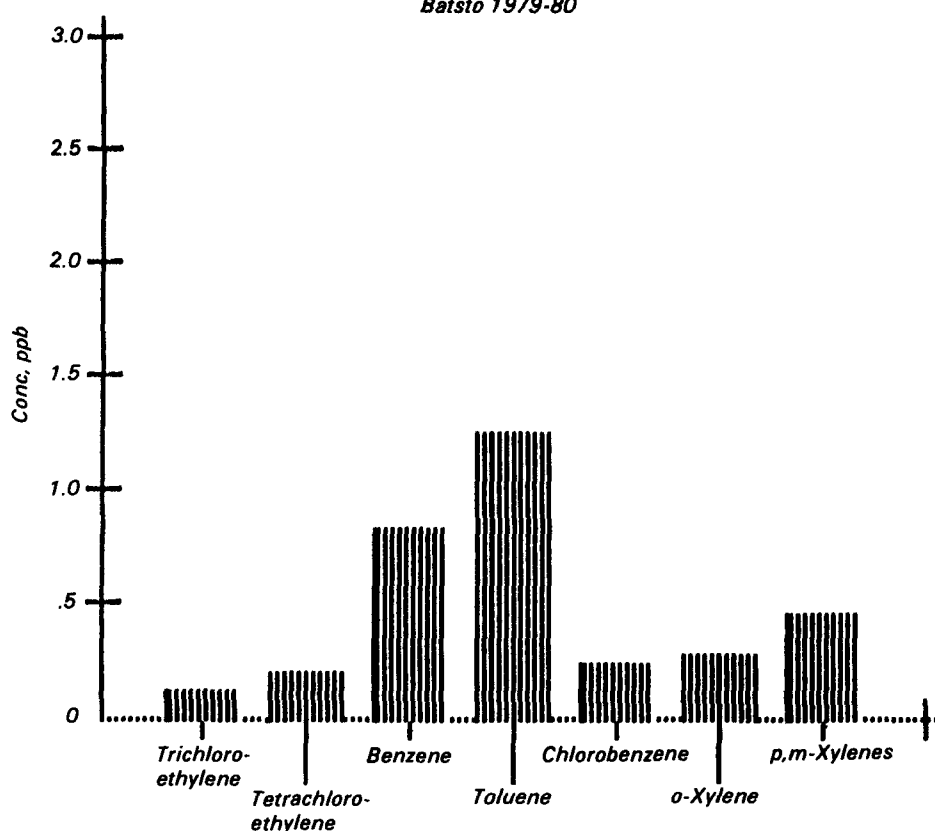


Figure 2. Average concentration of seven target compounds in the atmosphere of Batsto Village, NJ in 1979 and 1980.

Table 2. Compounds Observed by Mass Spectrometry in more than 70% of Samples Desorbed from Tenax Cartridges\*

Butanes	(C <sub>4</sub> H <sub>10</sub> )	Butenes	(C <sub>4</sub> H <sub>8</sub> )
Methylene chloride		Pentenes	(C <sub>5</sub> H <sub>10</sub> )
Chlorotrifluoromethane (Freon 13)		Hexenes	(C <sub>6</sub> H <sub>12</sub> )
Pentanes	(C <sub>5</sub> H <sub>12</sub> )	Heptenes	(C <sub>7</sub> H <sub>14</sub> )
Chloroform (Trace levels)		Octenes	(C <sub>8</sub> H <sub>16</sub> )
Hexanes	(C <sub>6</sub> H <sub>14</sub> )	Nonenes	(C <sub>9</sub> H <sub>18</sub> )
Benzene		Decenes	(C <sub>10</sub> H <sub>20</sub> )
Carbon tetrachloride (Trace levels)		Undecanes	(C <sub>11</sub> H <sub>24</sub> )
Heptanes	(C <sub>7</sub> H <sub>16</sub> )	Isobutylbenzene	
Trichloroethylene		Ethyl-dimethylbenzenes	
Toluene		Propyl-methylbenzenes	
Octanes	(C <sub>8</sub> H <sub>18</sub> )	Tetramethylbenzenes	
Perchloroethylene (Tetrachloroethene)			
Ethylbenzene			
Xylenes			
Styrene (Low levels)			
Nonanes	(C <sub>9</sub> H <sub>20</sub> )		
Trimethylbenzenes			
Propylbenzenes			
Chlorobenzenes			
Decanes	(C <sub>10</sub> H <sub>22</sub> )		
Diethyl benzenes			
Butylbenzenes			
Naphthalene (Low levels)			

\*Acetophenone and benzaldehyde are also routinely found. These species are known to be breakdown products of Tenax, and may occur as a result of the desorption of the cartridge.

Average Concentrations (PPbv) Versus Wind Direction

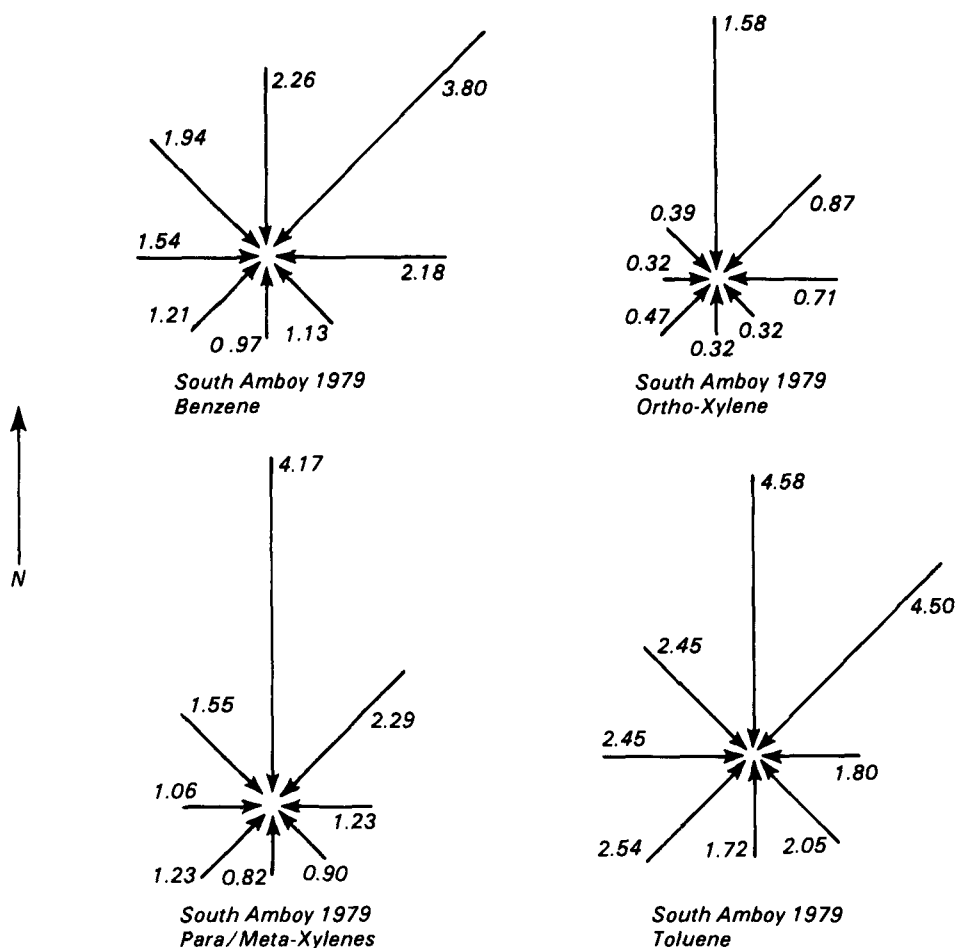


Figure 3. Pollution rose plate of average concentrations of four target compounds versus prevailing wind direction for South Amboy, NJ.

Barbara B. Kebbekus and Joseph W. Bozzelli are with the New Jersey Institute of Technology, Newark, NJ 07102.

Robert R. Arnts is the EPA Project Officer (see below).

The complete report, entitled "Volatile Organic Compounds in the Ambient Atmosphere of the New Jersey, New York Area," (Order No. PB 83-191 403; Cost: \$20.50, subject to change) will be available only from:

National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Environmental Sciences Research Laboratory  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

United States  
Environmental Protection  
Agency

Center for Environmental Research  
Information  
Cincinnati OH 45268

Postage and  
Fees Paid  
Environmental  
Protection  
Agency  
EPA 335



Official Business  
Penalty for Private Use \$300

PS 0000329  
U S ENVIR PROTECTION AGENCY  
REGION 5 LIBRARY  
230 S DEARBORN STREET  
CHICAGO IL 60604