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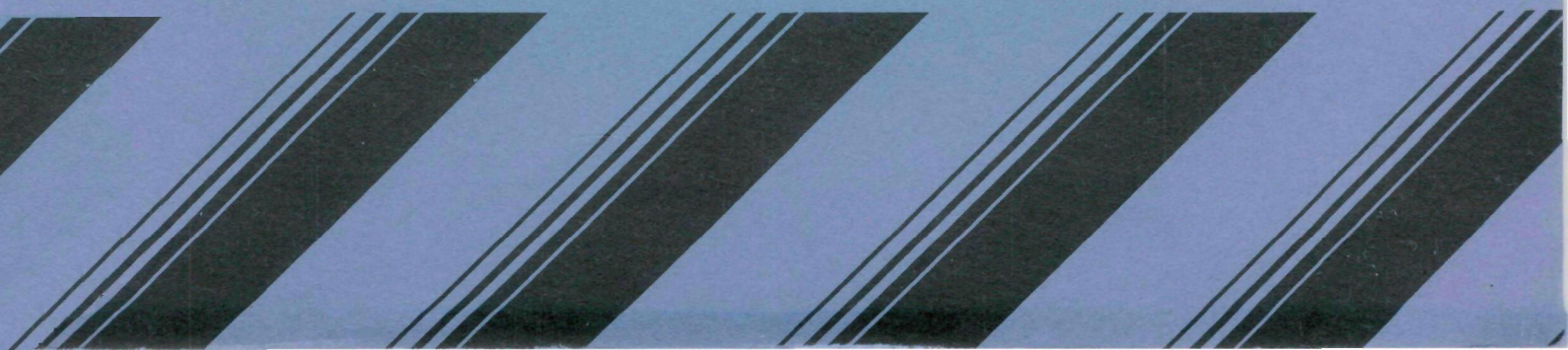
Toxic Substances

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# Environmental Monitoring

## Benzene



ENVIRONMENTAL MONITORING  
BENZENE

by

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## ABSTRACT

Procedures were developed for the collection and analysis of benzene in environmental samples. These procedures were employed in air, water, and soil sampling for benzene in the vicinity of five industrial facilities using or producing benzene. In addition, these procedures were employed in air sampling for benzene in the vicinity of two other industrial facilities, in the area around three gasoline service station locations, and at three urban locations in Columbus, Ohio.

Air samples were collected by pulling air through a bed of Tenax GC. The benzene was thermally desorbed from the Tenax and analyzed by cryogenic capillary gas chromatography. Benzene present in water and soil samples was determined by sparging it from the water or soil with nitrogen, adsorbing it in Tenax absorption tubes, and analyzing the Tenax tubes in the same manner as air samples.

Average 24-hour benzene concentrations at the air-sampling stations around the industrial facilities ranged from 2 to 51  $\mu\text{g}/\text{m}^3$  (0.5 to 19 ppb). In general, the highest concentrations in air were found at sampling stations downwind of the facilities or at stations closest to the facilities. The benzene concentrations found in environmental water samples ranged from <1 to 13 ppb, with levels higher than these being observed in plant effluents. Downstream of the plant outfalls the concentrations were 1 to 2 ppb or less. The highest benzene concentrations were found in soil samples, ranging from 2 to 191 ppb.

At air-sampling points around the service stations the average benzene concentrations were in the range of 1 to 7  $\mu\text{g}/\text{m}^3$  (0.3 to 2.0 ppb). These averages are for periods between 12 and 30 hours. The levels in residential neighborhoods upwind of the service stations ranged from 0.6 to 1.4  $\mu\text{g}/\text{m}^3$  (0.2 to 0.4 ppb). Maximum concentrations of 32.4  $\mu\text{g}/\text{m}^3$  (10.3 ppb) and 68.6  $\mu\text{g}/\text{m}^3$  (21.5 ppb) were measured downwind of a service station during refueling of that station's underground tanks. Automobile traffic was found to contribute to the benzene levels at the service station locations and at the three urban locations near the business district in Columbus. In a residential neighborhood near the business district, the 25-hour average benzene level was 5  $\mu\text{g}/\text{m}^3$  (1.5 ppb). In the center of the business district it was 12  $\mu\text{g}/\text{m}^3$  (4 ppb). Immediately adjacent to a busy highway leading into the business district, the average levels for the 25-hour period of the study were 9  $\mu\text{g}/\text{m}^3$  (3 ppb) on one side of the highway and 23  $\mu\text{g}/\text{m}^3$  (7 ppb) on the other side. The higher levels were on the side of the highway carrying the heavier traffic.



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INTRODUCTION

In recent years, there has been increasing concern about environmental levels of many organic compounds, including benzene. This study was undertaken for the United States Environmental Protection Agency in order to define environmental levels of benzene. To that end some potential benzene sources were chosen including industrial facilities where benzene is processed or used, gasoline service stations, and an urban area where traffic may be a source of benzene in the atmosphere. Accomplishment of the aims of this program required selection of suitable sampling locations, development of methodology for benzene sampling and analysis, and the collection and analysis of environmental samples. The major focus of the program was air sampling; however, a limited amount of data was obtained on water and soil samples collected in the vicinity of industrial facilities.

## PROCEDURES

### Development of Sample Collection System

This part of the program was divided into two parallel studies: evaluation of sorbents and design of the field sampling systems.

#### Evaluation of Sorbents

Little data are available on the environmental levels of benzene. Therefore, it was considered essential to use as sensitive an analytical method as possible and determine benzene levels down to less than 1 ppb ( $3 \mu\text{g}/\text{m}^3$ ). This made it necessary to use a sampling system which concentrates the benzene in a suitable medium. It was decided that an adsorbent system was the only feasible approach. Cold traps would not only be very inconvenient for field sampling, they would collect much more water than benzene, and it is questionable whether a cold trap would work efficiently for benzene in the parts per billion range.

Charcoal. Charcoal was considered as a sorbent, but discarded on the basis that desorption with any solvent would give a significant background of solvent impurities leading to reduced sensitivity. The NIOSH method for benzene utilizes  $\text{CS}_2$  as solvent. However, that method was designed for concentrations in the parts per million range, so that relatively large amounts of benzene are expected. Also, for low concentrations of benzene, the  $\text{CS}_2$  presents serious interferences to the quantitative analysis.<sup>(1)</sup> In addition humidity is known to have an adverse effect on the sorption capacity of charcoal, and no capacity or breakthrough data is available for benzene concentration in the parts per billion range.

Thermal desorption of benzene would avoid the interferences from the eluting solvent and the dilution effect. However, Pellizzari has found that the recovery of benzene from charcoal by thermal desorption is very low.<sup>(2)</sup>

Polymeric Microporous Sorbents. Two polymeric microporous adsorbents were considered. Chromosorb 102 and Tenax GC. In other work at Battelle, both have been used satisfactorily for atmospheric sampling. Tenax GC has superior thermal stability, but Chromosorb 102 is significantly cheaper, so it was chosen for initial evaluation.



Chromosorb 102. To determine the sorbent bed size and air flow rate for sampling, it is necessary to determine the retention volume for the sorbate, benzene in this case. The polymeric microporous sorbents function like a gas chromatographic column rather than by a sorption process by which charcoal and silica gel function. To determine this retention volume a gas chromatographic technique was used with a Chromosorb 102 column. A small amount of the benzene was injected into the gas chromatograph and the time at which the benzene peak started to elute was recorded. Plotting log of elution time ( $\log t$ ) versus the reciprocal absolute temperature [ $1/T(k)$ ], gives a straight line which can be extrapolated to room temperature (or any other desired temperature) to determine the elution time at the given flow rate. The determination was made at two flow rates to demonstrate that the retention volume was dependent upon the temperature. The data are given in Figure 1, along with similar data for Tenax GC. Based on these data, a large trap (4 cm I.D. x 10 cm length containing 50 g of Chromosorb 102) should have a retention time for benzene of over 24 hours at 30 C with a flow rate of 100 ml/min -- which was considered adequate for the program.

Checkout runs showed that 1-hour desorption of benzene on Chromosorb 102 gave essentially complete desorption of benzene. Benzene (30  $\mu$ l) was spiked into a Chromosorb 102 sample collection tube and laboratory air drawn through at 100 ml/min for 1/2 hour. Desorption was then carried out for 90 minutes at 185 C with nitrogen at a flow rate of 100 ml/min. The effluent was collected in three 18 in. x 1/4 in. stainless steel traps containing 1 g each of Tenax GC. Each trap was used for 30 minutes (0-30, 30-60, and 60-90 minutes). The Tenax traps were analyzed for benzene using gas chromatographic analysis. The traps were heated in a Wood's metal bath at 200 C while nitrogen was passed through the heated traps at 200 ml/min for 30 minutes and into a 3 m x 2 mm OD glass column packed with 5 percent DC510 on Gas Chrom Q and maintained at -50 C. The analyte is frozen on the head of the column under these conditions. The oven was then programmed from -50 C to 30 C at 20 C/min and from 30 C to 200 C at 4 C/min. The 0-30 and 30-60 min traps contained nearly all of the benzene; the 60-90 minute trap contained much less than 1 percent of the total amount of benzene in the three traps. The benzene peak was saturated for the first two traps so a more accurate estimate is not possible.

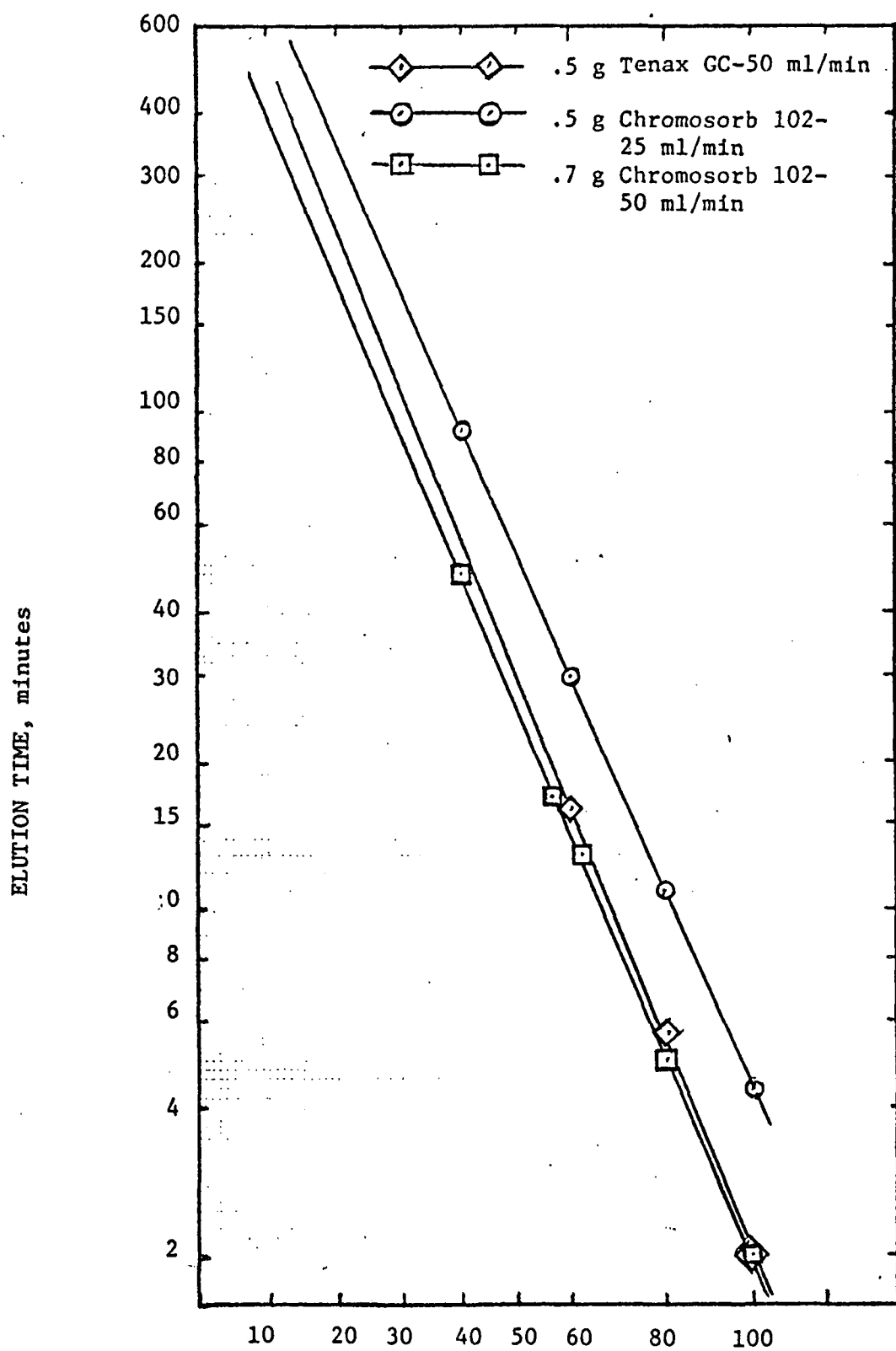


FIGURE 1. PLOT OF ELUTION DATA FOR BENZENE  
FROM CHROMOSORB 102 AND TENAX GC

Although these experiments showed that complete desorption could be obtained, it also showed that the overnight conditioning of (200 C with 50 ml/mm flow of dry nitrogen) Chromosorb did not clean up the Chromosorb adequately. A large number of peaks other than benzene also appeared on the chromatogram which were only attributable to "bleed" from the Chromosorb. Even 72-hour conditioning of the Chromosorb 102 did not lower the bleed sufficiently to permit its use as the adsorbent for collection of benzene.

Tenax GC. Since it was not possible to condition Chromosorb 102 adequately, it was decided to switch to Tenax GC. Because of the much higher cost of Tenax, however, it was decided that smaller traps should be used. Based on the retention time versus temperature plots for benzene on Tenax shown in Figure 1, a U-tube trap of .95 cm (3/8 in.) O.D. stainless steel tubing 30 cm (12 in.) long was selected. This design was expected to give somewhat over 8-hour retention for benzene at 40 C using a 30 ml/min flow rate, before breakthrough occurs. A lower flow rate would give longer retention time, but 30 ml/min is the minimum reasonable attainable with the field sampler system. The U-tube trap design was chosen because the U-tube traps fit directly onto the gas chromatographic system for direct desorption onto the column.

Tenax has been and is being used at Battelle as an adsorbent for hydrocarbons sparged from water samples with nitrogen gas. After adsorption of the hydrocarbons, the water vapor is flushed from the Tenax with dry nitrogen. The Tenax is then heated to desorb the hydrocarbons onto the chromatographic column. For this work, the Tenax is conditioned by heating overnight in a slow stream of dry nitrogen at 250 C.

For this program several hundred traps were required; so conditioning traps one at a time is impractical. Conditioning was carried out by hooking six traps in series. A Varian 2100 biomedical gas chromatograph with controls for four columns permitted activation of 24 traps (four groups of six traps each) at one time. The traps were conditioned overnight at 250 C with a flow of 100 ml/mm of helium. Selected traps were then run through the thermal desorption procedure described above and a chromatogram of the desorption products was obtained. Overnight conditioning did not clean up the Tenax satisfactorily. There was a large amount of background including a

peak exactly where benzene elutes. Conditioning for 48 hours gave a significant improvement and in some cases the traps were considered to be satisfactory. However, in subsequent studies, some of the "cleaned" traps were still found to give unacceptable background levels.

A search of the literature gave several clues about the source of the problem. Pellizzari, et al<sup>(3)</sup> report the use of Tenax GC for GC-MS analysis of atmospheric pollutants. They prepare Tenax GC for use by extracting 24 hours with methanol (or acetone<sup>(2)</sup>), vacuum drying, and thermal conditioning at 275 C for 20 minutes in a stream of dry helium. Bertsch, et al<sup>(4)</sup> also report the use of Tenax GC for collection of atmospheric volatiles for GC-MS analysis. Their conditioning consists of heating Tenax at 340 C for 1 hour in a stream of dry nitrogen.

After rather extensive study, it was found that much more drastic conditions than Pellizzari and Bertsch used were required to clean up the Tenax GC satisfactorily for this program. Details of the experimental studies are given in Appendix A. The procedure developed is:

- (1) Extract with methanol for 48 hours in Soxhlet Extractor
- (2) Vacuum dry overnight at 100-125 C
- (3) Condition in a large glass tube at 300 C for 16-20 hr, with a purified nitrogen stream flowing through the tube.
- (4) Pack in stainless steel traps
- (5) Condition at 275 C for 16-20 hr, with a purified nitrogen stream flowing through the trap at ~25 ml/min.

A variation of this procedure was used, at the suggestion of Pellizzari<sup>(2)</sup>, for cleanup of Tenax which had been used previously for benzene sampling:

- (1) Extract successively with methanol for 48 hours and then with pentane for 24 hours in Soxhlet Extractor
- (2) Vacuum dry overnight at 100 to 125 C
- (3) Pack in stainless steel traps
- (4) Condition traps at 275 C for 24 hours with a purified nitrogen stream flowing through the trap at ~25 ml/min.

The pentane is used to ensure removal of any hydrocarbons that may be present from the previous use.

Calculation of breakthrough capacity based on the breakthrough data shown in Figure 1 indicated that a breakthrough time of 8 to 9 hours was expected for benzene at 40 C (the maximum temperature that should be encountered during sampling) and a flow of 30 ml/min. However, those data were based on a small lot of Tenax already on hand. A new batch of Tenax ordered to fill the first 100 traps had a lower bulk density. It took 3.5 g of the original material to fill one trap, and only 2.2 g of the new lot. The effect of the lower bulk density on breakthrough time was not known. Consequently, breakthrough was determined for the new lot of Tenax using one of the stainless steel U-tubes.

Breakthrough was determined by a gas chromatographic procedure using the trap as a column at 40 C. The analyte was injected through the standard injection port and swept onto the trap by the carrier gas. Since peak broadening after several hours retention time becomes severe, direct observation of breakthrough is difficult. Consequently, a second Tenax trap was attached to the effluent end of the first trap and changed hourly. These backup traps were then gas chromatographically analyzed by thermal desorption. The retention time of benzene was 10-12 hours based on a 30 ml/min flow rate. Precise breakthrough times are not determined by this method since only hourly values are obtained. However, the data clearly show that adequate breakthrough time is available for the needs of this program.

#### Ambient Air Sampling System

The system shown in Figure 2 was developed to sample for benzene in ambient air. The system permits concurrent sampling with up to four 0.95 cm O.D. (3/8 in.) x 30 cm (12 in.) U-tube traps or other trap configurations. Two traps may also be connected in series to check for breakthrough during sampling. Flow through each trap is controlled by a calibrated jewel orifice. A flow meter is used to monitor total system flow. Sample system vacuum is monitored on a gauge and controlled by a vacuum relief valve. A Gast carbon vane, continuous duty pump is used to provide air flow through the system. The system is contained in a weather-proof housing. Air inlet to the system is through a filter mounted about 5 ft above ground level. Six systems were constructed for field use. Necessary spare parts were available to repair or replace system components in the field, if necessary.

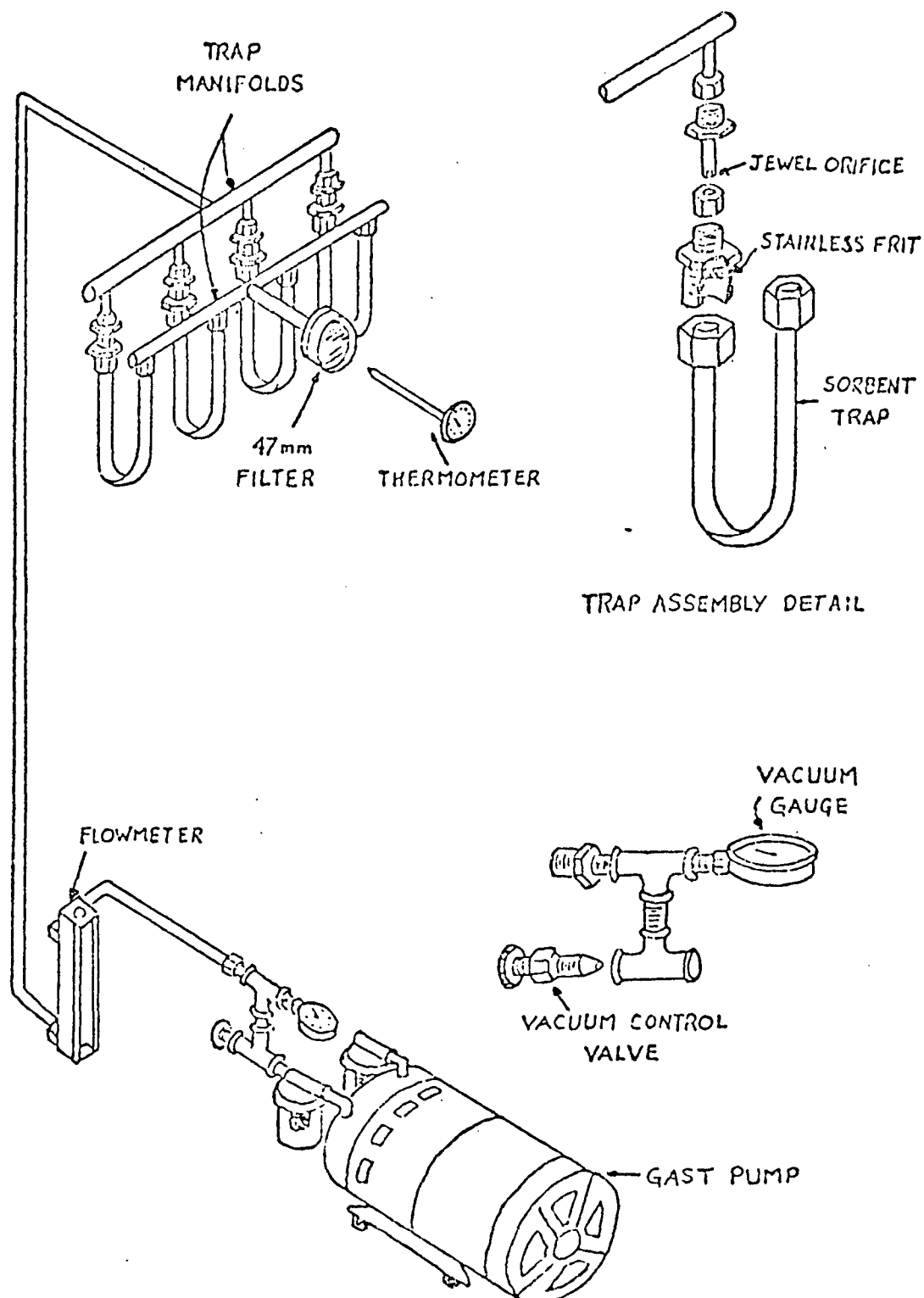


FIGURE 2. AMBIENT AIR SAMPLING SYSTEM

Two types of situations are encountered in which it is expedient to operate air sampling devices without dependence on 110 volts alternating current utility lines.

One of these situations entails traversing an air current downwind of a suspect source. Such traversals are made by hand-carrying a personal-type battery operated sampler for as far as a mile or more perpendicular to the wind; connections to mains is impractical in such situations.

The second situation involves continuous samplings of 24 hours or longer on sites which are remote from electrical services. The sites may be chosen to deliberately avoid extraneous emission sources (motor vehicles, incinerators, space heaters, paint, black-top, etc.) usually associated with 117 VAC terminals. To provide extended sampling capability on fixed remote sites, a battery-powered pumping system was assembled.

The system consists of a small 30 ampere-hour 12-volt lead-acid battery, a Trico 70 112-1 Electr-Vac vacuum windshield wiper booster pump, a pair of check-valves, a 30-pound refrigerant can, a Barksdale No. D2T-H18 pressure switch and protective relay, a plywood box (fitted with a hinged lid and handles) to contain the above, and appropriate plumbing, wiring, and hardware. Sketches of the pumping system appear in Figure 3.

#### Analytical Procedure for Benzene

A cryogenic capillary GC technique was chosen for analyses of benzene in environmental substrates on the basis of previous studies performed at BCL on analysis of hydrocarbons in marine materials. No extensive developmental work was required other than modification of a Varian 1400 gas chromatograph to operate under cryogenic conditions and establishment of appropriate gas chromatographic conditions to achieve satisfactory resolution of benzene from other volatile components in environmental substrates.



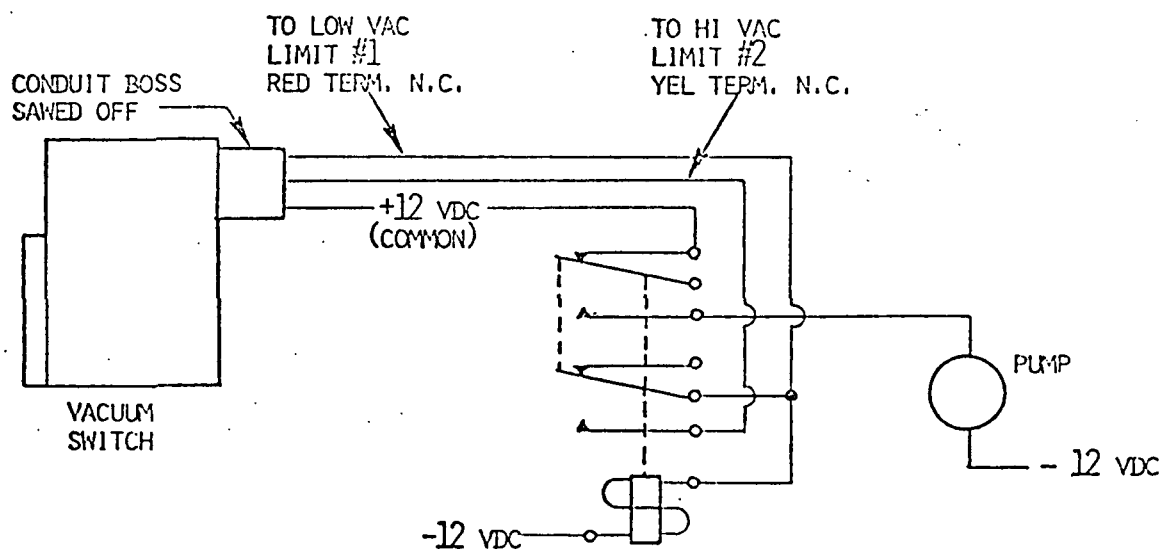
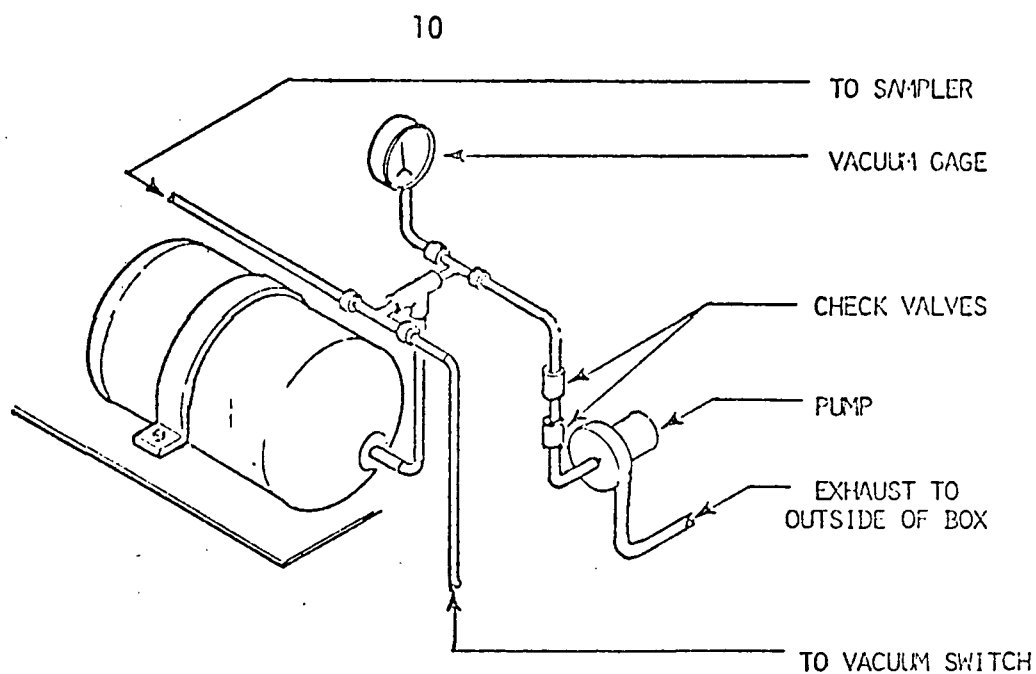


FIGURE 3. PUMPING SYSTEM FOR PORTABLE SAMPLER

### Analytical Method

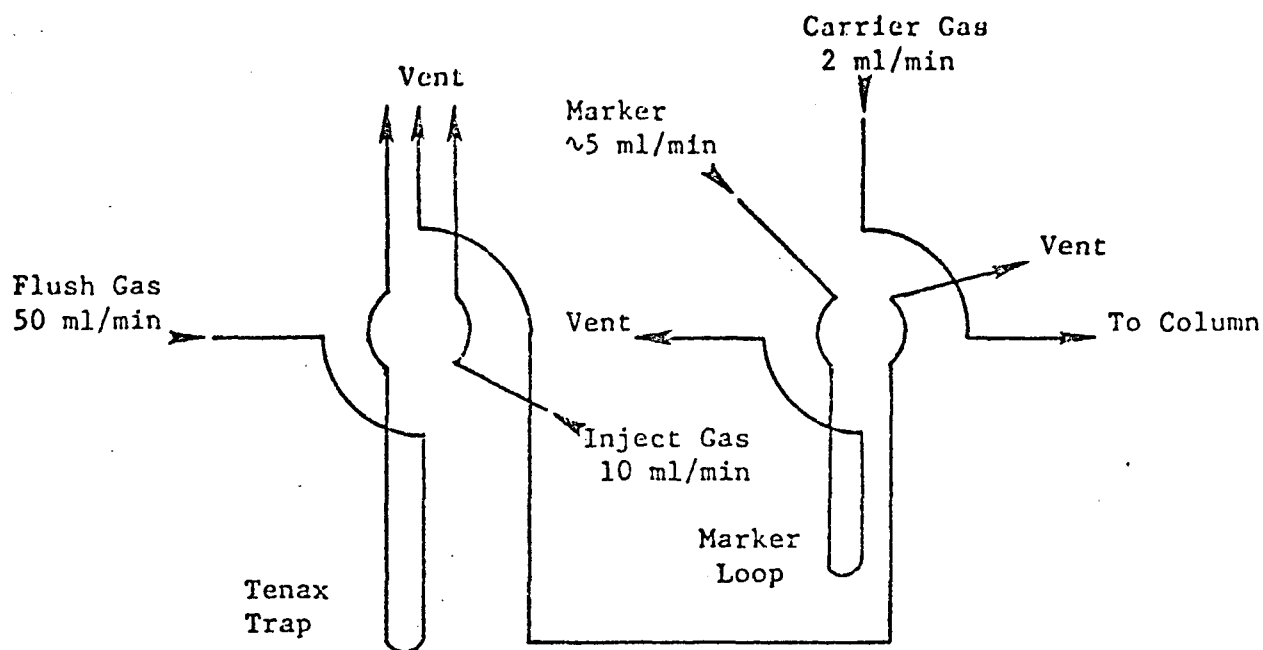
Benzene adsorbed on conditioned Tenax GC ( $\approx 2.7$  g) packed in 3/8 in. x 12 in. stainless steel U-shaped tubes is injected into a capillary GC by means of a dual valving arrangement utilizing two Carle 8-part valves as shown in Figure 4. The tubes are flushed with helium at 50 ml/min at room temperature to remove air and water. The flush period varies depending upon the environmental substrate being analyzed for benzene. For air samples, the flush period is 10 minutes and for water and soil samples, 60 minutes.

The Tenax tube is then rapidly heated to 200 C with a Woods metal bath. The flushed gas is vented. The benzene is desorbed from the Tenax with a 10 ml/min stream of helium for 10 minutes and collected on the head of the column at -70 C. A 50-meter glass capillary column (.01 in. I.D.) with SF96 as the liquid phase is employed. The oven is allowed to warm for 3 minutes (which brings the oven temperature to about 0 C). It is then temperature programmed at a rate of 1 C/min with 0 C as the starting point. Under these conditions, benzene elution time is approximately 14.5 minutes. Peak areas are determined by a computer or electronic integration system. A Spectra Physics SP4000 computer was used in this work.

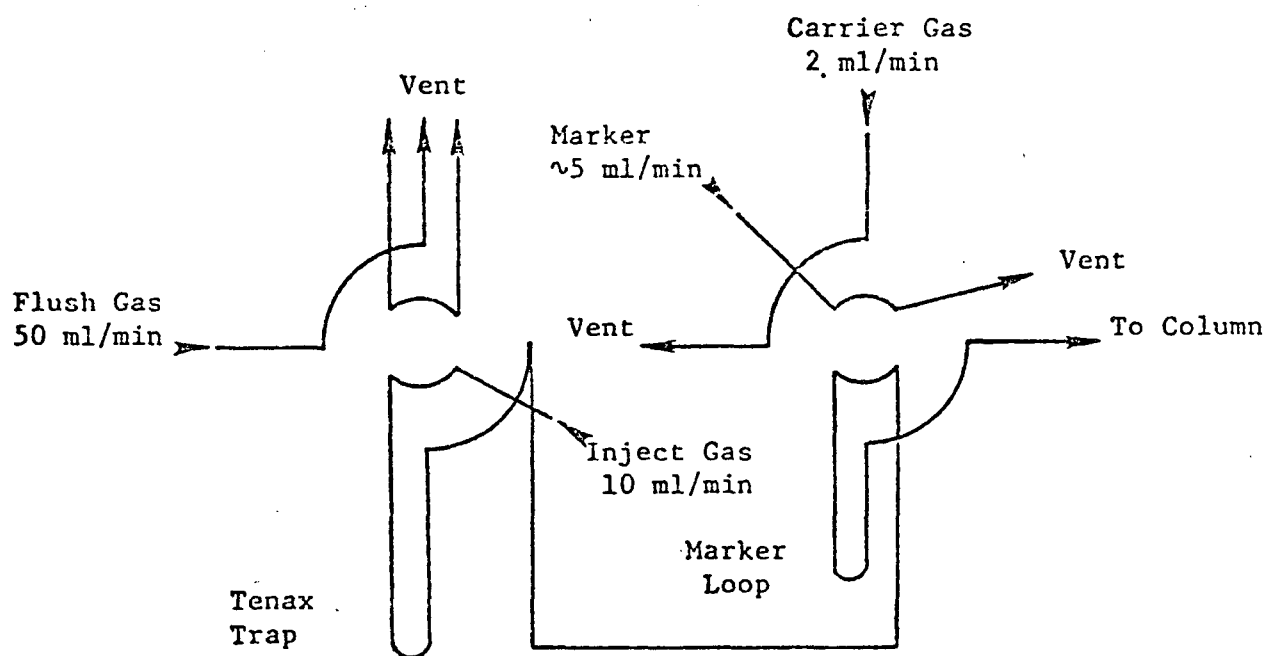
A schematic diagram of the valving system used for injecting the sample into the GC is shown in Figure 4. The trap is flushed in the same direction as it is sampled. By convention the traps are made with one arm 1/2 in. shorter -- this is the inlet used for sampling. During the flush mode (Figure 4a) the marker gas loop is also flushed with marker gas (150 ppm chloroform in nitrogen).

Figure 4b shows the system in the "inject" mode. In this mode a 10 ml/min stream of helium is flushed through the sample trap for 10 minutes through the chloroform marker loop and onto the head of the column. After the 10-minute inject cycle, the system is returned to the flush mode and the GC oven temperature program is started.

The chloroform marker gas can be useful as an aid in identifying the benzene peak if there are no interfering peaks in the vicinity of the chloroform peak. With the particular column, packing, column length, carrier gas flow rate and temperature program, used in the current work, chloroform elutes at 11.5 minutes and benzene at 14.5 minutes, exactly 3 minutes later. However, because the Varian 1400 gas chromatograph used is not under temperature control



a. Flush Mode



b. Inject Mode

FIGURE 4. VALVE INLET SYSTEM FOR ANALYSIS OF TENAX TRAPS

for the first three minutes (-70 to 0C), the time of chloroform and benzene can vary  $\pm \sim 0.2$  minutes. Actually the chloroform marker was of little value in this work because of the interferences encountered.

The identity of benzene in a random selection of air, water, and soil samples was confirmed by GC-MS. In all samples analyzed, the benzene peak was always the largest peak eluting in the benzene region. In air samples the closest interferences were methylchloroform and cyclohexane, for water the only close peaks were so small that they could not be identified, and for soil the interferences were methylcyclopentane and, to a small extent, methylchloroform.

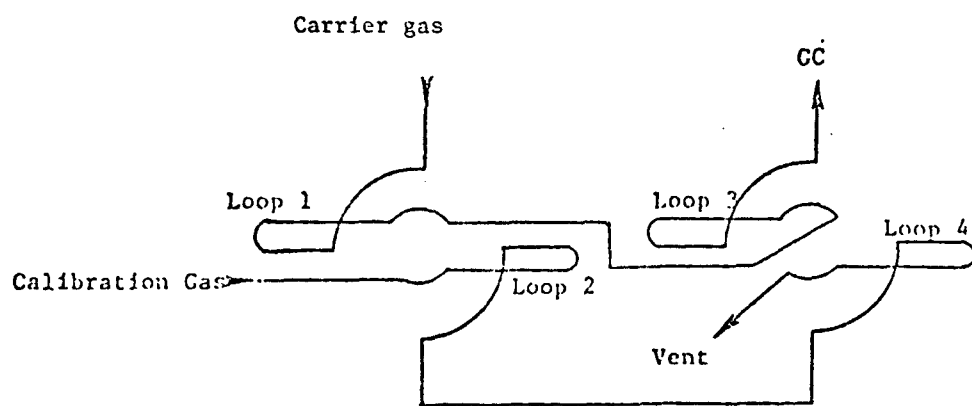
The minimum detectable level of benzene on column above background by this analytical method is approximately 2 ng which is equivalent to about  $0.2 \mu\text{g}/\text{m}^3$  or  $>0.1$  ppb.

#### Calibration of Gas Chromatograph

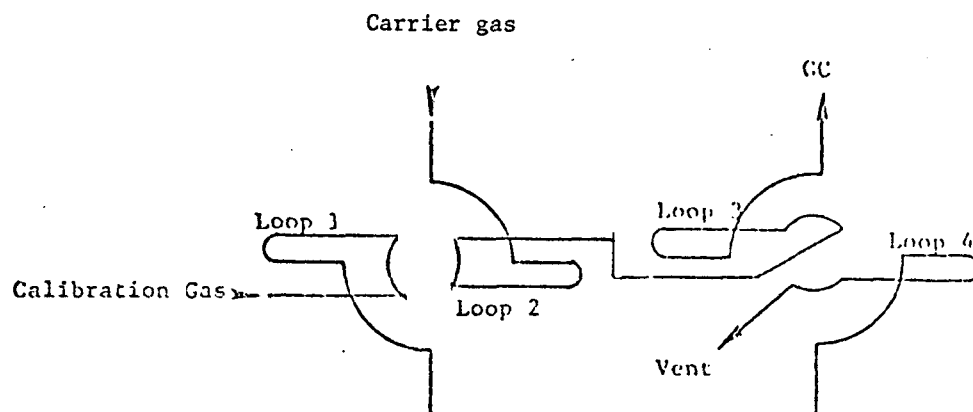
Calibration of the gas chromatograph was performed two or three times weekly by use of a calibrated gas mixture and a loop injector system. A variety of valve configurations can be employed, and the loop sizes and standard gas concentrations can be varied over fairly wide limits, provided that the total amount of benzene injected for each loop covers the range of interest. In this work, four loops and two standard gas mixtures of 183 and 25 ppm of benzene in nitrogen obtained from Matheson Coleman and Bell were used. The volumes of the loops and weight of benzene in each are:

<u>Volume of Loop, <math>\mu\text{l}</math></u>	<u>Benzene Weight, ng</u>	
	<u>25 ppm Std</u>	<u>183 ppm Std</u>
126	10	72
360	28	205
982	77	559
2,236	175	--(not used)

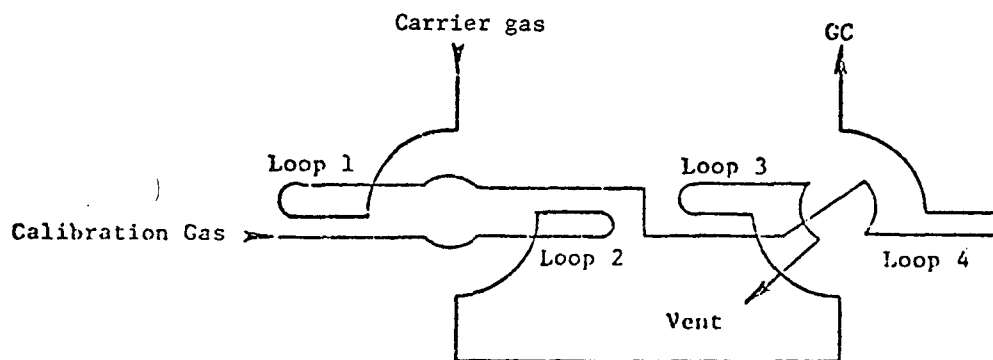
Figure 5 shows the calibration valve system used. It consists of two Hamilton Micro-Volume, 8-port valves (Model #2013). There are two loops on each valve. In Figure 5a, loops 2 and 4 are being filled with calibration gas and loops 1 and 3 are being swept by carrier gas. In Figure 5b, the valve on the left has been turned to inject loop 2 and fill loop 1 with calibration gas. In Figure 5c, the valve on the right has been turned to inject loop 4 and fill loop 3 with calibration gas.



a. Fill Loops 2 and 4



b. Inject Loop 2, Fill Loop 1



c. Inject Loop 4, Fill Loop 3

FIGURE 5. LOOP SYSTEM FOR CALIBRATION OF GC

The calibration curve is prepared by plotting the weight of benzene injected versus the integrator output. For the SP4000, the output is in units of microvolt seconds. At least one calibration point should be checked daily, and if significant discrepancy (greater than 2-4 percent) is found, the entire calibration curve is rerun.

### Quality Assurance Studies

In addition to routine quality assurance procedures a series of experiments were performed to confirm the validity of the data obtained in the sampling and analysis of benzene in ambient air.

### Sample Collection

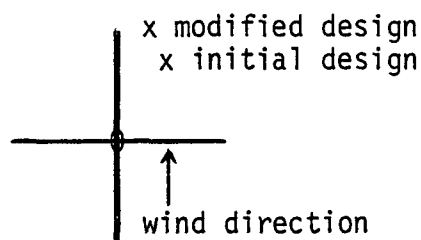
The issues addressed regarding the influence of the sample collection procedures on data validity were the effects of sampling system design and the collection efficiency of Tenax under various conditions.

Sampling System Design. During the conduct of this program two points of concern arose regarding the sampling system design:

- (1) The effect of the positioning of the sampling tube inlet on representative sampling of ambient air
- (2) The possibility of sampling pump exhaust mixing with the ambient air and resulting in an erroneously low analysis for benzene.

Through the end of 1977, the sampling tube inlet was situated below a flat protective surface of aluminum foil. When concern about the design was raised, a new design was adopted for use in subsequent sampling, and an experiment was performed to compare the two. The modified design involved an extension of the sampling tube (with an inverted funnel at the end) upwards through the protective aluminum cover. The experiment was conducted at a busy traffic intersection in Columbus, Ohio.

The sampling period was 11 hours (0730 to 1830) and the sampling rate 31 to 35 ml per minute. Sampling was performed in duplicate with two traps in tandem (foretrap and backup trap). The two sampling systems were positioned about 6 feet apart downwind and approximately equidistant (about 50 feet) from the center of the intersection which was controlled by a traffic light. The systems were oriented so that pump exhausts were also downwind:



The analytical data are presented in Table 1. The samples collected on the initial design analyzed 6.1 and 6.7 ppb and those collected on the modified design, 5.7 and 5.9 ppm. Based on these data the current design was just as effective as the modified one in collecting representative samples of ambient air.

TABLE 1. EFFECT OF SAMPLING SYSTEM DESIGN IN COLLECTION OF AMBIENT AIR SAMPLES

Sampling Period: December 30, 1977, 0730-1830				
Rate: 31 to 35 ml/min				
Temperature: 30 to 36 F				
RH: 57 to 65 percent				
Wind: Speed, calm to 1 m/sec; Direction, 124-235°				
Sampling Design	Volume Sampled, $\ell$	Benzene Analysis		Benzene Breakthrough on Backup Trap, ng
		$\mu\text{g}/\text{m}^3$	ppb	
Initial 1	22.8	21.1	6.1	<1
2	23.1	23.4	6.7	<2
			Avg. <u>6.4</u>	
Modified 1	22.8	19.7	5.7	<1
2	20.8	20.4	5.9	<1
			Avg. <u>5.8</u>	



During the first two sampling trips (in 1976), 3 in. x 8 ft cardboard tubes were used to divert pump exhaust away from the sampling systems. When this practice was abandoned in the 1977 sampling, the question was raised of the effect of possible mixing of exhaust with sampled ambient air. To alleviate this concern, 25 feet of exhaust hose was used in the 1978 sampling. In addition, an analysis was made of a sample of the exhaust taken 1 inch from the exhaust port of the box in which the pump is housed and compared with an analysis of ambient air. The benzene content of the exhaust was 2.5 ppb, which was essentially the same as the 3.2 ppb found in the ambient air.

The sampling system utilizes a Gast carbon valve pump modified by an air bleed valve on the low pressure side adjusted to achieve a vacuum of 20 inches of mercury when the air flow through the inlet to the Tenax traps (controlled by calibrated orifice) is 30 cc/min. When sampling in duplicate the ratio of exit air from two Tenax traps to exhaust air\* is approximately 0.06  $\ell$ /28.3  $\ell$  or stated another way, the exhaust air is approximately 99.8 percent ambient air. Also, the sampling systems are always positioned so that the exhaust ports, which are 4 feet below and to the side of the sample inlets, are downwind. Hence, on the basis of these facts, it must be concluded, even when wind speed and direction are variable, that pump exhaust will not constitute a significant fraction nor have any significant effect on benzene composition of ambient air samples.

Collection Efficiency of Tenax. Backup traps were used routinely in field sampling to confirm that breakthrough of benzene was not occurring. Data from these traps indicate that retention of benzene by Tenax is essentially quantitative; in two typical instances foretraps analyzed 278 ng (7.5 ppb) and 32 ng (0.8 ppb) of benzene while the corresponding backup traps in each case analyzed less than 2 ng of benzene (<0.1 ppb). The largest quantity of benzene found on any backup trap was about 15 percent of the quantity on the foretrap.

\* Manufacturer's data cites exhaust rate of 0.95 cfm (approximately 26.9  $\ell$ ) at 20 inches of mercury vacuum.

Experiments were conducted to determine the effects of high temperature, high humidity, and flow rate through the sampler.

Atmospheres of 12 ppb of benzene in nitrogen and 100 percent relative humidity (RH) were prepared by injection of 585 ng of benzene by calibrated loop into evacuated 20 L Tedlar bags followed by introduction of sufficient water to provide 100 percent RH at 72 F (~320 mg water) and 102 F (~700 mg water). The bags were charged with 15 to 17 L of nitrogen and the contents allowed to equilibrate about 1 hour at the temperature of collection. The entire contents of the bags were collected on two Tenax traps in tandem (foretrap and backup trap) at a sampling rate of 30 to 35 cc/min using the BCL sampling rig. Traps were analyzed in the usual manner by cryogenic capillary GC. The experiments were performed in duplicate at each temperature. Control experiments were performed in the same manner using the same bags prior to the actual benzene runs. The analytical data are shown in Table 2. Recoveries of benzene were 99 and 109 percent at 72 F and 115 and 98 percent at 102 F. Backup traps analyzed 1 to 3 ng of benzene background, corresponding to a breakthrough of 0.2 to 0.5 percent, which can be considered negligible.

TABLE 2. BENZENE RECOVERY STUDIES OF TENAX

Atmosphere: 12 ppb benzene (585  
ng in 15 to 17 L  
nitrogen); 100% RH.

Experi- ment	Temp, F	Benzene Charge, ng	Collection Rate, cc/min	Volume Collected, L	Break- through, ng	Benzene Recovered(a) ng	%
1	72	585	35	15.0	<2	580	99
2	72	585	35	15.2	<2	635	109
3	102	585	32	15.5	<3	675	115
4	102	585	31	16.3	1	575	98

(a) The Tedlar bags used in these experiments had a background interference to 10 to 15 ng of benzene.

The collection efficiency of Tenax for benzene at the 1 ppb level was determined at collection rates of 10, 100, and 1,000 cc/min. The data in Table 3 indicate that the collection efficiency at the 1 ppb level is independent of collection rate; average collection efficiency at the three rates was 104 percent. The benzene atmospheres were prepared in 20 L Tedlar bags (~72 to 80 ng benzene in 15.5 L air or nitrogen (equivalent to approximately 1.5 ppb) and sampled at the indicated rates on Tenax traps. The traps were analyzed by cryogenic GC in the usual manner.

TABLE 3. EFFECT OF COLLECTION RATE ON COLLECTION EFFICIENCY OF TENAX FOR BENZENE AT 1 PPB

Temperature, 72 F; RH, 0; Benzene Concentration, 72 to 80 ng in 15.5 L of air or nitrogen.

Experiment No.	Benzene Concentration, ng	Collection		Benzene Analysis <sup>(a)</sup>	
		Rate, cc/min	Time, hr	ng	Efficiency, %
1	72	11.1 <sup>(b)</sup>	22.5	81	113
2	80	16.0 <sup>(c)</sup>	17.0	85	106
3	72	95.0 <sup>(b)</sup>	2.7	91	126
4	80	100.0 <sup>(c)</sup>	2.5	55	69
5	72	800.0 <sup>(b)</sup>	0.33	81	113
6	80	1,000.0 <sup>(c)</sup>	0.25	70	88

(a) The Tedlar bags used in these experiments had a background interference equivalent to 10 to 20 ng of benzene.

(b) In air.

(c) In nitrogen.

#### Benzene Analysis

Three methods were used routinely to judge the accuracy of the data: (1) by spiking of the Tenax GC traps with known concentrations (10 to 1000 ng) of benzene in methanol; (2) calibrated loop injections (62 to 1100 ng) directly onto the GC column, and (3) spiking of the Tenax GC traps using the calibrated loops. The three methods agree within 10 to 15 percent of each other over the concentration range of 10 to 1100 ng.

On two occasions (in conjunction with the urban location sampling in Columbus, Ohio, and the U.S. Steel Corp. sampling in Clairton, Pennsylvania) Tenax traps were sent to EPA where they were spiked with known quantities of benzene by a gas-permeation technique. The traps were returned and analyzed periodically during the analysis of the field samples. The results are shown in Tables 4 and 5. Agreement with the EPA values was good in all cases.

TABLE 4. DETERMINATION OF BENZENE IN EPA-SPIKED SAMPLING TUBES FOR QUALITY CONTROL -- URBAN COLUMBUS SAMPLING

Trap No.	Amount of Benzene <sup>(a)</sup>		Difference, %
	Determined, ng	EPA Values, ng	
234	131	124	+5.6
181	132	124	6.5
290	135	124	8.8
111	127	124	2.4
		Average	+5.8
96	410	388	5.7
177	423	388	8.5
67	444	388	14.6
170	382	388	-1.5
		Average	+6.8

(a) Tubes supplied by Battelle-Columbus were spiked by the Quality Assurance Branch of the U.S. EPA at Research Triangle Park, N.C., and returned for analyses

TABLE 5. DETERMINATION OF BENZENE IN EPA-SPIKED TRAPS FOR QUALITY CONTROL -- U.S. STEEL CORP. SAMPLING

Trap No.	Amount of Benzene <sup>(a)</sup>		Difference, %
	Determined, ng	EPA Values, ng	
133	96.3	110	-12.5
76	97.0	110	-11.8
63	96.9	110	-11.9
223	99.7	110	- 9.4
65	99.9	110	- 9.2
257	100.5	110	- 8.6
		Average	-10.6
288	350.4	379	- 7.5
259	366.9	379	- 3.2
236	368.5	379	- 2.8
159	340.5	379	-10.2
		Average	- 5.9

(a) Traps supplied by Battelle-Columbus were spiked by the Quality Assurance Branch of the U.S. EPA at Research Triangle Park, NC., and returned for analyses

At least one or two field blanks were taken on each sampling trip and analyzed with the field samples. No more than negligible quantities of benzene were found in any of the field blanks.

Prior to the end of 1977, the 183 ppm benzene standard used for calibration of the gas chromatograph was checked only twice. An assay of the standard by mass spectrometry in December, 1977, showed 179 ppm and by gas chromatography, 187 ppm. The assay in February, 1977, by mass spectrometry was 183 ppm. In early 1978, a new 25 ppm gas standard was obtained. In order to increase calibration reliability of the cryogenic gas chromatograph, this standard was assayed daily by an independent GC method which is calibrated against liquid standards of benzene in carbon disulfide (50 to 500 ng).

To verify that no benzene is lost during the flushing of the Tenax trap to remove water, an experiment was performed to monitor the effluent from the flushing operation. A Tenax trap sample (15  $\mu$ ) of a 10 ppb benzene atmosphere at 100 percent RH was prepared and backflushed at room temperature onto the GC capillary column at the highest flow rate possible, 10 ml/min for 50 minutes; this is equivalent to the normal flush of 50 ml/min for 10 minutes. The Tenax trap was then replaced with an empty trap and the analysis of the flush effluent performed in the normal manner. No benzene peak was detected in the region 12.1 to 12.4 minutes where benzene normally elutes. This result was not unexpected since the previous studies showed a collection efficiency of >99 percent at 100 F and 100 percent RH for a 15  $\mu$  sample.

### Statistical Analysis

It was not considered necessary nor would it have been cost-effective to analyze all samples in duplicate. However, a sufficient number of duplicate analyses (and two triplicate) were performed to provide data for a variance analysis.

An analysis of variance for a one-way design was run using the Battelle Computer Center's version of the BMD programs<sup>(5)</sup>. A logarithmic transformation was used. From the variance analysis, a pooled standard deviation was obtained. This value,  $s$ , with the Students "t" value for 95 percent confidence and appropriate number of degrees of freedom was then

applied to the individual measurements to determine the 95 percent confidence limits according to the following formulas:

$$\text{Upper Confidence Limit} = 10^{(\log x + ts/\sqrt{n})}$$

$$\text{Lower Confidence Limit} = 10^{(\log x - ts/\sqrt{n})}$$

where

x is each individual value (or average if replicates were run),

n is the number of replicates,

s is the standard derivatives described above (.053 is the actual value), and

t is Students "t" value, 2.069 was used, representing 95 percent confidence limits for 23 degrees of freedom.

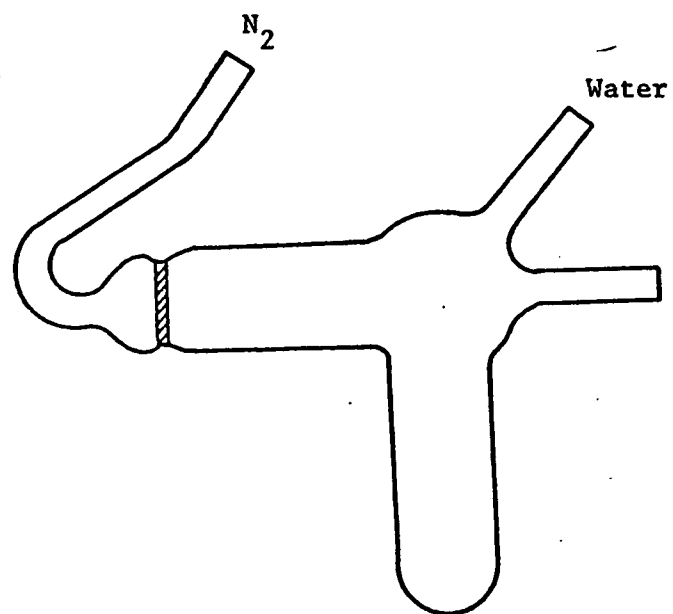
#### Analysis of Environmental Samples for Benzene

##### Air

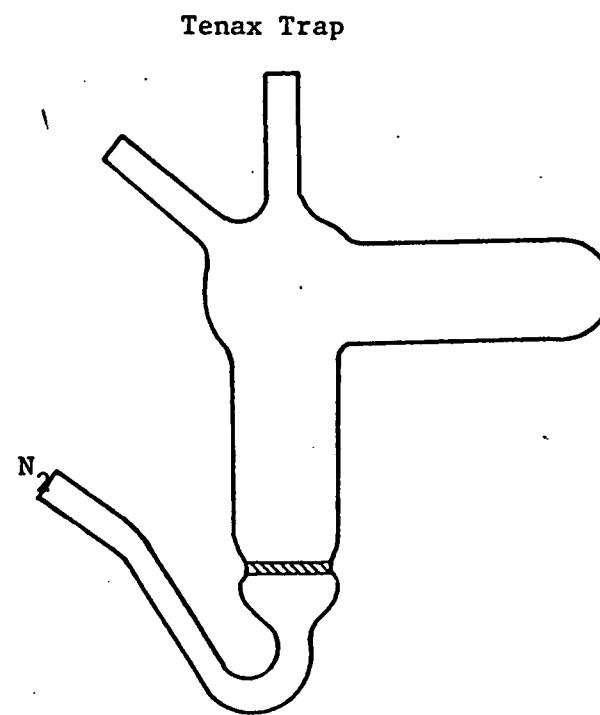
Samples of ambient air, collected in 2 to 12 hours at the rate of 30 ml/min on Tenax GC, were analyzed directly for benzene as described above. Most of the samples were collected for 8 hours. At some locations, grab samples were also collected, at flow rates of 200 to 220 ml/min for 10 to 20-minute periods.

##### Water

Samples were analyzed by sparging for 45 minutes with nitrogen at 100 ml/min at room temperature onto a Tenax GC tube which was then analyzed for benzene in the same manner as air samples. The sparging was conducted in the apparatus shown in Figure 6. The volume of sample used varied from 0.5 to about 20 ml depending upon the concentration of benzene. The volume of the first sample analyzed was approximately 10 ml and if the benzene content exceeded 500 ng (50 ppb), the analysis was repeated using a sample volume calculated to give about 75 to 100 ng of benzene on column. The smaller sample volumes were added to approximately 20 ml of presparged distilled water previously analyzed for benzene then sparged onto the Tenax tube.



Fill Position



Sparge Position

FIGURE 6. SPARGING APPARATUS FOR WATER SAMPLES



Soil

Samples of 3 to 6 g of soil were transferred to the sparging apparatus shown in Figure 7 containing 15 ml of  $H_2O$  and then sparged one hour at 75-80 C with a stream of nitrogen at 100 ml/min. The sample was stirred with a magnetic stirring bar during sparging. The spargate was collected on a Tenax GC tube and analyzed for benzene in the manner previously described. Prior to injection of the sample into GC, the tube was flushed 45 minutes to remove water.

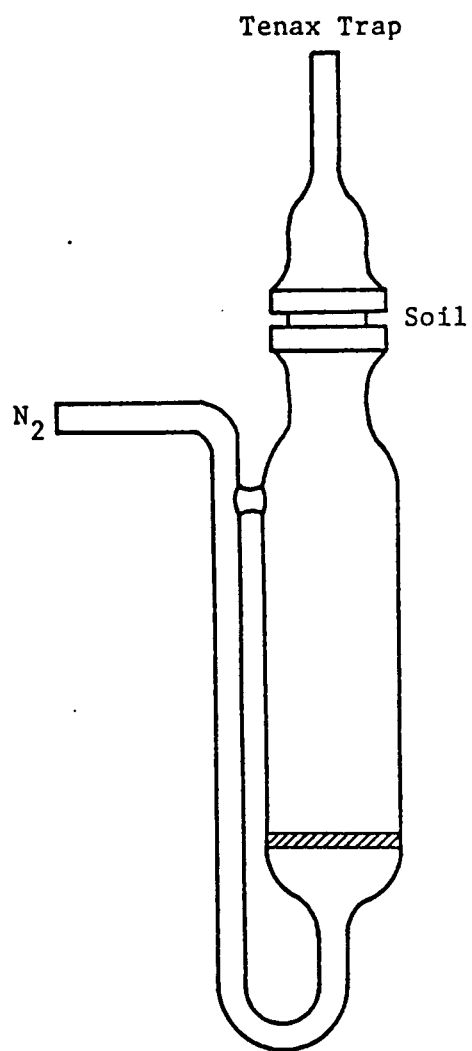


FIGURE 7. SPARGING APPARATUS FOR SOIL SAMPLES

## RESULTS AND DISCUSSION

Three types of locations where benzene is likely to be present were chosen for study in this program. Industrial locations where benzene is either produced or consumed represent one type. Service stations that dispense gasoline containing benzene represent a second type. An urban area with a heavy traffic volume was chosen as a third type of location.

### Industrial Locations

#### Selection of Sampling Locations

The first step in selection of sites for collection of samples was collection of data concerning the production and consumption of benzene by industrial plants. The original goal was to study storage and transportation facilities, as well, but in the case of benzene, the major storage facilities are located at the manufacturing or using facility. These are normally very close so that there is little "transportation" in the usual sense.

Table 6 lists the U.S. cities with the largest production and/or consumption of benzene. From this list a preliminary selection of plants for sampling was made, based on covering as many types of processes as possible, but sampling at the largest plants where practicable. This list of plants is given in Table 7. Appendix B gives a listing of benzene production and consumption facilities by various categories (Tables B-1 through B-8).

The selection of plants to be sampled was made from this list, based on discussions with the Sponsor. Later in the program a coke oven plant in Clairton, Pennsylvania, and a maleic anhydride plant in Neal, West Virginia, were added at the request of the Sponsor. The plants sampled are listed in Table 8.

At each location, air sampling sites were chosen on the basis of the following factors:

- (1) Prevailing weather conditions
- (2) Topographical details
- (3) The availability of electric current to power the samplers
- (4) The locations of populated areas that might be exposed
- (5) The presence of other potential sources of benzene.

At those locations where soil and water sampling was done, the soil samples were taken at the same sites as the air samples, and the water samples were taken upstream and downstream of the plant.

TABLE 6. MAJOR U.S. BENZENE CENTERS

State/City	Total Benzene Capacity (in millions of pounds)		Total
	Production	Consumption	
California/Los Angeles	256	107	363
San Francisco		107	107
Illinois/Chicago	176	181	357
Kansas/Wichita	95	108	203
Kentucky/Ashland	366	280	646
Louisiana/Baton Rouge	476	1254	1730
Lake Charles	183	--	183
New Orleans	1099	564	1663
Shreveport	117	--	117
Maryland/Baltimore	110	104	214
Michigan/Midland	220	701	921
Missouri/St. Louis	293	257	550
New Jersey/Elizabeth	--	130	130
New York/Buffalo	169	14	183
Oklahoma/Tulsa	176	--	176
Pennsylvania/Philadelphia	931	568	1499
Pittsburgh	403	100	503
Texas/Houston	4988	5254	10242
Corpus Christi	959	655	1614
Odessa	374	248	622
West Virginia/Parkersburg	--	402	402
Puerto Rico	2161	734	2895
Virgin Islands	183	--	183
Others	80	162	208
Grand Total	13815	11930	25711

TABLE 7. PRELIMINARY PLAN FOR BENZENE SAMPLING LOCATIONS

Process	Location	Nearest Large City, miles	Company	Capacity <sup>(a)</sup>	Benzene Capacity Within 100 Miles of Large City	
					Number of Plants	Capacity <sup>(a)</sup>
Benzene (Cat.-Ref.)	Texas City, TX	Houston (30)	Amoco	623	34	10242
Benzene (Py. Gas.)	Taft, LA	New Orleans (20)	Union Carbide	513	7	1663
Benzene (Toluene)	Corpus Christi, TX	Corpus Christi	Coastal St. Gas	513	9	1614
Ethylbenzene	Baton Rouge, LA	Baton Rouge	Foster Grant	720	3	1730
Cumene	Philadelphia, PA	Philadelphia	Gulf Oil	360	5	1499
Nitrobenzene	New Martinsville, WV	Wheeling (20)	Mobay	88	6	402
Chlorobenzene	Midland, MI	Midland	Dow	285	4	701
Detergent Alkylate	Richmond, CA	San Francisco (10)	Chevron	107	1	107
Cyclohexane	Sweeny, TX	Houston (50)	Phillips Pet.	80	34	10242
Maleic Anhydride	St. Louis, MO	St. Louis	Monsanto	141	4	550

(a) Capacity figures given in millions of pounds.

TABLE 8. BENZENE SAMPLING LOCATIONS

Company	Location	Process/Product
Petro-Tex	Houston, TX <sup>(a)</sup>	Maleic anhydride from benzene
Union Carbide	Taft, LA	Benzene from pyrolysis gas
Chevron	Richmond, CA	Detergent alkylate from benzene
Mobay	New Martinsville, WV	Nitrobenzene from benzene
Gulf Oil	Philadelphia, PA	Cumene from benzene
Ashland	Neal, WV <sup>(a)</sup>	Maleic anhydride from benzene
U.S.Steel	Clairton, PA <sup>(a)</sup>	Coke ovens

(a) Selected at recommendation of Sponsor.

#### Analysis of the Air Monitoring Data

During the benzene sampling exercises, data were gathered for several meteorological parameters which were expected to help explain the benzene concentrations measured around the different plants. These parameters were wind speed, wind direction, temperature, cloud cover, and weather type. The last two parameters in combination with wind speed and time of day provided an estimate of atmospheric stability. Temperature can be related to evaporation rate. Wind speed can be used to estimate dilution as well as rate of transport. Calm conditions indicate a potential buildup of emissions in the vicinity of the source. Wind direction is an indicator of the direction from which the benzene came to the monitor.

In analyzing the benzene sampling data with relation to these meteorological conditions, the most striking observation was the number of benzene measurements which appeared to have little or no relation to the meteorological parameters. The conclusion was that some of the most notable benzene measurements were the result of sources other than the one being monitored or of a marked change in the emission rate of the source under observation. High benzene concentrations were obtained in grab samples when the wind was not blowing from the Chevron plant. A local transitory source was indicated. High concentrations measured to the north of Petro-Tex when

the wind was from a northerly direction pointed to a large stationary source of benzene to the north of the plant site. There was a marked rise in the benzene measured at all four monitors around the Gulf Oil Company during a nighttime sampling period. One possible explanation for this phenomenon would be a sharp increase in emissions from the source company or one of its neighbors.

Analyses of the monitoring results from each of the plants are discussed in the following sections. In some of these analyses, estimates are made of maximum benzene concentrations. For these estimates, considerable use was made of the nomograms (Figures 8 and 9) in Turner's Workbook of Atmospheric Dispersion Estimates.<sup>(6)</sup> It was assumed that the effective height of emission of benzene from the plants was 15 to 20 meters which would correspond to a height greater than the height of large storage tanks, one of the principal sources of escaping benzene. As shown by Turner's Figure 3-9, the magnitude of the maximum  $\chi u/Q^*$  for these heights is relatively uniform for different atmospheric stabilities, while the distance from the source at which the maximum concentration will occur varies by a factor of 10. Thus, if the wind speed does not change, the major result of a change in atmospheric stability is that the distance from the source to the point of maximum benzene downwind will change. The concentration will remain approximately constant.

Turner's Figure 3-5 provides an estimate of the ratio of the maximum benzene concentration and the concentration at some other downwind point.

Thus, from the information in these two nomograms and the field observations, an estimate can be made of the maximum concentration and the point at which it occurs. It is assumed that no chemical transformation of the benzene takes place within the distance from the source to the monitors.

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\*  $\chi$  = ambient concentration;  $u$  = wind velocity; and  $Q$  = source strength.

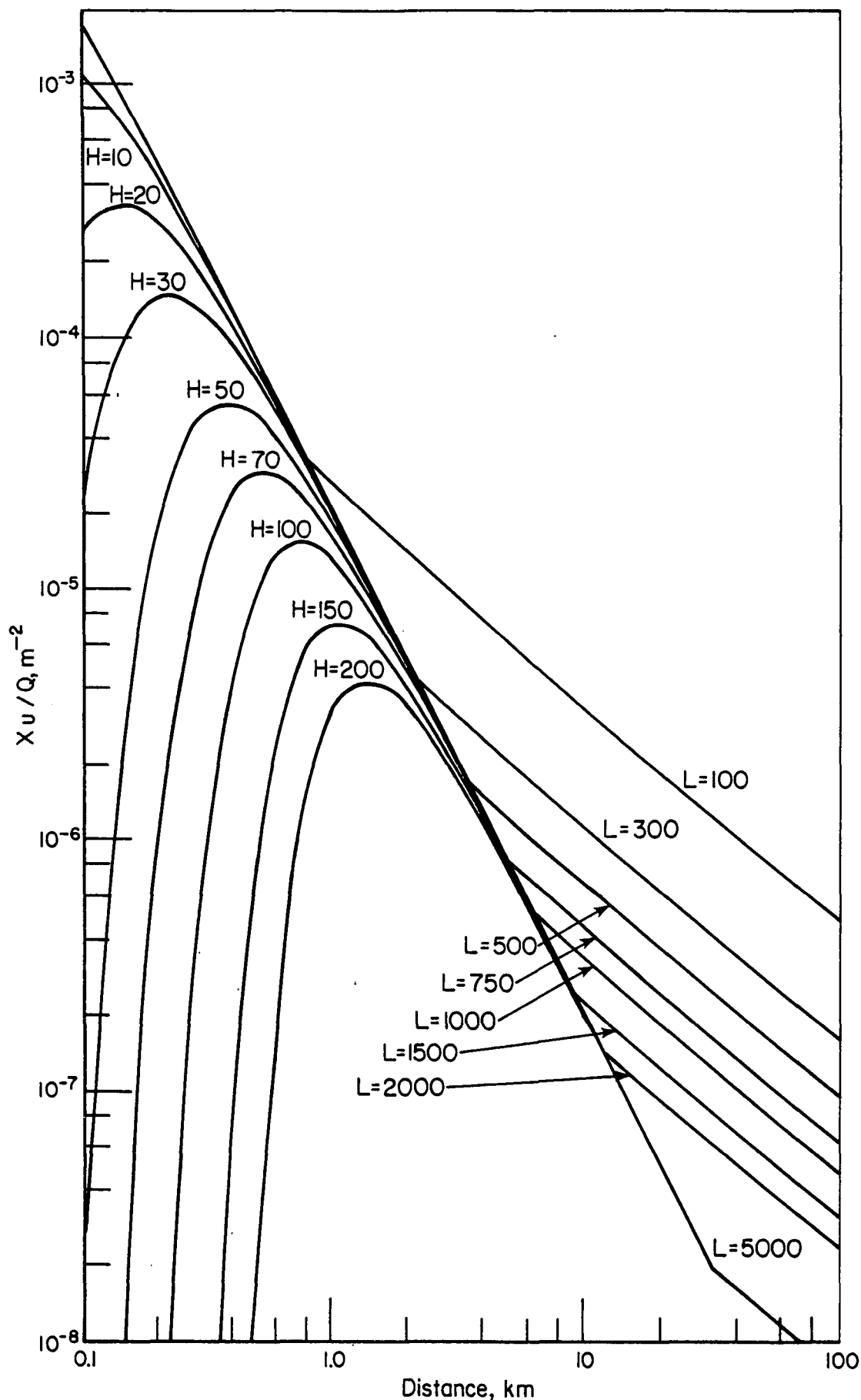


FIGURE 8.  $x_u/Q$  WITH DISTANCE FOR VARIOUS HEIGHTS OF EMISSION ( $H$ ) AND LIMITS TO VERTICAL DISPERSION ( $L$ ), B STABILITY

Source: Figure 3-5B from Turner, D.B., Workbook of Atmospheric Estimates.



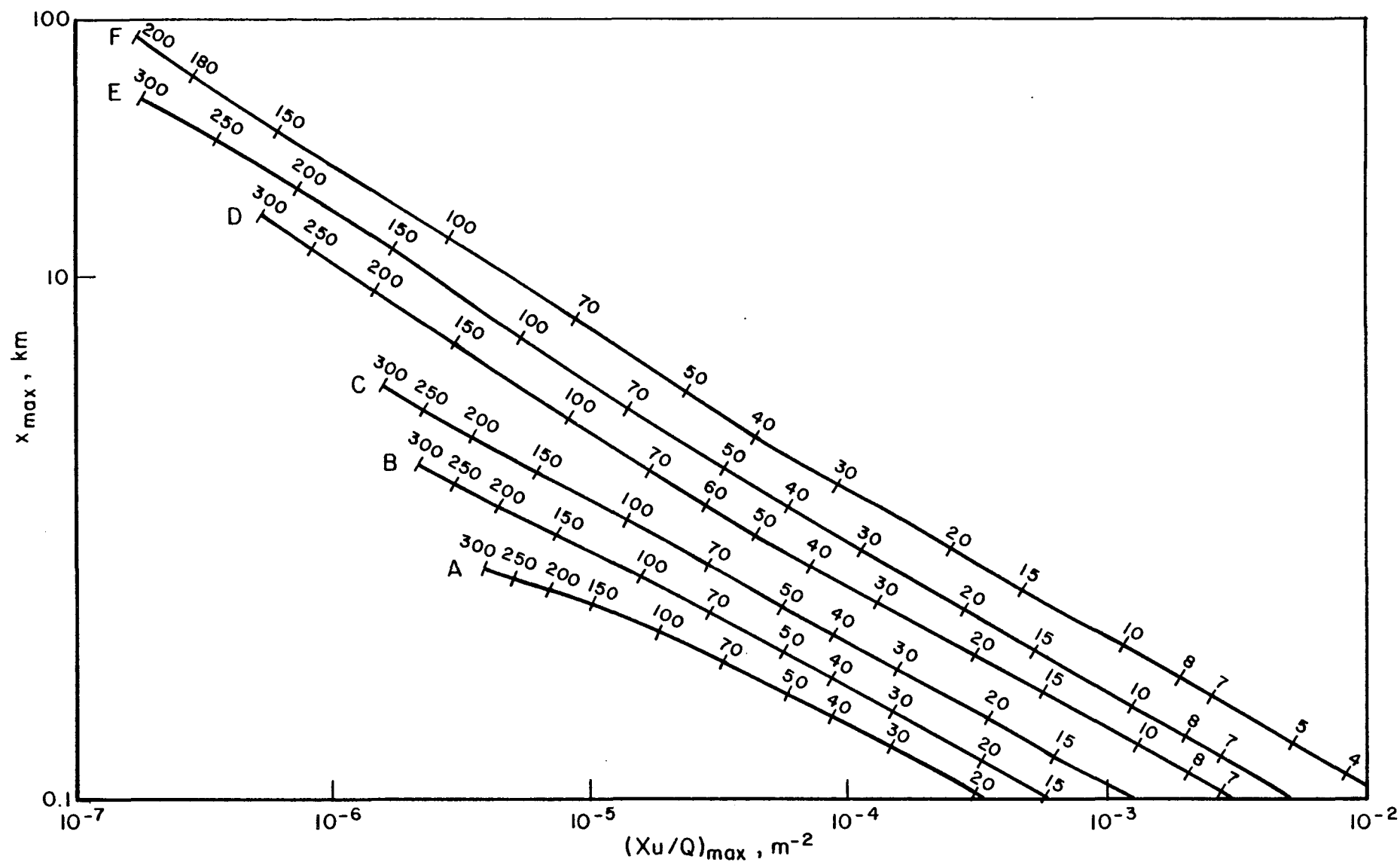


FIGURE 9. DISTANCE OF MAXIMUM CONCENTRATION AND MAXIMUM  $x_u/Q$  AS A FUNCTION OF STABILITY (CURVES) AND EFFECTIVE HEIGHT OF EMISSION (NUMBERS)

Source: Figure 3-9 from Turner, D.B., Workbook at Atmospheric Estimates.

### Analysis of Water and Soil Data

Water. Benzene levels in water ranged from <1 ppb to a high of 179 ppb, which was found in a plant effluent. In general, benzene in plant effluents quickly dispersed in rivers or streams to levels of 1 to 2 ppb or less.

Soil. The highest levels of benzene observed in the three environmental media were found in soil. Levels ranged from <2 ppb to a high of 191 ppb. These benzene levels in soil are to be expected; since soil is a natural adsorbent and benzene would accumulate through the process of absorption from air or water (rain). With one or two exceptions the highest levels of benzene were usually found in samples taken closest to the plant. Comparison of soil concentrations from different plants or even from different quadrants around one plant is restricted by the differences in soils.

### Mobay Chemical Company -- November, 1976

The benzene monitoring sites for the Mobay Chemical Company nitrobenzene plant at New Martinsville, West Virginia, are shown in Figure 10. Results for air, water, and soil samples are given in Tables 9 and 10.

During the air sampling period at this plant, there were no occasions when the wind blew directly toward a monitoring site during an 8-hour integrated sampling period. During the first 8-hour sample (noon to evening), the winds were relatively strong (4.4-7.5 m/sec) and from the west. In the second period (evening to before sunrise), conditions were calm with a temperature inversion indicated.

The maximum measured benzene concentration was  $18.7 \mu\text{g}/\text{m}^3$ , observed during the calm period at the monitoring site closest to the plant fence. The lowest concentration ( $1.2 \mu\text{g}/\text{m}^3$ ) was observed during a period of strong winds at the site farthest from the plant. The second highest measurement ( $14.1 \mu\text{g}/\text{m}^3$ ) was observed when the wind was blowing in the general direction of one of the monitors but not directly toward it.

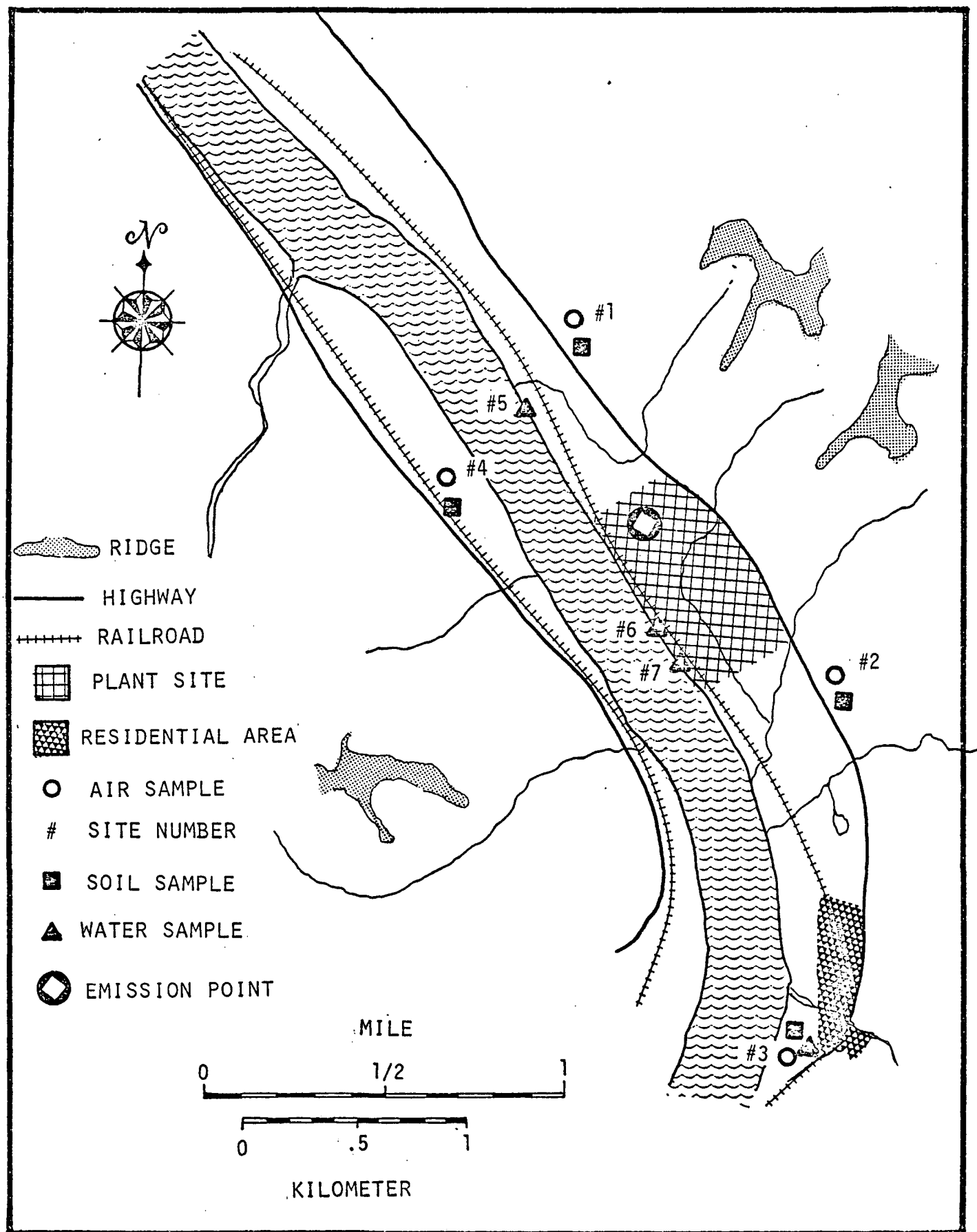


FIGURE 10. BENZENE MONITORING SITES AT MOBAY CHEMICAL COMPANY

TABLE 9. ANALYTICAL DATA FOR AIR SAMPLES FROM MOBAY CHEMICAL COMPANY

Sampling Station	Wind		Weather Conditions		Sampling Period	Benzene Analysis	
	Direction	Speed, m/sec	Temp. Range, F	General		ppb (v/v)	µg/m <sup>3</sup> (a)
1	270 <sup>0</sup>	4.4-7.5	37-60	Clear-dry front passed through	11/19/76 1110-1925	1.3	3.4 (2.7-4.4)
	--	Calm	28-37	Clear and still	11/19/76 1945-0525	3.7	9.9 (8.6-11.5) (3)
	225 <sup>0</sup>	3.5-4.8	28-43	Calm-sl haze	11/20/76 0545-1120	5.2	14.1 (12.0-16.5)(3)
					24 hour average	4	11
2	270 <sup>0</sup>	4.4-7.5	37-60	Clear-dry front passed through	11/19/76 1200-2015	2.8	7.6 (6.5-8.9) (3)
	--	Calm	28-37	Clear and still	11/19/76 1230-0555	7.0	18.7 (14.5-24.0)
	225 <sup>0</sup>	3.5-4.8	28-43	Haze to clear and bright	11/20/76 0615-1210	2.8	7.5 (5.8-9.7)
					24 hour average	4	11
3	270 <sup>0</sup>	4.4-7.5	37-60	Dry front passage	11/19/76 1400-2200	0.4	1.2 (0-1.6)
	--	Calm	28-37	Clear and still	11/19/76 2210-0635	1.2	3.3 (2.8-4.0) (2)
	225 <sup>0</sup>	3.5-4.8	28-43	--	11/20/76 0647-1410	1.3	3.4 (2.7-4.4)
					24 hour average	1	3
4	279 <sup>0</sup>	4.4-7.5	37-60	Clear-dry front passed through	11/19/76 1525-2245	1.4	3.8 (2.9-4.9)
	--	Calm	28-37	Clear and still	11/19/76 2300-0815	3.0	8.1 (6.3-10.5)
	225 <sup>0</sup>	3.5-4.8	28-43	Haze to bright and clear	11/20/76 0835-1525	1.2	3.2 (2.5-4.1)
					24 hour average	2	5

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

TABLE 10. ANALYTICAL DATA FOR WATER AND SOIL SAMPLES  
FROM MOBAY CHEMICAL COMPANY

Sampling Station	Benzene Analysis, ppb <sup>(a)</sup>		
	Water		Soil
1	--		2 (1.6-2.6)
2	--		Not analyzed
3	Ohio River, downstream:		
	surface	3.3 (2.6-4.3)	51 (40-66)
	6-ft depth	4.9 (3.8-6.3)	
4	--		17 (13-22)
5	Ohio River, upstream:		
	surface	12.0 (9.3-15.4)	--
	6-ft depth	11.9 (9.2-15.3)	--
6	Plant Influent	4.2 (3.3-5.4)	--
7	Plant Effluent	104. (81-134)	--

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

This plant lies in a deep vally; thus the only opportunity for the benzene to escape from the area is with winds up or down the Ohio River. The 24-hour average concentrations ranged from  $3 \mu\text{g}/\text{m}^3$  (1 ppb) to  $11 \mu\text{g}/\text{m}^3$  (4 ppb), with  $48.7 \mu\text{g}/\text{m}^3$  (7 ppb) representing the peak concentration observed during a calm 18-hour period.

Water samples were obtained upstream and downstream from the plant and in the plant influent and effluent. The higher level in the upstream as opposed to the downstream sample is very possibly due to a contribution from the PPG plant upstream of Mobay which manufactures chlorobenzene from benzene. This same contribution could also account for the Mobay plant influent having a benzene concentration of 4.2 ppb.

The benzene concentrations found in soil ranged from 2 to 51 ppb. The highest level found at this location was at the site most distant from the plant.

#### Gulf Oil Corporation -- December, 1976

The benzene monitoring sites for the Gulf Oil Corporation cumene plant at Philadelphia, Pennsylvania, are shown in Figure 11. Air, water, and soil samples were obtained, and the results are given in Tables 11 and 12.

Three integrated air samples varying from 7 to 21 hours were taken at sites in each of the four quadrants around the plant site. During the first sampling period, winds were generally from the south-southwest or southwest directions ( $202.5^\circ - 225^\circ$ ) away from Site No. 3 and toward Site No. 1. This correlates with the benzene concentrations being twice as high at Site No. 1 as at Site No. 3. Winds were light during this period (1-3 meters/second) and thus the plume rise would be expected to be greater than at higher speeds. These light speeds would also mean little dilution and a small distance traveled from the source. It is probable that the atmosphere was neutrally stable and that dispersion was relatively good.

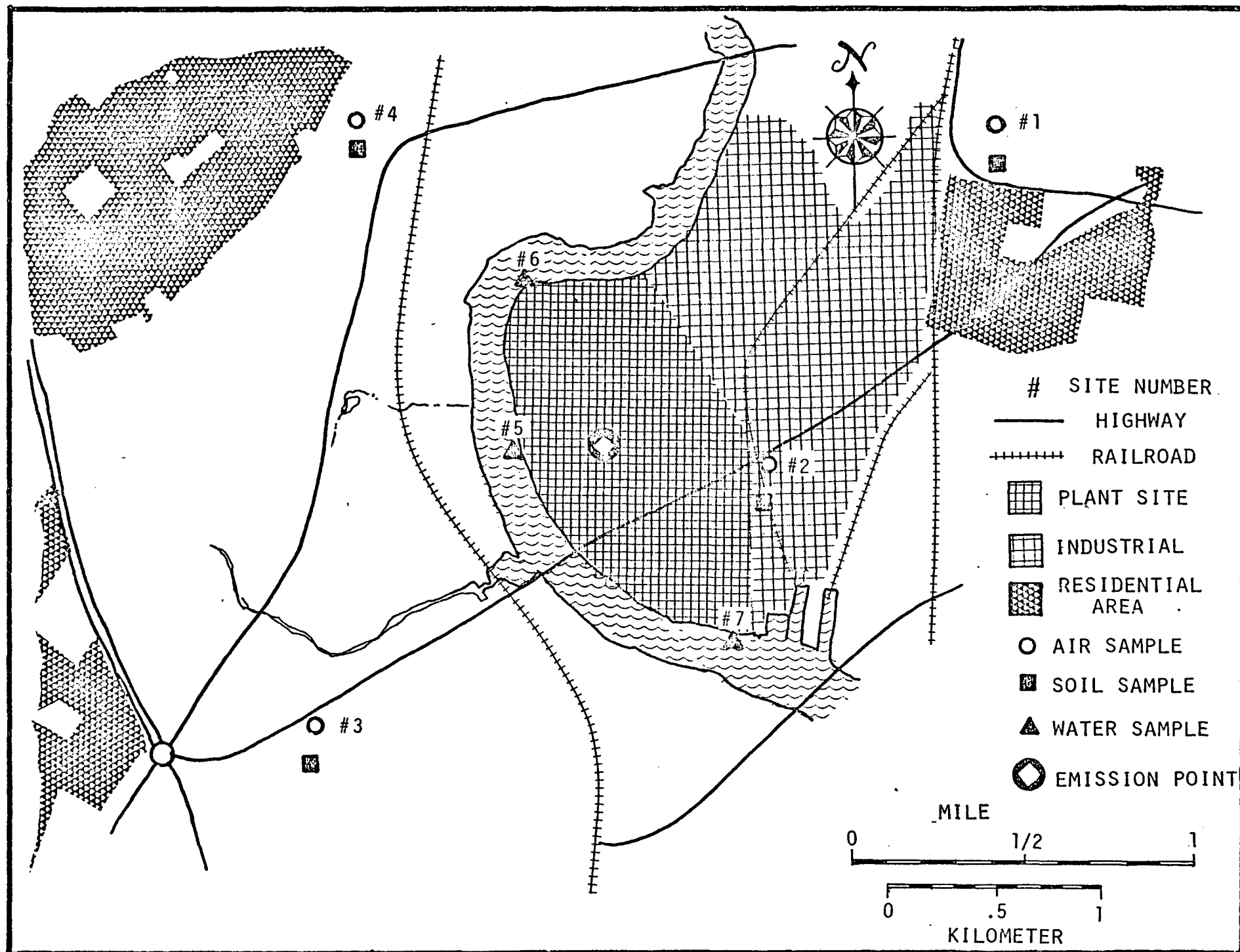


FIGURE 11. BENZENE MONITORING SITES AT GULF OIL COMPANY

TABLE 11. ANALYTICAL DATA FOR AIR SAMPLES FROM GULF OIL CORPORATION

Sampling Station	Weather Conditions				Sampling Period	Benzene Analysis	
	Wind Direction	Wind Speed, m/sec	Temp. Range, F	General		ppb (v/v)	μg/m <sup>3</sup> (a)
1	202.5 <sup>0</sup>	1.8	34-42	Overcast	12/15/76 0900-1620	9.1	24.4 (18.9-31.4)
	202.5 <sup>0</sup>	1.8	42-40	Partly cloudy	12/15/76 1620-1300	34.8	93.5 (78.0-112.0)(2)
	45 <sup>0</sup>	0.1	40-40	Partly cloudy	12/16/76 1300-2103	10.7	28.8 (22.4-37.1)
					24 hour average	19	51
2	202.5 <sup>0</sup>	1.0	34-40	--	12/15/76 0957-1720	1.2	3.1 (2.4-4.0)
	202.5 <sup>0</sup>	0.5	40-30	Partly cloudy	12/15/76 1720-0130	19.4	52.2 (40.6-67.4)
	45 <sup>0</sup>	0.01	30-40	Partly cloudy-overcast	12/16/76 0130-1023	9.7	26.1 (20.2-33.6)
					24 hour average	10	28
3	202.5 <sup>0</sup>	1.01	40	Partly sunny	12/15/76 1053-1920	5.4	14.5 (11.3-18.7)
	Calm	--	40	Overcast	12/15/76 1920-0220	20.5	55.0 (45.2-65.9)(2)
	Calm	--	40	Overcast	12/16/76 0220-1520	11.2	30.2 (23.4-88.9)
					24 hour average	12	31
4	225 <sup>0</sup>	3	42-40	--	12/15/76 1130-2018	7.4	20.0 (15.5-25.8)
	Calm	--	40-40	Cloudy	12/15/76 2018-0300	14.4	38.7 (30.1-50.0)
	45 <sup>0</sup>	0.9	40-44	--	12/16/76 0390-1138	7.4	19.8 (15.4-25.5)
					24 hour average	9	25

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.



TABLE 12. ANALYTICAL DATA FOR WATER AND SOIL SAMPLES  
FROM GULF OIL CORPORATION

Sampling Station	Benzene Analysis, ppb <sup>(a)</sup>		
	Water		Soil
1	--		34 (27-44)
2	--		<u>≥</u> 73 <sup>(b)</sup>
3	--		18 (14-23)
4	--		<u>≥</u> 34 <sup>(b)</sup>
5	Wastewater treatment unit: outfall	4.3 (3.3-5.4)	--
	from pump	56.6 (43.9-72.9)	--
6	River	1 (0-1.3)	--
7	Gulf Dock	1.9 (1.5-2.4)	--

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

(b) Sample not heated; so this is a minimum value.

In the second sampling period which was primarily during nighttime hours, calm conditions or very light winds prevailed. The sky was partly cloudy to overcast; therefore, if there was a temperature inversion, it was not a strong one. Benzene concentrations rose sharply at all monitoring sites increasing from 3 to 15 times above their values for the first sampling period.

In the third sampling period, the wind speeds picked up very slightly and the direction was generally from the northeast. In agreement with this shift, the benzene concentration at Site No. 3 to the southwest was slightly greater than the concentrations at the other sites. Concentrations in all quadrants dropped between the second and third periods but were rather uniform throughout the area. This may have been the result of the calm conditions during Period No. 2 when the benzene probably formed a stationary cloud over the area. When the wind picked up, this cloud plus the new emissions from the source moved toward the southwest.

Considering that wind speeds were relatively light throughout the three sampling periods, the low benzene concentrations measured at Site No. 2 during Period 1 is surprising. It is the site closest to the refinery. While the wind did not blow directly toward this site, the benzene concentration was markedly lower than at Site No. 3 which was upwind of the refinery. It is possible that there is enough plume rise so that the benzene plume passes above Site No. 2. This explanation loses some validity when it is recalled that the benzene concentrations were high at Site No. 2 during Periods 2 and 3 which had even lighter winds.

The benzene concentrations in water samples obtained from the river were only 1 to 2 ppb. Higher concentrations were found in water from the plant wastewater treatment unit.

The benzene levels in soil were the highest of the three media, and the highest level was found closest to the plant.

Petro-Tex Corporation -- July, 1977

Figure 12 shows the benzene monitoring sites for the Petro-Tex Corporation maleic anhydride plant at Houston, Texas. The analytical data for the air, water, and soil samples are given in Tables 13 and 14.

Winds were light (0-1.59 m/s) and variable in direction during the entire air sampling period at the Petro-Tex plant. Benzene concentrations measured by the 8-hour integrating samplers ranged from 6.9 to 44.0  $\mu\text{g}/\text{m}^3$ . The highest of these 8-hour concentrations was observed at Site No. 3 located about 0.5 km northeast of the plant. It was measured in the third period during daytime hours when the winds were calm to 0.5 m/sec.

In the sampling Period #2 from 0300 to 1115, the benzene concentration was only slightly smaller (39.1  $\mu\text{g}/\text{m}^3$ ). During this night-to-midday period the winds were similar to those in the following period, but the atmosphere was more stable. It is possible that there was a cloud of benzene from the Petro-Tex plant and the winds dispersed it or carried it aloft during either Period #2 or #3. The central portion of the plume downwind of the plant had benzene concentrations of about 45  $\mu\text{g}/\text{m}^3$ .

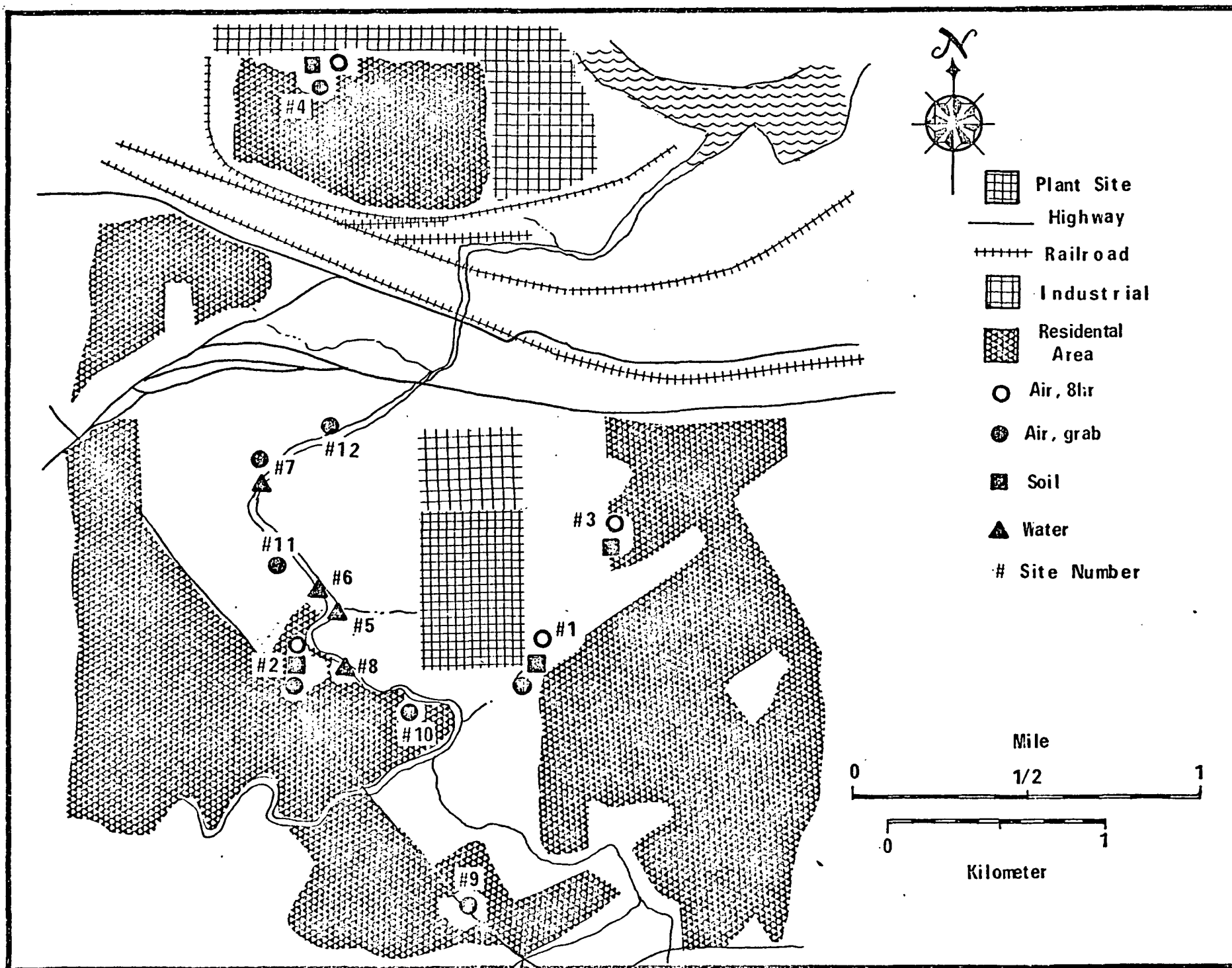


FIGURE 12. BENZENE MONITORING SITES AT PETRO-TEX CORPORATION

TABLE 13. ANALYTICAL DATA FOR AIR SAMPLES FROM PETRO-TEX CORPORATION

Sampling Station	Weather Conditions				Sampling Period	Benzene Analysis	
	Wind		Temp. Range, F	General		ppb (v/v)	μg/m <sup>3</sup> (a)
	Direction	Speed, m/sec					
<u>Continuous Monitoring Stations</u>							
1	180 <sup>0</sup> -calm	0.48-calm	58-37	Clear	1/20/77 1650-0210	3.9	10.6 (8.2-13.7)
	Calm-225 <sup>0</sup>	Calm-0.48	37-67	Partly cloudy	1/21/77 0210-1040	9.0	24.3 (18.9-31.3)
	225 <sup>0</sup> -190 <sup>0</sup>	0.48-1.45	67-57	Sunny	1/21/77 1040-1532	3.4	9.3 (7.8-11.1) (2)
	24 hour average					6	15
2	Calm	0.48-0	57-39	Clear	1/20/77 1605-0100	2.6	7.0 (5.4-9.0)
	Calm-90 <sup>0</sup>	0-1.45	37-59	Partly cloudy	1/21/77 0100-0845	9.1	24.5 (20.1-29.7) (2)
	90 <sup>0</sup> -calm	1.45-0	59-50	Clear	1/21/77 0805-1615	6.2	16.6 (13.7-20.2) (2)
	24 hour average					8	22
3	Calm	0.97-0	50-39	Clear	1/20/77 1810-0300	4.5	12.0 (9.3-15.4)
	Calm-225 <sup>0</sup>	0-0.48	39-62	Partly cloudy	1/21/77 0300-1115	14.5	39.1 (30.4-50.5)
	225 <sup>0</sup> -calm	0.48-0	62-50	Clear	1/21/77 1115-1830	16.4	44.0
	24 hour average					11	31
4	225 <sup>0</sup> -calm	1.45-0	50-39	Sunny	1/20/77 1935-0355	6.6	17.7 (14.6-21.2) (2)
	Calm-315 <sup>0</sup>	0-0.97	39-78	Partly cloudy	1/21/77 0355-1200	3.2	8.6 (6.7-11.1)
	315 <sup>0</sup> -135 <sup>0</sup>	0.97-0.48	78-51	Clear	1/21/77 1200-1935	3.1	6.9 (5.3-8.9)
	24 hour average					4	11
<u>Grab Samples</u>							
1	Calm	0	38	Partly cloudy	1/21/77 0225-0245	5.2	13.9 (10.8-17.9)
2	135 <sup>0</sup>	0.48	62	Clear	1/21/77 0920-0940	10.5	28.1 (21.8-36.2)
	45 <sup>0</sup>	0.48	62	Rain	1/22/77 1530-1540	1.9	5.0 (3.9-6.5)
	90 <sup>0</sup>	1.59	57	Clear	1/22/77 1643-1703	0.2	0.45 (0-.6)
4	Calm	0	38	Partly cloudy	1/21/77 1540-1600	12.1	32.5 (25.2-41.8)
	67.5 <sup>0</sup>	1.45	50	Rain	1/22/77 1610-1620	21.2	57.0 (44.3-73.4)

TABLE 13. (Continued)

Sampling Station	Weather			General	Sampling Period	Benzene Analysis		
	Wind		Temp. Range, F			ppb (v/v)	µg/m <sup>3</sup> (a)	
	Direction	Speed, m/sec						
Grab Samples (Continued)								
7	30 <sup>0</sup>	0.44	50	Rain	1/22/77 1410-1430	9.2	24.6 (19.1-31.7)	
	45 <sup>0</sup>	0.48	50	Rain	1/22/77 1500-1510	8.1	21.9 (17.0-28.2)	
9	Calm	0	38	Partly cloudy	1/21/77 0140-0154	3.2	8.6 (6.7-11.1)	
10	Calm	0	38	Partly cloudy	1/21/77 1256-1310	2.2	5.8 (4.5-7.5)	
11	135 <sup>0</sup>	0.43	62	Sunny	1/21/77 1100-1120	7.9	21.3 (16.5-27.4)	
12	Calm	0	78	Partly cloudy	1/21/77 1330-1350	2.6	6.9 (5.3-8.9)	

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

TABLE 14. ANALYTICAL DATA FOR WATER AND SOIL SAMPLES  
FROM PETRO-TEX CORPORATION

Sampling Station	Benzene Analysis, ppb <sup>(a)</sup>		
	Water		Soil
1	--	--	22 (17-28)
2	--	--	Not analyzed
3	--	--	Not analyzed
4	--	--	Not analyzed
5	Plant outfall	8 (6.2-10.3)	--
6	Midway	13.0 (10.1-16.7)	--
7	Upstream	<1	--
8	Downstream of outfall	2 (1.6-2.6)	--

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

Two of the grab samples from Site No. 2 were taken with a light wind blowing from the source toward this site which is one kilometer away. Nevertheless, the concentrations that were measured there were the lowest observed during the entire sampling period ( $0.45 \mu\text{g}/\text{m}^3$  and  $5.0 \mu\text{g}/\text{m}^3$ ). There are several possible reasons for these low readings including: (1) light winds and large plume rise caused the plume to pass over this site, (2) winds taken during these grab samples were too light and did not persist long enough to bring the benzene to the site, (3) the rain removed the benzene from the plume, or (4) the vegetation in the park setting of this site removed the benzene. There is at least one other reading taken during the Petro-Tex sampling that was made under similar conditions, but which had a higher benzene concentration.

A reading that might have been selected as a background because the wind was directed toward the plant occurred at Site No. 4 on January 22, 1977. However, instead of being a low concentration, it was the highest ( $57.0 \mu\text{g}/\text{m}^3$ ). A possible explanation of this reading is that it was the result of benzene being blown in from the refinery complex which is on the other side of the Houston Ship Channel.

In the water samples, a benzene concentration of 13 ppb was found in the stream near the plant outfall. The concentration measured in the outfall itself was 8 ppb. Downstream of the outfall, the concentration was down to 2 ppb.

A concentration of 22 ppb of benzene was found in a soil sample taken near the plant. This is the only soil sample which was analyzed.

#### Chevron Corporation -- January, 1977

The sites for benzene monitoring near the Chevron Corporation detergent alkylate plant at Richmond, California, are shown in Figure 13. The results for air, water, and soil samples are given in Tables 15 and 16.



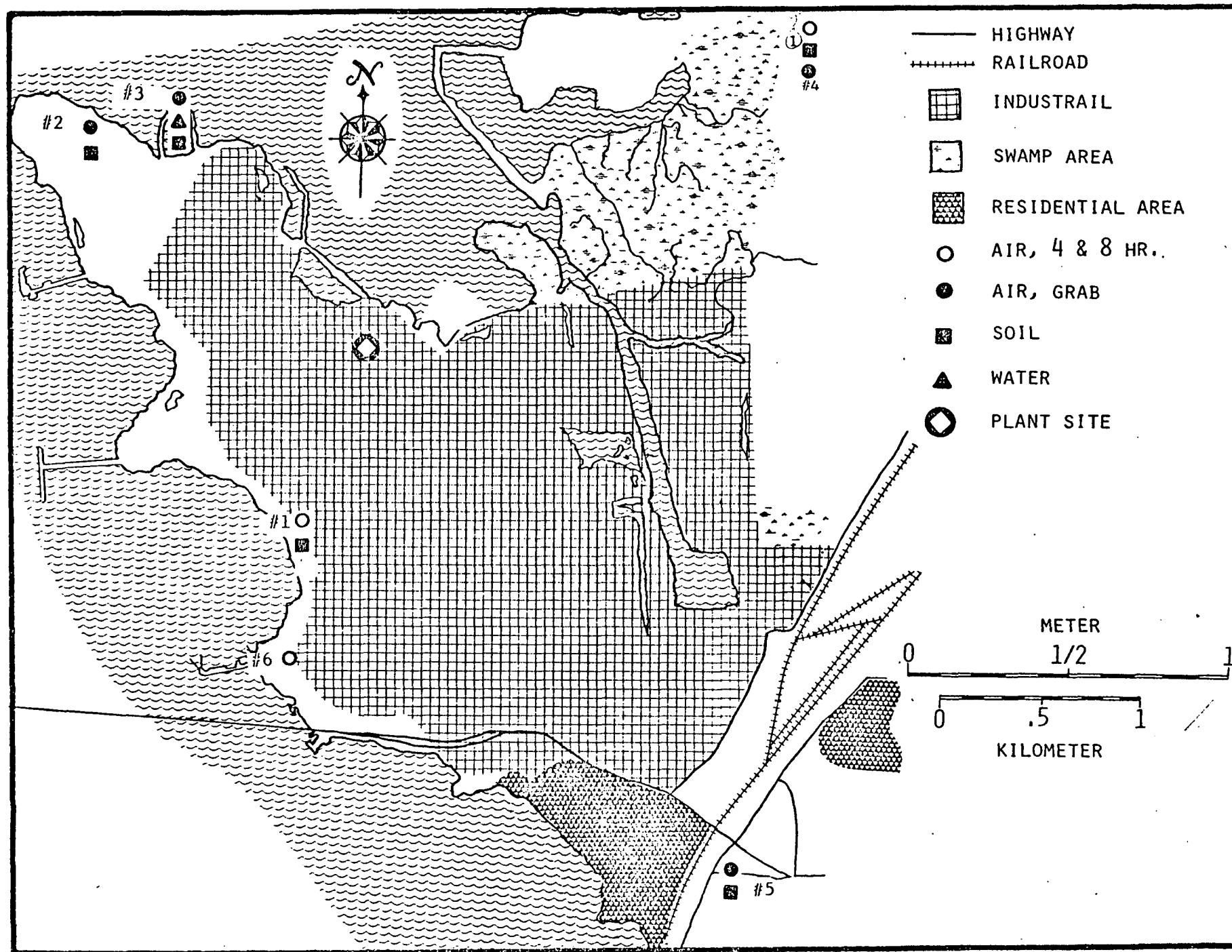


FIGURE 13. BENZENE MONITORING SITES AT CHEVRON, INC.

TABLE 15. ANALYTICAL DATA FOR AIR SAMPLES FROM CHEVRON CORPORATION

Sampling Station	Weather Conditions <sup>(a)</sup>			Sampling Period	Benzene Analysis	
	Wind		Temp. Range, F		ppb (v/v)	μg/m <sup>3</sup> (b)
	Direction	Speed, m/sec				
<u>Continuous Monitoring Stations</u>						
1	180-360 <sup>o</sup>	1.1-1.5	49-52	1/4/77 1345-1750	3	7.3 (6.1-8.8)(2)
	60-180	0.2-0.7	41-48	1/4/77 1840-2240	2	3.9 (3.3-4.7)(2)
4	60-180 <sup>o</sup>	1.6-4.1	42-45	1/5/77 0820-1620	1	3.0 (2.5-3.6)(2)
6	60-180 <sup>o</sup>	1.6-4.1	42-45	1/5/77 0900-1700	3	6.8 (5.7-8.1)(2)
<u>Grab Samples</u>						
2	240 <sup>o</sup>	1.1	54	1/4/77 1515-1535	1	2.7 (2.1-3.5)
	180	2.1	46	1/5/77 1012-1032	1	3.5 (2.7-4.5)
	110	4.1	49	1/6/77 1337-1357	1	2.9 (2.2-3.7)
	90	3.7	47	1/5/77 1400-1420	1	3.0 (2.3-3.9)
3	240 <sup>o</sup>	1.2	52	1/4/77 1630-1650	18	55.4 (43.0-71.4)
	180	2.1	46	1/5/77 1043-1103	8	25.9 (19.7-32.8)
	90	3.7	47	1/5/77 1431-1451	1	3.1 (2.4-4.0)
	90	3.7	47	1/5/77 1454-1514	1	3.0 (2.3-3.9)
4	180 <sup>o</sup>	1.1	49	1/5/77 1745-1805	3	8.9 (6.9-11.5)
5	180 <sup>o</sup>	0.7	48	1/4/77 1835-1855	6	18.7 (14.5-24.0)
	60	1.6	45	1/5/77 0925-0945	12	36.8 (28.6-47.4)

(a) General: sunny with a few light clouds. No precipitation during sampling period. Winds variable to highly variable.

(b) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

TABLE 16. ANALYTICAL DATA FOR WATER AND SOIL SAMPLES  
FOR CHEVRON CORPORATION

Sampling Station	Benzene Analysis, ppb <sup>(a)</sup>		
	Water		Soil
1	--		Not analyzed
2	--		191 (159-229)(2)
3	Yacht basin	<1	70 (54-90)
4	--		51 (40-66)
5	--		<u>&lt;148</u> <sup>(b)</sup>
7	Municipal water	<1	--

(a) The numbers in parentheses are the 95 percent confidence limits determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

(b) Sample is not heated; so this is a minimum value.

The large size of this plant and its location on a peninsula prevented air samples being taken any closer than 1 kilometer from the benzene source. One set of grab samples was made as far away as 3 kilometers from the benzene source. Winds were variable in direction during the sampling at all the sites. They ranged from light to moderate in speed. Two long periods of calm winds occurred during the monitoring.

There were several instances when benzene measurements were made at sites upwind of the plant's benzene source. One of these was the grab sample taken at Site No. 3. This was the highest observed concentration and suggests the possibility that the observed benzene did not originate at the Chevron benzene source but was produced by a source near the monitoring site. The other high readings (25.5, 36.8, and 18.7  $\mu\text{g}/\text{m}^3$ ) were also not observed downwind of the suspected benzene sources. If there are no other benzene sources in the area, the answer for these high readings would have to be a complicated trajectory.

One grab sample measurement taken at Site No. 2 with a 4.1 m/sec wind blowing from  $110^\circ$  is a possible example of a downwind sample. Site No. 2 was 1.9 km away from the suspected benzene source. The wind speed, cloud cover, and time of day indicated a B-type atmospheric stability. With B stability and an effective emission height of 15-20 meters, the maximum concentration would occur between 0.1 and 0.14 km downwind according to Turner's Figure 3-9. His nomogram for B stability (Figure 3-5B) shows that the ratio between the maximum concentration at 0.14 km and the concentration at 1.9 km would be:

$$\frac{x_1 \mu/Q}{x_2 \mu/Q} = \frac{x_1}{x_2} = \frac{3.5 \times 10^{-4}}{5 \times 10^{-6}} = 70.$$

The benzene concentration observed at Site No. 2 was 2.9  $\mu\text{g}/\text{m}^3$  so the expected maximum would be 243  $\mu\text{g}/\text{m}^3$  under this line of reasoning. The concentration 1 kilometer from the source (the property line) would be about 60  $\mu\text{g}/\text{m}^3$ . However, there is some doubt that this reasoning is correct. Four grab samples were taken at Site No. 2 at different times for different wind speed and direction conditions. The readings varied from 2.7 to 3.5  $\mu\text{g}/\text{m}^3$ . These observations could be interpreted as a local source effect, a background concentration, or a complicated trajectory.

Access to suitable water sampling sites was severely restricted by the condition that we not sample on plant property. Without access via plant property, it was necessary to obtain water samples about 1 to 1-1/2 miles from the plant discharge point into San Pablo Bay at the Yacht basin. Benzene levels in samples of brackish water and municipal water taken at this site were less than 1 ppb.

In view of the relatively low levels of benzene found in the air samples from this location, it is difficult to explain levels as high as 191 ppb of benzene being found in the soil samples. It is conceivable that the benzene may have come from a source other than the Chevron plant (old oil spills, gasoline spills, etc.).

Union Carbide Corporation -- January, 1977

The benzene monitoring sites for the Union Carbide Corporation benzene plant at Taft, Louisiana, are shown in Figure 14. Results of the air, water, and soil sampling are given in Tables 17 and 18.

Winds during the Union Carbide air sampling were light to moderate (0.2 to 3.8 m/s) and generally with a southerly component. Areas to the north of the plant were across the Mississippi River and were ruled out as sampling sites because of the lack of bridges or ferries across the river in this vicinity. Consequently, there were several measurements which can be considered as representative of background (0.6 to 2.9  $\mu\text{g}/\text{m}^3$ ). The others could give little information on maximum off-plant observations.

There is one phenomenon -- the sharp increase in benzene concentration during the 0200 to 1130 monitoring period at Sites 1 and 2 -- that does not appear explainable by changes in the weather parameters. This increase in ambient concentration may have been the result of an increase in emissions. If not, then a more detailed monitoring program will be required to determine causes of similar occurrences.

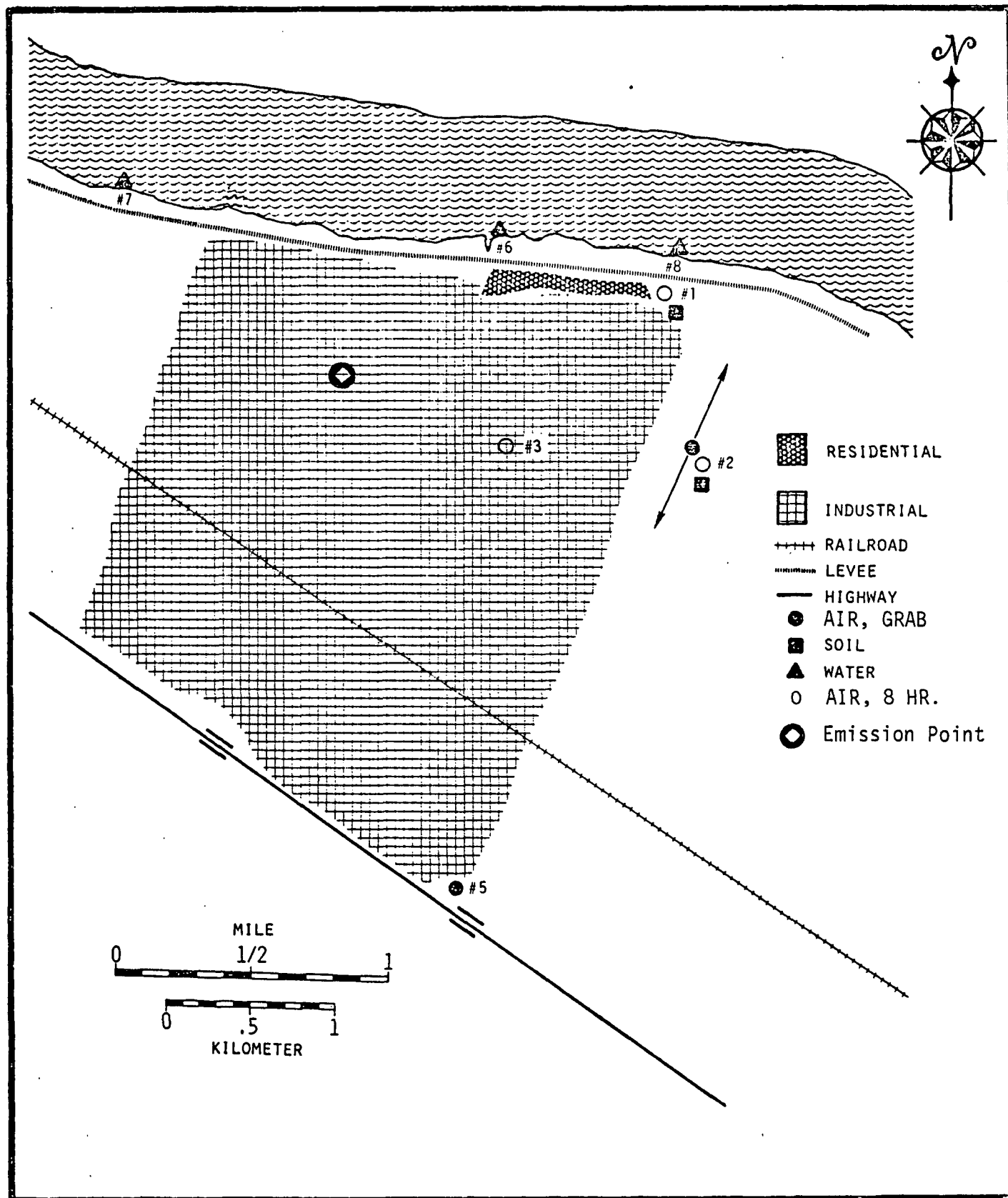


FIGURE 14. BENZENE MONITORING SITES AT UNION CARBIDE

TABLE 17. ANALYTICAL DATA FOR AIR SAMPLES FROM UNION CARBIDE CORPORATION

Sampling Station	Weather Conditions				Sampling Period	Benzene Analysis	
	Wind		Temp. Range, F	General		ppb (v/v)	μg/m <sup>3</sup> (a)
	Direction	Speed, m/sec					
Continuous Monitoring Stations							
1	202.5 <sup>o</sup>	1.5	48-54	Overcast	1/26/77 0945-1920	0.7	1.8 (1.5-2.1)(2)
	180 <sup>o</sup>	0.2	54-56	Overcast and int. rain	1/26/77 1920-0225	0.6	1.6 (1.3-1.9)(2)
	180 <sup>o</sup>	1.6	56-61	Partly cloudy w/mist and lt. fog	1/27/77 0225-1015	4.5	12.1 (10.1-14.5)(2)
					24 hour average	<u>2</u>	<u>6</u>
2	202.5 <sup>o</sup>	1.3	49-58	Overcast	1/26/77 1030-1955	2.6	7.0 (5.8-8.4)(2)
	135 <sup>o</sup>	0.6	58-54	Overcast	1/27/77 1955-0255	1.1	2.9 (2.4-3.5)(2)
	202.5 <sup>o</sup>	1.8	54-59	Partly cloudy	1/27/77 0255-1125	6.4	17.3 (14.4-20.7)(2)
					24 hour average	<u>4</u>	<u>9</u>
3	180 <sup>o</sup>	3.8	54	Overcast	1/26/77 1110-2025	12.8	34.4 (26.7-44.4)
	135 <sup>o</sup>	0.6	58-54	Partly cloudy	1/27/77 2025-0335	13.5	36.2 (28.1-46.5)
					16 hour average	<u>13</u>	<u>35</u>
Grab Samples							
5	180 <sup>o</sup>	1.4	58	Overcast	1/26/77 0346-0426	0.6	1.5 (1.2-1.9)
	157.5 <sup>o</sup>	1.5	55	Overcast	1/26/77 0923-1003	0.2	0.6 (0.0-0.8)
2 <sup>(b)</sup>	292.5 <sup>o</sup>	2.1	69	Partly cloudy	1/28/77 1111-1157	3.9	10.4 (8.1-13.4)
	292.5 <sup>o</sup>	2.1	69	Partly cloudy	1/28/77 2420-2430	2.4	6.4 (5.0-8.2)

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

(b) Traversed along line shown in Figure 14.

TABLE 18. ANALYTICAL DATA FOR WATER AND SOIL SAMPLES  
FROM UNION CARBIDE CORPORATION

Sampling Station	Benzene Analysis, ppb <sup>(a)</sup>		
	Water		Soil
1	--		12 (9.3-15.4)
2	--		14 (11-18)
6	Plant Effluent	179 (155-207)(3)	--
7	Mississippi River: upstream	2 (1.6-2.6)	--
8	Mississippi River: downstream	1 (0-1.3)	--

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.



Two grab samples in the vicinity of Site No. 2 were taken when this site was downwind of the suspected benzene source. The distance between this site and the source was about 2 km. A combination of the 2.1 m/sec wind speed, partly cloudy sky, and daytime conditions indicate a B-type atmospheric stability. Under these conditions, the maximum concentration is expected to have been within 0.2 km of the source (from Turner's Figure 3-9). Thus, it would have fallen on the plant property. Using the observed benzene concentration at Site No. 2 ( $10.4 \mu\text{g}/\text{m}^3$ ) and Turner's nomogram (Figure 3-5B), one can estimate that the maximum short-term concentration was on the order of  $700 \mu\text{g}/\text{m}^3$  on plant property and  $40 \mu\text{g}/\text{m}^3$  at the plant's fence line.

Water samples were obtained from the Mississippi River upstream and downstream from the plant and from the plant effluent. The benzene levels in the river were only 1 to 2 ppb though the concentration in the effluent was 179 ppb.

The benzene concentrations found in soil samples were 12 to 14 ppb.

#### U.S. Steel Corporation -- July, 1978

The benzene sampling sites for the U.S. Steel coke oven facility at Clairton, Pennsylvania, are shown in Figure 15. Site No. 1 was at 1035 Monongahela Avenue, at the south end of the Westinghouse Apartment Division. Site No. 1B was at the South Allegheny High School approximately a mile and one-half from the coke ovens and on a ridge above the coke ovens. Site No. 1A was at the Allegheny County Airport, and was generally downwind from the plant, but somewhat further removed (about 4 miles) from the coke ovens and on a ridge.

Site No. 2, at Belle Bridge, Pennsylvania, was generally out of the air plume crossing the coke ovens and was intended for background purposes. Sites 3 and 4, as shown in Figure 15, were at the Clairton Sewage Plant and the Clairton Auxiliary Police Stations, respectively. These two sites were the closest to the plant, but because of the variable wind direction were only periodically in the emission plume from the coke ovens.

Only air sampling was done at this location, and the results are given in Table 19.

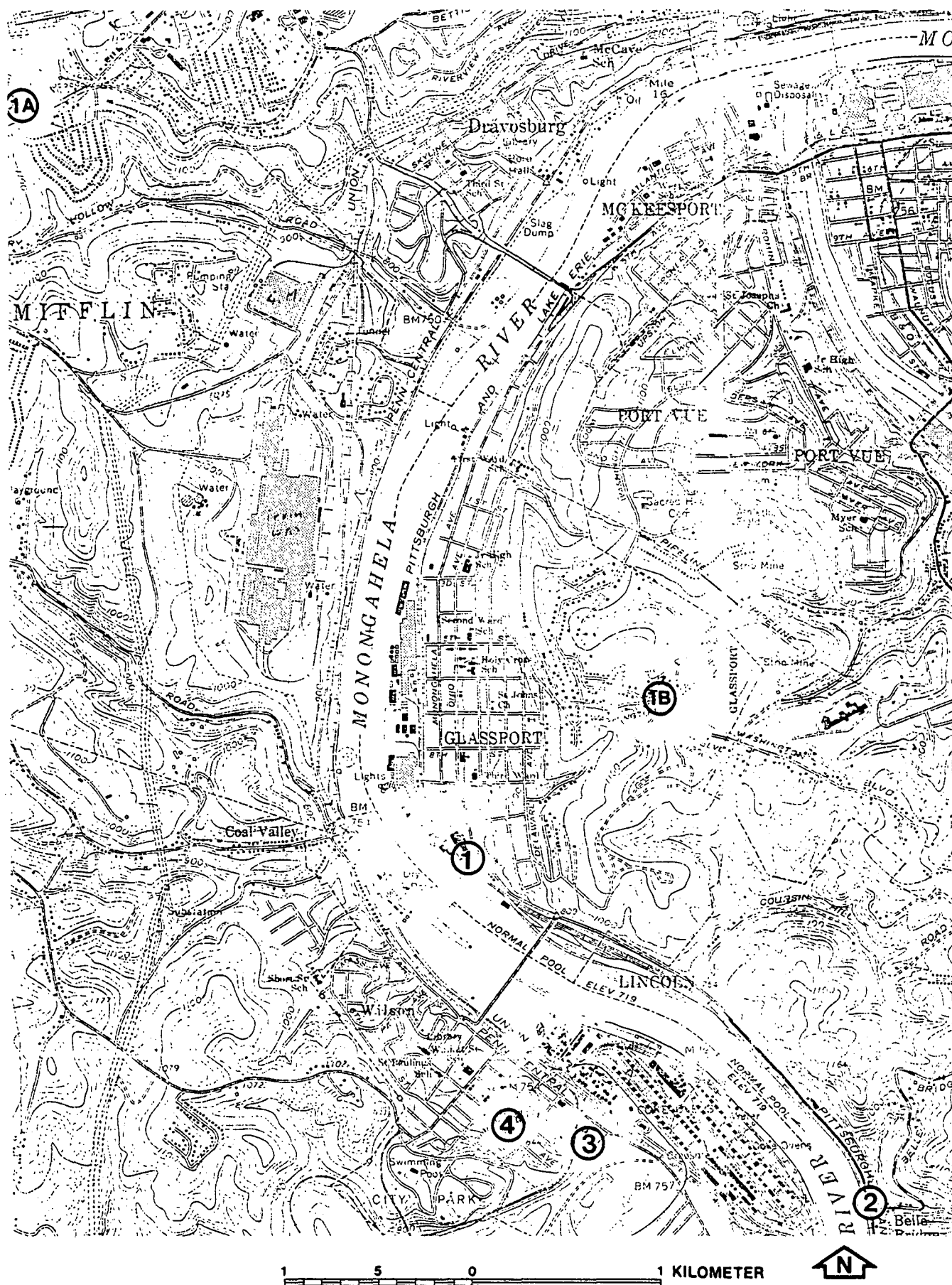


FIGURE 15. BENZENE MONITORING SITES AT U.S. STEEL

TABLE 19. ANALYTICAL DATA FOR AIR SAMPLES FROM U. S. STEEL CORPORATION

Sampling Station	Weather Conditions					General	Sampling Period	Benzene Analysis	
	Wind <sup>(a)</sup>		Temp. Range, F	Relative Humidity, percent	ppb (v/v)			μg/m <sup>3</sup> <sup>(b)</sup>	
	Direction	Speed, m/sec							
1A	110 <sup>0</sup> -180 <sup>0</sup>	1.6-4.1	77-73	31	Calm	7/12/78 1230-2103	2.0	6.5 (5.0-8.4)	
	110 <sup>0</sup> -180 <sup>0</sup>	1.6-4.1	73-62	--	Clear, calm	7/17/78 2103-0425	6.0	19.2 (14.9-24.8)	
	180 <sup>0</sup> -220 <sup>0</sup>	3.6-6.2	62-81	--	Partly sunny	7/13/78 0425-1323	2.3	7.3 (5.7-9.4)	
	24 hour average						3	10	
1B	110 <sup>0</sup> -180 <sup>0</sup>	2.1-4.1	64-82	43	Clear, calm	7/12/78 0957-1809	0.4	1.2 (0-1.6)	
	180 <sup>0</sup> -110 <sup>0</sup>	1.6-4.1	84-59	55	Clear	7/12/78 1809-0202	0.6	2.0 (1.6-2.6)	
1	340 <sup>0</sup> -90 <sup>0</sup>	1.8-2.5	70-82	--	Clear	7/12/78 1041-1835	2.3	7.5 (5.8-9.7)	
	90 <sup>0</sup> -180 <sup>0</sup>	1.2-2.2	79-58	--	Clear, calm	7/12/78 1835-0228	3.7	12.0 (9.3-15.4)	
	180 <sup>0</sup>	0.6-2.4	58-74	51	Clear, calm	7/13/78 0228-1039	12.9	41.5 (32.2-53.5)	
	24 hour average						6	19	
2	340 <sup>0</sup> -90 <sup>0</sup>	1.7-2.5	69-75	--	Clear, calm	7/12/78 1102-1911	0.7	2.4 (1.9-3.1)	
	90 <sup>0</sup> -180 <sup>0</sup>	1.3-1.7	75-56	--	--	7/12/78 1911-0251	0.7	2.2 (1.7-2.8)	
	180 <sup>0</sup>	0.6-2.5	58-74	--	Partly cloudy, haze	7/13/78 0261-1103	2.0	6.4 (5.0-8.2)	
	24 hour average						1	4	
3	340 <sup>0</sup> -90 <sup>0</sup>	1.3-2.5	70-76	--	--	7/12/78 1148-2019	1.5	4.9 (3.8-6.3)	
	180 <sup>0</sup>	0.9-1.6	72-51	--	--	7/12/78 2019-0352	3.0	9.7 (7.5-12.5)	
	180 <sup>0</sup> -70 <sup>0</sup>	0.6-3.2	51-79	59	--	7/13/78 0352-1250	2.5	8.0 (6.7-9.6)(2)	
	24 hour average						2	7	
4	180 <sup>0</sup>	1.2-1.7	71-57	--	Clear, calm	7/12/78 1947-0323	3.5	11.4 (8.8-14.7)	
	180 <sup>0</sup> -70 <sup>0</sup>	0.6-2.5	57-75	46	--	7/13/78 0323-1226	6.0	19.3 (16.2-23.1)(2)	

- (a) Wind direction and speed were determined separately for ridge sites (1A and 1B) and valley sites (1 to 4).  
 (b) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

The highest concentration observed was 12.9 ppb which was at Site No. 1 in the valley, across the river from the coke ovens. The readings at Site 1B were lower than expected. This site was downwind from the coke ovens during most of the sampling periods and the sampling team could smell "coke oven odors" at this site. However, the site is on a ridge and the winds were slightly stronger on the ridges than they were in the valley. Background levels appear to be in the 0.4 to 0.7 ppb range as judged from Site 1B and Site 2 when upwind from the coke ovens. The levels at the airport are relatively high, 2 to 6 ppb, compared to values obtained at the closer sites. Other sources of benzene at the airport may have contributed to these higher values.

The winds were generally out of the South and Southeast, but the direction was rather variable during any given sampling period.

Ashland Chemical Company -- September, 1978

The benzene sampling sites for the Ashland Chemical Company maleic anhydride plant at Neal, West Virginia, are shown in Figure 16. Site No. 1 is on a dairy farm north and east of the plant. Site No. 2 is in Neal, West Virginia, at a greenhouse at 2244 Big Sandy Road. Site No. 3 is across the river on U.S. Route 23, west of the Novamont Chemical Company's polypropylene plant. Site No. 4 is in Neal on Big Sandy Road. Site No. 5 is north of Neal, across from the southernmost regions of the refinery. Site No. 6 is farthest from the maleic anhydride plant, south of Neal on Big Sandy Road; and Site No. 7 is at the corner of Route 52 and Big Sandy Road, slightly north and east of the plant.

Directly across the river from Sites 1 and 7 is the Ashland refinery. This is a possible source of benzene which may complicate the interpretation of the results. Approximately 2 miles north of the plant, there are coke ovens in Catlettsburg, Kentucky. In addition, there are coke ovens in South Point, Ohio, which is approximately 3 miles north of the maleic anhydride plant. These coke ovens are also possible sources of benzene which may make the results difficult to interpret.

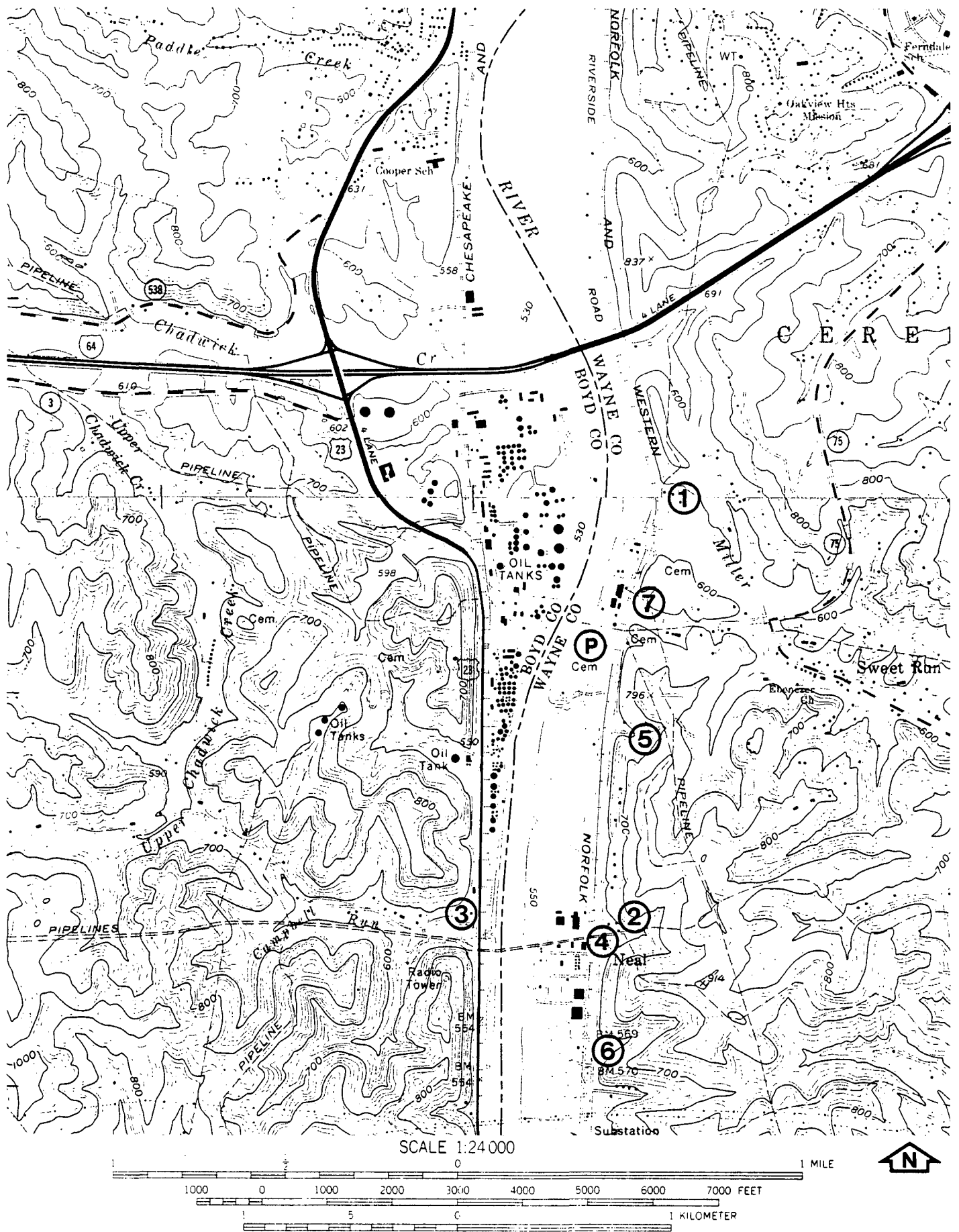


FIGURE 16. BENZENE MONITORING SITES AT ASHLAND CHEMICAL

The meteorological data were obtained from the Tri-State Airport which is not shown on the map, but which is just slightly over 1-1/2 miles east of the maleic anhydride plant.

Only air sampling was done at this location, and the results are given in Table 20.

In general, the highest determinations were made on samples taken at Sites 1 and 7 which were closest to the maleic anhydride plant, but also closest to the refinery. At Site 4 the highest level, 29.7 ppb, was determined; but there is no obvious explanation for this high value when all other values at Site 4 were 1.1 ppb or below. In general, the benzene levels within the town of Neal (Sites 2, 4, and 6) directly across the river from Neal (Site 3) were less than 2 ppb.

The prevailing wind was out of the south and west which makes most of the sites upwind from the maleic anhydride plant. Only Sites 1 and 7 were downwind of the maleic anhydride plant.

There was good agreement between duplicates, and confidence can be placed in the analytical results. However, because of the location of the plant in relationship to the river and the refinery, it was difficult to obtain samples that would accurately reflect the benzene emissions from the maleic anhydride plant.

TABLE 20. ANALYTICAL DATA FOR AIR SAMPLES FROM ASHLAND CHEMICAL COMPANY

Sampling Station	Weather Conditions <sup>(a)</sup>					Sampling Period	Benzene Analysis	
	Wind		Temp. Range, F	Relative Humidity, percent	General		ppb (v/v)	μg/m <sup>3</sup> <sup>(b)</sup>
	Direction	Speed, m/sec						
1	260 <sup>0</sup> -270 <sup>0</sup>	2.6-5.7	85-75	55-80	--	9/12/78 1428-2225	9.3	30.0 (23.2-38.6)
	240 <sup>0</sup> -120 <sup>0</sup>	1.6-2.6	75-70	80-91	--	9/12/78 2240-0904	4.0	12.9 (10.0-16.6)
	340 <sup>0</sup> -200 <sup>0</sup>	1.6-3.1	70-87	91-59	Cloudy, calm	9/13/78 0904-1647	5.1	16.5 (12.8-21.3)
	24 hour average					6	19	
2	270 <sup>0</sup> -240 <sup>0</sup>	2.6-5.7	85-73	57-84	Cloudy, windy	9/12/78 1517-2337	0.3	0.9 (0-1.2)
	240 <sup>0</sup> -120 <sup>0</sup>	1.6-2.6	73-70	84-91	--	9/12/78 2337-0949	0.8	2.7 (2.1-3.5)
	340 <sup>0</sup> -180 <sup>0</sup>	1.6-3.1	73-87	91-59	Cloudy, calm	9/13/78 0949-1725	1.1	3.4 (2.8-4.1) (2)
	24 hour average					1	2	
3	270 <sup>0</sup> -250 <sup>0</sup>	2.6-5.7	85-77	55-80	--	9/12/78 1345-2155	0.8	2.5 (1.9-3.2)
	340 <sup>0</sup> -180 <sup>0</sup>	1.6-3.1	72-87	91-59	Very cloudy	9/13/78 0825-1625	1.7	5.4 (4.2-7.0)
3	180 <sup>0</sup> -220 <sup>0</sup>	2.6-4.6	80-74	68-85	Cloudy	9/14/78 1112-2130	1.1	3.7 (2.9-4.8)
	220 <sup>0</sup> -310 <sup>0</sup>	2.6-3.6	80-70	88-55	Clear, sunny	9/14/78 2130-1112	0.3	1.1 (0-1.4)
	24 hour average					1	2	
4	260 <sup>0</sup> -230 <sup>0</sup>	2.1-5.7	84-72	57-85	Cloudy, windy	9/12/78 1530-0003	1.1	3.6 (2.8-4.7)
	230 <sup>0</sup> -280 <sup>0</sup>	1.6-2.6	70-76	85-91	--	9/13/78 0003-1017	0.7	2.2 (1.8-2.6) (2)
	280 <sup>0</sup> -340 <sup>0</sup>	1.6-3.1	76-87	91-59	Cloudy, calm	9/13/78 1017-1757	0.7	2.1 (1.6-2.7)
	24 hour average					1	2	
4	180 <sup>0</sup> -220 <sup>0</sup>	2.6-4.6	80-75	80-85	Cloudy, windy	9/14/78 1323-2040	29.7	95.8 (74.3-123.5)
	220 <sup>0</sup> -250 <sup>0</sup>	2.6-4.1	75-72	82-85	--	9/14/78 2040-0425	0.3	1.1 (0-1.4)
	250 <sup>0</sup> -310 <sup>0</sup>	2.6-4.6	70-84	87-40	Sunny, Calm	9/15/78 0425-1430	0.9	2.8 (2.2-36)
	24 hour average					9	29	
5	270 <sup>0</sup> -240 <sup>0</sup>	2.6-5.7	84-74	55-83	Cloudy, windy	9/12/78 1450-2310	6.8	21.9 (18.2-26.2) (2)
	240 <sup>0</sup> -120 <sup>0</sup>	1.6-2.6	74-70	83-91	--	9/12/78 2310-0926	0.7	2.3 (1.8-3.0)
	340 <sup>0</sup> -180 <sup>0</sup>	1.6-3.1	74-87	91-59	Cloudy, calm	9/13/78 0926-1710	1.6	5.3 (4.1-6.8)
	24 hour average					3	10	

TABLE 20. (Continued)

Sampling Station	Weather Conditions (a)					General	Sampling Period	Benzene Analysis	
	Wind		Temp. Range, F	Relative Humidity, percent	ppb (v/v)			μg/m <sup>3</sup> (b)	
	Direction	Speed, m/sec							
6	260 <sup>0</sup> -230 <sup>0</sup>	2.1-5.7	84-73	57-85	Cloudy, calm	9/12/78 1545-0025	0.3	1.0 (0-1.3)	
	120 <sup>0</sup> -300 <sup>0</sup>	1.6-2.6	74-70	85-91	--	9/13/78 0025-1037	0.7	2.1 (1.6-2.7)	
	340 <sup>0</sup> -180 <sup>0</sup>	1.6-3.1	74-87	91-59	Cloudy, calm	9/13/78 1037-1813	1.1	3.5 (2.7-4.5)	
	24 hour average						1	2	
6	190 <sup>0</sup> -210 <sup>0</sup>	2.6-4.6	87-77	80-85	--	9/14/78 1355-2100	0.6	2.0 (1.7-2.4) (2)	
	210 <sup>0</sup> -250 <sup>0</sup>	2.6-4.1	77-70	85-82	--	9/14/78 2100-0445	0.5	1.5 (1.2-1.9)	
7	180 <sup>0</sup> -200 <sup>0</sup>	2.6-4.6	80-75	85-75	--	9/14/78 1240-2000	1.0	3.2 (2.5-4.1)	
	200 <sup>0</sup> -320 <sup>0</sup>	2.6-4.1	70-84	87-40	--	9/14/78 2000-1345	13.8	44.5 (34.6-57.5)	
	24 hour average						10	32	

(a) Barometric pressure throughout the sampling was 29.1 to 29.2 in. Hg.

(b) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.



### Service Station Locations

Benzene is an important ingredient of motor fuels, with the amount fluctuating with the grade of fuel. Samples of the benzene content of U.S. gasolines in a 1968 study<sup>(7)</sup> showed that the mean benzene content averaged about 1 percent by volume, with a range between 0.54 and 2.0 percent. As a consequence of the requirements for reduced levels of lead anti-knock additives, the average benzene percentage in one oil company's gasolines was increased from less than 1 percent to less than 2 percent between 1974 and 1976.<sup>(8)</sup> Samples from this company's refineries in 1976 indicated an overall average of 1.25 percent among three grades of gasoline with individual measurements ranging from 0.54 to 2.39 percent.

### Selection of Sampling Locations

Ambient air was sampled around three gasoline service station locations in Columbus, Ohio. Sampling was performed at each location with the objective of determining maximum benzene concentrations to which inhabitants of the area are exposed in their daily activities.

The service station locations selected represented different sets of source conditions. These were:

- (1) Three or four stations at a busy intersection or beside each other along a roadway with residences nearby. A location at I-71 and Morse Road was selected to satisfy this condition.
- (2) A single heavily patronized full-service/self - service station in a residential area. Fishinger Road and Mountview Avenue was chosen to meet this condition.
- (3) A fully self-service station with residences nearby. A location at Morse and Maize Roads was chosen to satisfy this condition.

The following additional criteria were used in selecting the service station locations:

- Maximum throughput of gallons of gasoline pumped
- High traffic density near the station
- Large population affected
- Grades of gasolines available include those high in benzene content
- Minimum obstructions to wind flow between the station(s) and the surrounding neighborhood.

### Sampling Protocol

Monitoring for atmospheric benzene levels was performed during the period the stations were in operation, 16-20 hours, at seven or eight sites around each location taking both continuous and grab samples of air.

Samples at the stationary monitors were collected in duplicate at 8 to 10-hour intervals on Tenax GC traps at a rate of 30 ml/min. Grab samples were collected for 20-minute periods at the rate of 200 to 220 ml/min. The continuous monitors were placed where the impact on people living or working in the area could be determined and where the changes in concentration with distance downwind could be distinguished. Four monitors were placed in the downwind quadrant (to the southeast or northeast depending on the expected wind direction) at distances of 50, 100, 150, and 200 m from the station or station complex. One monitor was placed in each of the other three quadrants between 50 to 150 m from the station complex. Grab samples were taken at various sites off the station property with the objectives of estimating areas of peak benzene concentrations, determining the ambient concentrations directly downwind of the stations, comparing short-term averages with long-term averages, and measuring the variations in ambient benzene concentrations between hours of high and low gasoline sales.

During the sampling periods at Locations 2 and 3 (but not Location 1) wind direction, wind speed, and temperature were monitored with a battery-operated weather station. Intermittently, additional checks on the wind measurements were made with a hand-held anemometer. Periodic observations of cloud cover, current weather type, and humidity were also made. Hourly observations of all these variables were obtained for the sampling periods from the National Weather Service station at Port Columbus Airport.

### Analysis of the Benzene Sampling Data

In the discussions of the ambient data from the three service station locations, an attempt has been made to develop some hypotheses which are consistent with the measured ambient concentrations of benzene, the known or suspected sources, and the meteorological parameters. One can assume a benzene dispersion model which has service station emissions being injected into the ambient air near the ground (within 1 m of the surface) with little or no plume rise and then these emissions being diffused laterally and vertically as they move downwind. The benzene emissions are generated as a series of puffs from each vehicle's gasoline tank as gasoline is being pumped into the tank and vapors are being forced out. Some benzene may also be emitted by evaporation from the hot engine block as the gas pumping operation proceeds. Under very high ambient temperatures gasoline vapors, including benzene, from normal service station operations (pumping and storage) may be emitted to the atmosphere at an accelerated rate.

All of the ambient measurements made during the service station monitoring program cannot be explained by this model. In some cases the explanation probably lies in the uncertainties of the measurement themselves, for example, short-term variations of wind speed and wind direction. It is also likely that the sampler network was unable to pick up the maximum benzene concentration during each sampling period. In some cases, the discrepancy between hypothesis and observation was probably a benzene source which was not included in the original model.

One source of benzene emissions which was unexpectedly significant in this measurement program was motor vehicles -- in traffic, idling, or parked. Concentrations at several sampling sites were apparently the result of benzene evaporated from engine blocks or emitted from exhausts. Automobile emissions were suspected as a source when: (a) no service station was upwind of the sampler, (b) the benzene concentration was higher than background, and (c) the increases of benzene concentration during the day coincided with the presence of automobiles upwind of the sampler. Some of the highest 8-hour averages were obtained at sites which appeared to be more auto-traffic related than service-station related.

At one service station location the sampling program was fortunate to include a period when a tank truck was filling the underground storage tanks. The highest grab sample concentrations of benzene measured during the entire service station sampling program were obtained downwind of the station during this operation. Eight-hour average concentrations at the samplers in the vicinity of these grab samples were markedly higher during this period than the 8-hour concentrations downwind of the station during other periods.

Location 1. The Morse Road and I-71 Monitoring  
(Friday, June 10--Saturday, June 11, 1977)

This location (Figures 17, 18, and 19) fulfilled source condition (1) and comprised three adjacent stations (T, S, and H) on the south side of Morse Road and one station (M) north of Morse Road and directly across from Station T. The location was approximately 200 m east of the I-71-Morse Road interchange. The point where the I-71 exit and entrance ramps join Morse Road is depressed below the area of the service stations. A motel at the same elevation as the service stations lies on the south side of Morse Road between the stations and the I-71 exit ramp. A group of two-story apartment buildings with several mature trees is located on the south side of Morse Road to the east of the stations. There are three 50-car and six 10-car parking lots in this complex. One-story houses with a few trees are located to the south of the service stations. On the north side of Morse Road there are no trees. It is generally open with an auto agency, a theater, and a restaurant being the closest buildings.

While this location was chosen for the high density of service stations it is also an area of heavy traffic -- commuters into Columbus via Interstate 71 and vehicles going to or from the shopping complexes which are on Morse Road east of the sampling location. Morse Road is a six-lane thoroughfare east of I-71

Table 21 lists the ambient benzene concentrations measured at each sampling site, the gasoline pumped at the various service stations, the benzene content of the gasoline, and the range of meteorological parameters measured at the Port Columbus Airport during the sampling. Hourly values of the meteorological variables measured at the airport's National Weather Service station during the sampling are provided in Table 22. No continuous meteorological measurements were taken at Location 1.

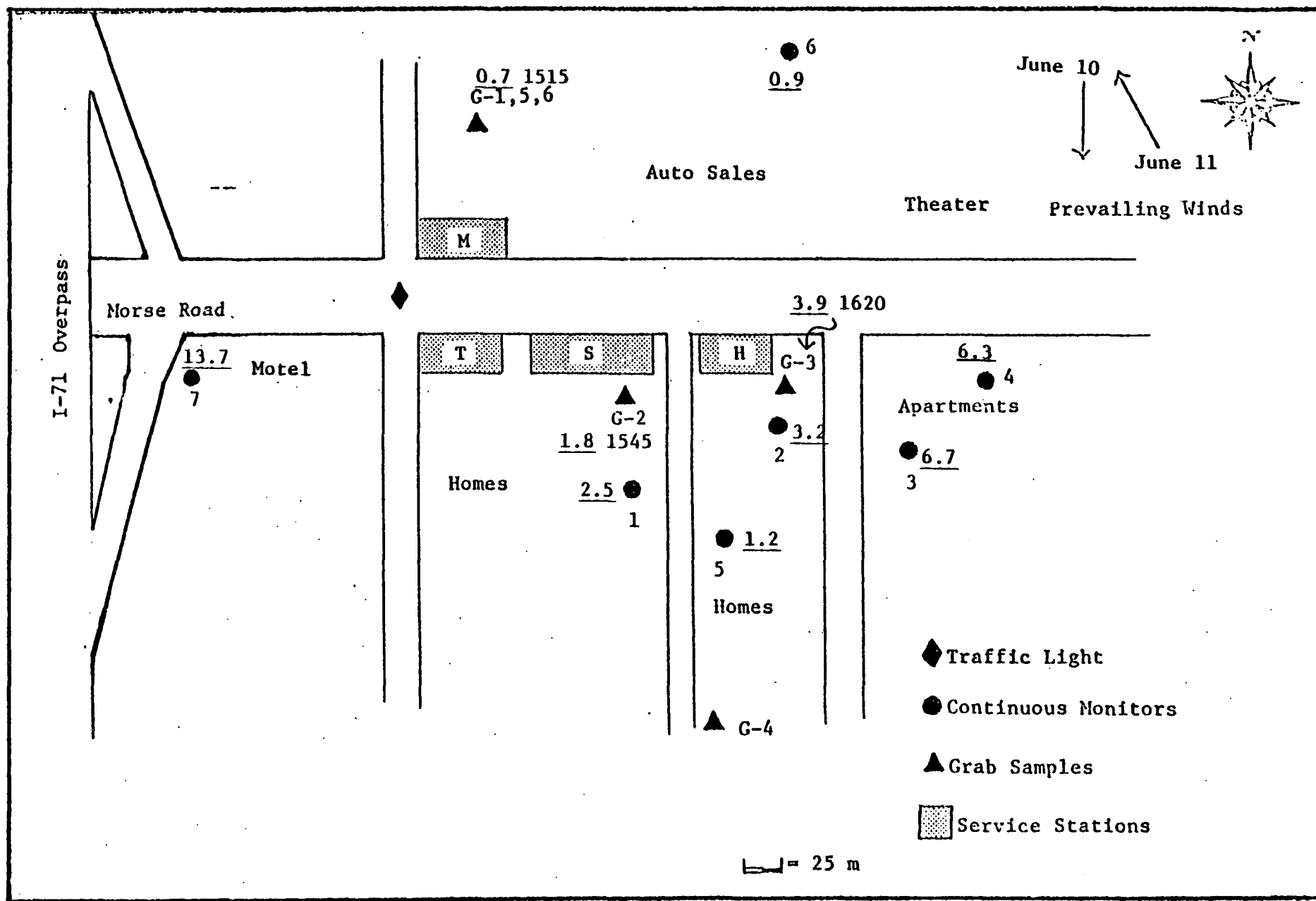


FIGURE 17. LOCATION 1 -- BEI CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ ) AT MORSE ROAD AND I-71 DURING PERIOD 1 (1320-2100, JUNE 10, 1977)



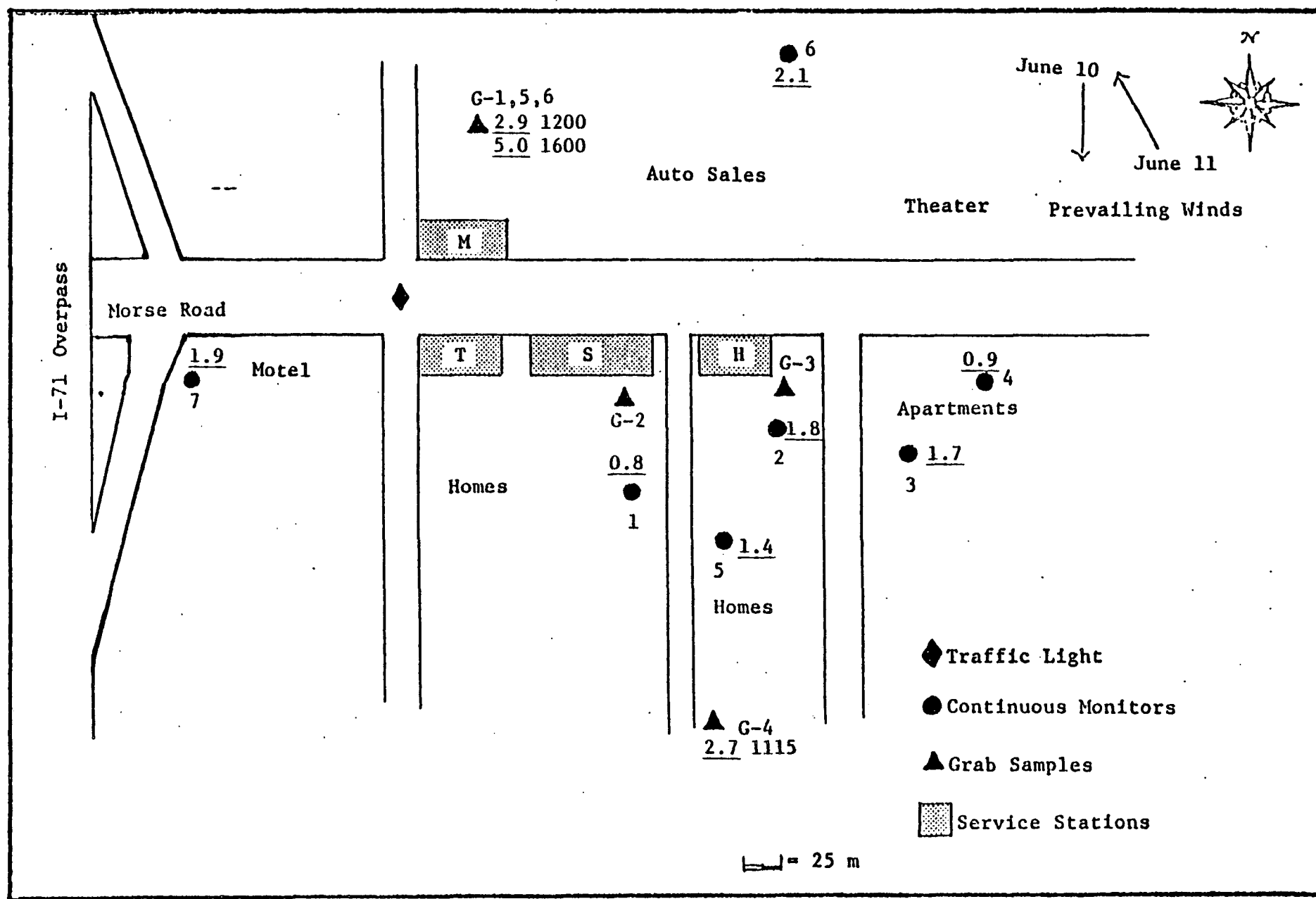


FIGURE 19. LOCATION 1 -- BENZENE CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ ) AT MORSE ROAD AND I-71 DURING PERIOD 3 (1000-1800, JUNE 11, 1977)

TABLE 21. BENZENE ANALYSES OF AIR SAMPLES FROM SERVICE STATION LOCATION AT I-71 AND MORSE ROAD

Sampling Station	Weather Conditions					General	Sampling Period	Benzene Analysis <sup>(a)(b)</sup>	
	Wind Direction	Wind Speed, m/sec	Temp. Range, F	Atmos Pressure, mm Hg	Relative Humidity, percent			ppb (v/v)	µg/m <sup>3</sup>
1	320-360	1.5-4.1	71-61	742-745	43-54	Clear	6/10, 1240-2145	0.8	2.5 (2.1-3.0)*
	030-calm	2.1-calm	61-48	741-742	52-86	Partly cloudy	6/10, 2145-0825	0.2	0.5 (0-0.7)
	Calm-250	1.5-4.1	56-62	739-742	60-75	Overcast intermittent rain	6/11, 0825-1800	0.3	0.8 (0-1.0)
							29 hr avg	0.5	1
2	Ditto	Ditto	Ditto	Ditto	Ditto	Ditto	6/10, 1320-2300	1.0	3.2 (2.7-8.8)*
							6/10, 2300-0950	0.7	2.2 (1.8-2.6)*
							6/11, 0950-1800	0.6	1.8 (1.5-2.1)*
							29 hr avg	0.8	2
3	Ditto	Ditto	Ditto	Ditto	Ditto	Ditto	6/10, 1330-2235	2.1	6.7 (5.1-8.7)
							6/10, 2235-1010	1.7	5.5 (4.3-7.1)
							6/11, 1010-1800	0.5	1.7 (1.3-2.2)
							29 hr avg	1.5	5
4	Ditto	Ditto	Ditto	Ditto	Ditto	Ditto	6/10, 1355-2320	2.0	6.3 (4.9-8.1)
							6/10, 2320-1030	1.1	3.4 (2.7-4.4)
							6/11, 1030-1800	0.3	0.9 (0-1.2)
							28 hr avg	1.1	4
5	Ditto	Ditto	Ditto	Ditto	Ditto	Ditto	6/10, 1300-2210	0.4	1.2 (0-1.6)
							6/10, 2210-0845	0.1	0.4 (0-0.6)
							6/11, 0845-1800	0.4	1.4 (1.1-1.8)
							29 hr avg	0.3	1
6	Ditto	Ditto	Ditto	Ditto	Ditto	Ditto	6/10, 1410-2340	0.3	0.9 (0-1.1)*
							6/10, 2340-1045	0.6	1.9 (1.6-2.3)*
							6/11, 1045-1800	0.7	2.1 (1.6-2.7)
							28 hr avg	0.5	2
7	Ditto	Ditto	Ditto	Ditto	Ditto	Ditto	6/10, 1220-2120	4.3	13.7 (10.6-17.6)
							6/10, 2120-0745	1.3	4.3 (3.3-5.5)
							6/11, 0745-1800	0.6	1.9 (1.6-2.3)*
							30 hr avg	2.0	7



TABLE 21. (Continued)

Sampling Station	Weather Conditions					General	Sampling Period	Benzene Analysis <sup>(a)(b)</sup>	
	Wind		Temp. Range, F	Atmos. Pressure, mm Hg	Relative Humidity, percent			ppb (v/v)	μg/m <sup>3</sup>
	Direction	Speed, m/sec							
<u>Grab Samples</u>									
G-1	360	4.1	71	743	47	Clear	6/10, 1510-1530	0.2	0.7 (0-0.9
G-2	360	4.1	71	743	46	Clear	6/10, 1539-1559	0.6	1.8 (1.4-2.3)
G-3	360	4.1	71	743	43	Clear	6/10, 1608-1633	1.2	3.9 (3.0-5.0)
G-4	250	1.5	62	741	60	Overcast	6/11, 1106-1129	0.8	2.7 (2.1-3.5)
G-5	130	2.6	62	740	75	Overcast	6/11, 1545-1605	1.6	5.0 (3.9-6.5)
G-6	250	3.6	62	742	60	Overcast	6/11, 1140-1200	0.9	2.9 (2.2-3.7)

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. Values marked \* are based on duplicate determinations, otherwise the result is based on a single sample.

(b) Gasoline Data:

Station	Date	Gallons Pumped			
		Regular	Unleaded	Premium	Totals
T	6/10, 0600-2200	--	--	--	750
	6/11, 0600-2200	--	--	--	800
	LV % Benzene	1.1	0.9	1.0	1550
S	6/10, 0600-2200	--	--	--	3400
	6/11, 0600-2200	--	--	--	3400
	LV % Benzene	1.4	1.3	1.3	6800
H	6/10, 0600-2400	1487	5182	1095	7764
	6/11, 0600-2400	1650	5700	1200	8500
	LV % Benzene	0.6	0.5	0.5	16264
M	6/10, 1200-1800	--	--	--	1184
	LV % Benzene	1.6	1.3	--	

TABLE 22. HOURLY WEATHER OBSERVATIONS FOR I-71 AND MORSE ROAD LOCATION<sup>(a)</sup>

Time	Pressure, mm Hg	Temp, F	Wind		Relative Humidity, percent	Character
			Direction	Speed, m/sec		
<u>June 10</u>						
1200	745	65	360	1.5	54	Clear
1300	744	66	350	3.6	52	Ditto
1400	744	69	320	2.6	47	"
1500	743	71	360	4.1	47	"
1600	743	71	360	4.1	46	"
1700	743	71	360	3.6	43	"
1800	743	71	360	3.6	44	"
1900	743	70	350	3.1	44	"
2000	743	68	350	3.1	49	"
2100	742	65	030	2.1	52	Partly Cloudy
2200	742	61	030	2.1	62	Ditto
2300	742	60	030	2.1	64	"
2400	743	58	040	2.1	72	"
<u>June 11</u>						
0100	743	55	040	2.1	72	Partly Cloudy
0200	743	55	Calm	--	69	Ditto
0300	742	55	"	--	66	"
0400	742	54	"	--	69	"
0500	742	52	"	--	74	"
0600	741	48	"	--	86	"
0700	742	49	"	--	83	"
0800	742	56	"	--	72	"
0900	741	61	170	3.6	60	Overcast
1000	741	61	130	2.6	60	Ditto
1100	742	62	170	1.5	60	Overcast, inter- mittent rain
1200	742	62	250	3.6	60	Ditto
1300	741	62	160	3.1	60	"
1400	740	62	150	4.1	60	"
1500	740	61	140	2.1	67	"
1600	739	62	130	2.6	75	"
1700	739	62	120	3.1	75	"
1800	739	61	120	4.1	72	"

(a) National Weather Service data.

During the first two sampling periods (Figures 17 and 18) at Location 1 (approximately 1300 to 2100 local daylight time on Friday, June 10, and 2100 on June 10 to 1000 on June 11) the most significant observations were the high benzene concentrations to the east and west of the service station complex in comparison with concentrations downwind (south) of the complex. Eight-hour concentrations at the downwind sites (Numbers 1, 2, and 3) were from 2 to 10 times smaller than concentrations on the east (Sites 3 and 4) and west (Site 7). A possible explanation of these higher concentrations crosswind from the service stations is motor vehicle emissions. Sites 3 and 4 are in the apartment complex. It can be hypothesized that over 150 automobiles returned to this area during the evening of the 10th and benzene from the engines evaporated while the engines cooled off. Low wind or calm conditions during the night (Period 2) in addition to a nocturnal temperature inversion caused the benzene to remain in the area. Benzene concentrations in this apartment area during Period 3 (Figure 19) were among the lowest measured by the monitoring network. During this last period (approximately 1000 to 1800 LDT on June 11) the evaporated benzene was dispersed by light winds and unstable conditions while little new benzene was evaporated in the apartment parking lots.

Site 7 was on the east side of the exit ramp from northbound I-71. This exit ramp handles a large volume of evening commuter traffic from downtown Columbus as well as cars going to the shopping centers on the eastern portion of Morse Road. At 6:00 p.m. cars are lined up in this exit ramp and along one lane of I-71 waiting to enter Morse Road going both east and west. Morse Road passes under I-71 and the exit ramp is depressed beneath the level of the service station complex. The high benzene concentrations at Site 7 during sampling Period 1 are possibly the result of "hot soak" emissions from automobiles waiting to enter Morse Road plus emissions blown from I-71 toward the sampler by the north wind. Another important source for this site is an oil company's small tank field about 1 km to the north. Because Morse Road and the exit-entrance ramps are depressed in this area benzene probably built up in this topographical depression. The high concentration remained there during the light-wind and temperature-inversion conditions of the nighttime portion of Period 2.

Ambient benzene concentrations which are probably related to gasoline station emissions did show a decrease with increasing distance. In Period 1 the highest long-term measurement was  $3.7 \mu\text{g}/\text{m}^3$  at Site 2 dropping off to  $1.2 \mu\text{g}/\text{m}^3$  at Site 5 further downwind. As a consequence of the southeast wind direction during Period 3 (Figure 19) the highest ambient concentrations attributable to the service stations probably were to the northwest of the stations in the area of grab sample Sites 5 and 6. This supposition is borne out by the  $5.0 \mu\text{g}/\text{m}^3$  observation at G-5 at 1600 and the fact that Site 6 measured the highest concentration in the network during the period.

Background benzene concentrations upwind of service stations, highways, and parking lots appear to be about  $1.0 \mu\text{g}/\text{m}^3$ . Support for this conclusion comes from the measurements at Site 6 during Period 1 and Sites 1 and 4 during Period 3. However, it should be noted that the minimum long-term observations were about  $0.5 \mu\text{g}/\text{m}^3$  at Sites 1 and 5 during Period 2.

Grab samples at Sites G-2 and G-3 during Period 1 are in the range of values that would be expected from the long-term measurements. However, it is difficult to explain the grab-sample measurement of  $2.7 \mu\text{g}/\text{m}^3$  taken at G-4 during mid-morning of Period 3. No known large source is near and upwind of this site.

Location 2. The Fishinger Road  
and Mountview Avenue Monitoring  
(Thursday, July 7, 1977)

This location (Figures 20 and 21) fulfilled source condition (2) and comprised a single full-service/self-service station (Station D) at the southwest corner of Fishinger Road and Mountview Avenue. The area around the church north of the service station is open while the homes to the west, south, and east of the station have mature trees. The home on the southeast corner of Fishinger Road and Mountview Avenue is shielded from the service station by a hedge six feet high. Shoreham Road which is parallel to Fishinger on the north is depressed below the level of Fishinger. Fishinger Road is four lanes wide and serves as a feeder to two commuter arteries at its east and west ends each about 1.5 km from Mountview.



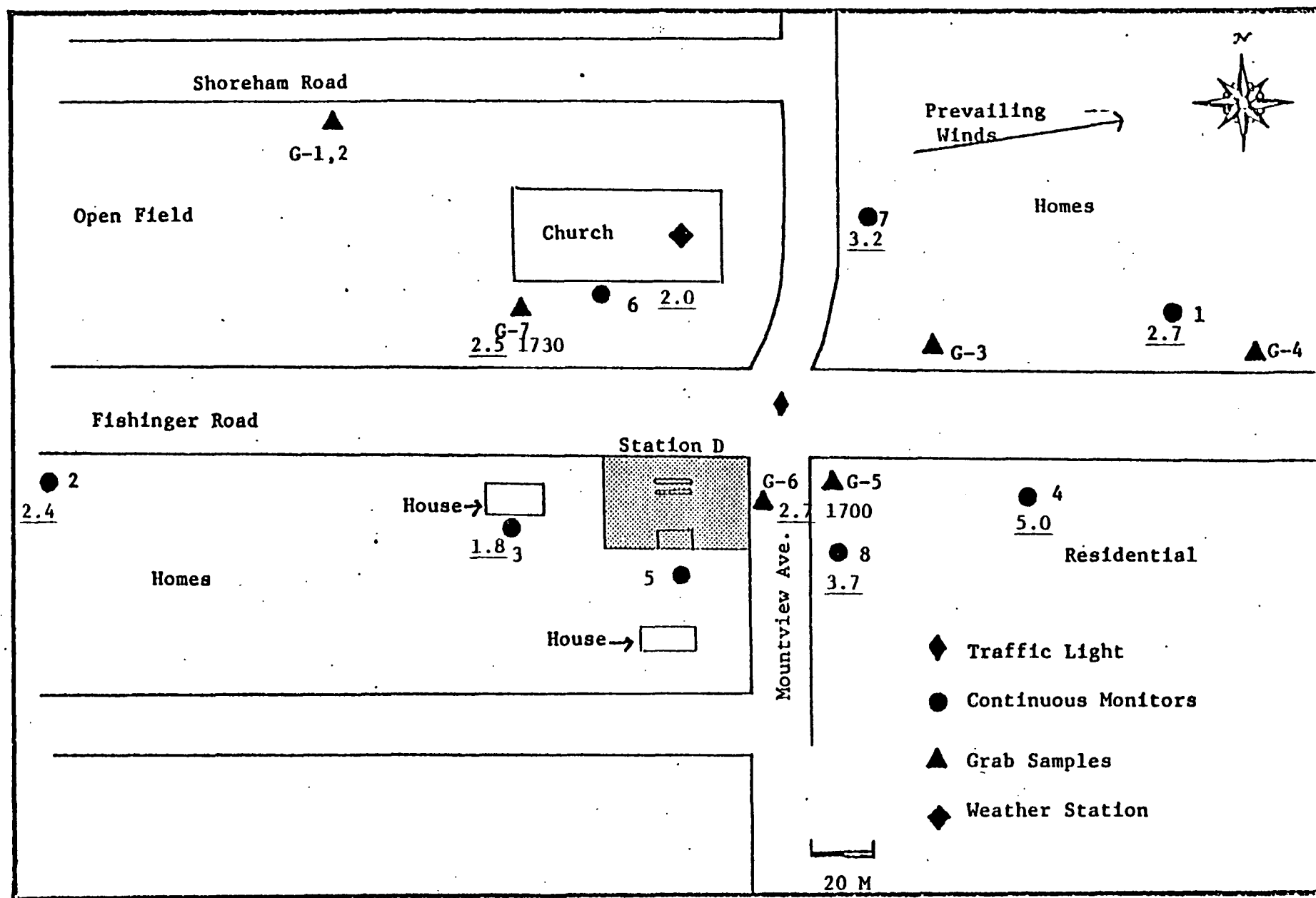


FIGURE 21. LOCATION 2 -- BENZENE CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ ) AT FISHINGER ROAD AND MOUNTVIEW AVENUE DURING PERIOD 2 (1500-2000, JULY 7, 1977)

This sampling took place in a residential neighborhood along a busy road, but one that does not carry nearly the amount of traffic that travels over Morse Road. There was only a single station at the Fishinger Road location and the volume of gasoline pumped was considerably less than at the Morse Road station complex. The benzene content of the gasolines at this location were similar to those at Location 1.

Despite the differences in amounts of gasoline pumped, the benzene concentrations downwind of the Fishinger Road service station were of a magnitude comparable to those measured downwind of the stations on Morse Road. One explanation for the Fishinger Road concentrations being larger than expected may lie in the meteorological conditions -- specifically, the extremely high temperatures (over 35 C). These temperatures could have caused an increase in the benzene vaporization rate which resulted in higher ambient concentrations.

Sampling at this location was conducted simultaneously by Battelle and by personnel from the Sohio Research Center, Cleveland, Ohio. Sohio collected NIOSH charcoal tube samples (600 mg) at 8-hour intervals with a sampling flow rate of 1 L/min.. The benzene analyses of these tubes by Sohio personnel were in good agreement with Battelle data (see values in brackets in Table 23).

An MRI Mechanical Weather Station was placed on the roof of a church across the street from the service station. Continuous measurements of wind speed and wind direction were made with this instrument. Hourly meteorological readings taken by the National Weather Service at the Port Columbus Airport are presented in Table 24. Variables between the National Weather Service hourly average wind direction measurements and those made on location ranged from  $-40^{\circ}$  to  $+40^{\circ}$  with an average deviation of  $17^{\circ}$ .

During the first sampling period, extending from approximately 0700 to 1500 local daylight time (Figure 20), benzene measurements at the continuous sampling sites indicated a pattern of benzene transport and diffusion along the downwind direction. The maximum observation in the neighborhood was  $2.9 \mu\text{g}/\text{m}^3$  made at Site 4. Benzene concentrations dropped off to  $1.2 \mu\text{g}/\text{m}^3$  further downwind at Site 1. Based on the pattern of 8-hour measurements, the highest concentrations in the neighborhood probably occurred in the area just north of Sites G-5 and G-6. The grab sample measurement of  $5.9 \mu\text{g}/\text{m}^3$  taken at G-5 about 9:30 a.m. fits this pattern.

TABLE 23. BENZENE ANALYSES OF AIR SAMPLES FROM SERVICE STATION LOCATION  
AT FISHINGER ROAD AND MOUNTVIEW AVENUE

Sampling Station	Weather Conditions						Benzene Analysis <sup>(a)(b)</sup>		
	Wind		Temp, F	Atmos Pressure, mm Hg	Relative Humidity, percent	General	Sampling Period	ppb	
	Direction	Speed, m/sec						(v/v)	µg/m <sup>3</sup>
1	270-360	4.6-7.2	86	760	48-74	Clear-cloudy	0600-1435	0.4	1.2 (0-1.4)*[<1]
	225-270	7.2-9.3	94	760	45-48	Cloudy	1435-2030	0.8	2.7 (2.1-3.5)[<1]
							14 hr avg	0.7	2
2	270-360	4.6-7.3	87	Ditto	48-74	Clear-cloudy	0715-1525	0.2	0.6 (0-0.8)[<1]
	225-270	7.2-9.3	94	"	45-48	Cloudy	1525-2000	0.8	2.4 (1.9-3.1)[<1]
							13 hr avg	0.5	1.5
3	225-270	7.2-9.3	87	"	45-48	Cloudy	1155-2005	0.6	1.8 (1.5-2.1)*[<1]
4	270-360	4.6-7.2	89	"	48-74	Clear-cloudy	0640-1550	0.9	2.9 (2.2-3.7) [?]
	225-270	7.2-9.3	99	"	45-48	Cloudy	1550-2035	1.6	5.0 (3.9-6.5) [1]
							13 hr avg	1.3	4
5	270-360	4.6-7.2	86	"	48-74	Clear-cloudy	0700-1555	0.7	2.3 (1.8-3.0) [<1]
	225-270	7.2-9.3		"	45-48	Cloudy	1555-2015	Lost	[1]
6	270-360	4.6-7.2	85	"	48-74	Clear-cloudy	0540-1410	0.4	1.3 (1.1-1.6)*[<1]
	225-270	7.2-9.3		"	45-48	Cloudy	1410-2100	0.6	2.0 (1.7-2.4)*[1]
							15 hr avg	0.5	2
7	270-360	4.6-7.2	86	"	48-74	Clear-cloudy	0730-1505	0.5	1.5 (1.2-1.9) [<1]
	225-270	7.2-9.3		"	45-48	Cloudy	1505-2030	1.0	3.2 (2.5-4.1) [1]
							13 hr avg	0.8	2
8	270-360	4.6-7.2	86	"	48-74	Cloudy	0815-1615	0.7	2.3 (1.9-2.8)*
	225-270	7.2-9.3		"	45-48	Rain	1615-2050	1.2	3.7 (3.1-4.5)*
							13 hr avg	1.0	3



TABLE 23. (Continued)

Sampling Station	Weather Conditions					Benzene Analysis <sup>(a)(b)</sup>		
	Wind		Temp, F	Atmos Pressure, mm hg	General	Sampling Period	ppb (v/v)	µg/m <sup>3</sup>
	Direction	Speed, m/sec						
Grab Samples								
G-1	250	4.1	83	760	Clear-hazy	0900-0905	0.5	1.7 (1.3-2.2)
G-2	240	2.6	81	Ditto	Clear	0740-0800	0.2	0.7 (0-0.9)
G-3	260	5.7	86	"	Hazy	0929-0949	1.9	5.9 (4.6-7.6)
G-4	260	5.7	86	"	Hazy	0955-1005	0.8	2.5 (1.9-3.2)
G-5	280	7.2	90	"	Hazy	1200-1220	Lost	
G-6	210	8.2	95	"	Cloudy	1645-1715	0.8	2.7 (2.1-3.5)
G-7	210	9.3	95	"	Cloudy	1725-1745	0.8	2.5 (1.9-3.2)
G-8	Incomplete sample - rain							

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(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. Values marked \* are based on duplicate determinations, otherwise the result is based on a single sample. Values in brackets are results of analyses reported by personnel of Sohio Research Center of charcoal tube samples taken simultaneously with the Battelle samples. The unit is ppb.

(b) Gasoline data:

Station	Date	Gallons Pumped			Totals
		Regular	Unleaded	Premium	
D	7/7, 0600-2030	--	--	--	2000 (estimate)
	LV % Benzene	0.3	1.0	0.6	

TABLE 24. HOURLY WEATHER OBSERVATIONS FOR FISHINGER ROAD AND MOUNTVIEW AVENUE LOCATION(a)

Time	Pressure, mm Hg	Temp, F	Wind		Relative Humidity, percent	Character
			Direction	Speed, m/sec		
<u>July 7</u>						
0600	760	79	240	4.6	74	Clear
0700	760	75	240	4.6	77	Ditto
0800	700	81	240	2.6	69	"
0900	760	83	250	4.1	67	Hazy
1000	760	86	260	5.7	63	Ditto
1100	760	88	291	5.2	61	"
1200	760	90	280	7.2	58	"
1300	760	91	270	6.2	54	Cloudy
1400	760	94	230	7.2	48	Ditto
1500	759	94	240	8.8	48	"
1600	760	95	240	8.2	45	"
1700	760	95	210	8.2	45	"
1800	760	94	220	9.3	46	"
1900	760	93	230	9.3	46	"
2000	759	91	250	8.8	47	Cloudy, rain

(a) National Weather Service data.

All grab samples taken in the 9:30 to 10:00 a.m. period are higher than the longer term averages which may indicate a benzene buildup over the entire area during this time.

Site 2 was selected as an upwind background measurement for this location. A comparison of the Site 2 measurement of  $0.6 \mu\text{g}/\text{m}^3$  and the Site 6 measurement of  $1.3 \mu\text{g}/\text{m}^3$  offers some indication of the magnitudes of benzene emissions from Fishinger Road Traffic.

During the second sampling period extending from 1500 to 2000 local daylight time (Figure 21) the same general pattern of benzene distribution prevailed downwind of the service station as existed during Period 1. However, the concentrations were 1.5 to 2.0 times as great. The increase resulted from an areawide benzene increase as well as an increase in emissions from the service station.

The reading at Site 2's background sampler was  $2.5 \mu\text{g}/\text{m}^3$ . This was larger than the measurements at Sites 6 ( $2.0 \mu\text{g}/\text{m}^3$ ) and 3 ( $1.8 \mu\text{g}/\text{m}^3$ ) which were downwind of Site 2. This suggests that benzene from some other source may have affected Site 2 during this period.

From the general pattern of benzene distribution downwind of the service station, it is suggested that the maximum 5-hour concentration in the residential neighborhood was probably in excess of  $6 \mu\text{g}/\text{m}^3$  and occurred in the vicinity of Sites G-5 and G-6. However, the grab sample taken at 1700 at G-6 was only  $2.7 \mu\text{g}/\text{m}^3$ . An examination of the on-location wind direction trace for this period indicated that the winds varied from southwesterly to westerly to northerly. The low reading for the G-6 samples was possibly made when the wind was not blowing directly from the station to the sampler.

Location 3. The Morse Road and Maize Road Monitoring  
(Friday, August 5--Saturday, August 6, 1977)

This location (Figures 22 and 23) fulfilled source condition (3) and comprised a full self-service station (Station P) located on the northeast corner of the Morse Road and Maize Road intersection. This corner is approximately 1000 m east of the first location. A station (Station B) which was closed during the sampling at Location 3, is on the southeast corner of the Morse and Maize Roads intersection. A full-service station (Station L) is located on the southwest corner of the intersection. With

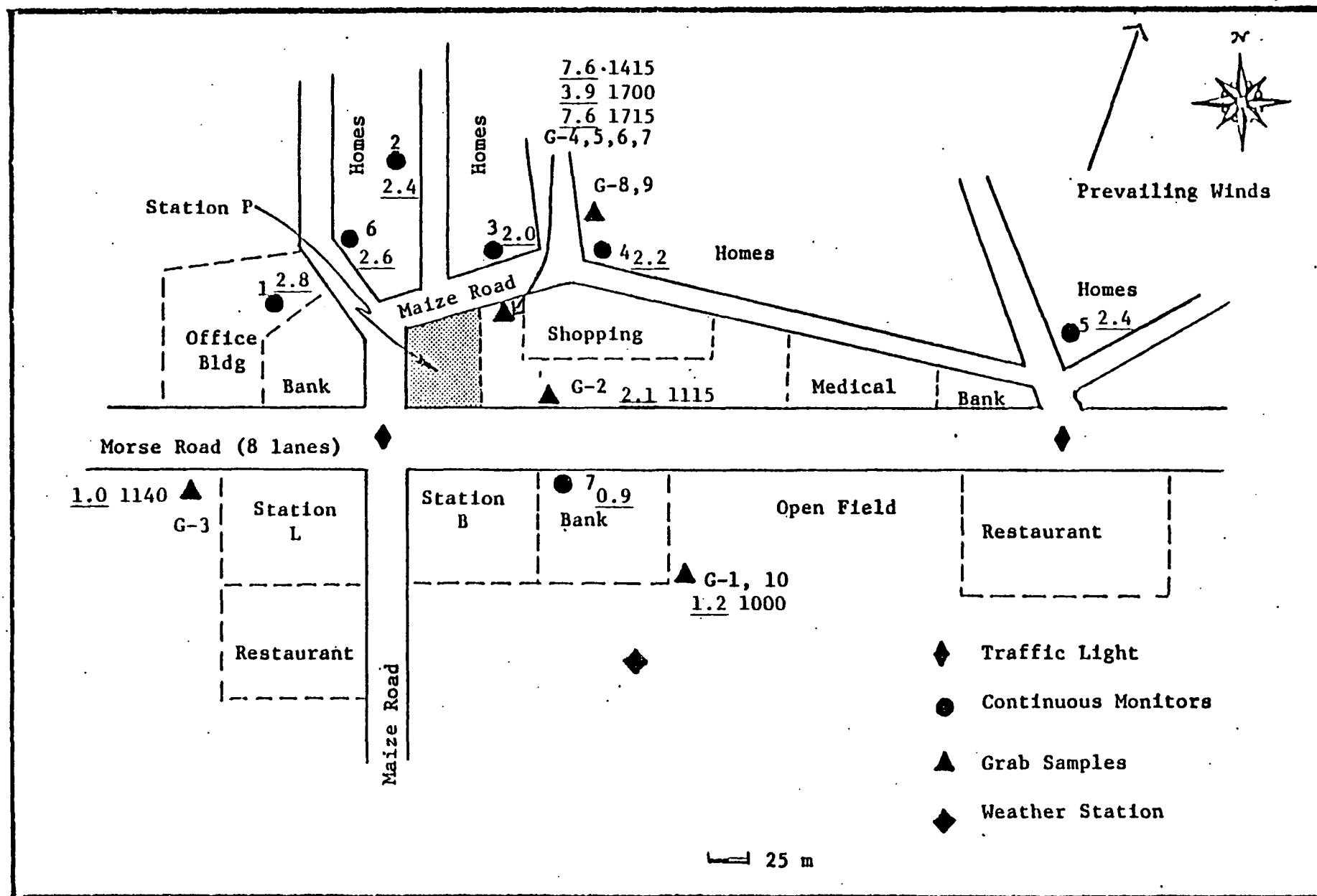


FIGURE 22. LOCATION 3 -- BENZENE CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ ) AT MORSE AND MAIZE ROADS DURING PERIOD 1 (0800-1800, AUGUST 5, 1977)

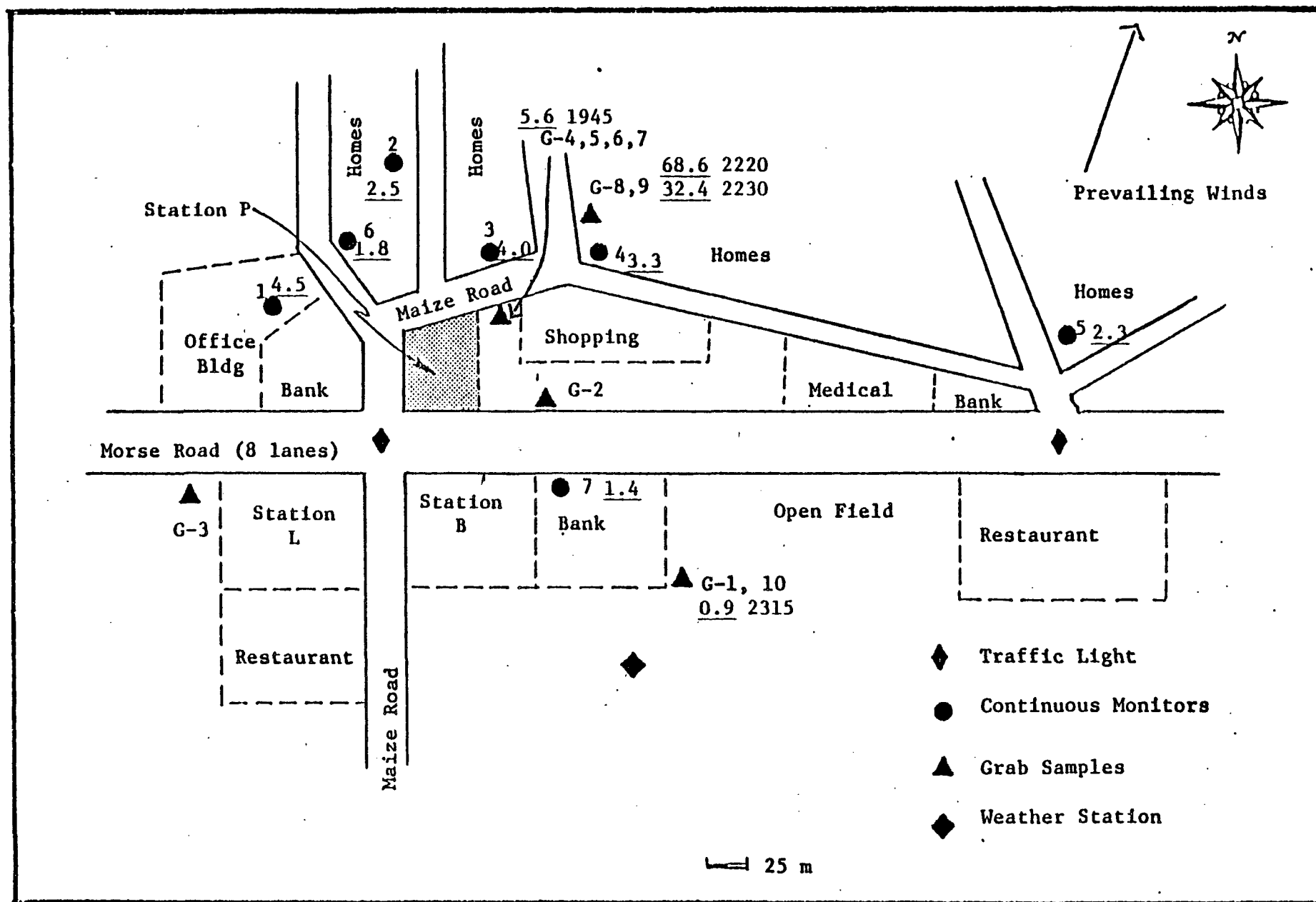


FIGURE 23. LOCATION 3 -- BENZENE CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ ) AT MORSE AND MAIZE ROADS DURING PERIOD 2 (1800, AUGUST 5 -- 0200, AUGUST 6, 1977)

the exception of a small three-story office building one block west of Station P the area west, north, and east of the station is composed of homes and commercial establishments which are one-story buildings. On the south side on this stretch of Morse Road the area is generally flat and open with only a small one-story bank located to the east of Station B. There are no mature trees in this vicinity.

The sampling was conducted at a location approximately 1/4 mile to the east of the first sampling area (Location 1) on Morse Road. This location was deemed to be beyond the influence of the other service station complex. Even if this assumption were not true, the wind direction during the third sampling program would have transported the benzene emissions from I-71 and Morse Road along a line generally to the west of Maize Road.

On-location wind measurements were made with the Mechanical Weather Station in an open field south of Morse Road. Hourly weather data taken by the National Weather Service at Port Columbus are presented in Table 25. Variations between hourly average measurements made at the sampling location and at the airport ranged from  $0^{\circ}$  to  $40^{\circ}$  with an average  $16^{\circ}$  deviation for the entire sampling time. Hourly average wind directions at Location 3 varied from  $200^{\circ}$  to  $250^{\circ}$  while at the airport the range was between  $180^{\circ}$  and  $240^{\circ}$ .

At this third location, Site 7 served as a background measurement upwind of Morse Road and Site 5 measured benzene concentrations downwind of this thoroughfare at a point well removed from service stations. The measurements of  $0.9 \mu\text{g}/\text{m}^3$  at Site 7 and  $2.4 \mu\text{g}/\text{m}^3$  at Site 5 represent the background values upwind and downwind of Morse Road against which the other measurements can be compared. Measurements at the first sampling location also indicated that  $1 \mu\text{g}/\text{m}^3$  might be a reasonable benzene background concentration for a suburban-residential area such as Location 2.

In the first sampling period (Figure 22, Tables 25 and 26) the winds were generally from the southwest. To the south of Morse Road (upwind) long-term and grab-sample measurements indicated benzene concentrations of about  $1 \mu\text{g}/\text{m}^3$ . On the downwind side of the road long-term concentrations ranged from 2.0 to  $2.8 \mu\text{g}/\text{m}^3$ . Decreasing concentrations from Site 1 to

TABLE 25. HOURLY WEATHER OBSERVATIONS FOR MORSE AND  
MAIZE ROADS LOCATION(a)

Time	Pressure, mm Hg	Temp, F	Wind		Relative Humidity, percent	Character
			Direction	Speed, m/sec		
<u>August 5</u>						
0600	765	73	186	4.1	82	Cloudy
0700	765	73	220	3.6	82	Ditto
0800	766	74	190	4.1	79	"
0900	766	75	190	4.6	76	"
1000	766	80	230	5.2	69	Partly cloudy
1100	766	82	220	5.7	65	Cloudy
1200	766	85	210	6.1	59	Ditto
1300	766	87	240	8.2	57	"
1400	766	87	230	9.3	55	"
1500	765	87	230	7.2	55	"
1600	765	90	240	8.8	49	Partly cloudy
1700	765	88	220	4.7	50	Ditto
1800	765	88	200	8.8	54	"
1900	765	88	210	5.2	50	"
2000	765	86	220	7.2	53	"
2100	765	83	200	3.6	59	"
2200	765	81	190	3.6	63	"
2300	765	79	210	3.1	67	"
2400	765	76	190	3.1	71	"
0100	766	75	180	2.6	74	"
0200	765	75	180	2.6	74	"

(a) National Weather Service data.

TABLE 26. BENZENE ANALYSES OF AIR SAMPLES FROM SERVICE STATION LOCATION AT MORSE AND MAIZE ROADS

Sampling Station	Weather Conditions					General	Sampling Period	Benzene Analysis <sup>(a)(b)</sup>	
	Wind Direction	Wind Speed, m/sec	Temp. Range, F	Atmos Pressure, mm Hg	Relative Humidity, percent			ppb (v/v)	μg/m <sup>3</sup>
1	200-240	4.7-9.3	82-88	765	54-59	Cloudy	1138-1820	0.9	2.8 (2.2-3.6)
	200-220	3.6-8.8	88-83	765	54-59	Cloudy	1820-2100	1.4	4.5 (3.5-5.8)
							9 hr avg	<u>1.2</u>	<u>4</u>
2	190-240	3.6-8.8	73-88	Ditto	54-82	Ditto	0700-1745	0.7	2.4 (1.9-3.1)
	180-210	2.6-7.2	88-75		54-74		1745-0153	0.7	2.5 (1.9-3.2)
							19 hr avg	<u>0.7</u>	<u>2</u>
3	190-240	Ditto	Ditto	Ditto	Ditto	Ditto	0735-1840	0.6	2.0 (1.6-2.6)
	180-210						1840-0142	1.3	4.0 (3.3-4.8)*
							18 hr avg	<u>1.0</u>	<u>3</u>
4	190-240	Ditto	Ditto	Ditto	Ditto	Ditto	0825-1855	0.7	2.2 (1.7-2.8)
	180-210						1855-0130	1.1	3.3 (2.8-4.0)*
							18 hr avg	<u>0.9</u>	<u>2</u>
5	199-240	Ditto	Ditto	Ditto	Ditto	Ditto	0806-1910	0.8	2.4 (1.9-3.1)
	180-210						1910-0118	0.7	2.3 (1.9-2.8)*
							17 hr avg	<u>0.8</u>	<u>2</u>
6	190-240	Ditto	Ditto	Ditto	Ditto	Ditto	0705-1810	0.8	2.6 (2.0-3.3)
	180-210						1810-0200	0.6	1.8 (1.5-2.1)*
							19 hr avg	<u>0.7</u>	<u>2</u>
7	190-240	Ditto	Ditto	Ditto	Ditto	Ditto	0850-1935	0.3	0.9 (0-1.1)*
	180-210						1935-0210	0.4	1.4 (1.1-1.8)
							17 hr avg	<u>0.3</u>	<u>1</u>



TABLE 26. (Continued)

Sampling Station	Weather		Temp. Range, F	Atmos Pressure, mm Hg	Relative Humidity, percent	General	Sampling Period	Benzene Analysis <sup>(a)(b)</sup>	
	Wind	Speed, m/sec						ppb (v/v)	µg/m <sup>3</sup>
	Direction								
Grab Samples									
G-1	210	4.6	75	766	69	Cloudy	0943-1003	0.4	1.2 (0-1.6)
G-2	210	4.7	85	766	65	Ditto	1102-1122	0.7	2.1 (1.6-2.7)
G-3	210	6.2	85	766	59	"	1139-1158	0.3	1.0 (0-1.3)
G-4	230	9.3	87	766	55	"	1414-1434	2.4	7.6 (5.9-9.8)
G-5	240	4.7	89	765	50	"	1644-1704	1.2	3.9 (3.0-5.0)
G-6	220	4.7	89	765	54	"	1710-1730	2.4	7.6 (5.9-9.8)
G-7	210	4.7	88	765	53	"	1930-1950	1.8	5.6 (4.4-7.2)
G-8	220	3.6	81	765	67	"	2217-2227	21.5	68.6 (54.5-90.5)
G-9	220	3.1	81	765	67	"	2227-2237	10.3	32.4 (25.2-41.7)
G-10	210	3.1	79	765	71	"	2303-2323	0.3	0.9 (0-1.2)

(a) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section (page B-5). Values marked \* are based on duplicate determinations, otherwise the result is based on a single sample.

(b) Gasoline data:

Station	Date	Gallons Pumped			Totals
		Regular	Unleaded	Premium	
P	8/5, 0600-1700	2960	1191	--	4151
	1700-1900	1025	379	--	1404
	1900-0230	1745	662	--	2407
	LV % Benzene	1.2	0.7		7692
L	8/5, 0600-0600	2900	4350	1550	8800
	LV % Benzene	0.8	1.1	1.2	

Site 6 to Site 2 could be attributed to downwind dispersion of the traffic emissions. The position of Site 5 would recommend it as a good control site to compare concentrations downwind of the road at a place without a gasoline station. Thus, it was believed that the benzene concentration at Site 5 could be deducted from the concentrations at Sites 3 and 4 to isolate the effect of the Station P emissions at Morse and Maize Roads.

Unexpectedly, the long-term benzene concentrations at Sites 3 and 4 during this period were less than the concentration at Sites 5, 1, 6, and 2. Unless there were some unidentified benzene sources affecting Sites 5, 1, 6, and 2, or some chemical reaction destroying benzene, or some microscale dispersion fluctuations causing the benzene from Station P to bypass Sites 3 and 4, the measurements at these two sites are suspect.

During the second sampling period at Location 3 (Figure 23) the north side of Morse Road was again downwind in relation to traffic emissions. The magnitude of traffic emissions of benzene during this time is best portrayed by the difference between the measurements at Site 5 ( $2.3 \mu\text{g}/\text{m}^3$ ) and Site 7 ( $1.4 \mu\text{g}/\text{m}^3$ ).

There was considerable variation among the benzene measurements at the other monitoring sites. Some of these variations can be explained, at least partially, by differences in sampling times or sources. However, there are still some unexplained measurements.

The largest concentration during this period was observed at Site 1 ( $4.5 \mu\text{g}/\text{m}^3$ ). During Period 1 the gradient from Site 1 to Site 2 was attributed to downwind dispersion. In Period 2 there was no uniform gradient. Sampling at Site 1 during this period lasted only 2.5 hours while at the other sites the sampling covered 5 to 8 hours. The 2.5 hours at Site 1 was done between 6:30 p.m. and 9:00 p.m. when auto traffic and activities at the bank and at Station L were at a maximum for the period. If the benzene concentration at Site 1 had averaged  $2.5 \mu\text{g}/\text{m}^3$  for an additional 4.5 hours, the overall concentration average would have been  $3.2 \mu\text{g}/\text{m}^3$  which is more in line with the concentrations at Sites 2 and 5.

The  $1.8 \mu\text{g}/\text{m}^3$  concentration at Site 6 is lower than would be predicted considering the  $2.5 \mu\text{g}/\text{m}^3$  at Site 2 and the potential  $3.2 \mu\text{g}/\text{m}^3$  at Site 1.

For 20 minutes at about 10:30 p.m. a tank truck refilled the underground gasoline storage tanks at Station P. During this operation, two 10-minute grab samples (G-8 and G-9) were taken downwind of the station near continuous sampling Site 4. Average concentrations for these 10-minute periods were  $68.6 \mu\text{g}/\text{m}^3$  and  $32.4 \mu\text{g}/\text{m}^3$ , which were the highest levels observed during the service station monitoring program.

It would seem that the large benzene levels during this 20-minute period would result in concentrations at Sites 3 and 4 which were higher than other sites (e.g., 5 and 2) not downwind of the service station. What is revealed by a computation, however, is that the effect of the tank truck emissions should have resulted in an even higher concentration at Site 4 than was actually measured. Even if the prevailing benzene concentration for the remainder of Period 2 was only  $2.2 \mu\text{g}/\text{m}^3$ , then the 20 minutes of tank-truck emissions should have caused an overall average of  $4.7 \mu\text{g}/\text{m}^3$  instead of the  $3.3 \mu\text{g}/\text{m}^3$  that was observed. The measurement at Site 3 should also have been higher under these calculations. The lower than expected readings at these two samplers during Period 2 adds to the questionability of the low readings at these sites during Period 1.

The series of grab samples taken at the downwind edge of Station P property (G-4 through G-7) at different times indicate the range of benzene concentration variations that might be experienced at a site during a day's operations. A dispersion calculation to check on long-term values was made based on the G-4 and G-5 grab samples. These had concentrations of  $7.6 \mu\text{g}/\text{m}^3$  and  $3.9 \mu\text{g}/\text{m}^3$ , respectively, minus  $2.0 \mu\text{g}/\text{m}^3$  of background benzene downwind of the road. It was found that the benzene contribution to Site 3 might vary between  $0.7 \mu\text{g}/\text{m}^3$  and  $2.1 \mu\text{g}/\text{m}^3$ . When these concentrations are added to the  $2.0 \mu\text{g}/\text{m}^3$  of assumed background the resulting 2.7 to  $4.1 \mu\text{g}/\text{m}^3$  is greater than the  $2.0 \mu\text{g}/\text{m}^3$  observed during Period 1.

#### Emission Calculations

Table 27 presents several estimates of benzene emission rates based on grab samples taken during the three programs. The samples selected for calculating emissions were those for which the wind blew from the service station to the monitor. In each case the source was considered to be a point source, which is actually incorrect since at several locations there was more

than one service station. In one case the monitor was so close to the station that the calculation of emissions was made as though the source was an area source projected backward to a virtual point source. Thus, the values listed in the table should be considered only as rough estimates.

TABLE 27. ESTIMATED BENZENE EMISSION RATES

Location	Site No.	Background Concentration Subtracted, $\mu\text{g}/\text{m}^3$	Atmospheric Stability Type	Distance From Source, m	Time	Emission Rate, g/sec
1	G-5	2.1	D	200	Day	0.0145
2	G-3	1.2	C	100	Day	0.0069
2	G-4	1.2	C	200	Day	0.0083
3	G-4	2.0	D	35 <sup>(a)</sup>	Day	0.0139
3	G-8	1.8	D	155	Night	0.061 <sup>(b)</sup>

(a) Virtual distance is 160 m when source is treated as an area source.

(b) During refilling of storage tanks.

No attempt has been made to carry the calculations on to the emission-factor stage. As mentioned in the last paragraph there is only limited confidence in the emission-rate calculations. The large amount of benzene produced by highway traffic adds to the uncertainty. The complications of different volumes of gasoline of various grades pumped by various gasolines are too complex to allow derivation of emission factors at this time. Furthermore, there are indications from the Fishinger Road sampling that the benzene emissions may be related to ambient temperature. If this is true, then climate can be a significant factor in predicting benzene emissions and ambient concentrations. The concentrations measured during this sampling program may be low compared to those found near similar sources in a very hot climate.

### Urban Locations

The purpose of this part of the program was to determine atmospheric benzene levels at urban locations having different traffic densities.

#### Selection of Sampling Locations

Three types of sites were chosen in the vicinity of the main business district of Columbus, Ohio. Air at these sites was sampled and the benzene concentrations determined. Types of sites included are:

- (1) A midtown intersection having a high traffic load throughout normal business hours,
- (2) A highway leading into the business district. Traffic volume was determined for the sampling period at this site, and
- (3) A residential area situated near the business district, but relatively isolated from normal business traffic and having a low service station density.

The locations of the three sites are indicated on Figure 24. Site No. 1 was on the Ohio Statehouse lawn at the intersection of Broad (Route 40) and High (Route 23) Streets, the center of the city. During the sampling period of March 15 and March 16, 1978, this position was essentially directly downwind of the traffic passing through that intersection. At Site No. 2, two samplers, indicated as 2a and 2b in Figure 24, were operated on opposite sides of the highway between 520 and 550 East Broad Street. Automatic traffic counters were placed by the City on each side of the street in the same block and approximately 75 feet west of Jefferson Avenue. Site No. 3, Figure 24, was located in the German Village section of Columbus, south of the business district. The exact locations of the sites are listed in Table 28. Sketched maps of each of the sampling locations showing approximate building placements in the vicinity of the samplers are given in Figures 25, 26, and 27.

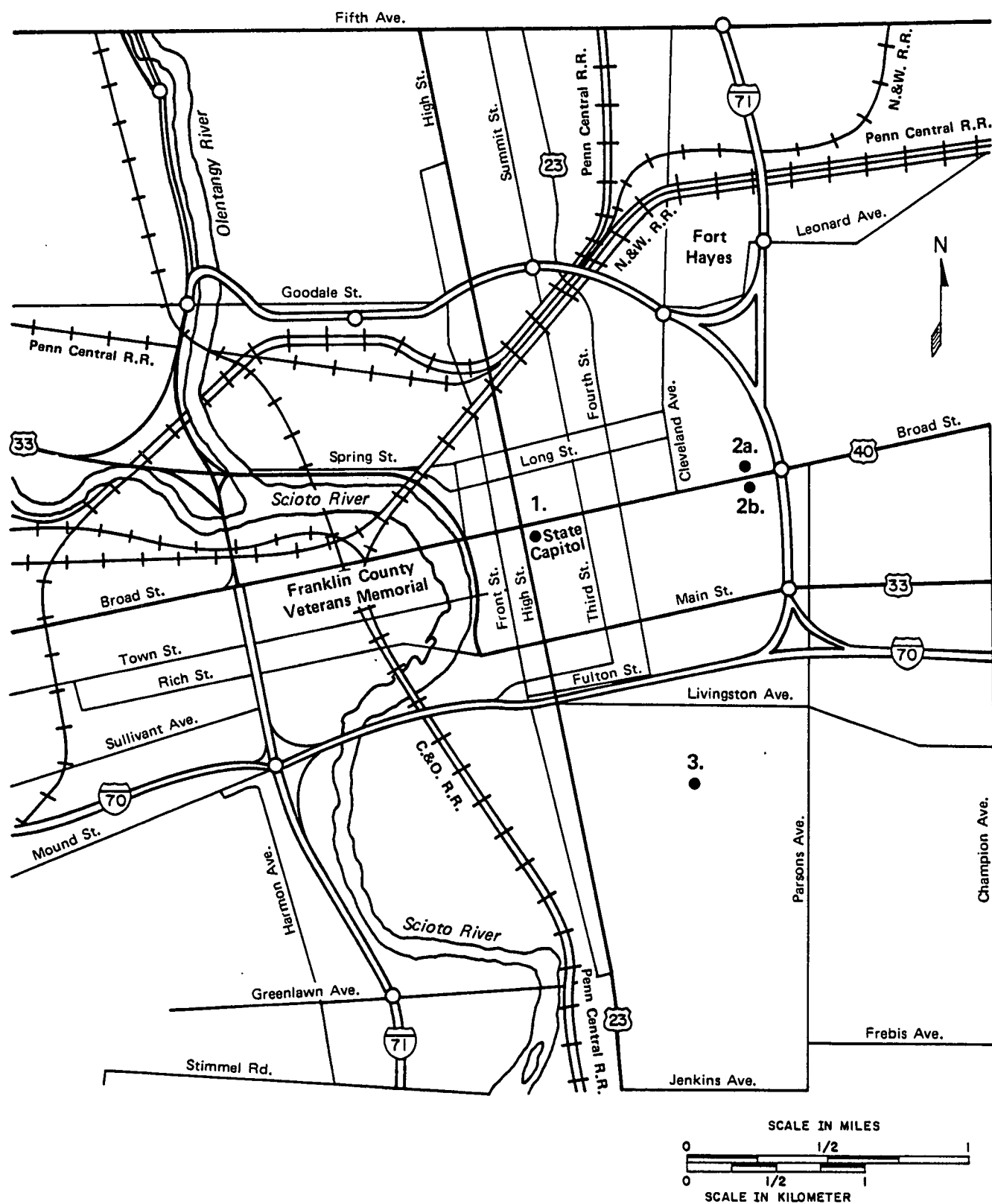


FIGURE 24. BENZENE MONITORING SITES AT URBAN LOCATIONS IN COLUMBUS, OHIO

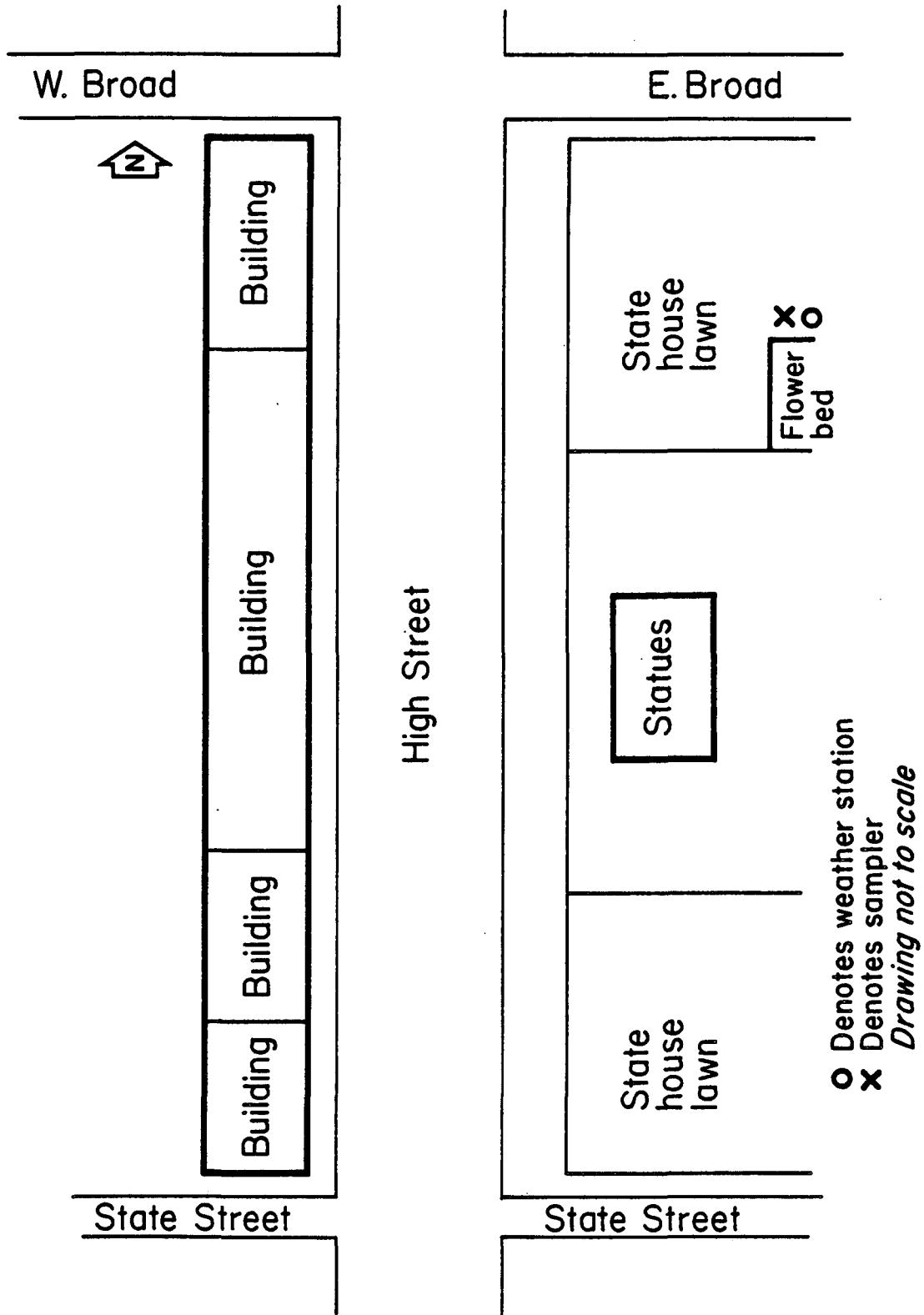


FIGURE 25. BENZENE SAMPLING SITE NO. 1 IN COLUMBUS, OHIO

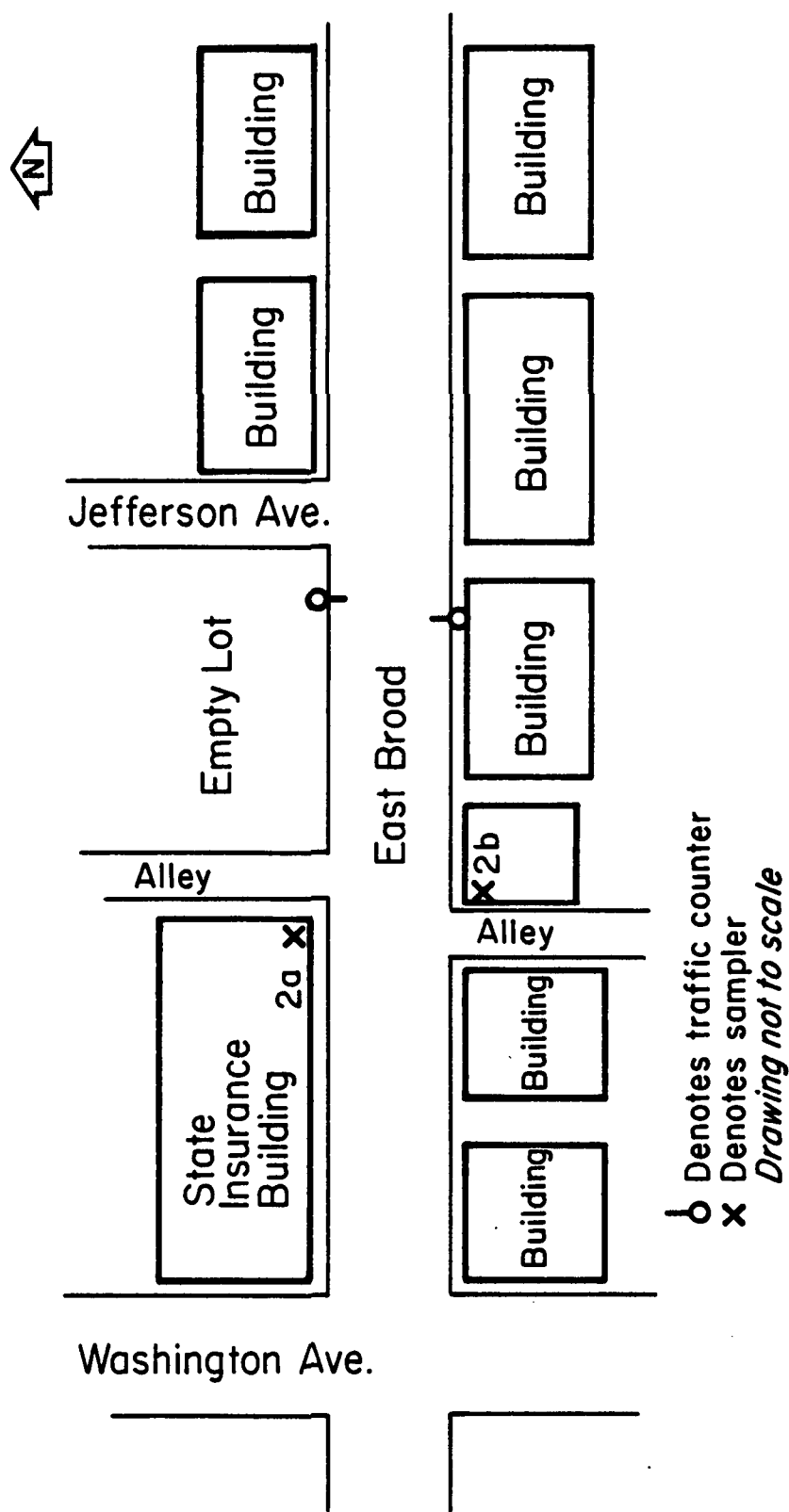


FIGURE 26. BENZENE SAMPLING SITES 2a AND 2b IN COLUMBUS, OHIO



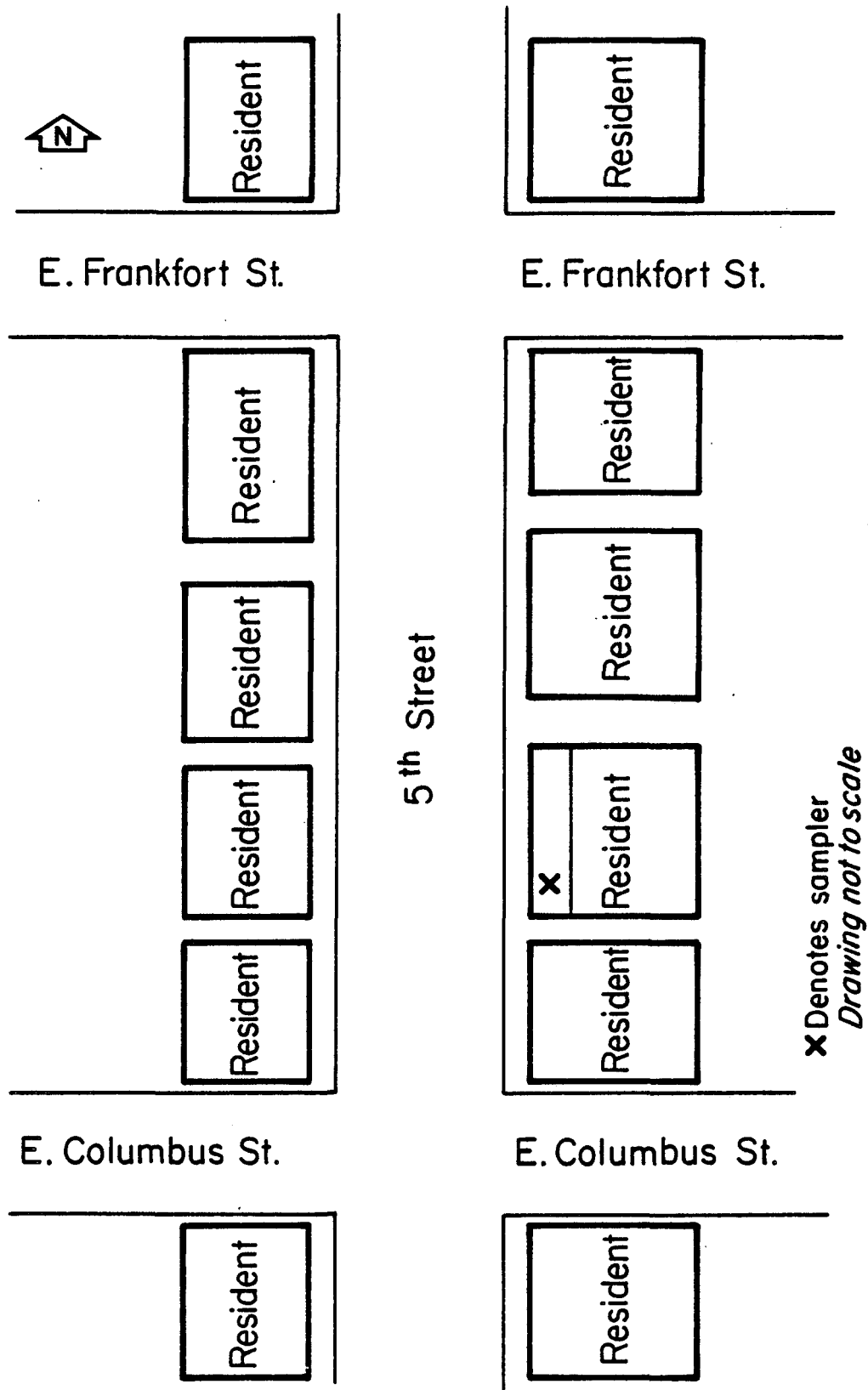


FIGURE 27. BENZENE SAMPLING SITE NO. 3 IN COLUMBUS, OHIO

TABLE 28. URBAN SAMPLING LOCATIONS IN COLUMBUS, OHIO

Site No.	Location
1	Statehouse lawn -- about 100 feet east of High Street (Route 23) and 250 feet south of Broad Street (Route 40)
2a	518 East Broad Street (Route 40) -- about 6 feet north of the north sidewalk
2b	547 East Broad Street (Route 40) -- about 10 feet south of the south sidewalk
3	766 South Fifth Street (in German Village) about 3 feet east of the east sidewalk

#### Sampling Protocol

Air was sampled at all three sites. At Site No. 1, three 8-hour samples, one duplicate 8-hour sample, and one backup sample were collected during the sampling period. At the second site, samples consisted of

- 3 - 8-hour samples at each of the two stations
- 2 - duplicate samples (one at each station)
- 2 - backup samples (one at each station)
- 2 - 2-hour (rush hour) samples at each station
- 2 - backup samples for the rush-hour samples.

At the residential site, Site No. 3, samples were collected in the same manner as those at Site No. 1.

In addition, meteorological data were collected at each site. At Site No. 1, continuous measurements were made of the temperature, wind speed, and wind direction using a Model 1071 Meteorological Research Inc. instrument. Spot checks of relative humidity, wind speed, wind direction, and temperature were made at each of the sites using portable instruments. These data were supplemented by hourly readings made by the U.S. Weather Bureau at Port Columbus.

### Traffic Data

With the cooperation of the City of Columbus, Division of Traffic Engineering, it was possible to obtain an exact count of the vehicles passing the samplers at Site No. 2. This was done with automatic traffic counters which had hoses extending across all lanes of East Broad Street and counted the vehicles in both directions. Tables 29 and 30 show the data that were supplied to us by the Division of Traffic Engineering. Figure 28 is a plot of the data showing the rush hours and the total movement of traffic during the sampling period.

### Benzene Monitoring Results

Table 31 summarizes the analytical data for the valid determinations of benzene in the collected samples. Some of the samples at Sites 2a and 2b were lost due to mechanical failures. This prevented determination of a 24-hour average benzene concentration at Site 2a and the morning rush-hour benzene concentration at Site 2b.

In general, the observed benzene levels correlate very well with traffic density. The lowest levels were found in the residential area (Site No. 3) which is somewhat removed (1/4 to 1/2 mile) from major thoroughfares. The levels at the midtown location (Site No. 1) were within the range of concentrations observed along the highway leading into the business district (Site No. 2). At all three locations, the lowest levels were measured during the night when the traffic was the lightest.

A comparison of the benzene levels with the traffic volume is given in Table 32 for Site No. 2, the only location where traffic counts were made. The highest benzene levels were observed on the same side of the highway as the heavy traffic flow, the north side. The only time the levels measured on the south side approached the north-side levels was during the evening rush hour when the eastbound traffic was heavy. This was true even though the wind during most of the day was blowing toward the sampler on the south side and away from the sampler on the north side. However, the winds were light throughout the day.

TABLE 29. TRAFFIC COUNT SUPPLIED BY CITY OF COLUMBUS --  
DIVISION OF TRAFFIC ENGINEERING<sup>(a)</sup>

(East Broad Street at Jefferson,  
Westbound Traffic)

One-Hour Period Starting	15-Minute Period Starting				One-Hour Period Totals	Percent of Total
	:00	:15	:30	:45		
<u>March 15</u>						
9:00 a.m.	392	364	391	305	1452	6.93
10:00 a.m.	305	285	310	264	1164	5.55
11:00 a.m.	285	280	332	335	1232	5.88
12:00 p.m.	280	313	345	356	1294	6.17
1:00 p.m.	291	291	321	289	1192	5.69
2:00 p.m.	287	324	324	269	1204	5.74
3:00 p.m.	272	301	300	295	1168	5.57
4:00 p.m.	274	336	308	317	1235	5.89
5:00 p.m.	273	767	725	255	2040	9.73
6:00 p.m.	212	180	181	180	753	3.59
7:00 p.m.	189	239	211	169	808	3.85
8:00 p.m.	117	117	97	108	439	2.09
9:00 p.m.	110	107	98	90	405	1.93
10:00 p.m.	105	107	88	68	368	1.76
11:00 p.m.	51	73	40	47	211	1.01
<u>March 16</u>						
12:00 a.m.	58	30	31	24	143	0.68
1:00 a.m.	24	17	17	16	74	0.35
2:00 a.m.	8	13	15	11	47	0.22
3:00 a.m.	7	4	15	10	36	0.17
4:00 a.m.	7	21	23	22	73	0.35
5:00 a.m.	33	52	78	76	239	1.14
6:00 a.m.	119	200	244	358	921	4.39
7:00 a.m.	479	580	685	617	2361	11.26
8:00 a.m.	573	590	494	447	2104	10.04

(a) Total over 24-hr period: 20963.

TABLE 30. TRAFFIC COUNT SUPPLIED BY CITY OF COLUMBUS --  
DIVISION OF TRAFFIC ENGINEERING(a)(East Broad Street at Jefferson,  
Eastbound Traffic)

One-Hour Period Starting	15-Minute Period Starting				One-Hour Period Totals	Percent of Total
	:00	:15	:30	:45		
<u>March 15</u>						
9:00 a.m.	170	130	153	184	637	4.04
10:00 a.m.	172	179	184	197	732	4.64
11:00 a.m.	229	233	235	257	954	6.05
12:00 p.m.	279	257	227	223	986	6.25
1:00 p.m.	196	229	213	228	866	5.49
2:00 p.m.	259	264	281	302	1106	7.01
3:00 p.m.	297	316	450	231	1294	8.21
4:00 p.m.	443	390	554	638	2025	12.84
5:00 p.m.	609	503	409	305	1826	11.58
6:00 p.m.	258	197	169	180	804	5.10
7:00 p.m.	147	175	147	153	622	3.94
8:00 p.m.	147	139	171	141	598	3.79
9:00 p.m.	157	164	155	121	597	3.79
10:00 p.m.	134	85	109	83	411	2.61
11:00 p.m.	117	79	74	61	331	2.10
<u>March 16</u>						
12:00 a.m.	82	41	45	43	211	1.34
1:00 a.m.	22	22	21	25	95	0.60
2:00 a.m.	15	16	25	20	76	0.48
3:00 a.m.	14	13	7	14	48	0.30
4:00 a.m.	6	9	15	17	47	0.30
5:00 a.m.	10	23	27	31	91	0.58
6:00 a.m.	29	48	70	85	232	1.47
7:00 a.m.	101	118	150	188	557	3.53
8:00 a.m.	168	155	153	147	623	3.95

(a) Total over 24-hr period: 15769.

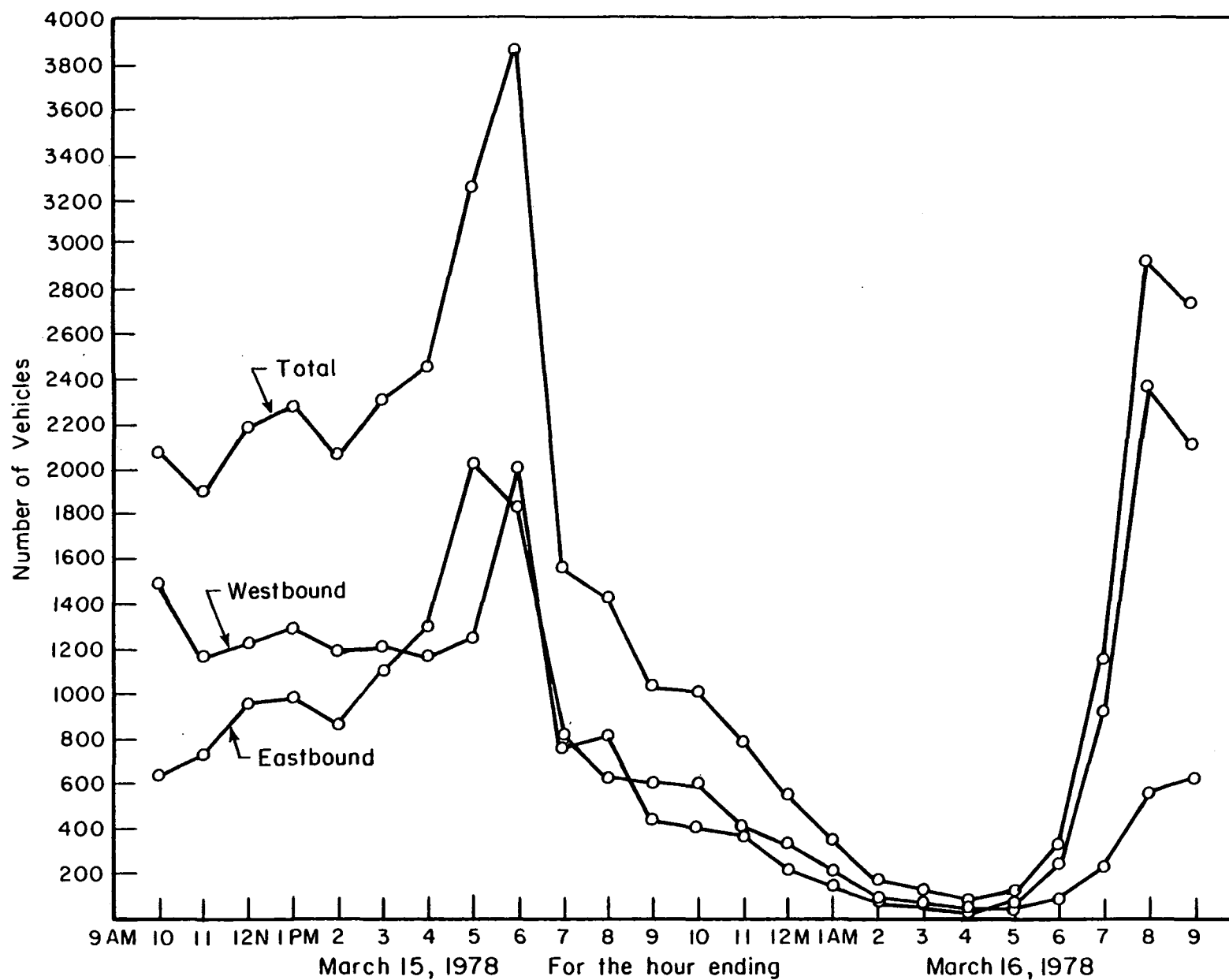


FIGURE 28. TRAFFIC FLOW ON ROUTE 40 INTO AND OUT OF THE BUSINESS DISTRICT IN COLUMBUS, OHIO

TABLE 31. ANALYTICAL DATA FOR AIR SAMPLES FROM URBAN SITES IN COLUMBUS, OHIO

Sampling Station	Weather Conditions <sup>(a)</sup>					Benzene Analysis			
	Wind		Temp. Range, F	Relative Humidity, percent	General	Sampling Period	ppb (v/v)	μg/m <sup>3</sup> <sup>(b)</sup>	
	Direction	Speed, m/sec							
1	150 <sup>0</sup> -350 <sup>0</sup>	1.7-2.2	33-39	87-61	Drizzle	3/15/78 0712-1455	5.1	16.5 (12.8-21.3)	
	350 <sup>0</sup> -360 <sup>0</sup>	1.0-2.0	37-40	57-67	Overcast	3/15/78 1455-2230	4.0	12.8 (10.7-15.3)(2)	
	360 <sup>0</sup> -45 <sup>0</sup>	0.9-2.2	32-40	59-75	Overcast	3/15/78 2237-0815	2.4	7.6 (5.9-9.8)	
	25 hr average						3.8	12	
2a	150 <sup>0</sup>	1.7-1.9	33-36	78	Drizzle	3/15/78 0743-0945	8.6	27.8 (21.6-35.9)	
	150 <sup>0</sup> -350 <sup>0</sup>	1.7-2.2	33-40	78-61	Overcast	3/15/78 0743-1528	7.5	24.2 (18.8-31.2)	
	350 <sup>0</sup> -360 <sup>0</sup>	1.4-1.8	37-40	57-62	Overcast	3/15/78 1528-1754	6.9	22.2 (17.2-28.6)	
	330 <sup>0</sup> -360 <sup>0</sup>	1.4-2.2	32-33	77	Overcast	3/16/78 0658-0901	5.5	17.8 (13.8-23.9)	
2b	150 <sup>0</sup> -350 <sup>0</sup>	1.7-2.2	33-40	78-61	Drizzle	3/15/78 0812-1542	3.4	11.0 (8.5-14.2)	
	350 <sup>0</sup> -360 <sup>0</sup>	1.0-2.0	37-40	57-67	Overcast	3/15/78 1542-2320	3.3	10.5 (8.1-13.6)	
	360 <sup>0</sup> -45 <sup>0</sup>	0.9-2.2	32-37	59-75	Overcast	3/15/78 2320-0907	2.2	7.2 (5.6-9.3)	
	25 hr average						3.0	9	
3	350 <sup>0</sup> -360 <sup>0</sup>	1.4-1.8	37-40	57-62	Overcast	3/15/78 1542-1759	5.3	17.1 (13.3-22.1)	
	150 <sup>0</sup> -350 <sup>0</sup>	1.7-2.2	34-39	78-61	Drizzle	3/15/78 0645-1416	2.0	6.3 (4.9-8.1)	
	350 <sup>0</sup> -360 <sup>0</sup>	1.2-2.0	35-40	67-57	Overcast	3/15/78 1416-2157	1.5	4.8 (4.0-5.8)(2)	
	360 <sup>0</sup> -45 <sup>0</sup>	0.9-2.2	33-40	60-75	Overcast	3/15/78 2157-0804	1.3	4.1 (3.2-5.3)	
25 hr average						1.5	5		

(a) Barometric pressure throughout the sampling was 741 to 744 mm Hg.

(b) The numbers in parentheses are the 95 percent confidence limits, determined as discussed under the quality assurance section. A single number appearing in parentheses is the number of replicates, otherwise the result is based on a single sample.

(c) A continuous 25-hour period was not covered due to loss of samples during analysis.

TABLE 32. CORRELATION OF BENZENE LEVELS WITH TRAFFIC VOLUME AT SITE NO. 2 IN COLUMBUS, OHIO

Sampling Period	Traffic Volume (Vehicles/Hour)		Without Background Subtraction			With Background Subtraction <sup>(a)</sup>		
			Benzene Concentration, ppb	Benzene Concentration per Traffic Unit (ppb/1,000 Vehicles/Hour)		Benzene Concentration ppb	Benzene Concentration per Traffic Unit (ppb/1,000 Vehicles/Hour)	
	One-Way Traffic	Total Traffic		One-Way Traffic	Total Traffic		One-Way Traffic	Total Traffic
<u>Sampling Site No. 2a (North Side of Highway)</u>								
	Westbound Traffic (Same Side of Highway as Sampler)			Westbound Traffic			Westbound Traffic	
3/15/78 0743-0945	1,903 <sup>(b)</sup>	2,524 <sup>(b)</sup>	8.6	4.5	3.4	7.3	3.8	2.9
3/15/78 0743-1528	1,398 <sup>(b)</sup>	2,263 <sup>(b)</sup>	7.5	5.4	3.3	6.2	4.4	2.7
3/15/78 1528-1754	1,591	3,453	6.9	4.3	2.0	5.6	3.5	1.6
3/16/78 0658-0901	2,126	2,688	5.5	2.6	2.0	4.2	2.0	1.6
<u>Sampling Site No. 2b (South Side of Highway)</u>								
	Eastbound Traffic (Same Side of Highway as Sampler)			Eastbound Traffic			Eastbound Traffic	
3/15/78 0812-1542	907 <sup>(b)</sup>	2,232 <sup>(b)</sup>	3.4	3.7	1.5	2.1	2.3	0.9
3/15/78 1542-2320	947	1,785	3.3	3.5	1.8	2.0	2.1	1.1
3/15/78 2320-0907	224	854	2.2	9.8	2.6	0.9	4.0	1.1
25 hr average	652	1,555	3.0	4.6	1.9	1.7	2.6	1.1
3/15/78 1542-1759	1,788	3,352	5.3	3.0	1.6	4.0	2.2	1.2

(a) The background employed was 1.3 ppb, the lowest value observed in the residential neighborhood (Site No. 3).

(b) Portions of this count were estimated from the following morning's count.



Since the results indicated a correlation between benzene concentration and traffic volume, the data were further compared by calculation of a benzene concentration per unit of traffic. This was done by dividing the benzene levels (ppb) by the traffic volume (1000 vehicles per hour). The calculation was performed for both the traffic volume on the same side of the highway as the sampler and the total traffic volume. It was also done with and without the subtraction of a background benzene concentration that might be expected if there were no traffic. The background concentration used was 1.3 ppb, the night-time level observed in the residential neighborhood (Site No. 3). The results of these calculations are also shown in Table 32. The best correlations with traffic volume were achieved with the subtraction of a benzene background. This is most apparent in the data obtained on the south side of the highway, where an excellent correlation was obtained with the use of the total traffic volume and with background subtraction. The wind was blowing from the highway toward the south side sampler during all of the sampling periods except for a portion of the first. The reverse situation was true on the north side. There the wind blew toward the sampler only during the first sampling period and part of the second, which may have contributed to a poorer correlation of the north side data with traffic volume. Comparison of the data for the two sides of the highway is better when only one-way traffic is considered.

SUMMARY

Procedures were developed for the collection and analysis of benzene in air, water, and soil samples. The procedures were applied to air monitoring for benzene in the vicinity of seven industrial facilities, in the area around three gasoline service station locations, and at three urban locations in Columbus, Ohio, and to water and soil sampling for benzene near five of the industrial facilities.

The procedure for collection of benzene in air samples involved pulling the air through a bed of Tenax GC. It was found that preparation of the Tenax prior to its use required much more drastic cleanup conditions than indicated in the literature. The benzene was thermally desorbed from the Tenax and analyzed by cryogenic capillary gas chromatography. Benzene present in water and soil samples was determined by sparging it from the water or soil with nitrogen, adsorbing it in Tenax adsorption tubes, and analyzing the Tenax tubes in the same manner as air samples.

Results of the air monitoring at the various locations are summarized in Table 33. The 24-hour average benzene concentrations at the air sampling stations around the seven industrial facilities ranged from 2 to 51  $\mu\text{g}/\text{m}^3$  (0.5 to 19 ppb) as compared with background concentrations of 0.5 to 3  $\mu\text{g}/\text{m}^3$  (0.2 to 1.2 ppb). At the Mobay Chemical Company nitrobenzene plant, the average levels were in the range of 3 to 11  $\mu\text{g}/\text{m}^3$  (1 to 4 ppb), with the lowest concentration being observed at the station most distant from the plant. The average concentrations found near the Gulf Oil Corporation cumene plant ranged from 25 to 51  $\mu\text{g}/\text{m}^3$  (9 to 19 ppb). Near the Petro-Tex Corporation maleic anhydride plant, the average concentrations were in the range of 11 to 31  $\mu\text{g}/\text{m}^3$  (4 to 11 ppb). The highest levels were observed at a station near the plant when the wind, though relatively calm, blew toward this station. At the Ashland Chemical Company maleic anhydride plant, the average concentrations ranged from 2 to 32  $\mu\text{g}/\text{m}^3$  (1 to 10 ppb). The highest levels were found downwind of the plant at stations close to the plant. The presence of a refinery near this plant complicates the interpretation of the results. Near the Chevron Corporation detergent alkylate plant the average benzene levels were in the range of 3 to 7  $\mu\text{g}/\text{m}^3$  (1 to 3 ppb). The location of this plant prevented samples being taken any closer than 1 km from the suspected benzene source. The average concentrations near the Union Carbide Corporation benzene plant ranged from 6 to 35  $\mu\text{g}/\text{m}^3$  (2 to 13 ppb). The

TABLE 33. SUMMARY OF BENZENE AIR-MONITORING DATA.

Facility or Location Monitored	Sampling Station	Location of Source Relative to Sampler		Wind		Benzene Concentrations <sup>(a)</sup>			
		Distance, km	Direction, degrees	Direction, degrees	Speed, m/sec	ppb (v/v)		$\mu\text{g}/\text{m}^3$	
						Avg.	Range	Avg.	Range
Mobay Nitrobenzene Plant <sup>(b)</sup>	1	1.0	160	225/270	Calm-7.5	4	1.3-5.2	11	3.4-14.1
	2	1.0	305	225/270	Calm-7.5	4	2.8-7.0	11	7.5-18.7
	3	2.5	340	225/270	Calm-7.5	1	0.4-1.3	3	1.2-3.4
	4	0.9	100	225/279	Calm-7.5	2	1.2-3.0	5	3.2-8.1
Gulf Oil Cumene Plant <sup>(b)</sup>	1	2.5	230	45/202.5	0.1-1.8	19	9.1-34.8	51	24.4-93.5
	2	0.8	275	45/202.5	0.01-1.0	10	1.2-19.4	28	3.1-52.2
	3	2.0	45	202.5	Calm-1.01	12	5.4-20.5	31	14.5-55.0
	4	2.0	145	45/225	Calm-3	9	7.4-14.4	25	19.8-38.7
Petro-Tex Maleic Anhydride Plant <sup>(b)</sup>	1	0.2-0.5	270-320	180-225	Calm-1.45	6	3.4-9.0	15	9.3-24.3
	2	1.0	45-90	90	Calm-1.45	8	2.6-9.1	22	7.0-24.5
	3	0.5	220-270	225	Calm-0.97	11	4.5-16.4	31	12.0-39.1
	4	2.0	150	135-315	Calm-0.97	4	3.1-6.6	11	6.9-17.7
Ashland Maleic Anhydride Plant <sup>(b)</sup>	1	0.8	210	120-340	1.6-5.7	6	4.0-9.3	19	12.9-30.0
	2	1.6	350	120-340	1.6-5.7	1	0.3-1.1	2	0.9-3.4
	3	1.4	20	180-340	1.6-5.7	1	0.3-1.7	3	1.1-5.4
	4	1.5	355	180-340	1.6-5.7	5	0.3-29.7	16	1.1-95.8
	5	0.5	330	120-340	1.6-5.7	3	0.7-6.8	10	2.3-21.9
	6	1.9	360	120-340	1.6-5.7	1	0.3-1.1	2	1.0-3.5
	7	0.3	230	180-320	2.6-4.6	10	1.0-13.8	32	3.2-44.5
Chevron Detergent Alkylate Plant <sup>(b)</sup>	1	1.0	15	60-360	0.2-1.5	2	2-3	6	3.9-7.3
	4	2.7	240	60-180	1.6-4.1	1	1	3	3
	6	1.6	10	60-180	1.6-4.1	3	3	7	6.8
Union Carbide Benzene Plant <sup>(b)</sup>	1	2.0	250	180-202.5	0.2-1.6	2	0.6-4.5	6	1.6-12.1
	2	2.0	280	135/202.5	0.6-1.8	4	1.1-6.4	9	2.9-17.3
	3	1.0	290	135/180	0.6-3.8	13	12.8-13.5	35	34.4-36.2

TABLE 33. (Continued)

Facility or Location Monitored	Sampling Station	Location of Source Relative to Sampler		Wind		Benzene Concentrations <sup>(a)</sup>			
		Distance, km	Direction, degrees	Direction, degrees	Speed, m/sec	ppb (v/v)		$\mu\text{g}/\text{m}^3$	
						Avg.	Range	Avg.	Range
U.S. Steel Coke Oven Facility <sup>(b)</sup>	1A	7.0	145	110-220	1.6-6.2	3	2.0-6.0	10	6.5-19.2
	1B	2.5	170	110-180	1.6-4.1	0.5	0.4-0.6	2	1.2-2.0
	1	2.2	135	90-340	0.6-2.5	6	2.3-12.3	19	7.5-41.5
	2	0.5	280	90-340	0.6-2.5	1	0.7-2.0	4	2.2-6.4
	3	1.0	100	70-340	0.6-3.2	2	1.5-3.0	7	4.9-9.7
	4	1.4	100	70-180	0.6-2.5	5	3.5-6.0	15	11.4-19.3
Location 1: Four-Station Intersection <sup>(c)</sup>	1	0.1-0.2	300-45	30-360	Calm-4.1	0.5	0.2-0.8	1	0.5-2.5
	2	0.05-0.25	280-360	30-360	Calm-4.1	0.8	0.6-1.0	2	1.8-3.2
	3	0.1-0.4	285-310	30-360	Calm-4.1	1.5	0.5-2.1	5	1.7-6.7
	4	0.15-0.4	270-290	30-360	Calm-4.1	1.1	0.3-2.0	4	0.9-6.3
	5	0.15-0.3	300-10	30-360	Calm-4.1	0.3	0.1-0.4	1	0.4-1.4
	6	0.2-0.3	185-245	30-360	Calm-4.1	0.5	0.3-0.7	2	0.9-2.1
	7	0.2-0.4	40-90	30-360	Calm-4.1	2.0	0.6-4.3	7	1.9-13.7
Location 2: Single Full-Service/ Self-Service Station <sup>(c)</sup>	1	0.2	250	225-360	4.6-9.3	0.7	0.4-0.8	2	1.2-2.7
	2	0.2	90	225-360	4.6-9.3	0.5	0.2-0.8	2	0.6-2.4
	3	0.05	75	225-270	7.2-9.3	0.6	0.6	2	1.8
	4	0.1	270	225-360	4.6-9.3	1.3	0.9-1.6	4	2.9-5.0
	5	0.03	360	225-360	4.6-9.3	0.7	0.7	2	2.3
	6	0.07	160	225-360	4.6-9.3	0.5	0.4-0.6	2	1.3-2.0
	7	0.1	210	225-360	4.6-9.3	0.8	0.5-1.0	2	1.5-3.2
	8	0.05	290	225-360	4.6-9.3	1.0	0.7-1.2	3	2.3-3.7
Location 3: Single Self-Service Station <sup>(c)</sup>	1	0.1	110	200-240	3.6-9.3	1.2	0.9-1.4	4	2.8-4.5
	2	0.15	170	180-240	2.6-8.8	0.7	0.7	2	2.4-2.5
	3	0.05	190	180-240	2.6-8.8	1.0	0.6-1.3	3	2.0-4.0
	4	0.1	220	180-240	2.6-8.8	0.9	0.7-1.1	2	2.2-3.3
	5	0.25	270	180-240	2.6-8.8	0.8	0.7-0.8	2	2.3-2.4
	6	0.1	135	180-240	2.6-8.8	0.7	0.6-0.8	2	1.8-2.6
	7	0.1	315	180-240	2.6-8.8	0.3	0.3-0.4	1	0.9-1.4
Location 1: Center of the City <sup>(d)</sup>	1	--	--	150-45	0.9-2.2	4	2.4-5.1	12	7.6-16.5
Location 2: Both Sides of a Busy Highway <sup>(d)</sup>	2a	--	180	150-360	1.4-2.2	7	5.5-8.6	23	17.8-27.8
	2b	--	260	150-45	0.9-2.2	3	2.2-5.3	9	7.2-17.1
Location 3: Residential Neighborhood <sup>(d)</sup>	3	--	--	150-45	0.9-2.2	1.5	1.3-2.0	5	4.1-6.3

(a) These data are for the continuous monitoring only (grab samples are not included).

(b) Industrial locations.

(c) Service Station locations in Columbus, Ohio.

(d) Urban locations in Columbus, Ohio.

highest concentration was observed at the sampling station closest to the emission point. At the U.S. Steel Corporation coke oven facility, the average concentrations ranged from 2 to 19  $\mu\text{g}/\text{m}^3$  (0.5 to 6 ppb). The highest level was found in the valley across the river from the coke ovens. The lowest levels were observed at a station on a ridge above the ovens, though it was downwind.

A limited number of soil and water samples were obtained near five of the industrial facilities and analyzed for benzene. The results are summarized in Table 34. Exclusive of plant effluent samples, the benzene concentrations found in water samples ranged from <1 to 13 ppb. In general, the downstream levels were 1 to 2 ppb or less. The higher levels were found near the plant outfall in one case and upstream of the plant in another case where a chlorobenzene plant was located upstream. The highest levels of benzene found in any of the three environmental media were found in the soil samples. The levels ranged from 2 to 191 ppb.

Also summarized in Table 33 are the results of air sampling in Columbus, Ohio, near three service station locations and at three urban locations near the center of the city. At sampling points near the service stations, the 12-to-30-hour average benzene concentrations were in the range of 1 to 7  $\mu\text{g}/\text{m}^3$  (0.3 to 2.0 ppb), with individual measurements ranging from 0.4 to 13.7  $\mu\text{g}/\text{m}^3$  (0.1 to 4.3 ppb). Analysis of the data revealed that emissions from automobiles (idling, parked after a trip, or in traffic) contribute to observed benzene concentrations. Background benzene concentrations in neighborhoods upwind of the service stations and automobile traffic ranged from 0.6 to 1.4  $\mu\text{g}/\text{m}^3$  (0.2 to 0.4 ppb). Levels of 32 to 69  $\mu\text{g}/\text{m}^3$  (10 to 22 ppb) were observed in the residential neighborhood near one station in grab samples taken during the filling of underground storage tanks.

Generally higher benzene concentrations were found at the three urban Columbus locations, all of which were nearer the center of the city than the service station locations. In a residential neighborhood near the business district, the 25-hour average benzene level was 5  $\mu\text{g}/\text{m}^3$  (1.5 ppb). In the center of the business district, it was 12  $\mu\text{g}/\text{m}^3$  (4 ppb). Immediately adjacent to a busy highway leading into the business district, the average levels were 9  $\mu\text{g}/\text{m}^3$  (3 ppb) on one side of the highway and 23  $\mu\text{g}/\text{m}^3$  (7 ppb) on the other side. The higher levels were observed on the side of the highway carrying the heavier traffic. The individual measurements made at this location correlate well with the traffic counts.

TABLE 34. SUMMARY OF BENZENE SOIL- AND WATER-MONITORING DATA

Facility Monitored	Sampling Station	Sample Description	Water	Distance from the Plant, km	Soil
			Benzene Concentration, ppb		Benzene Concentration, ppb
Mobay Nitrobenzene Plant	1	--	--	1.0	2
	3	Downstream: Surface	3.3	2.5	51
		6 ft depth	4.9		
	4	--	--	0.9	17
	5	Upstream: Surface	12.0	--	--
		6 ft depth	11.9	--	--
	6	Plant Influent	4.2	--	--
Gulf Oil Cumene Plant	7	Plant Effluent	104.	--	--
	1	--	--	2.5	34
	2	--	--	0.8	>73(a)
	3	--	--	2.0	18
	4	--	--	2.0	>34(a)
	5	Wastewater Treatment Unit: Outfall	4.3	--	--
		From pump	56.6	--	--
	6	River	1	--	--
Petro-Tex Maleic Anhydride Plant	7	Gulf Dock	1.9	--	--
	1	--	--	0.2-0.5	22
	5	Plant Outfall	8	--	--
	6	Midway, Near Outfall	13	--	--
	7	Upstream	<1	--	--
	8	Downstream	2	--	--
Chevron Detergent Alkylate Plant	2	--	--	1.7	191
	3	Yacht Basin	<1	1.3	70
	4	--	--	2.7	51
	5	--	--	3.2	≥148(a)
	7	Municipal Water	<1	--	--
Union Carbide Benzene Plant	1	--	--	1-2	12
	2	--	--	~2	14
	6	Plant Effluent	179	--	--
	7	Upstream	2	--	--
	8	Downstream	1	--	--

(a) Sample not heated, so this is a minimum value.

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- (8) H. E. Runion. 1977. Benzene in Gasoline II. *American Industrial Hygiene Association Journal*. 38:391-393.

APPENDIX A

CONDITIONING OF TENAX GC FOR BENZENE ANALYSES



## APPENDIX A

CONDITIONING OF TENAX GC FOR BENZENE ANALYSIS

Preparation of satisfactory traps is dependent upon several important variables; solvent extraction and time and temperature of conditioning. To check out these variables several experiments were made. Exploration of all possible combinations was precluded by limitations of time, but the primary variables were studied as discussed below.

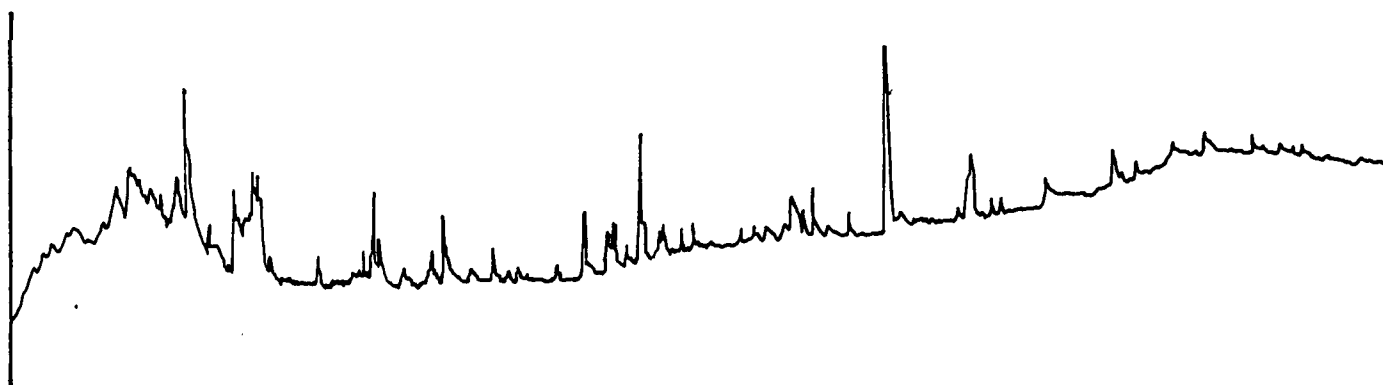
Stainless Steel Versus Glass

Stainless steel and glass traps (U tube, 3/8 in. O.D. x 12 in. long)\* were packed with Tenax GC that was solvent extracted in a Soxhlet extractor with distilled-in-glass methanol for 48 hours, then vacuum dried at 135-150 C for 16 hours. The traps were then conditioned for 45 min at 200 C with a helium flow of 40 ml/min on the GC analytical system (see later section on analysis). The traps were then evaluated by being subjected to essentially the standard analytical procedure for benzene. Each trap was heated for 5 minutes at 200 C while helium at 10 ml/min was passed through the trap and swept onto the GC column at -70 C. For trap evaluation, the column was programmed from 0 C at 8 C/min. This is the standard procedure for evaluation of Tenax traps. Figure A-1a and A-1b are chromatograms for evaluation of Tenax conditioned in the glass and stainless steel traps, respectively. To simulate the effect of aging (storage), the traps were capped and heated overnight (16 hr) at 100 C. Figure A-1c shows a check of the stainless steel trap. The seal\*\* on the glass trap apparently leaked air, as the chromatogram of the glass trap had peaks completely off scale.

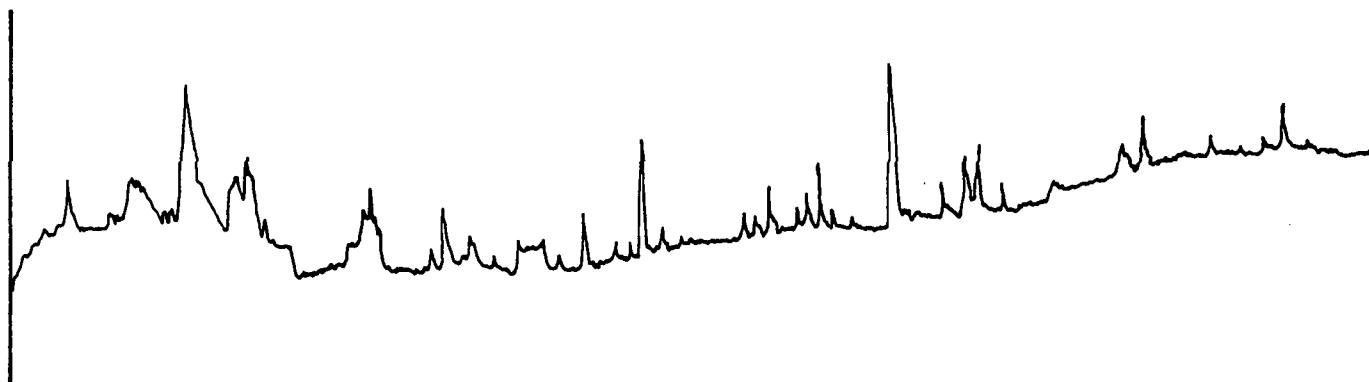
These data indicate that stainless steel does not appear to affect the stability of Tenax.

\* All stainless steel traps are this size unless otherwise indicated.

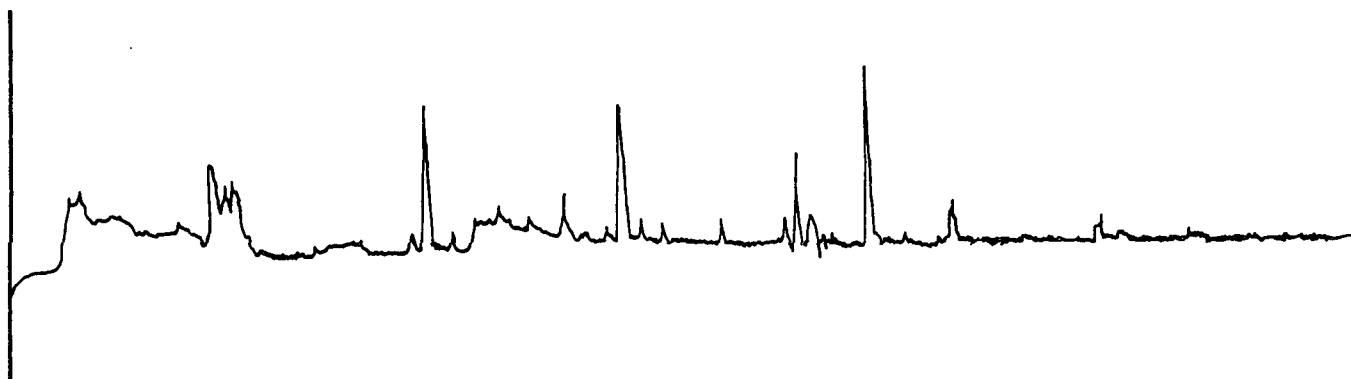
\*\* Swagelok caps with graphite ferrules were used.



a. Glass Trap



b. Stainless Steel Trap



c. Stainless Steel Trap After Heating Overnight at 100 C

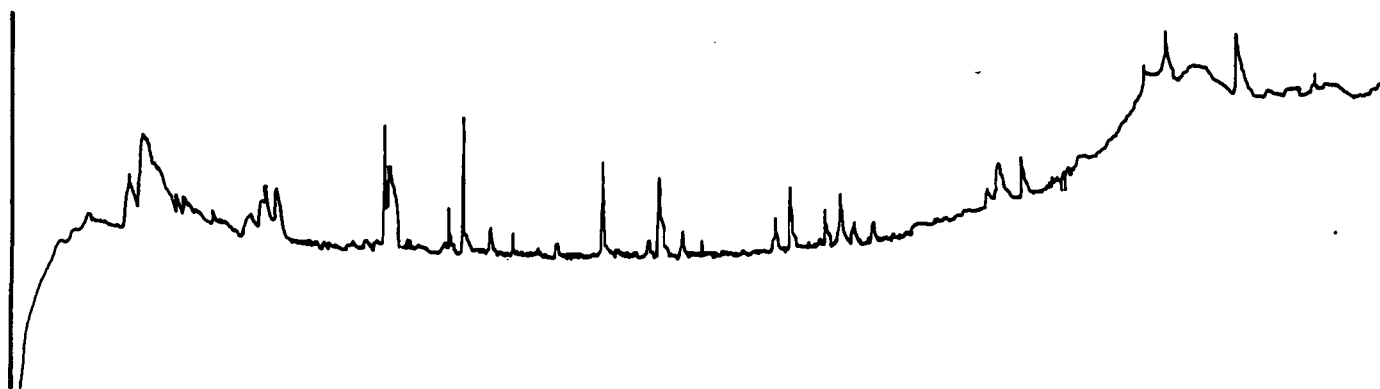
FIGURE A-1. CHROMATOGRAMS FOR COMPARISON OF GLASS AND STAINLESS STEEL TRAPS

Extracted Versus Unextracted Tenax GC

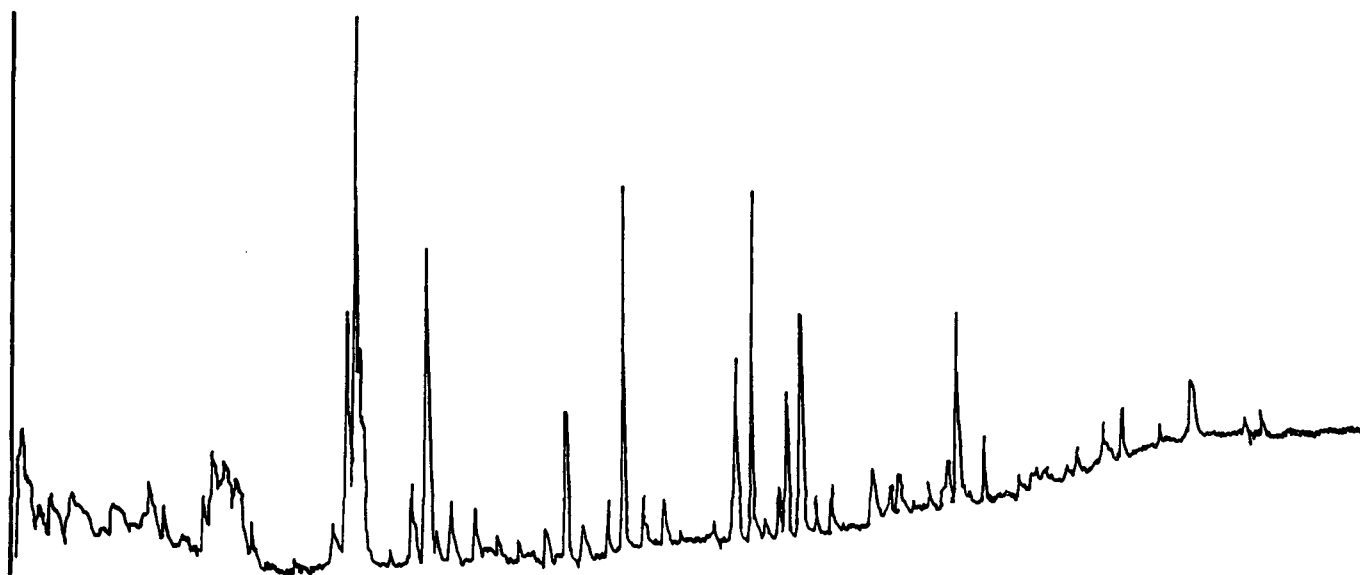
A stainless steel trap was packed with unextracted Tenax GC and conditioned at 200 C for 1 hour. It was evaluated by the standard procedure. The chromatogram is shown in Figure A-2a. This trap was then capped and heated overnight at 60 C. Figure A-2b is the chromatogram obtained upon evaluation of the trap. Comparison\* of Figure A-2a with Figure A-1b indicates the extraction makes little difference in the cleanliness of traps immediately after conditioning. However, comparison of Figure A-2b with Figure A-1c indicates that extracted Tenax is superior to unextracted Tenax for stability. Except for one series to be discussed later, all traps have been packed with extracted Tenax GC.

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\* A single column GC is used, and thus baseline drift should be ignored.



a. Initial Evaluation



b. After Aging Overnight at 60 C

FIGURE A-2. CHROMATOGRAMS OF STAINLESS STEEL TRAP FILLED WITH UNEXTRACTED TENAX

Effect of Temperature and Time  
in Thermal Conditioning of Tenax GC

Two times and temperatures were picked for a brief preliminary study of these two variables, 200 C (used in earlier work at BCL on another project) and 275 C, and 20 minutes and 2 hours chromatograms for evaluation of these traps are given in Figure A-3. All were run 24 hours after conditioning. The chromatogram for the trap conditioned 20 minutes at 200 C had numerous peaks off-scale. Chromatograms for evaluation of the other three traps are shown in Figure A-3 as follows:

200 C, 2 hr - Figure A-3a

275 C, 20 min - Figure A-3b

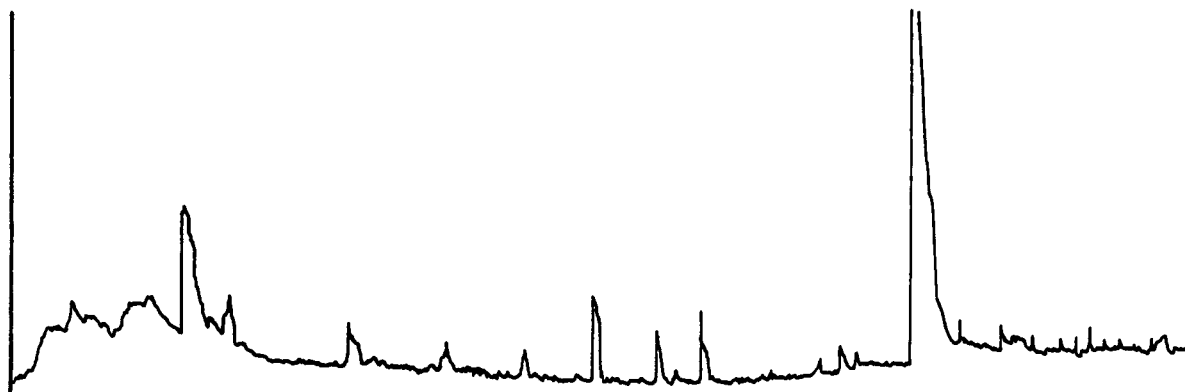
275 C, 2 hr - Figure A-3c.

Based on these chromatograms, 20 minutes is obviously too short a time for conditioning and 2 hours at 200 C seems better than 2 hours at 275 C.

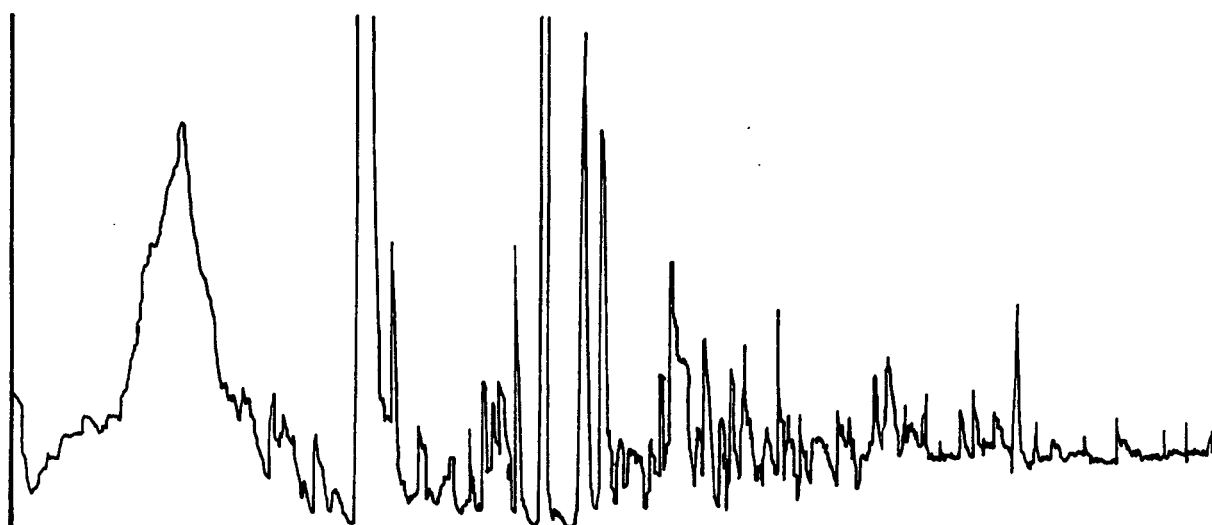
Logically, however, higher temperatures should give better conditioning, provided that the decomposition temperature of Tenax is avoided. Previous attempts to condition traps in groups were reported earlier and had not been successful. Several more attempts were made to condition traps in groups of from four to twelve at 275 C for 16 hours. The traps were fastened together in series with 3/8 in. Swagelok unions and heated in a GC oven. Results were variable; some traps were good -- others bad. A manifold was constructed to permit conditioning of four groups of traps in parallel, three traps in series in each group. Again, results were variable; some traps were good, others were marginal, and others poor. The difficulty was finally traced to leaks in the Swagelok connections. Since the Swagelok connection was heated, air oxidation of the surfaces occurred. The oxidation made it more difficult to tighten the connections with each successive experiment. Connections that were tight before heating would develop leaks after being heated and cooled to room temperature. Leaks permit diffusion of air into the traps, and Tenax GC oxidizes at the elevated temperatures.

At this point there was a critical need for traps and no really good method of conditioning Tenax traps more than one at a time had been found. The only reliable method was to condition traps individually on the GC analytical system; 200-225 C for 2 hours gave good traps. Long-term stability tests had

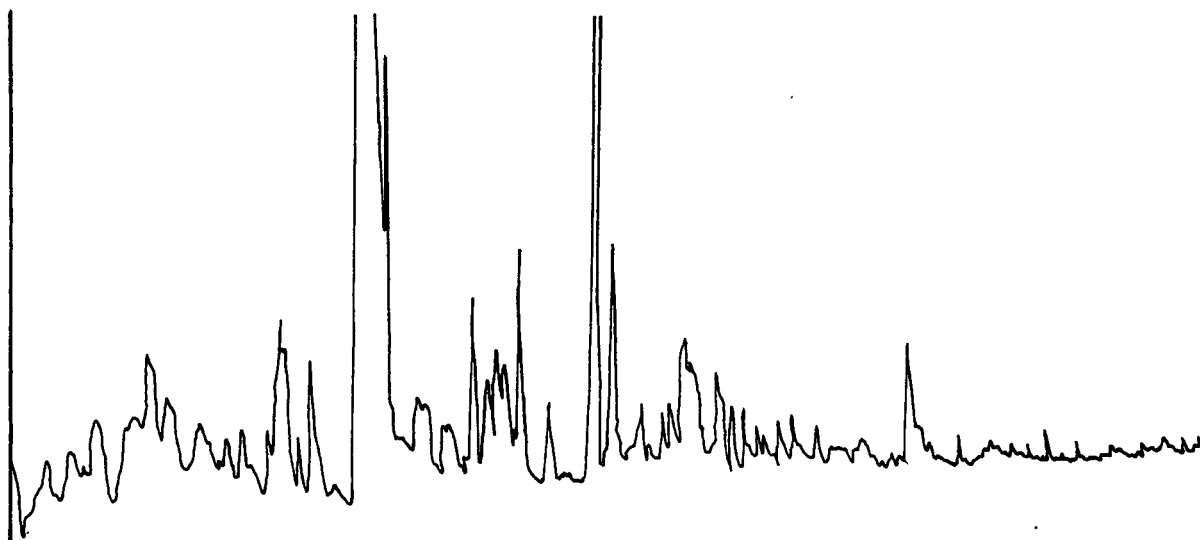
A-6



a. 200 C - 2 hr



b. 275 C - 20 min



c. 275 C - 2 hr

FIGURE A-3. CHROMATOGRAMS FOR COMPARISON OF TIME AND TEMPERATURE  
IN TENAX CONDITIONING

not been performed at room temperature but it had been found that traps were stable when stored at -70 C. Therefore, 40 traps were packed with solvent-extracted Tenax, conditioned at 225 C for 2 hours on the GC system, and stored at dry-ice temperature. It had been learned from Pellizzari<sup>(2)</sup> that cold storage of traps after sampling was advisable if the traps could not be analyzed quickly, so it was planned to keep them cold after sampling. These traps were used to sample at Mobay Chemical Company, New Martinsville, West Virginia.

Figure A-4a is the chromatogram for evaluation of one of these traps. Figure A-4b is the chromatogram of a control trap, taken on the sampling trip and returned with the samples. No significant deterioration of the traps occurred. However, storage at room temperature for 1 week led to significant worsening of the traps, Figure A-4c; therefore, the short conditioning time is not satisfactory.

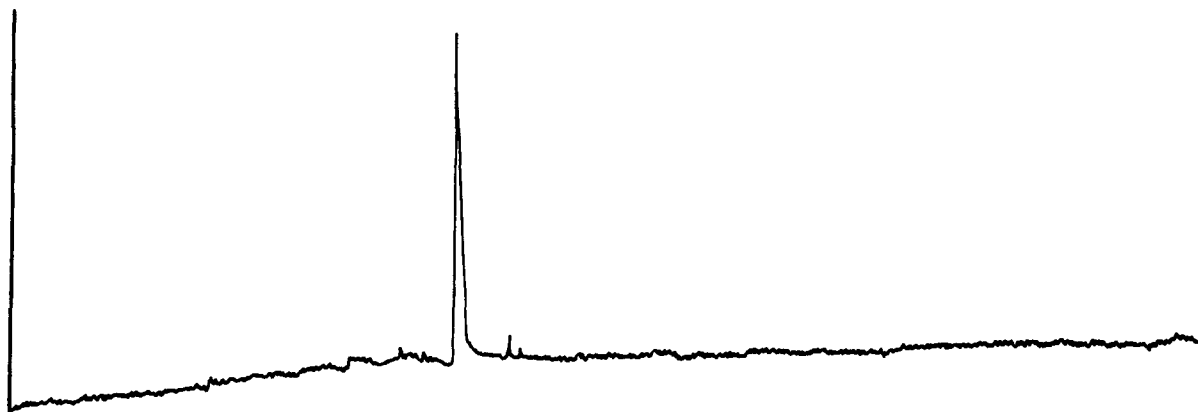
#### Tenax Conditioning System

To overcome this difficulty, a new system for conditioning Tenax traps was designed. This system consists of a stainless steel manifold onto which 12 Tenax traps can be fastened individually so that the traps are connected in parallel. Each trap is closed with a stainless steel cap into which a 1-inch piece of .01 in. I.D. stainless steel capillary is silver soldered. A 300 ml/min flow of nitrogen through the manifold provides a flow of 25 ml/min through each trap. High purity nitrogen is used. It is further purified by passing it through an Oxy-Trap and a Drierite-molecular sieve trap. The traps mounted on the manifold are heated by lowering the assembly into the Wood's metal bath. This bath is made from an aluminum block, machined to provide a slot for each tube.\* Since the connections are not in the bath they are not subjected to the maximum temperature, thus reducing oxidation problems. The top is covered with fiberglass and aluminum foil during the conditioning period, and the enclosed space is constantly flushed with nitrogen, further reducing oxidation.

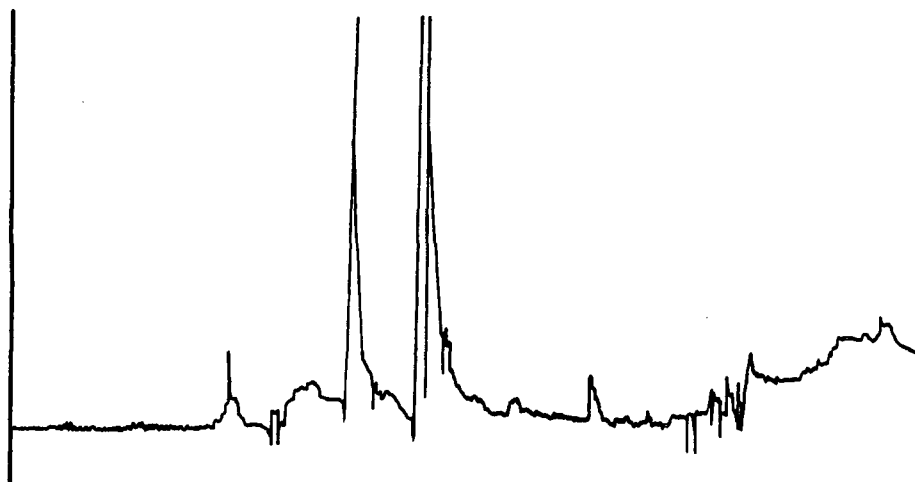
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\* The slots are not necessary, but substantially reduce the amount of Wood's metal required.

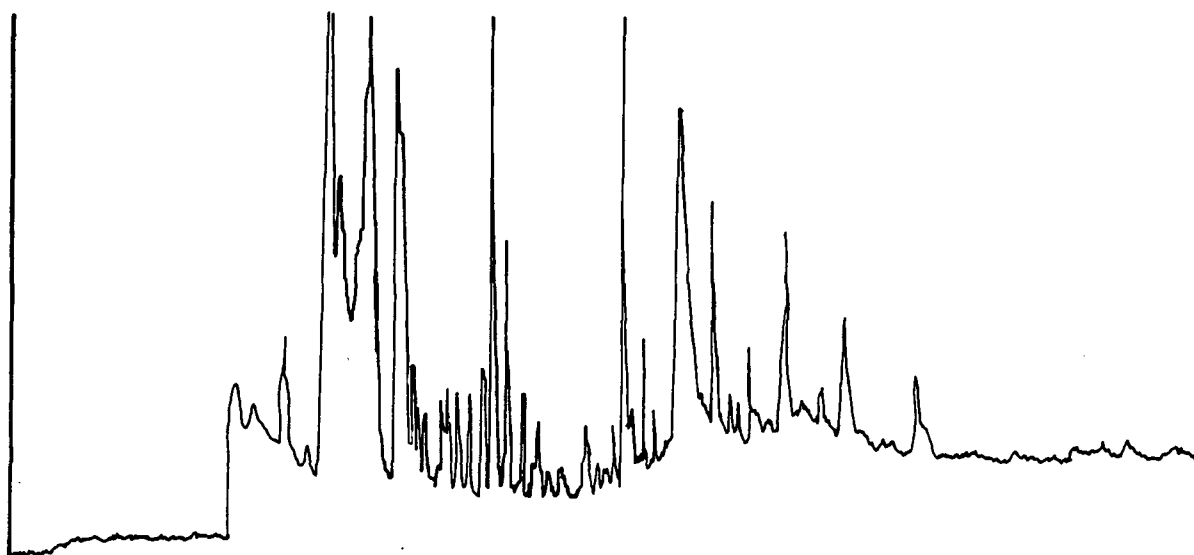
A-8



a. 24 Hours After Conditioning



b. Control Trap Taken on Mobay Sampling  
Trip (Stored 3 Weeks at  $-70^{\circ}\text{C}$ )



c. Stored 1 Week at Room Temperature

FIGURE A-4. CHROMATOGRAMS FROM EVALUATION OF TRAPS CONDITIONED FOR  
2 HR AT  $225^{\circ}\text{C}$



The first experiments with this apparatus employed Tenax GC which had been extracted for at least 48 hours with methanol and vacuum dried before packing the traps. Three sets of traps (12 in each set) were conditioned overnight (16-20 hours) and evaluated as described previously. Of the 36 traps, slightly over one-half were considered good, the rest were only fair, and a few poor. Figure A-5 shows chromatograms of the evaluation of four typical traps. These traps were reasonably good. However, since so many traps were marginal or unsatisfactory, this method of preparation of traps was not considered satisfactory.

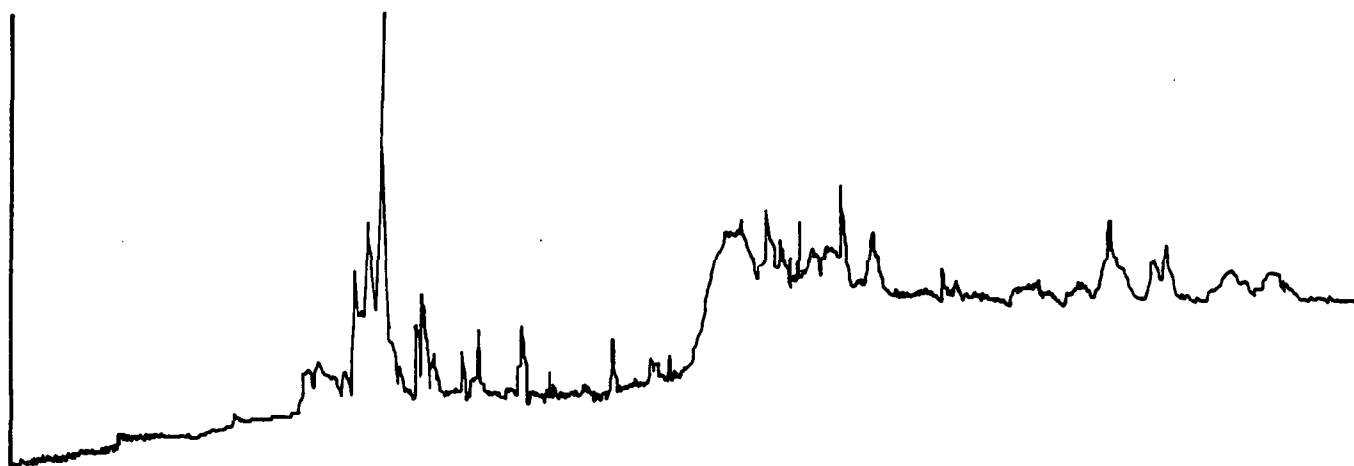
#### Preconditioning of Tenax

More thorough conditioning of Tenax would have to involve higher temperature, longer time, or both. Bertsch et al,<sup>(4)</sup> recommended 340 C. Because of the possible catalytic effects of stainless steel surfaces, conditioning in the stainless steel tubes did not seem safe. Moreover, the problem of oxidation of joints would be more severe at higher temperatures. Longer time also was undesirable from the standpoint of reasonable production rate.

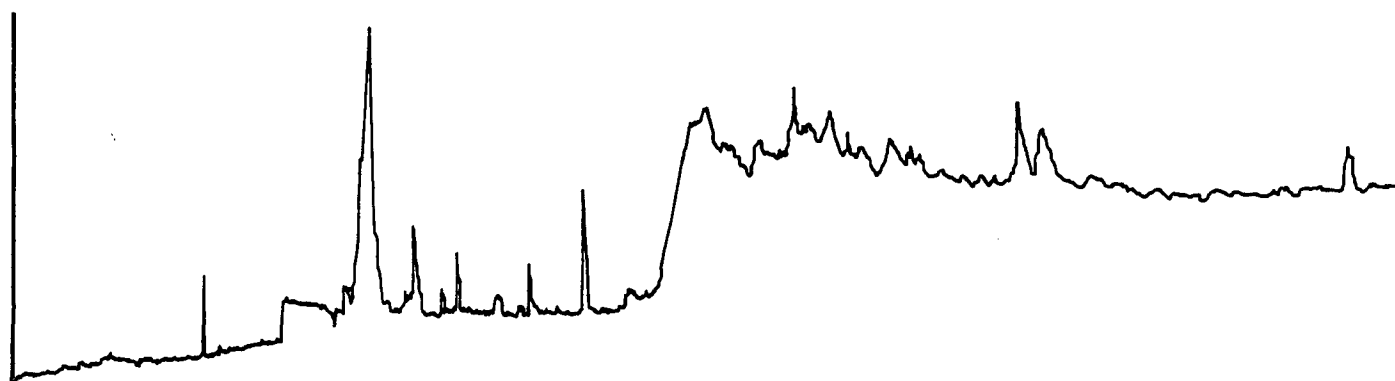
It was decided to precondition Tenax at a higher temperature in large glass tubes. Accordingly, several experiments were run in which the solvent extracted Tenax GC was heated at 300 C in a large glass tube, with purified nitrogen flow. Four different conditions were evaluated:

- (A) Re-extract with methanol for 72 hours, vacuum dry.  
Heat with nitrogen flow for 8 hours at 300 C.
- (B) No re-extraction -- heat with nitrogen flow for  
8 hours at 300 C.
- (C) Similar to (B), but 16 hours at 300 C.
- (D) Similar to (B) and (C), but 40 hours at 300 C.

At this point all of the Tenax on hand had been extracted with methanol at least once and packed into traps. All traps that were marginal or poor were unpacked, screened to remove any debris, and blended into one large batch of recovered Tenax. Experiments A and B above were run concurrently to determine



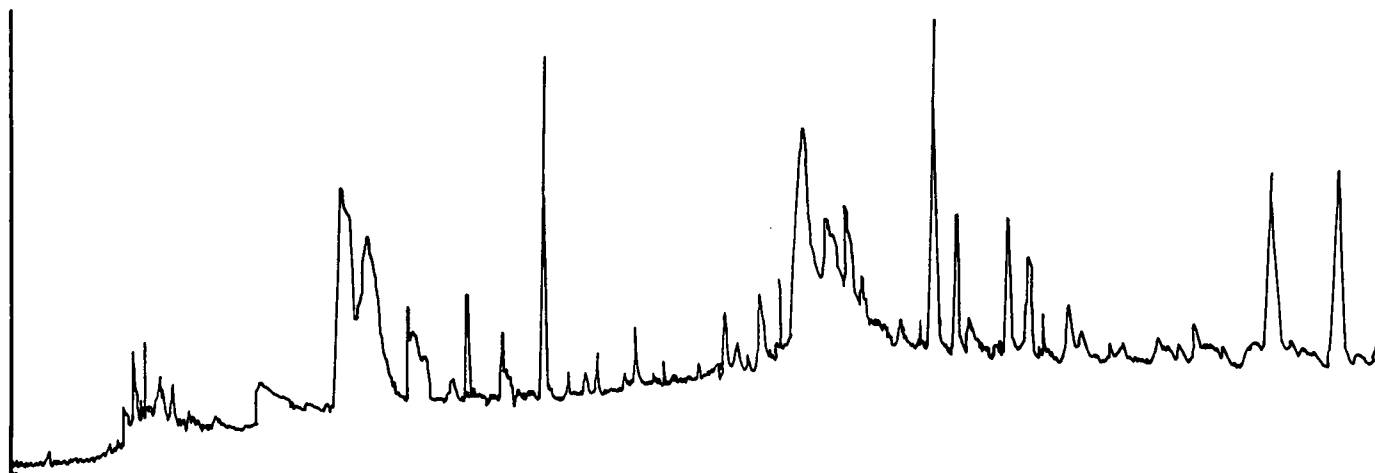
**a. Typical Good Traps**



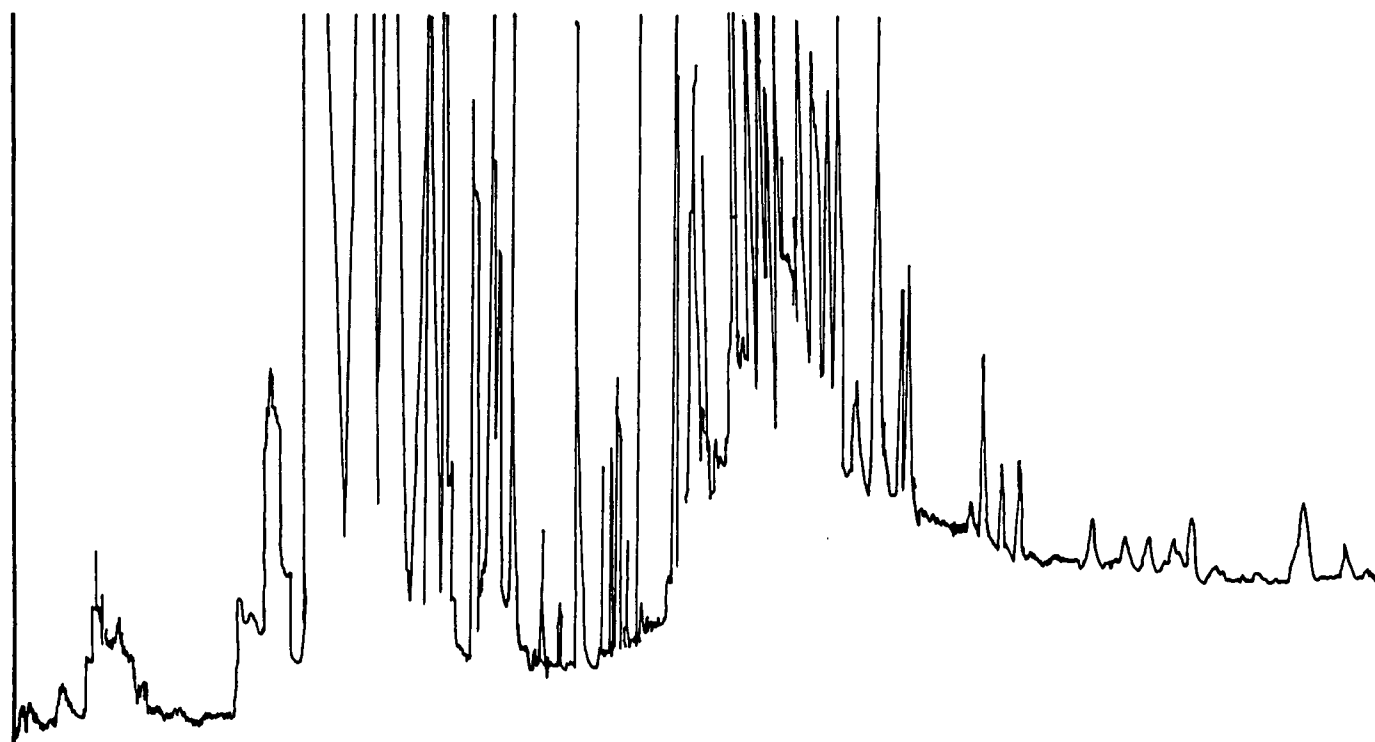
**b. Typical Good Traps**

**FIGURE A-5. CHROMATOGRAMS FOR EVALUATION OF SOLVENT EXTRACTED TENAX**

A-11



c. A Fair Trap



d. A Poor Trap

FIGURE A-5. (CONTINUED)

whether a re-extraction of the recycled Tenax was required. Experiments (C) and (D) were done later. Several sets of traps were packed with each of the four kinds of preconditioned Tenax and conditioned in the 12-tube conditioning system described previously.

The following sections briefly describe the results of the evaluation of the conditioned traps. Overall, Tenax (A) is slightly better than (B), (C), or (D). Therefore, in all further reconditioning of Tenax a combination of solvent extraction and thermal conditioning was used.

In evaluation of traps, however, it should be noted that the gas chromatograph with flame-ionization detector is much more sensitive than GC/MS. Peaks considered unacceptable interferences for this program are not detectable by GC/MS, unless the latter is operating in the SIM mode and looking for a specific ion (or ions). The worst traps in the whole series have peaks corresponding to only about 2 to 4 ng of benzene. Thus, using even the bad traps on a 14-liter sample would provide an uncertainty of less than 0.1 ppb (volume).

#### Preconditioned Tenax, Type A

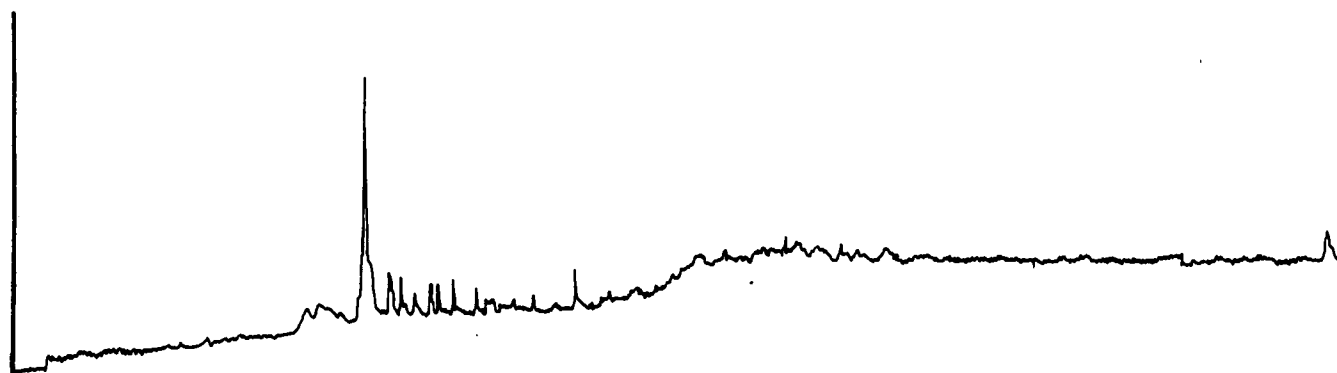
A total of 26 traps were conditioned and checked. Most of these traps were quite good. The chromatogram given in Figure A-6a is typical.\* Two had larger than usual peaks in the early part of the chromatogram as shown in Figure A-6c.

#### Preconditioned Tenax, Type B

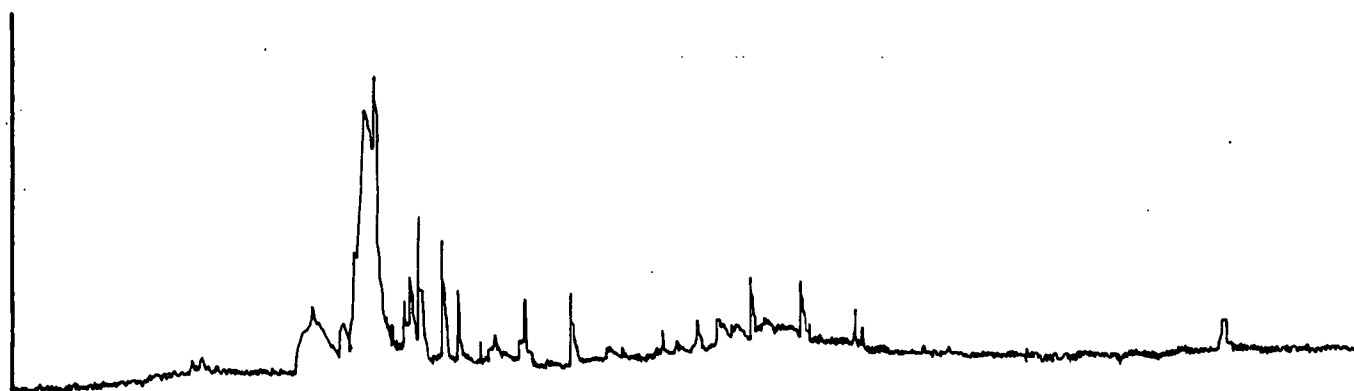
Most of these traps were also quite good, as illustrated by Figure A-7a.\*\* However, two of the traps had significantly larger peaks, in and following the benzene regions, as shown in Figure A-7c.

\* Storage stability of these traps was good. Figure A-6b shows the same trap after 21 days aging.

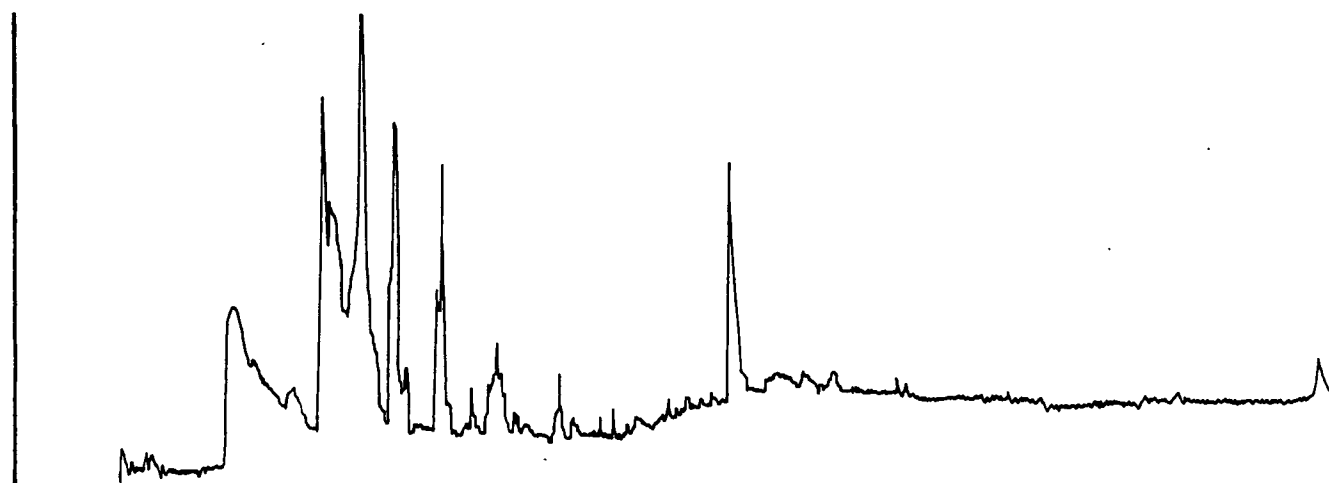
\*\* Storage stability of these traps was good. Figure A-7b shows the same trap after 14 days aging.



a. Typical Good Trap



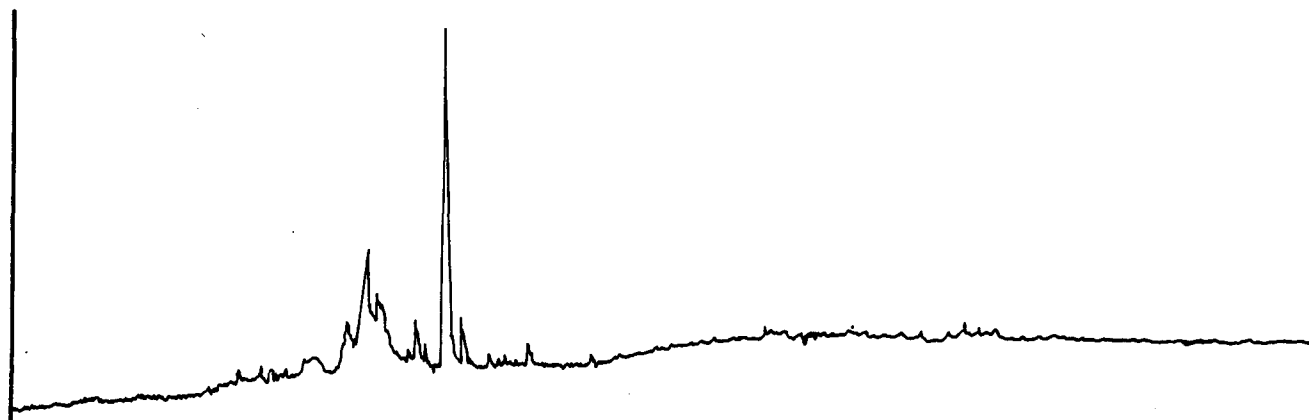
b. Trap A, Aged 14 Days



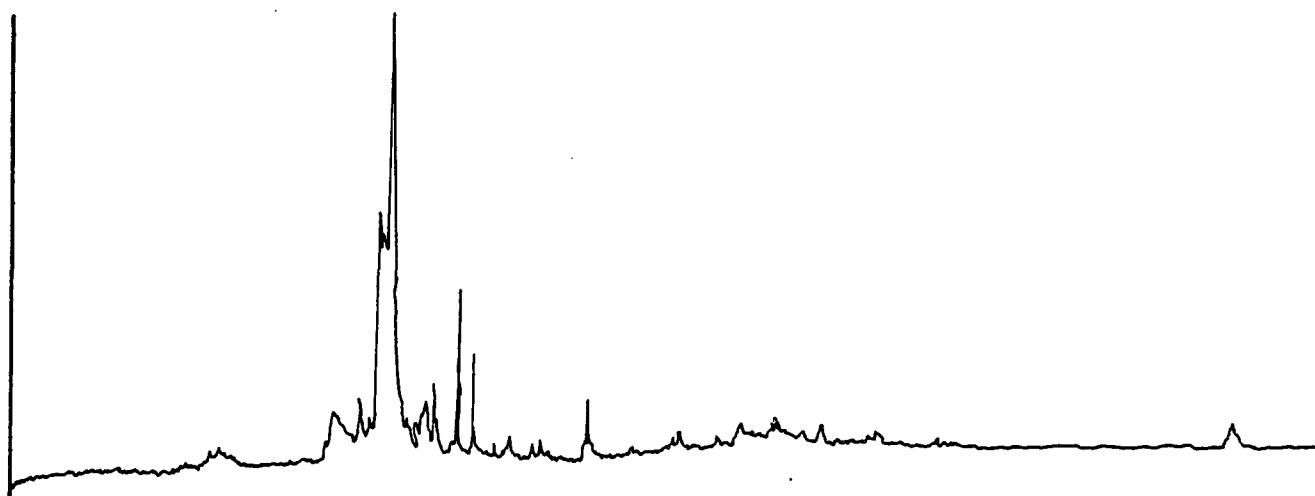
c. Trap With Early Peaks

FIGURE A-6. CHROMATOGRAMS FOR EVALUATION OF PRECONDITIONED TENAX TYPE A

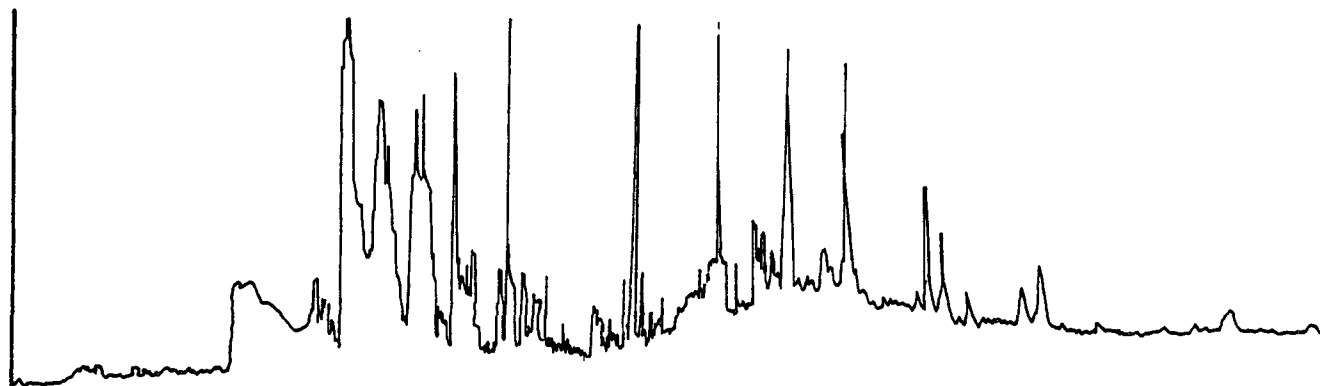
A-14



a. Typical Good Trap



b. Trap A, Aged 14 Days



c. Trap With Larger Peaks

FIGURE A-7. CHROMATOGRAMS FOR EVALUATION OF PRECONDITIONED TENAX TYPE B

Preconditioned Tenax, Type C

There were 25 traps in this series; all but three were good. Figure A-8a is typical of the good traps.\* The other three were rated fair and are exemplified by Figure A-8b. These traps were also fairly stable as shown in Figure A-8c.

Preconditioned Tenax, Type D

There were 59 traps in this series. Most of these were found to be good. Figure A-9a is representative of the good traps. Two were found to be fair (Figure A-9b) and two were poor (Figure A-9c).

Alltech Associates Preconditioned Tenax

Alltech Associates markets a preconditioned Tenax, advertised as being ready for use. It is made from Tenax GC by thermal conditioning at 300 C for 3-4 hours in a tube furnace with a stream of purified nitrogen. A 15-g lot of this material in stainless steel traps was conditioned overnight at 275 C in the conditioning apparatus previously described. These traps were all found to be good. Figure A-10a is representative. In addition, traps stored for up to 3 weeks at room temperature remained good (Figures A-10b and A-10c).

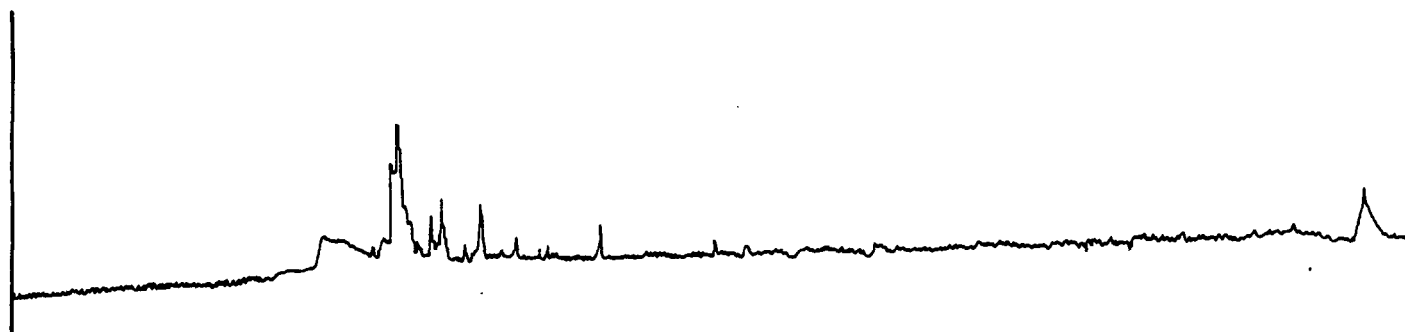
Several more lots of the Alltech preconditioned Tenax were ordered for additional tests. Unfortunately, traps packed from these later lots did not respond as favorably to conditioning. Many traps from these later were rated as only fair. However, these traps were not checked immediately after conditioning, whereas most traps have been checked initially within a few days of conditioning. Also as noted previously, their peaks are not large enough to cause an uncertainty of more than about 0.1 ppb.

It has been observed that any trap will be better after the first evaluation. Several of the traps packed with the later lots of Alltech preconditioned Tenax were re-checked after the initial evaluation. Figure A-11\*\* shows one of these traps. On re-checking it is much better.

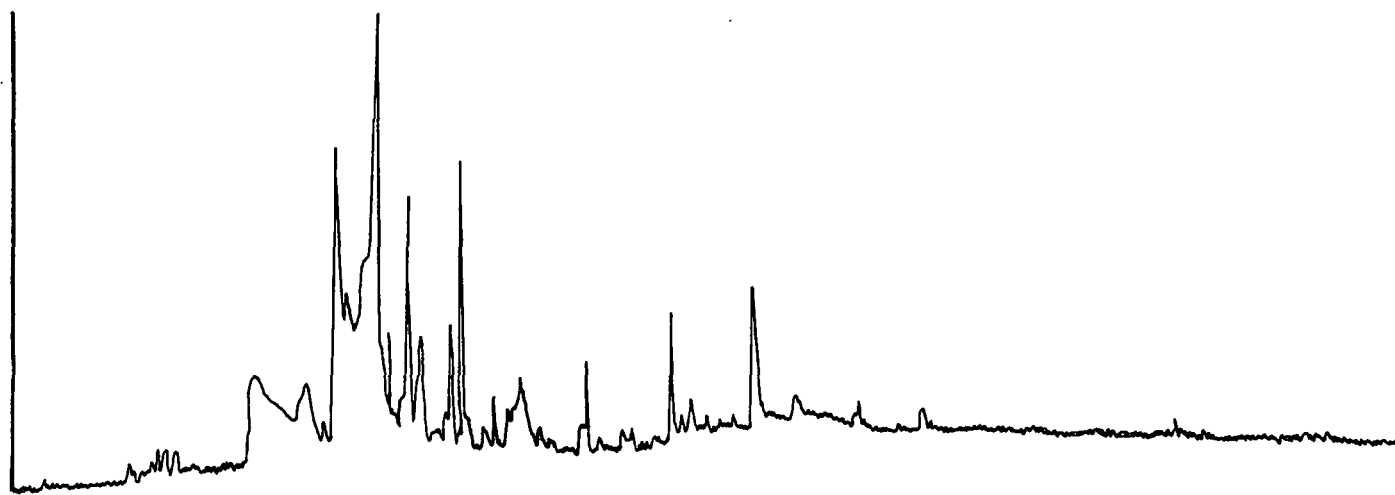
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\* Storage stability of these traps was good. Figure A-8b shows the same trap after 10 days aging.

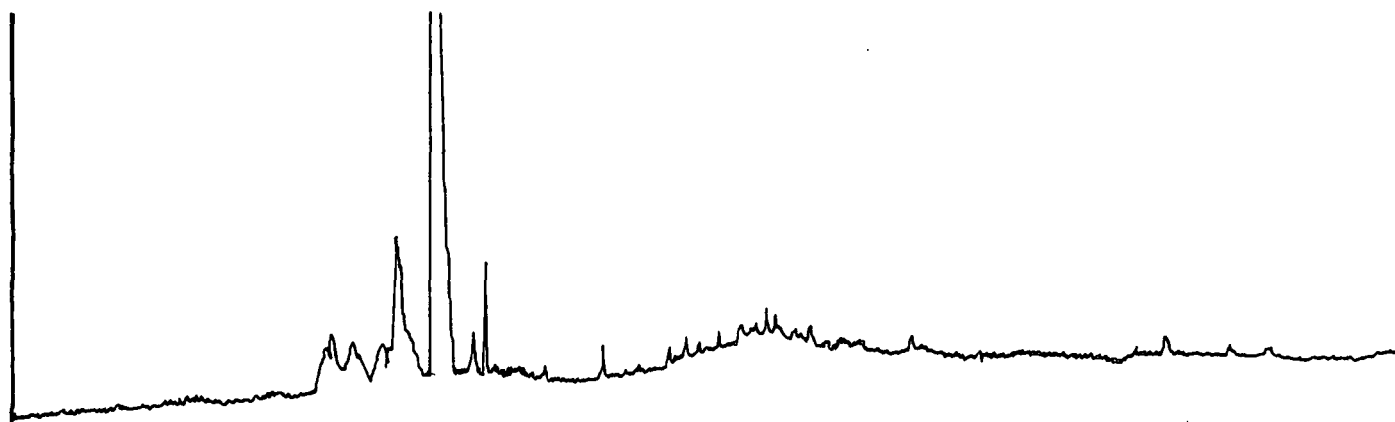
\*\* These chromatograms were run with a 50-meter column, whereas all the other chromatograms were run with a 25-meter column. Consequently, the chloroform marker peak is at about 9 minutes and benzene elutes at about 10 minutes.



a. Typical Good Trap



b. A Fair Trap

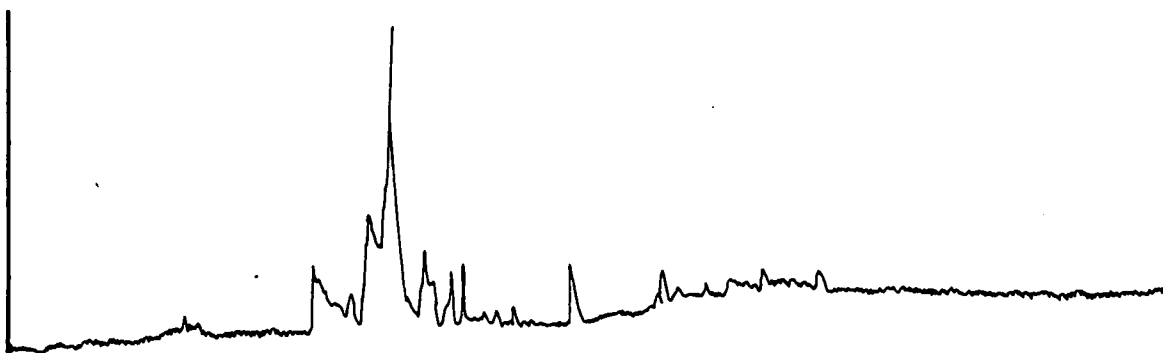


c. Trap C Aged 10 Days

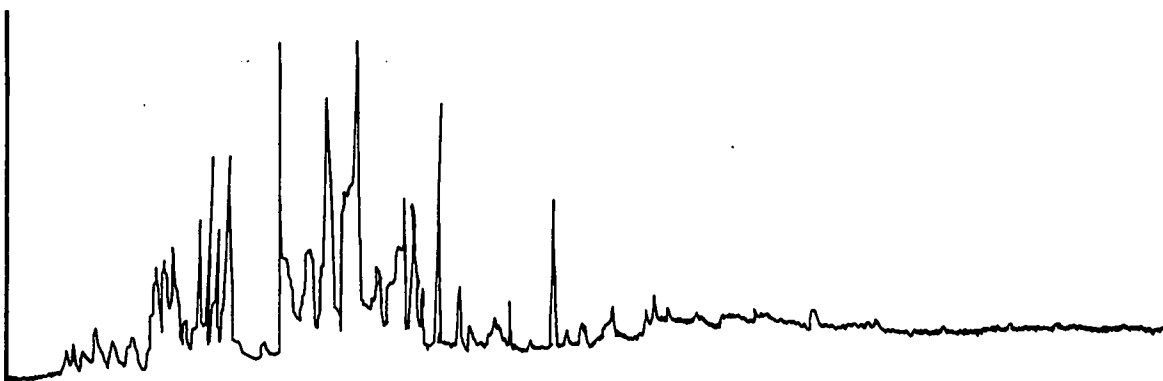
FIGURE A-8. CHROMATOGRAMS FOR EVALUATION OF PRECONDITIONED TENAX TYPE C



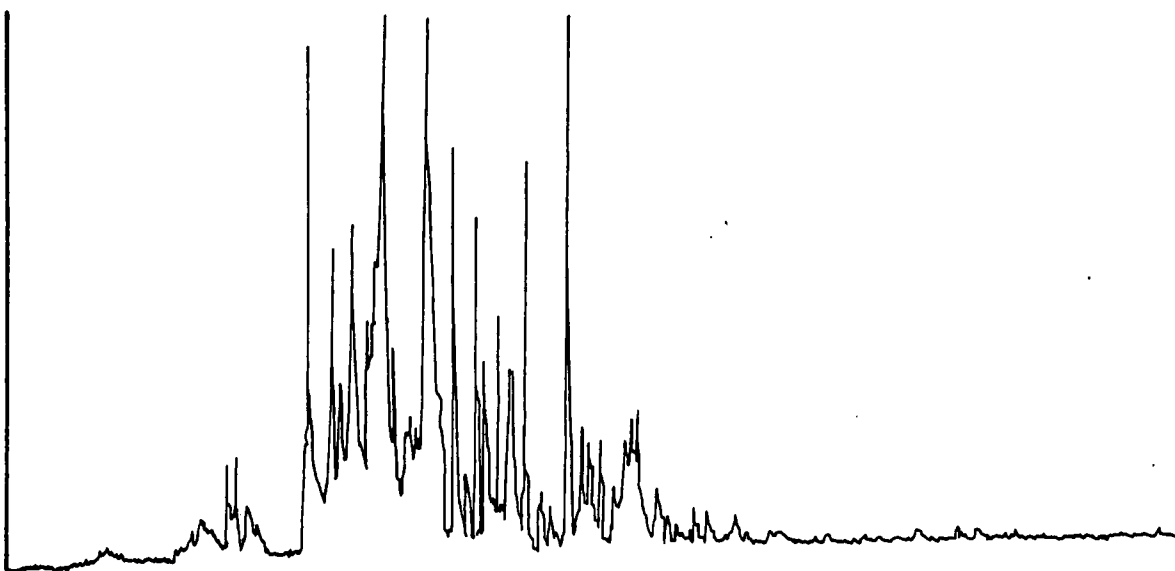
A-17



a. Typical Good Trap

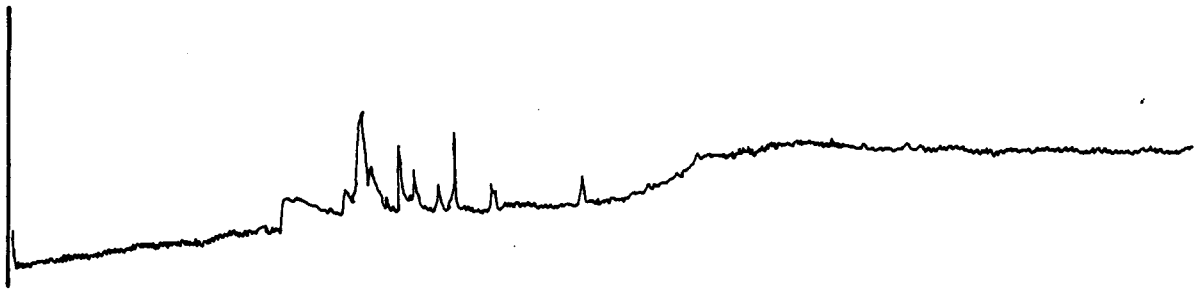


b. A Fair Trap

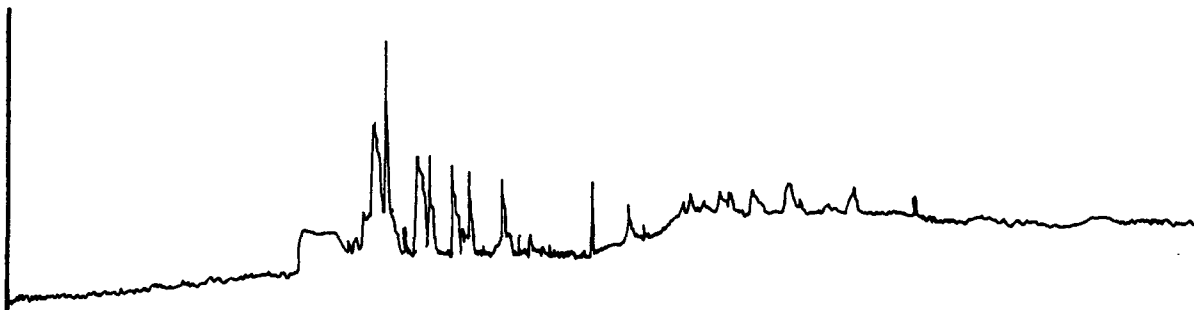


c. A Poor Trap

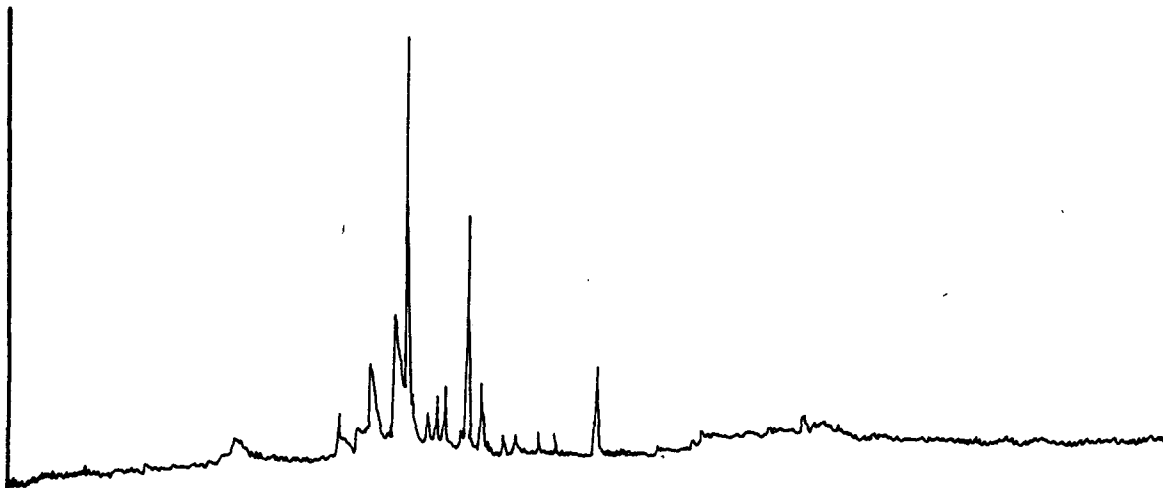
FIGURE A-9. CHROMATOGRAMS FOR EVALUATION OF PRECONDITIONED TENAX TYPE D



a. Typical Good Trap



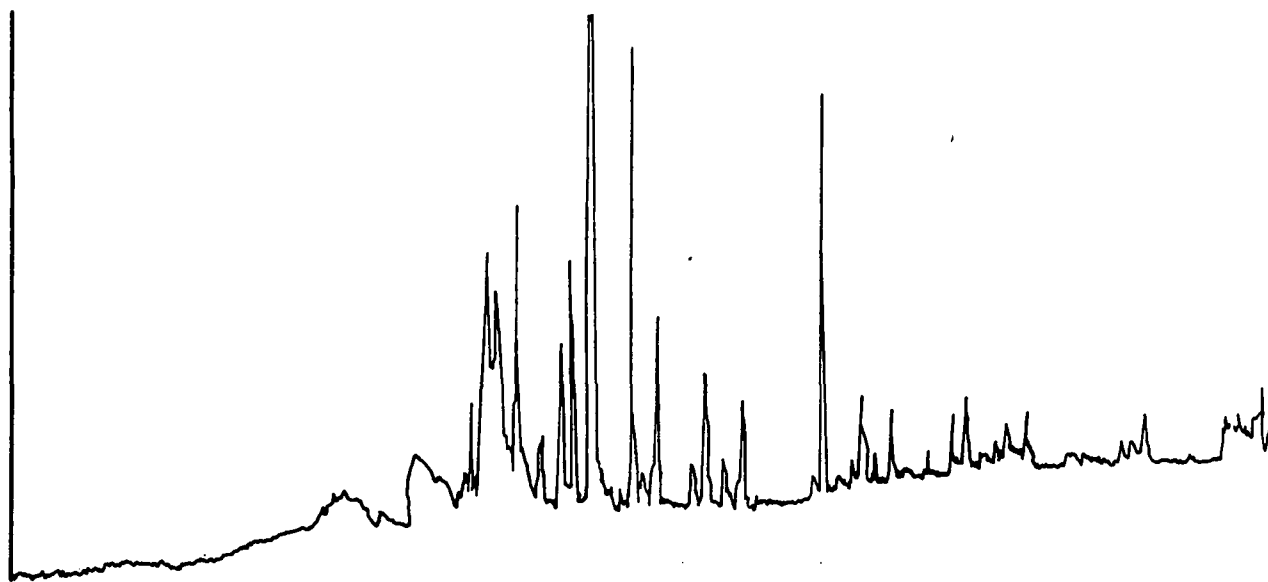
b. a, 7 Days Later



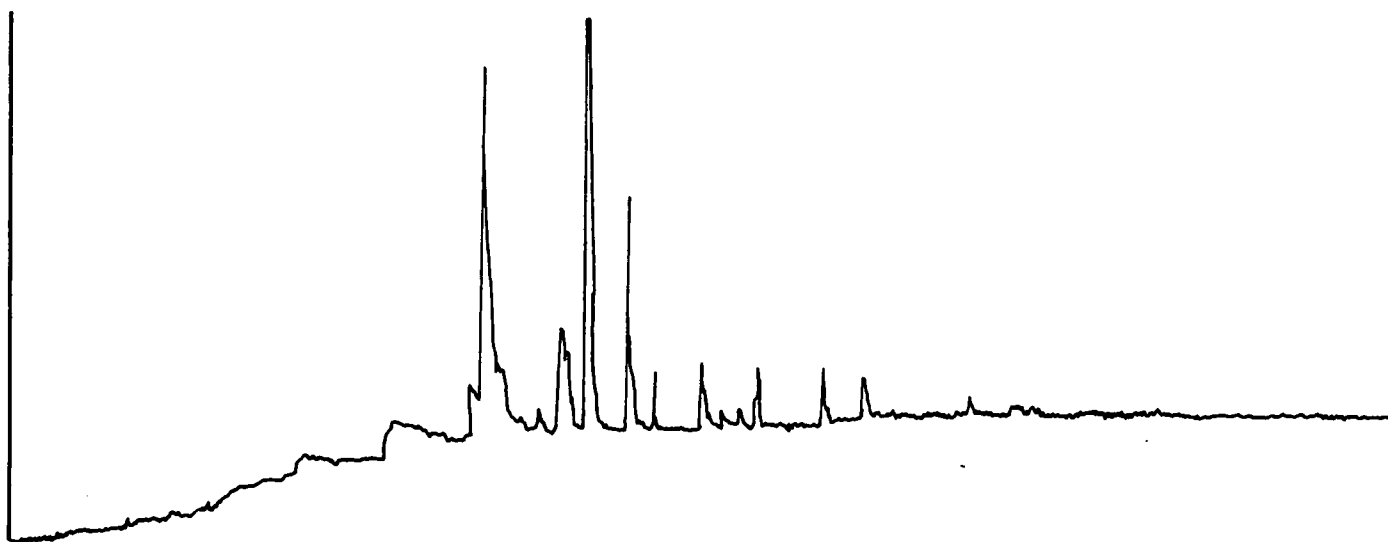
c. Another Good Trap, 21 Days Aging

FIGURE A-10. CHROMATOGRAMS FOR EVALUATION OF SAMPLE LOT OF ALLTECH PRECONDITIONED TENAX

A-19



a. Trap Rated as Fair



b. Same Trap Rechecked 2 Days Later

FIGURE A-11. CHROMATOGRAMS FROM EVALUATION OF LATER LOTS OF ALLTECH PRECONDITIONED TENAX

APPENDIX B

BENZENE PRODUCTION AND CONSUMPTION FACILITIES

## APPENDIX B

BENZENE PRODUCTION AND CONSUMPTION FACILITIES

To permit a logical choice of sampling locations, data were assembled on the production and consumption of benzene. Table B-1 lists all of the benzene manufacturing plants for which data were found, and includes the location, company, capacity, and process. Tables B-2 and B-3 give the benzene requirements for chemical manufacturing processes using benzene. Tables B-4 through B-10 contain data on plants using benzene in production of various organic industrial chemicals. Table B-11 lists the cities in which benzene production and consumption is largest.

TABLE B-1. BENZENE MANUFACTURING PLANTS  
(LOCATIONS, ANNUAL CAPACITIES, AND PROCESSES)

State/City	Company	Capacity		Process*
		(in millions of gallons)	(in millions of pounds)	(in millions of gallons)
California				
El Segundo	Standard Oil (Calif.)	23	168	23-R
Palo Alto	Beckman Instr.	NA		NA
Wilmington	Atlantic Richfield	12	88	12-R
Colorado				
Pueblo	CF&I Steel	3	22	3-C
Illinois				
Lemont	Union Oil	24	176	18-C 6-R
Wood River	Shell Chemical	40	293	40-R
Kansas				
ElDorado	Skelly Oil	13	95	13-R
Kentucky				
Ashland	Ashland Oil	50	366	40-C 10-H
Louisiana				
Alliance	Gulf Oil	70	513	45-D 25-R
Baton Rouge	Exxon	65	476	43-R 22-E
Chalmette	Tenneco	10	73	10-R
Lake Charles	Cities Service	25	183	25-R
Shreveport	Pennzoil	15	110	15-E
Taft	Union Carbide	70	513	70-E
Maryland				
Sparrows Point	Bethlehem Steel	15	110	15-C
Michigan				
Bay City	Dow	30	220	30-R
New Jersey				
Westville	Texaco	60	440	35-R 25-D
New York				
Lackawanna	Bethlehem Steel	8	59	8-C
North Tonawanda	Ashland Oil	15	110	12-C 3-R

TABLE B-1. (Continued)

State/City	Company	Capacity		Process*
		(in millions of gallons)	(in millions of pounds)	(in millions of gallons)
Ohio				
Middletown	Armco Steel	3	22	3-C
Toledo	Interlake	1	7	1-NA
Oklahoma				
Tulsa	Sun Oil	24	176	12-D 12-R
Pennsylvania				
Aliquippa	Jones & Laughlin	10	73	10-C
Bethlehem	Bethlehem Steel	4	29	4-C
Clairton	United States Steel	45	330	45-C
Marcus Hook	Sun Oil	15	110	15-R
Marcus Hook	Standard Oil (Ohio)	8	59	8-NA
Philadelphia	Gulf Oil	40	293	19-D 21-R
Puerto Rico				
Guayama	Phillips Petroleum	110	806	65-D 45-R
Penuelas	Commonwealth Oil	185	1355	110-D 70-R
Texas				
Baytown	Exxon	65	476	43-R 22-E
Beaumont	Mobil Oil	60	440	40-R 20-E
Beaumont	Union Oil	70	513	70-D
Big Spring	American Petrofina	45	330	30-D 15-R
Chocolate Bayou	Monsanto	75	549	35-D 40-E
Corpus Christi	Union Pacific (Champlin)	10	73	10-R
Corpus Christi	Kerr-McGee	16	117	16-NA
Corpus Christi	Sun Oil	35	256	20-D 15-R
Corpus Christi	Coastal States Gas	70	513	60-D 10-R
Deer Park	Shell	75	549	40-R 35-E
Freeport	Crown Central Petrol.	50	366	50-D
Houston	Charter Oil	5	37	5-R
Houston	Atlantic Richfield	44	322	32-R 12-D

TABLE B-1. (Continued)

State/City	Company	Capacity		Process*
		(in millions of gallons)	(in millions of pounds)	(in millions of gallons)
Texas (Continued)				
Lone Star	Northwest Ind.	1	7	1-C
Odessa	Shell	6	44	6-R
Pasadena	Crown Central Petrol.	23	168	18-D
				5-R
Port Arthur	American Petrofina	15	110	15-D
Port Arthur	Gulf Oil	38	278	30-R
				8-E
Port Arthur	Texaco	45	330	45-R
Sweeny	Phillips Petroleum	22	161	22-R
Texas City	Standard Oil (Ind.)(Amoco)	85	623	80-R
				5-E
Texas City	Marathon Oil	6	44	6-R
Winnie	Allied Chemical	3	22	3-R
Utah				
Geneva	U.S. Steel	4	29	4-C
Virgin Islands				
St. Crois	Amerada Hess	25	183	25-R
TOTALS		1886	13815	(see below)

	Totals	Percent
*C - Coal derived benzene from coke oven light oil:	163	8.6
D - Dealkylation of toluene	526	27.9
E - Petroleum product cracking operations for ethylene production	307	16.3
R - Catalytic reformat of petroleum products	865	45.9
NA - Not available	25	1.3
	1886	100.0



TABLE B-2. BENZENE REQUIREMENTS FOR MAJOR CHEMICAL PRODUCTS

Product	Benzene required at 100 percent capacity (Million pounds)	Percent of Total Benzene Capacity
Ethylbenzene	6,354	46
Cumene	3,028	22
Nitrobenzene	694	5
Chlorobenzene	656	5
Detergent Alkylate	420	3
Cyclohexane	389	3
Maleic Anhydride	389	3
	<u>11,930</u>	<u>87</u>
Total benzene capacity (See Table )	13,815	

TABLE B-3. ESTIMATED BENZENE REQUIREMENTS FOR MINOR CHEMICAL PRODUCTS

Product	Benzene Required at 100 percent capacity (Million pounds)	Locations
Biphenyl (diphenyl)	35	Anniston/Al., Sparrows Pt./Md, Bay City/Mich, Lyndhurst/NJ, Greensboro/NC, Woonsocket/RI, Freeport/Texas, Houston/Texas
Resorcinol	25	Petrolia/Pa
Hydroquinone	7	LaSalle/Ill., Kingsport/Tenn, Baysport/Texas
Anthraquinone	small	Toms River/NJ
Benzene hexachloride (Lindane)	small	Niagara Falls/NY, Newark/NJ
Trichlorophenol(245T)	small	Midland/Mich, Stamford/Conn, Jacksonville/Ark.
Pentachlorophenol	small	Midland/Mich
Solvent(paints, rubber cements, solvent extraction, etc.)	small	Widely scattered

TABLE B-4. MALEIC ANHYDRIDE MANUFACTURING PLANTS  
(PLANT LOCATIONS, COMPANIES, AND ANNUAL  
CAPACITY FOR BENZENE CONSUMPTION)

State/City	Company	Benzene Requirement at 100 Percent Capacity <sup>(a)</sup> (million pounds)
Illinois		
Cicero	Koppers	13
Morris	Reichold	80
Missouri		
St. Louis	Monsanto	141
New Jersey		
Elizabeth	Reichold	40
Fords	Tenneco	35
Pennsylvania		
Bridgeville	Koppers	46
Neville Island	U.S. Steel	54
Texas		
Houston	Petro-Tex	67
West Virginia		
Moundsville	Allied Chemical	80
TOTAL		389

(a) Based on the assumption that 1.34 pounds of benzene are required for each pound of maleic anhydride produced.

TABLE B-5. ETHYLBENZENE MANUFACTURING PLANTS (PLANT LOCATIONS, COMPANIES, AND ANNUAL CAPACITY FOR BENZENE CONSUMPTION)

State/City	Company	Benzene Requirement at 100 Percent Capacity <sup>(a)</sup> (million pounds)
Louisiana		
Baton Rouge	Foster Grant	720
Carville	Cos-Mar	534
Chalmette	Tenneco	19
Welcome	Gulf Oil	408
Michigan		
Midland	Dow	408
Puerto Rico		
Penuelas	Commonwealth Oil	119
Texas		
Big Spring	American Petrofina	33
Corpus Christi	Sun Oil	70
Freeport	Dow	1384
Houston	Charter Oil	26
Houston	ARCO	74
Houston	Joc Oil	NA
Odessa	El Paso	204
Phillips	Phillips Petroleum	NA
Port Arthur	ARCO	326
Seadrift	Union Carbide	252
Texas City	Monsanto	1076
Texas City	Standard Oil (ind.) (Amoco)	701
TOTAL		6354

(a) Based on the assumption that 0.742 pounds of benzene are required for each pound of ethylbenzene produced.

TABLE B-6. CUMENE MANUFACTURING PLANTS (PLANT LOCATIONS, COMPANIES, AND ANNUAL CAPACITY FOR BENZENE CONSUMPTION)

State/City	Company	Benzene Requirement at 100 Percent Capacity <sup>(a)</sup> (million pounds)
California		
El Segundo	Standard Oil (Calif.)(Chevron)	80
Illinois		
Blue Island	Clark Oil	88
Kansas		
El Dorado	Skelly Oil	108
Kentucky		
Ashland	Ashland Oil	280
Michigan		
Midland	Dow	8
New Jersey		
Westville	Texaco	208
Pennsylvania		
Philadelphia	Gulf Oil	360
Puerto Rico		
Penuelas	Union Carbide	512
Texas		
Chocolate Bayou	Monsanto	520
Corpus Christi	Coastal States Gas	112
Corpus Christi	Sun Oil	200
Port Arthur	Gulf Oil	360
Texas City	Marathon Oil	152
Texas City	Standard Oil (Ind.)(Amoco)	40
TOTAL		3028

(a) Based on the estimate that 0.80 pounds of benzene are required for each pound of cumene produced.

TABLE B-7. NITROBENZENE MANUFACTURING PLANTS (PLANT LOCATIONS, COMPANIES, AND ANNUAL CAPACITY FOR BENZENE CONSUMPTION)

State/City	Company	Benzene Requirement at 100 Percent Capacity <sup>(a)</sup> (million pounds)
Illinois		
Sauget	Monsanto	7
Louisiana		
Geismar	Rubicon Chemicals	49
Mississippi		
Pascagoula	First Mississippi	88
New Jersey		
Bound Brook	American Cyanamid	55
Gibbstown	DuPont	130
Texas		
Beaumont	DuPont	202
West Virginia		
Moundsville	Allied Chemical	36
New Martinsville	Mobay Chemicals	88
Willow Island	American Cyanamid	39
TOTAL		694

(a) Based on the assumption that 0.65 pounds of benzene are required for each pound of nitrobenzene produced.

TABLE B-8. CHLOROBENZENE MANUFACTURING PLANTS  
(PLANT LOCATIONS, COMPANIES, AND ANNUAL  
CAPACITY FOR BENZENE CONSUMPTION)

State/City	Company	Benzene Requirement at 100 Percent Capacity <sup>(a)</sup> (million pounds)
Delaware		
Delaware City	Standard Chlorine	71
Illinois		
Sauget	Monsanto	109
Michigan		
Midland	Dow	285
Nevada		
Henderson	Montrose Chemicals	67
New York		
Niagara Falls	Hooker	14
Syracuse	Allied Chemical	24
West Virginia		
Natrium	PPG	86
TOTAL		656

(a) Based on the assumption that 0.950 pounds of benzene are required for each pound of chlorobenzene produced.

TABLE B-9. DETERGENT ALKYLATE MANUFACTURING PLANTS  
(PLANT LOCATIONS, COMPANIES, AND ANNUAL  
CAPACITY FOR BENZENE CONSUMPTION)

State/City	Company	Benzene Requirement at 100 Percent Capacity <sup>(a)</sup> (million pounds)	
California			
Carson	Witco Chemicals	27	SC
Richmond	Standard Oil (Calif.)(Chevron)	107	BC
Maryland			
Baltimore	Continental Oil	92	SC
Baltimore	Continental Oil	12	BC
Texas			
Chocolate Bayou	Monsanto	109	SC
West Virginia			
South Charleston	Union Carbide	73	SC
TOTAL		420	

- (a) Based on the assumption that 0.485 pounds of benzene are required for each pound of detergent alkylate produced.  
SC = straight chain (biodegradable)  
BC = branched chain.

TABLE B-10. CYCLOHEXANE MANUFACTURING PLANTS (PLANT LOCATIONS, COMPANIES, AND ANNUAL CAPACITY FOR BENZENE CONSUMPTION)

State/City	Company	Benzene Requirement at 100 Percent Capacity <sup>(a)</sup> (million pounds)
Puerto Rico		
Guayama	Phillips Petroleum	66
Penuelas	Commonwealth Oil	37
Texas		
Baytown	Exxon	37
Beaumont	Union Oil	32
Big Spring	American Petrofina	11
Borger	Phillips Petroleum	37
Corpus Christi	Union Pacific (Champlin)	21
Port Arthur	Gulf Oil	31
Port Arthur	Texaco	37
Sweeny	Phillips Petroleum	80
TOTAL		389

(a) Based on the assumption that 0.935 pounds of benzene are required for each pound of cyclohexane produced.



TABLE B-11. MAJOR U.S. BENZENE CENTERS

State/City	Total Benzene Capacity		TOTAL
	Production	Consumption	
	(in millions of pounds)		
California/Los Angeles	256	107	363
San Francisco		107	107
Illinois/Chicago	176	181	357
Kansas/Wichita	95	108	203
Kentucky/Ashland	366	280	646
Louisiana/Baton Rouge	476	1254	1730
Lake Charles	183	--	183
New Orleans	1099	564	1663
Shreveport	117	--	117
Maryland/Baltimore	110	104	214
Michigan/Midland	220	701	921
Missouri/St. Louis	293	257	550
New Jersey/Elizabeth	--	130	130
New York/Buffalo	169	14	183
Oklahoma/Tulsa	176	--	176
Pennsylvania/Philadelphia	931	568	1499
Pittsburgh	403	100	503
Texas/Houston	4988	5254	10242
Corpus Christi	959	655	1614
Odessa	374	248	622
West Virginia/Parkersburg	--	402	402
Puerto Rico	2161	734	2895
Virgin Islands	183	--	183
Others	80	162	208
GRAND TOTAL	13815	11930	25711