United States
Environmental Protection
Agency

Office of Monitoring Systems
and Quality Assurance
Washington DC 20460

EPA-600/4-82-015
June 1983

Research and Development

EPA

Direct Measurement of Volatile Organic Compounds in Breathing-Zone Air, Drinking Water, Breath, Blood, and Urine

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Ruth Zweidinger, Mitch Erickson, S. Cooper,
Don Whittaker, and Edo Pellizzari
Analytical Sciences Division
Chemistry and Life Sciences Group
Research Triangle Institute

and

Lance Wallace
Office of Monitoring Systems and Quality Assurance
Office of Research & Development

DISCLAIMER

This study was designed to test methods of measuring individual exposure; it was not designed and cannot be used to characterize geographical areas or populations beyond the actual study groups themselves. No epidemiological conclusions regarding health effects of measured exposure levels can be drawn from this study.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Physical, chemical, and biological measurements of environmental quality are necessary to determine not only the extent of environmental damage but also the effects of environmental protection programs. The Office of Monitoring Systems and Quality Assurance has the responsibility of developing new monitoring methods, evaluating and improving existing methods, carrying out field monitoring programs, and assuring the quality of the environmental data collected by the Agency.

The present study was a pilot effort to evaluate new methods for measuring personal exposure to a number of toxic compounds in air, water, breath, and blood. The methods for collecting air and breath samples appear to be particularly effective, and are now being employed in large-scale studies.

H. Matthew Bills
Acting Director
Office of Monitoring Systems
and Quality Assurance

ACKNOWLEDGEMENTS

The authors wish to acknowledge Dr. Andrew J. Johnson of Lamar University and Dr. William McDonnell of the University of North Carolina for their willing help in locating student volunteers. To the volunteers themselves, who carried air monitors, collected water samples, and gave blood, breath, and urine samples, we are deeply indebted.

ABSTRACT

Methods for determining individual human exposure to volatile organic compounds (VOC) encountered during normal daily activities were field-tested on university student volunteers in two geographical areas. The following equipment and analytical protocols were tested:

- A personal air quality monitor employing the synthetic adsorbent Tenax-GC® to collect organic vapors for later analysis by gas chromatography/mass spectrometry (GC/MS).
- A specially-designed spirometer for collecting samples of expired human breath on duplicate Tenax-GC® cartridges for later GC/MS analysis.
- A purge and trap analytical protocol for determining VOC levels in blood and urine.

Results included the following:

- The personal monitor and spirometer proved feasible for collecting abundant quantitative data on most of the 15 target organic vapors.
- Air exposures to many VOC varied widely, sometimes over 3 orders of magnitude, among students on the same campus that had been monitored over the same time period and day.
- A log-linear relationship between breathing-zone air exposures and concentrations in exhaled breath was suggested for three chemicals: tetrachloroethylene, 1,1,1-trichloroethane, and vinylidene chloride.
- The analytical protocols for blood and urine gave different results in different laboratories. The cause of this problem is being investigated.
- Air was the main route of exposure for all target compounds except the two trihalomethanes (chloroform and bromodichloromethane), which were transmitted mainly through water.
- Estimated total daily intake through air and water of the target organics ranged from 0.3 to 12.6 mg, with 1,1,1-trichloroethane at the highest concentrations in both geographic areas.

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SECTION 1
CONCLUSIONS

- Sampling and analytical methods for measuring volatile organic compounds in breathing-zone air, drinking water, and exhaled breath appear to be suitable for use in field studies of the general population. However, more work needs to be done on the analytical methods for blood and urine before they are acceptable for field use.

- Five vapor-phase organic compounds were ubiquitous, occurring in 100% of both the air and breath samples in Lamar University and the University of North Carolina. These organics were benzene, chloroform, tetrachloroethylene, 1,1,1-trichloroethane, and dichlorobenzene isomer.

- Three of the five ubiquitous compounds (tetrachloroethylene, vinylidene chloride, and 1,1,1-trichloroethane) displayed an approximate log-linear relationship between air and breath levels. (That is, the logarithm of the breath concentration appears to vary directly with the logarithm of the concentration in breathing-zone air).

- Estimated total daily intake through air and water of the volatile organics measured ranged from 0.3-12.6 mg, with a geometric mean value of about 1.8 mg. Roughly one-third to one-half of this amount was supplied by 1,1,1-trichloroethane in air.

- Seven of the 10 most prevalent compounds measured by the personal air quality monitors exhibited high variability (2-3 orders of magnitude) despite being measured by students spending most of their time on a single campus at the same time of day on two consecutive days. If this preliminary observation is confirmed, it calls into question the practice of assigning similar exposures to a "cohort" of people in a given small geographic area.

- Two organics were found in appreciable quantities in drinking water: chloroform and bromodichloromethane. For both, the estimated daily intake through water was about three times that through air. The sum of the two trihalomethane concentrations in drinking water exceeded 100 parts per billion in all 38 samples.

- The high breath-air ratios of chloroform noted for University of North Carolina students compared to Lamar students is attributable to their greater exposure to chloroform through drinking water. However, the high breath-air ratios for two other compounds--tetrachloroethylene and dichlorobenzene isomer--could not be explained by levels in drinking water.

SECTION 2

RECOMMENDATIONS

- Further work is needed on the purge-and-trap analytical protocol for blood and urine.
- The observed great variability in personal exposure to organics needs further study. If validated, it should be considered in planning future environmental exposure studies.
- Further studies relating dose to exposure are required to validate or modify the log-linear relationship postulated in the present study.
- The anomalously high levels in breath of dichlorobenzene and tetrachloroethylene compared to measured exposure levels should be further investigated.

SECTION 3

INTRODUCTION

Few studies (1,2) have attempted to measure individual human exposure or body burden of volatile organic compounds (VOC) at normal ambient concentrations. Yet this information is crucial in arriving at decisions of great economic consequence concerning the regulation of these substances. The present study is a pilot effort to evaluate currently available methods required to determine individual human exposure and body burden of a number of VOC including several suspected carcinogens.

METHODS FOR MEASURING EXPOSURE

Air. Until now, methods for determining individual exposure to most organic vapors in air have been lacking. The main reasons have been

- lack of an adsorbent capable of collecting organic vapors and allowing quantitative recovery;
- lack of small quiet personal monitors capable of accompanying persons on their daily routines (3).

Both of these deficiencies appear to be well along toward a solution. For the past few years, a synthetic polymer called Tenax GC® has been undergoing laboratory and field tests to determine its performance characteristics (4-6). This polymer has an adsorption affinity for hundreds of organic compounds. By pumping ambient air across a cartridge of Tenax GC® and then inserting the cartridge into a thermal desorption until on a gas chromatograph/mass spectrometer (GC/MS)/computerized system, several

hundred compounds can be identified and several dozen quantified at the part per billion (ppb) level or below.

By combining the Tenax GC® cartridge with a small quiet pump, a personal monitor is created capable of measuring individual exposures over an 8-hour period. The present study is the first field test of a Tenax-based personal monitor to measure exposure to several compounds simultaneously.

Other Routes. Besides air, drinking water, food and beverages may be major routes of exposure to volatile organics. Analysis methods are adequate for drinking water, but are rudimentary for food and beverages. Therefore drinking water was included in this study, but food and beverages were not. (A more complete study of individual exposure through air, drinking water, some food groups and beverages, and house dust, has been recently completed by the U.S. Environmental Protection Agency) (7).

METHODS FOR CALCULATING BODY BURDEN

As with exposure, measurement methods for calculating body burden of many VOC have only recently been developed (1,2,7-9). Among these methods, two were selected for field testing in this study:

- Breath analyses. A specially designed spirometer employing Tenax GC® cartridges (1,2,7) was used to analyze the exhaled breath of volunteer subjects for the same organic vapors measured by the personal monitors.
- Blood and urine analyses. A recently developed analytical protocol for purgeable volatile organics (8) was used to measure concentrations of organic compounds in the blood and urine of the volunteer subjects.

Exposure/Body Burden Relationships

By combining measurements of exposure and body burden made for the same individual, it was hoped that relationships between exposure and body burden would be suggested for at least some compounds. The existence of such relationships would be of immense practical value in estimating levels of previous exposure in persons whose body burden had been determined, or, vice-versa, in estimating body burden of persons whose exposure had been measured.

SECTION 4

PROGRAM OBJECTIVES

The main objective of the study was to field-test the following methods for measuring human exposure to VOC:

- A personal air quality monitor to sample breathing-zone air;
- A specially designed spirometer to sample exhaled breath;
- Analytical protocols for measuring VOC in air, tap water, and breath, blood and urine.

Depending on the success of the various methods, a second objective was to compare levels of VOC in breathing-zone air and drinking water with levels of the same compounds in the human body fluids tested. Table 1 lists all compounds studied.

Selection of Sites.

Two areas were selected for study: a petrochemical manufacturing center in Texas and a nonindustrial community in North Carolina. Volunteers from local universities were sought to reduce the variability associated with age or occupation.

Beaumont, Texas was selected to represent the petrochemical area. Lamar University is bordered on the north and south by oil storage tank farms, and on the northwest by the urban area of Beaumont. (Fig. 1). Winds from the south cross over major refineries and petrochemical plants before reaching the University. Students who live on campus would be exposed 24 hours of the day. Both on- and off-campus residents were studied.

Table 1. CHEMICALS SOUGHT IN STUDY

	Chemical	Air and Breath[a]	Drinking Water, Blood, and Urine[a]	Blood[b] (Lamar only) (Dec. 79)	Blood[b] (Lamar only) (March 80)
1.	Chloroform	X	X	X	X
2.	Chlorobenzene	X	X	X	X
3.	Tetrachloroethylene	X	X	X	X
4.	1,2-Dichloroethane	X	X		X
5.	1,1,1-Trichloroethane	X	X	X	X
6.	1,1,2-Trichloroethane		X		
7.	Trichloroethylene	X	X	X	X
8.	Carbon tetrachloride		X	X	X
9.	Bromodichloromethane	X	X	X	X
10.	Vinylidene chloride	X		X	X
11.	1,1-Dichloroethane	X			
12.	1,2-Dichloropropane	X			
13.	Dibromochloromethane	X		X	
14.	Ethylene dibromide	X			
15.	m-dichlorobenzene	X			
16.	o-dichlorobenzene	X			X
17.	Benzene	X			
18.	Bromoform			X	X
19.	1,1,2,2-Tetrachloroethane			X	X
20.	Hexachloro-1,3-butadiene			X	X
21.	1,2-Dichloroethylene			X	

[a]Analyzed at Research Triangle Institute.

[b]Analyzed at University of Miami.

Chemicals could not be separated by gas chromatographic column employed.

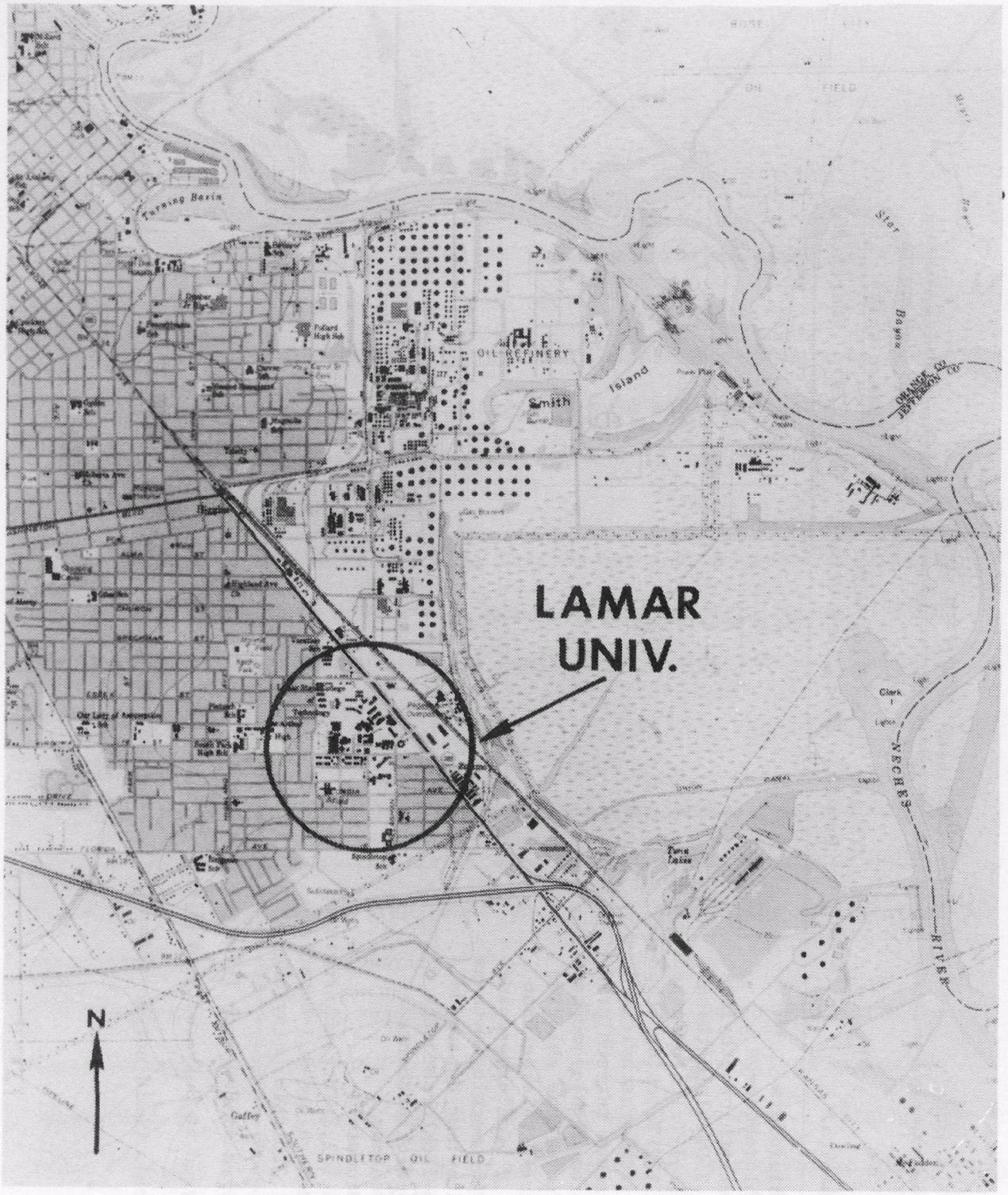

Figure 1. Map of Beaumont, Texas, including Lamar University area. Note the many oil storage tanks and oil fields north and south of the University.

Chapel Hill, N.C. was selected to represent the non-industrial area. Chapel Hill has essentially no heavy industry and is located near no industrial cities. Both on- and off-campus residents of the University of North Carolina were included in the study population.

Selection of Subjects.

At both universities, potential participants

1) had to be currently enrolled;
2) could not be enrolled in a course allowing direct contact with organic chemicals (e.g., chemistry, anatomy, biology, or hospital laboratories);
3) could not be employed in occupations allowing exposure to organic chemicals (e.g., chemical plants, service stations, garages); and
4) could not engage in hobbies allowing potential exposure to organic chemicals (e.g., painting, gardening, refinishing furniture or developing photographs).

A questionnaire developed by the University of Miami Medical School was administered to each student to determine factors that might be related to exposure, such as residence on or off campus, dietary habits, hobbies, parents' occupations. The human rights committee at the University of Miami Medical School approved the questionnaire (reproduced in Appendix A) for use in studies of human exposure to VOC.

In all, 17 students were selected: 11 at Lamar University (five sampled on March 4, 1980 and six on the following day); and six at UNC (three students sampled on June 10, 1980 and three on the following day). Each participant signed a consent form and received a small incentive when sampling was completed.

SECTION 5

SAMPLING AND ANALYSIS

SAMPLE COLLECTION--Lamar University

Tap water, air, breath, blood, and urine samples were collected from the 11 Lamar University Students (Table 2) according to specific sampling procedures (1).

Each morning an air monitor and water sample bottles were distributed to each participant with printed instructions on how to collect the tap water samples and what to expect during the sampling. Each participant carried the monitors for a 5-9 hour period (Tables 3 and 4). At the end of the day, air monitors and tap water samples were turned in and breath, blood, and urine samples were collected.

Water. The tap water samples were collected by each individual immediately after he or she drank. Each participant was provided with three 125 mL glass amber bottles with Teflon® lined caps. The participants were asked to fill at least one but not necessarily all three within the course of the day. It was preferred that one of the samples be from the subject's home or dormitory. Bottles were filled to overflowing and tightly capped. They were turned in at the end of the day and placed on ice. The samples were kept cold until analyzed.

Air. A personal sampler employing Tenax GC® polymer to collect organic compounds was used to collect all air samples in the study. The sampler consisted of an MSA Model C-200 pump and an attached Tenax cart-

Table 2. SAMPLES COLLECTED AT LAMAR UNIVERSTY, BEAUMONT, TX,

Participant No.	1980 Date	Air	Breath[a]	Water[b]	Blood	Urine
30001	3/4	1	1	1	1	1
30002	3/4	1	1	2	1	1
30003	3/4	1	1	1	1	1
30004	3/4	1	1	2	1	1
30005	3/4	1	1	3	1	1
30011	3/5	1	1	3	1	1
30012	3/5	1	1	3	1	1
30013	3/5	1	1	3	1	1
30014	3/5	1	1	3	1	1
30015	3/5	1	1	2	1	1
30016	3/5	1	1	3	1	1

[a]Breath samples were collected in duplicate.

[b]Each participant was asked to collect a water sample each time he or she drank--hence the range of 1, 2 or 3 samples.

Table 3. SAMPLING PROTOCOL FOR PERSONAL AIR SAMPLES - LAMAR UNIVERSITY

Participant No.	Date	Temperature (°C)	Pump[a] No.	Sampling Start	Sampling End	Starting Flow (mL/min)	Ending Flow (mL/min)	Average Flow (mL/min)	Volume Sampled (L)
30001	3/4/80	26.1	1	0754	1637	-	-	-	25.1
30002	3/4/80	26.1	2	0818	1706	-	-	-	24.4
30003	3/4/80	25.5	3	0818	1459	-	-	-	19.4
30004	3/4/80	26.1	4	0839	1550	-	-	-	24.6
30005	3/4/80	26.1	5	0848	1527	-	-	-	21.1
30011	3/5/80	25.3	1	0746	1420	-	-	-	14.9
30012	3/5/80	26.6	2	0800	1544	-	-	-	24.6
30013	3/5/80	26.6	3	0815	1517	-	-	-	19.9
30014	3/5/80	26.6	4	0858	1632	-	-	-	26.2
30015	3/5/80	26.6	5	0904	1657	-	-	-	25.3
30016	3/5/80	26.1	2D	0920	1440	49.2	48.0	48.6	15.6

[a]Pump Nos. 1-5 were MSA's, count rates were calibrated in mL/min, and total counts × rate gave volume sampled. 2D = Dupont sampler.

Table 4. METEOROLOGICAL CONDITIONS AT LAMAR UNIVERSITY:* MARCH 4-5, 1980

Time	Temperature		Relative Humidity (%)		Wind Direction		Wind Speed (mph)		Precipitation (inches)	
(hrs)	(3/4/80)	(3/5/80)	(3/4/80)	(3/5/80)	(3/5/80)	(3/5/80)	(3/4/80)	(3/5/80)	(3/4/80)	(3/5/80)
6	57	62	81	93	163	234	6	4	-	-
7	58	62			157	219	6	4	-	-
8	58	63			179	223	5	4	-	-
9	59	67	78	87	199	234	7	5	T	-
10	59	67			154	304	6	6	T	-
11	60	65			150	325	8	10	T	-
12	61		87	68	158		9		.01	-
31	60	63			156	340	9	10	.02	-
14	61	65			156	352	10	11	T	-
15	61	66	90	55	158	348	7	11	.03	-
16	61	65			172	344	6	11	.16	-
17	61	65			162	350	6	10	.03	-
18	61	63	90	61	164	341	6	7	T	-

Ozone Levels: 3/4/80 .02 to .04 ppm
3/5/80 .00 to .06 ppm

Fog and Thunderstorm on March 4th; Fog on March 5th

*Source: Texas Air Control Board: Lamar University station in Beaumont

ridge. Participants carried the sampler with them during a 5-9 hour period while they attended classes, ate lunch, commuted, or carried out other normal daily activities on the campuses of their universities.

The sampler pump flow rate was adjusted to about 0.05 L/min, providing a sampling volume of about 25 L of air. This volume was chosen to avoid exceeding the breakthrough volumes for most of the compounds selected for study. (Breakthrough volume is defined as that volume at which 50% of the compound is lost through the exit of the sampling cartridge). These breakthrough volumes ranged from 15 to 2000 liters (at 70 °F) for the amount (1.5g) of Tenax employed.

The sampling tubes consist of a glass tube 10 cm long with an inner diameter of 1.5 cm. Eight cm of 35/60 mesh Tenax particles were placed between glass wool plugs which provided support at both ends. The Tenax is prepared in the following way: virgin Tenax (or material to be recycled) is extracted in a Soxhlet apparatus for a minimum of 18 hours with methanol followed by n-pentane. Then it is dried for 3-5 hours in a vacuum oven at 120° and at a pressure of 28 inches of water. It is then meshed in a clean air room to provide a 35/60 particle size range. Cartridge samplers are then filled with the Tenax and conditioned by passing helium (first purified in a liquid-nitrogen-cooled cryogenic trap) at a rate of 30 mL/min through the cartridges for 120 minutes at a temperature of 270°C. To avoid recontamination of the Tenax sorbent bed, the conditioned cartridges are transferred to Kimax® culture tubes, immediately sealed using Teflon® - lined caps, and cooled. The culture tubes were then placed inside plain sealable paint cans.

Breath. Breath samples were collected on Tenax GC cartridges via a spirometer (Fig. 2). The valves in the Douglas mouthpiece were replaced with Tedlar. A bubbler filled with distilled deionized water was placed in-line with the air tank to humidify the air for the comfort of the participants.

The subject was seated in a comfortable chair, and the mouthpiece height adjusted to a convenient level. A long spring clamp was used to seal the air flow from Bag A to the mouthpiece. To prevent room air contamination, a plug was placed in the mouthpiece opening until the test began. Air flow from the pure-air tank was started, and when the 50-L Bag A was about half full, the clamp and plug were removed, the nose clipped, and the subject began to breathe on the apparatus. After a minute or two, the Nutech sampler pump was started with the flow at approximately 7 L/min. The flow was adjusted to approximate the individual subject's respiration rate. The subject was asked to breathe until about 75 L of exhaled breath passed through Bag B. The subject was then asked to stop, and the remainder of Bag B's contents were sampled. The Tenax cartridges were removed and stored in culture tubes. Bag B was then removed and flushed with helium to decontaminate it for future use. A clean bag was replaced in position for the next subject. The mouthpiece was sterilized by swabbing with alcohol after each use. The Tenax cartridges were desiccated over $CaSO_4$ placed in the bottom of a culture tube and covered with glass wool.

Blood. Blood was drawn in the afternoon by a qualified phlebotomist at the Student Health Center. Four 7-mL vacutainers (Kimble - Terumo Kt 200SKA) containing an anti-coagulant were filled from an arm vein. The

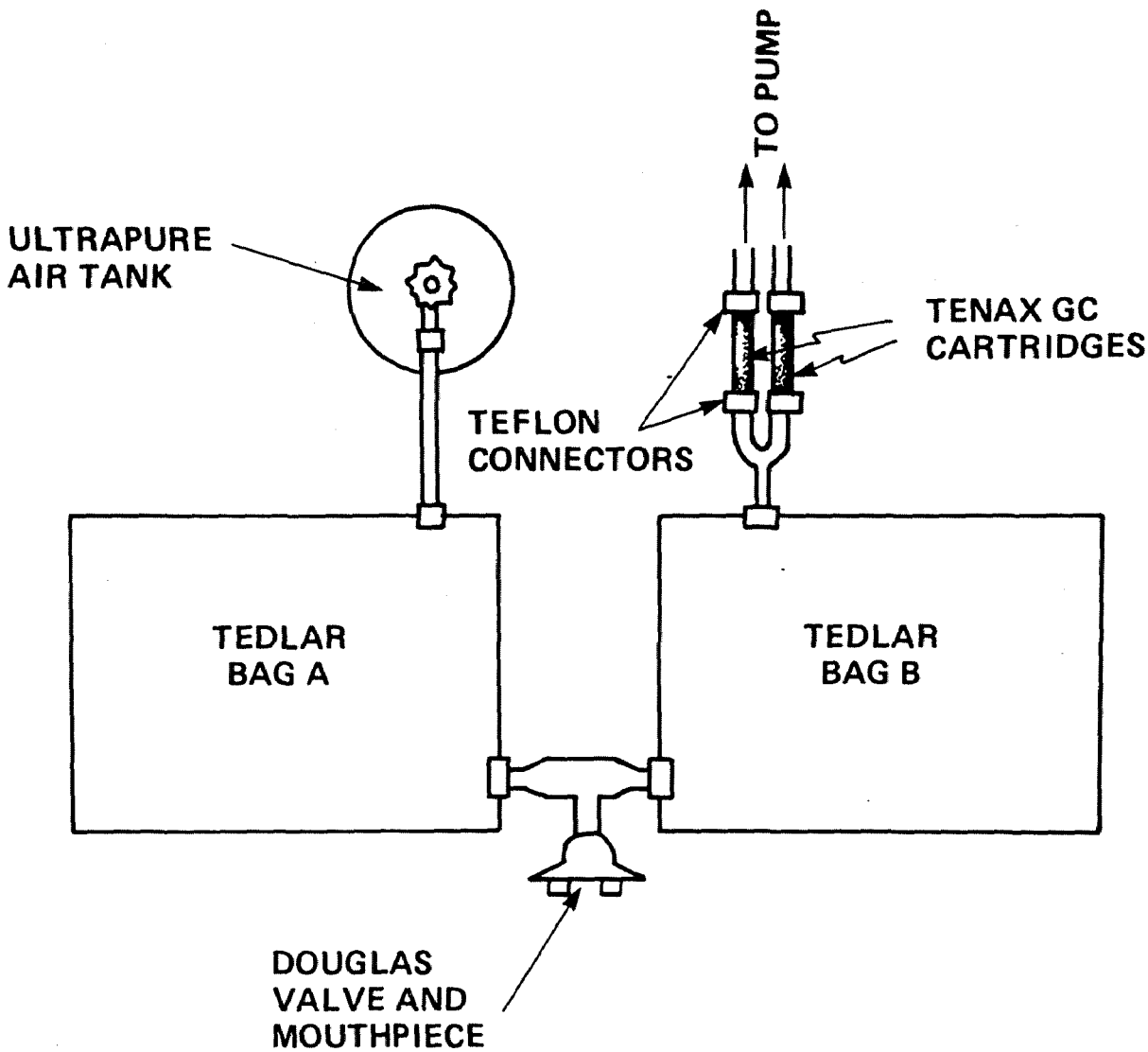

Figure 2. Schematic of spirometer for collection of breath samples.

containers were immediately chilled on ice, centrifuged and placed back in the ice. When chilled, the plasma was drawn off using a Pasteur pipet and transferred to several 4-mL glass vials fitted with Teflon® lined rubber septum caps. Each vial contained 4 mL of plasma and was kept cold until analyzed. One vial from each subject was packed on ice and shipped overnight to the University of Miami. The remaining vials were returned to Research Triangle Institute (RTI) to be analyzed.

Urine. Urine samples were collected immediately after the blood was drawn. Wide-mouth 240-ml amber bottles, sealed with a Teflon® lined cap were used. Samples were placed on ice and kept cold until analyzed.

University of North Carolina

During June, 1980, tap water, air, breath, blood and urine samples were collected at UNC (Table 5). Participants were screened and selected by EPA staff under the direction of Dr. William McDonnell of the Health Effects Research Laboratory's Inhalation Toxicology unit on the University of North Carolina campus. Samples were also collected in this building.

The criteria and methods of sampling remained the same as for the Lamar University study in Beaumont, Texas. Six students participated as subjects, and two more supplied blood and urine for blanks and controls. (Sampling protocols for air are displayed in Table 6.)

ANALYSIS PROCEDURES

All samples were analyzed at Research Triangle Institute (RTI), except for the blood samples, which were sent to the University of Miami.

Breath and Air. For analysis, the cartridges were placed in a preheated thermal desorption chamber and purged with helium gas (15-20 mL/min.)

Table 5. SAMPLES COLLECTED AT U. NORTH CAROLINA: CHAPEL HILL, NC

Participant No.	Date	Air	Breath[a]	Water	Blood	Urine
40001	6/10/80	1	1	2	1	1
40002	6/10/80	1	1	2	1	1
40003	6/10/80	1	1	2	1	1
40011	6/11/80	1	1	3	1	1
40012	6/11/80	1	1	2	1	1
40013	6/11/80	1	1	2	1	1

[a]Samples were collected in duplicate sets.

Table 6. SAMPLING PROTOCOL FOR PERSONAL AIR SAMPLES - UNIVERSTY OF NORTH CAROLINA

Participant No.	Date	Temperature (°C)	Relative Humidity	Pump No.	Sampling Start	Sampling End	Volume Sampled[b] (liters)	Wind Direction	Wind Velocity (knots)
40001	6/10/80	21.1	46%	1	0747	1535	27.0	WSW	10
40002	6/10/80			2,4[a]	0746 1002	0830 1601	- 19.1		
40003	6/10/80			3	0747	1612	23.7		
40011	6/11/80	21.1	58%	1	0734	1444	24.3	NNE	9
40012	6/11/80			4	0752	1539	23.7		
40013	6/11/80			3	0742	1539	22.4		

[a]Monitor dropped by subject, stopped functioning - second monitor employed.

[b]MSA sampler employed, 0.56 ml/count established by calibration; total counts multiplied by rate gave volume sampled.

into a liquid nitrogen capillary trap (5). After the desorption was completed, the temperature on the capillary loop was rapidly raised (faster than 100°C/min) and the carrier gas introduced the vapors onto the high resolution GC column. The glass capillary column was programmed from ambient temperature to 240°C at 4°C/min and held at the upper limit for a minumum of 10 minutes. After all the components eluted, the column was cooled to ambient temperatures and the next sample was run.

The helium carrier gas was precisely controlled at 2.25 mL/min by a Tylan mass flow controller. A jet separator connected the glass capillary column to the mass spectrometer (a Varian Mat CH-7 or LKB 2091). The mass spectrometer (resolution 1500-2000) was equipped with single ion monitoring capability and interfaced with a Varian 620/L or PDP 11/04 computer, respectively.

The mass spectral data were processed by scanning the original spectra and extracting the reconstructed ion chromatogram (RIC). The intensity was plotted against the spectrum number. Identities of constituents in the sample were established by comparing mass spectra obtained with those in the National Bureau of Standards (NBS) reference libraries.

Concentrations in air or breath of the target compounds were determined by the following technique (4). An external standard (hexafluoro-benzene or perfluorotoluene) was loaded at a known concentration onto each sample cartridge before analysis. The absolute peak height or area of the chemical to be measured was then compared to the peak height or area of the standard, by selecting characteristic ions in the mass spectra. These heights or areas are proportional to the number of moles of each substance. The proportionality constant, called the relative molar

response (RMR), is known or can be determined experimentally for any compound (10). The mass of the chemical on the cartridge was then determined from the following equation:

$$M_u = A_u W_u M_s / A_s W_s RMR$$

where subscripts u and s stand for the chemical of interest and the standard respectively, M= mass, W= molecular weight, RMR = the relative molar response of the unknown to the standard, and A = the response (area or peak height) of the characteristic ion.

The mean concentration of the substance in the air near the subject's breathing zone during his exposure period can then be determined by dividing the mass per cartridge by the volume of air drawn across the cartridge, provided that the sampling volume does not exceed the breakthrough volume (at sampling temperature) for the given compound. Even if the breakthrough volume has been exceeded, the mean concentration during the latter part of the exposure period (corresponding to the time required to pump the breakthrough volume of air across the cartridge) can be estimated by dividing the mass of the compound on the cartridge by the breakthrough volume. The calculated mass can be corrected for efficiency (i.e. thermal desorption plus storage losses), which varies by compound and by the length of time between collection and analysis (11). Thus the mean concentration can be calculated by C = M/V, where V = the volume of air sampled or the breakthrough volume, whichever is less, and M is the mass on the cartridge, corrected for recovery efficiency.

Drinking Water, Blood Serum and Urine

Tap water, blood serum, and urine samples were analyzed by a purge/

trap/desorb method based on that of Bellar and Lichtenberg (see ref. 7). The GC conditions were as follows: carrier gas flow rate of 30 mL/min, transfer line temperature 200°C, and inlet temperature 140°C. The column temperature was programmed at 60°C for 2 min, then increased at a rate of 10°C/min to 157°C. Both a Hall Electrolytic Conductivity Detector and a flame ionization detector were operated simultaneously to detect both the halogenated compounds and benzene. The column was 1.8m x 2mm 0.2% Carbowax 1500 on 60/80 Carbopack C. Standards, blanks and controls were interspersed throughout the analysis period. The standards were prepared fresh daily and transferred to smaller containers that were stored in the refrigerator until used.

Tap water. --A 5-mL water sample was transferred to a 5-mL purge device (Bellar and Lichtenberg design) via a glass syringe. The water was purged onto a Tenax GC trap at a flow/rate of 40 mL/min for 12 minutes. The compounds were then desorbed onto the analytical column. The purge device was rinsed several times with distilled water after each sample.

Urine. --The purge device was placed in a sand bath maintained at a temperature of 115°C during the entire analysis. A 1 mL aliquot of 1% aqueous antifoam was added to the 5 mL purge device and purged off-line at a flow/rate of 20 mL/min for about 20 minutes. A 2 mL aliquot of urine was then added to the purged antifoam and purged on-line for 15 min at a flow rate of 20 mL/min. To prevent contamination of the Tenax trap by steam, a small glass vapor trap was installed between the purging device and the trap (12). After the purge/trap period was complete the compounds were transferred to the analytical column. The purge device was cleaned with several rinsings of distilled water between samples.

Blood serum. --Foaming was a major problem encountered with the blood serum samples. Even with the 1 mL of 1% antifoam solution added to the serum, foam migrated into the vapor trap, necessitating dismantling and cleaning between each sample. This proved excessively time consuming so a larger purge device (25mL) was used and the amount of 1% antifoam was increased to 1.5mL. The purge device was placed in a constant temperature sand bath maintained at 115°C during the analysis. The antifoam solution was purged off-line for approximately 20 minutes with the flow-rate of 20 mL/min. A 0.5 mL aliquot of blood serum was injected into the purge device and purged onto the trap for 15 min at a flow rate of 20 mL/min. After the purge/trap period was complete, the compounds were transferred to the analytical column. The purge device was cleaned with several rinsings of distilled water.

Broad Spectrum Analysis.

Blood serum, urine and tap water samples (two each) were selected to be purged onto Tenax GC cartridges for broad spectrum analysis by GC/MS. Samples showing the largest number and amount of compounds detected by the purge/trap/desorb analysis were selected for the broad spectrum analysis. The blood and urine samples were purged by means of a headspace purge apparatus (Fig. 3). Four mL of blood serum and 25 mL of urine were diluted to 50 mL with purged distilled water. The samples were stirred while maintained at a temperature of 50°C. The samples purged for 90 min at a flow rate of 25 mL/min.

The conditions for the tap water purge were the same, but the purge apparatus used was of the through-solution type (Figure 4). A 50 mL sample of tap water was purged. The moisture trapped in the Tenax

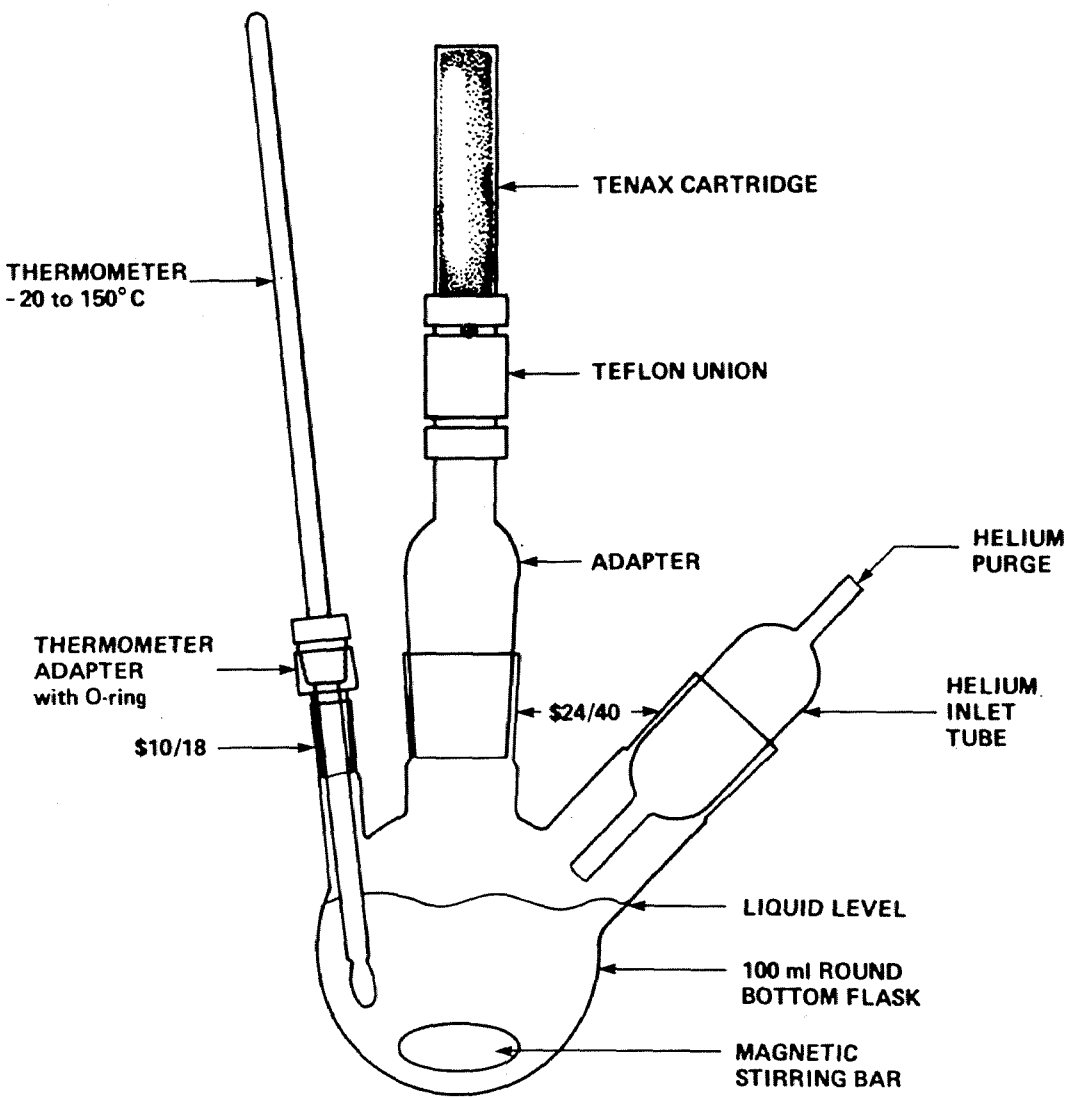

Figure 3. Headspace purge and trap apparatus for urine and blood.

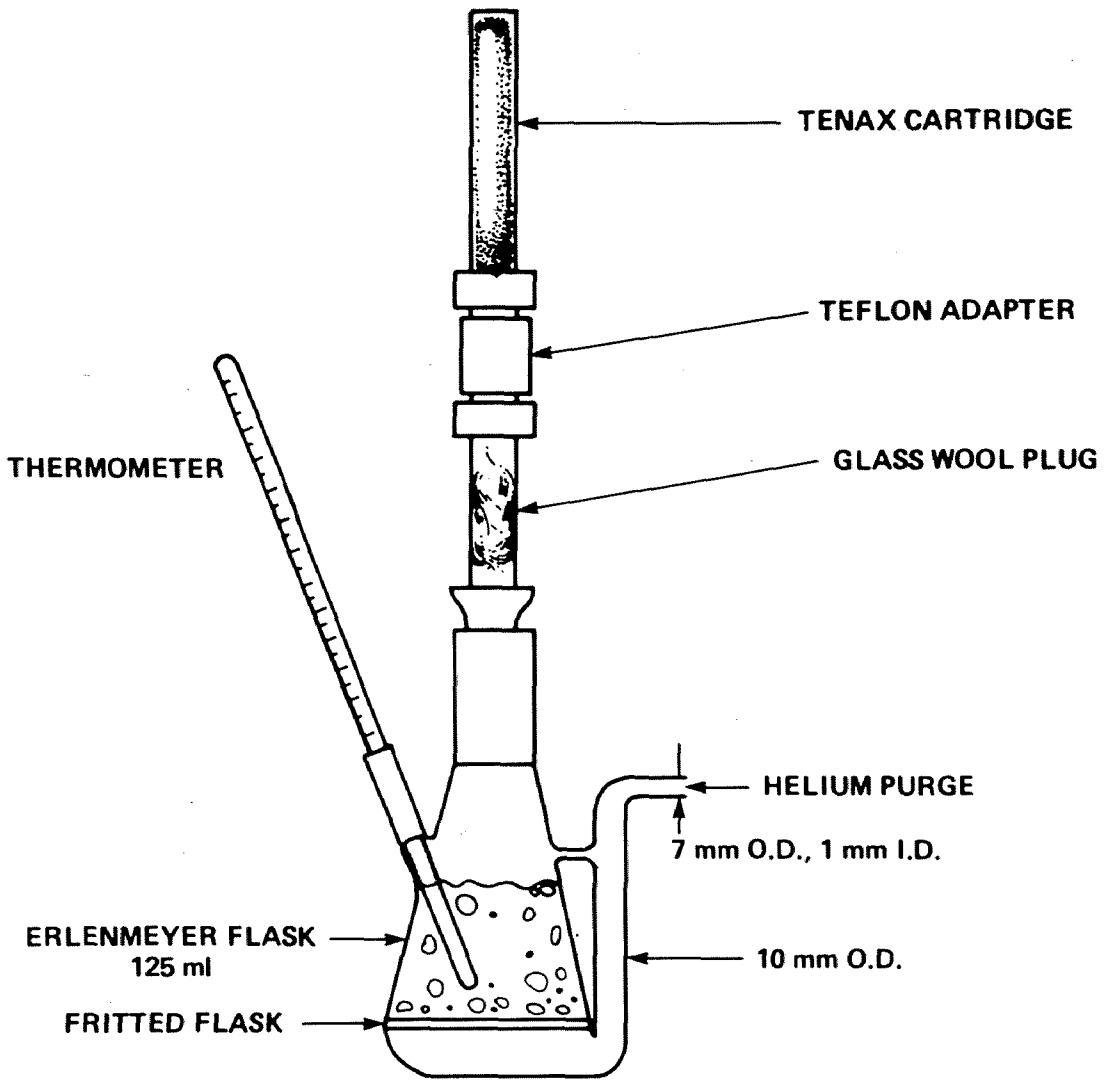

Figure 4. Purge and trap apparatus for water.

cartridge was dried by means of $CaSO_4$ (previously heated to 400°C for 3 hrs.) added to the culture storage tubes. They were desiccated overnight and then transferred to culture tubes without $CaSO_4$ for storage in the freezer until analysis.

Quality Control

The blanks and controls were prepared one day prior to the sampling trips (Tables 7 and 8). Lab blanks and controls remained at freezer temperatures (-20°C) in the laboratory during the field trip while the field blanks and controls were transported to and from the field, alongside the samples.

The air controls were spiked with the following seven compounds via a permeation system: chloroform, 1,2-dichloroethane, 1,1,1-trichlorethane, carbon tetrachloride, trichloroethylene, bromodichloromethane, and benzene.

The breath blanks were run on the spirometer with the mouthpiece plugged and the intake air forced through the exhaled bag. The controls were collected in the same manner, except that each cartridge was spiked with about 500 ng of each of the compounds listed.

Tap water blanks were prepared from distilled water. The bottles were filled to overflowing, capped with Teflon® lined caps, and refrigerated. Controls were spiked to give a concentration of 10 ng/mL of each of the following nine compounds: chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, tetrachloroethylene, chlorobenzene, o-dichlorobenzene, and bromodichloromethane. They were filled, capped and stored in the same manner as the blanks.

The blood plasma blanks and controls were prepared using combined plasma from four individuals. The plasma was collected as described in

Table 7. BLANKS AND CONTROLS--LAMAR UNIVERSITY

Sample type	Lab Blank	Lab Control	Field Blank	Field Control
Air	2	1	2[a]	2
Breath	2	1[b]	4	4
Water	2	2	3	3
Blood	1	1	4	4
Urine	1	1	2	2

[a]Lost due to mishandling in field.

[b]Invalid due to improper preparation.

Table 8. BLANKS AND CONTROLS--UNIVERSITY OF NORTH CAROLINA

Sample Matrix	Lab Blank	Lab Control	Field Blank	Field Control
Air	2	2[a]	2	2[a]
Breath	2		2	
Water	2	2	2	2
Blood				
Urine	2	2	2	2

[a]Controls are for both air and breath samples.

the section on sampling. The plasma was stored in 4mL vials and capped with Teflon® lined rubber septum caps. Controls were spiked at a concentration of 10 ng/mL with the same compounds as the water.

Urine blanks and controls were prepared from a composite of urine from three people. The urine controls were also spiked with the above compounds at a concentration of 10 ng/mL. Both blanks and controls were stored in clean 120-mL bottles filled with 100 mL of urine, sealed with Teflon® lined caps, and refrigerated (+4°C).

Section 6

RESULTS

Quality Control Results

Air and Breath. Percent recoveries for the air and breath analyses generally ranged between 95-140% (Tables 9 and 10). Coefficients of variance decreased to less than 10% for 1,1,1-trichloroethane and trichloroethylene between the Lamar and UNC visits, but remained between 20-30% for the other chemicals.

Water. Percent recoveries for tap water control samples at Lamar University varied widely, from 25% for tetrachloroethylene to >100% for chloroform (Table 11). The similarity of field controls to laboratory controls indicated that the problem did not lie in storage or transport of the sample. Adjustments in the analytical protocol led to the greatly improved percent recoveries observed at Chapel Hill three months later (Table 12). Mean recoveries ranged between 92% and 118% for the seven spiked compounds. The precision (i.e., relative standard deviation, or coefficients of variation) ranged between 4 and 12% at Chapel Hill. (The peaks for trichloroethylene and 1,1,2-trichloroethane overlap, so it was not possible to determine whether one or both compounds were present, nor to quantiate either compound).

Urine. As with the water samples, recovery efficiencies for urine samples showed sharp improvement between the Lamar and UNC visits. (Tables 13 and 14). From a range of 12-57% observed at Lamar University

Table 9. PERCENT RECOVERY OF SELECTED TEST SUBSTANCES IN AIR AND BREATH CONTROL SAMPLES (LAMAR UNIVERSITY STUDY)

	Air			Breath	
Compound	Observed (ng/cart.) $\bar{X}$ ± S.D. (C.V.)	Actual (ng/cart.)	Percent	Observed (ng/cart.) $\bar{X}$ ± S.D. (C.V.)	Percent
Benzene	570 ± 177 (31)	528	108 ± 33	643 ± 265 (41)	122 ± 50
Chloroform	270 ± 91 (33)	200	135 ± 45	219 ± 74 (34)	109 ± 37
1,2-Dichloroethane	750 ± 285 (38)	581	129 ± 49	707 ± 243 (34)	122 ± 41
1,1,1-Trichloroethane	505 ± 175 (35)	368	137 ± 47	501 ± 115 (23)	136 ± 31
Trichloroethylene	606 ± 155 (26)	605	100 ± 26	615 ± 140 (23)	102 ± 23
Tetrachloroethylene	694 ± 142 (21)	536	129 ± 26	572 ± 171 (30)	107 ± 32
Bromodichloromethane	286 ± 90 (32)	227	126 ± 40	249 ± 68 (27)	110 ± 30
Chlorobenzene	255 ± 49 (19)	219	116 ± 22	218 ± 90 (41)	99 ± 41
m-Dichlorobenzene	567 ± 174 (31)	490	116 ± 35	499 ± 124 (25)	102 ± 25

Table 10. PERCENT RECOVERY OF SELECTED TEST SUBSTANCES IN AIR AND BREATH CONTROL SAMPLES (UNIVERSITY OF NORTH CAROLINA STUDY)

	Air			Breath	
Compound	Observed (ng) $\bar{X}$ ± S.D. (C.V.)	Actual (ng)	Percent	Observed (ng) $\bar{X}$ ± S.D. (C.V.)	Percent
Benzene	450 ± 77 (17)	530	85 ± 14	501 ± 291 (58)	94 ± 55
Chloroform	208 ± 59 (28)	200	104 ± 29	-	-
1,2-Dichloroethane	548 ± 236 (43)	567	97 ± 42	644 ± 74 (11)	113 ± 13
1,1,1-Trichloroethane	600 ± 31 (5)	455	132 ± 7	456 ± 143 (31)	100 ± 31
Trichloroethylene	889 ± 56 (6)	742	119 ± 7	828 ± 41 (5)	111 ± 6
Tetrachloroethylene	852 ± 276 (32)	556	153 ± 50	-	-
Bromodichloromethane	292 ± 98 (33)	225	130 ± 43	-	-
Carbon tetrachloride	508 ± 39 (8)	343	148 ± 11	484 ± 145 (30)	141 ± 42

Table 11. QUANTITIES OF TARGET COMPOUNDS RECOVERED IN TAP WATER BLANKS AND CONTROLS FOR LAMAR UNIVERSITY STUDIES (ng/mL)

Sample	CF[a]	DE	MCF	CT	BCM	TCE	PERC	CB
Water Blank (T_o)	1.2 ± 2	-	-	-	0.5	-	-	-
Field Blank	0.3 ± 0.1	-	-	-	-	-	-	-
Lab Blank	3.0 ± 4	-	-	-	7.6	-	-	-
Field Control	9.4 ± 4 (94)[c]	8.7 ± 0.5 (87)	3.9 ± 2 (37)	-	5.5 (55)	NQ	2.4 ± 0.2 (26)	7.5 ± 0.2 (76)
Lab Control	11 ± 4 (109)	9.3 ± 1 (93)	4.6 ± 0.7 (46)	3.4 ± 0.1 (34)	5.8 ± 0.1 (58)	NQ	2.6 ± 0.1 (25)	7.5 ± 1 (75)

[a]CF = chloroform, DE = 1,2-dichloroethane, MCF = 1,1,1-trichloroethane, CT = carbon tetrachloride, BCM = bromodichloromethane, TCE = trichloroethylene/or 1,1,2-trichloroethane, PERC = tetrachloroethylene, CB = chlorobenzene.

[b]- not detected.

[c]Mean ± S.D. (percent recovered).

Table 12. QUANTITIES OF TARGET COMPOUNDS RECOVERED IN TAP WATER BLANKS AND CONTROLS FOR UNC STUDIES (ng/mL)

Sample	CF[a]	DE	MCF	BCM	TCF	PERC	CB
Field Blank	T[b]	-	-	-	-	-	-
Lab Blank	1.3 ± 0.5	-	-	-	-	-	-
Field Control	11 ± 1.4 (98)[c]	10 ± 0.9 (100)	12 ± 1 (118)	10 ± 1 (102)	11 ± 0 (108)	12.5 ± .2 (125)	10 ± 0.5 (102)
Lab Control	9.8 ± .3 (88)	9.2 ± 0.1 (92)	10.8 ± 0.1 (107)	9.5 ± 0 (95)	10.4 ± .2 (104)	12 ± 1 (107)	10 ± 0.5 (100)

[a]See Table 11 for codes.

[b]T = trace.

[c]Mean ± S.D. (percent recovered).

Table 13. QUANTITIES OF TARGET COMPOUNDS MEASURED IN URINE BLANKS AND CONTROLS--LAMAR UNIVERSITY (ng/mL)

Sample	Chloroform	1,2-Dichloro-ethane	1,1,1-Trichloro-ethylene	Carbon tetrachloride and/or bromodi-chloromethane	Trichloroethylene and/or 1,1,2-trichloroethane	Tetrachloro-ethylene	Chlorobenzene
Lab Control	9.3 (93)	9.0 (90)	5.3 (53)	4.6 (46)	2.9 (29)	4.0 (40)	13 (130)
Lab Blank	-	-	-	-	-	-	-
Field Blank-1	0.3	-	-	-	-	-	-
Field Blank-2	-	-	-	-	-	-	-
Field Control-1	5.0 (47)[a]	5.7 (57)	3.2 (32)	3.0 (30)	1.2 (12)	1.3 (13)	2.6 (26)
Field Control-2	4.7 (47)	5.7 (57)	3.2 (32)	3.0 (30)	1.2 (12)	1.4 (14)	4.3 (43)

[a]Numbers in parenthesis are percent recoveries of spiked compounds (with appropriate blank substracted).

Table 14. QUANTITIES OF TARGET COMPOUNDS MEASURED IN URINE BLANKS AND CONTROLS--CHAPEL HILL (ng/mL)

Sample	Chloro-form	1,2-Dichloro-ethane	1,1,1-Trichloro-ethane	Bromodichloro-methane	Trichloro-ethylene	Tetrachloro-ethylene	Chloro-benzene
Field Blank-1	0.2	-	ND	ND	0.1	T[a]	1.9
Field Blank-2	3.0	-	ND	ND	0.2	ND	ND
Lab Blank-1	-	-	0.7	ND	0.4	T	ND
Lab Blank-2	3.0	-	0.7	ND	0.3	ND	ND
Field Control-1	8.8 (86)[b]	10 (100)	12 (120)	9.7 (97)	9.7 (96)	9.0 (90)	9.0 (71)
Field Control-2	12 (90)	11 (110)	12 (120)	12 (120)	11 (108)	12 (120)	9.6 (96)
Lab Control-1	10 (100)	11 (110)	15 (143)	10 (100)	12 (116)	12 (120)	10 (100)
Lab Control-2	12 (90)	11 (110)	13 (123)	12 (120)	11 (107)	13 (130)	11 (110)

[a]Compound found in trace quantities.

[b]Numbers in parenthesis represent percent recoveries of spiked compounds (with appropriate blank subtracted).

[c]Median absolute recovery and percent recovery calculated independently.

mean recoveries of the seven spiked compounds improved to 92-126% at UNC. However, for all compounds in both study areas, field controls showed lower recoveries than laboratory controls, indicating a possible effect of transportation. At UNC, the precision was again high, ranging between 5 and 15%.

Blood. Blood controls for the Lamar University student study showed generally poor or variable recovery efficiencies, ranging from 20-140% (Table 15). For the UNC student study the efficiencies increased greatly, ranging from 80-165% (Table 16). Five of the seven spiked compounds were recovered at levels significantly higher than prepared, indicating the probable presence of these chemicals in the pooled blood samples donated as controls. This problem of accounting for the endogenous background has not been solved.

In addition to the quality control samples, three blind quality assurance samples were prepared for both blood and water. These samples were encoded prior to submission to the analyst. The results indicate variable recoveries except for chlorobenzene (Tables 17 and 18). Neither chloroform nor 1,1,1-trichloroethane could be recovered with good precision. Moreover, false positive identifications occurred consistently for tetrachloroethylene. The cause of these problems is being investigated.

Questionnaire Results

Demographic characteristics of the student volunteers from Lamar University and University of North Carolina are displayed in Tables 19 and 20.

Field Results

Air. Of 15 compounds sought, six were found in 100% of the samples:

Table 15. QUANTITIES OF TARGET COMPOUNDS MEASURED IN BLOOD PLASMA BLANKS AND CONTROLS--LAMAR UNIVERSITY (ng/mL)

Sample	Chloro-form	1,2-Dichloro-ethane	1,1,1-Trichloro-ethane	Bromodichloro-methane	Trichloro-ethylene	Tetrachloro-ethylene	Chloro-benzene
Lab Blank	9.0	21	13	-	-	0.5	-
Lab Control	17 (80)[a]	28 (70)	25 (120)	9.2 (92)	7.3 (73)	5.6 (51)	12 (120)
Field Blank-3	16	31	T[b]	-	17	-	-
Field Blank-4	16	30	T	1.2	-	T	-
Field Control-3	21 (50)	33 (20)	8.0 (80)	9.2 (90)	19 (20)	14 (140)	10 (100)
Field Control-4	20 (40)	32 (20)	4.4 (44)	3.2 (20)	17 (170)	12 (130)	9.6 (96)
System Blank[c]	-	-	-	-	-	-	-
System Blank	-	-	-	-	-	-	-
System Blank	-	-	-	-	-	-	-

[a]Numbers in parenthesis are percent recoveries of spiked compounds (with appropriate blank subtracted).

[b]Trace.

[c]Prepurged distilled water blank with 0.5 mL of antifoam added.

Table 16. QUANTITIES OF TARGET COMPOUNDS MEASURED IN BLOOD PLASMA BLANKS AND CONTROLS--CHAPEL HILL (ng/mL)

	Chloro-form	1,2-Dichloro-ethane	1,1,1-Tri-chloro-ethane	Bromodi-chloro-methane	Trichloro-ethylene	Tetrachloro-ethylene	Chloro-benzene	Mean	SD	CV	Median
Distilled Water Blank	ND	ND	ND	ND	ND	ND	ND				
Distilled Water Blank	ND	ND	ND	ND	ND	ND	ND				
Field Blank-2	14	ND	22	ND	ND	20	T[a]				
Field Blank-3	4.6	ND	21	ND	ND	15	ND				
Lab Blank-1	14	ND	22	ND	ND	20	ND				
Blank 40015[a]	14	ND	22	ND	T	20	ND				
Blank 40017[b]	14	ND	21	ND	ND	20	ND				
Field Control-2	28 (70)[d]	26 (130)	41 (95)	28 (140)	32 (160)	46 (130)	36 (180)	34 (128)	8 (37)	24 (29)	32 (130)
Field Control-3	23 (92)	18 (90)	39 (90)	36 (130)	31 (155)	41 (130)	30 (150)	30 (120)	8 (29)	27 (24)	30 (130)
Lab Control-1	30 (80)	36 (130)	42 (100)	29 (134)	33 (165)	47 (135)	36 (180)	35 (133)	8 (35)	23 (26)	33 (135)
Control 40014	29 (76)	26 (130)	37 (75)	28 (140)	30 (150)	41 (105)	35 (175)	32 (121)	6 (38)	19 (31)	30 (130)
Control 4001[c]	41 (81)	35 (105)	60 (117)	40 (120)	47 (141)	66 (138)	47 (141)	48 (120)	11 (22)	23 (18)	47 (120)
Mean	30 (80)	26 (117)	44 (95)	30 (135)	35 (154)	48 (218)	37 (165)	(124)			
SD	7 (8)	6 (19)	9 (15)	6 (10)	7 (9)	10 (13)	6 (18)	(6)			
CV (%)	23 (10)	23 (16)	20 (160)	20 (7)	20 (6)	21 (10)	16 (11)	(5)			
Median[f]	29 (80)	26 (130)	41 (95)	28 (140)	32 (155)	46 (130)	36 (175)	(121)			

[a]Blank 40015 corresponds to Control 40014.

[b]Blank 40017 corresponds to Control 40016.

[c]Control 40016 was spiked at a higher concentration than the other controls.

[d]Numbers in parenthesis are percent recoveries. The concentration of the blanks have been taken into account.

[e]Compound found in trace quantities.

[f]Absolute recovery and percent recovery calculated independently.

Table 17. RESULTS OF WATER BLIND STUDY[a]

Compound	Blank		Spike -1			Spike -2		
	Spike (ng/mL)	Found (ng/mL)	Spike (ng/mL)	Found (ng/mL)	Recovery (%)	Spike (ng/mL)	Found (ng/mL)	Recovery (%)
Benzene	0	ND[b]	0	ND		0	ND	
Chloroform	0	ND	15.5	15.6	100	1.5	1.7	116
1,2-Dichloroethane	0	ND	6	ND		0	ND	
1,1,1-Trichloroethane	0	ND	14.1	20	142	134	202	151
Carbon tetrachloride	0	ND	16.7	13.4	80	ND	ND	
Bromodichloromethane	0	ND	0	ND		0	ND	
Trichloroethylene and/or	0	ND	0	ND		0	0.02	
1,1,2-Trichloroethane	0	ND	0			0	ND	
Tetrachloromethylene	0	ND	17.0	9.2	54	0	ND	
Chlorobenzene	0	ND	11.6	12.4	107	0	ND	

[a]Samples prepared with known levels of the compounds as indicated and encoded prior to submission for analysis.

[b]Not detected.

Table 18. RESULTS OF BLOOD BLIND STUDY[a]

Compound	Blank		Spike -1			Spike -2		
	Spike (ng/mL)	Found (ng/mL)	Spike (ng/mL)	Found (ng/mL)	Recovery (%)	Spike (ng/mL)	Found (ng/mL)	Recovery (%)
Benzene	0	ND[b]	0	0		0	0	
Chloroform	0	ND	31	8.8	30	32.8	31.6	96
1,2-Dichloroethane	0	ND	0	0		0	0	
1,1,1-Trichloroethane	0	ND	28.2	24	85	28.2	15	53
Carbon tetrachloride	0	ND	0	0		0	0	
Bromodichloromethane	0	ND	0	0		0	0	
Trichloroethylene and/or 1,1,2-Trichloroethane	0	ND	23.2	-[c]	-	23.2	-	
Tetrachloroethylene	0	28	0	20	0	0	7.8	0
Chlorobenzene	0	ND	11.6	9.5	8.2	23.2	18.6	80
Mean					66			76

[a]Three samples prepared with known levels as indicated and encoded prior to submission for analysis.

[b]Not detected.

[c]Not quantitated - interferences.

[d]Not included in calculation.

Table 19. DEMOGRAPHIC CHARACTERISTICS OF LAMAR UNIVERSITY VOLUNTEERS

Participant Code	Sex	Race	Age	Residence	Possible Exposure Activities
A	M	W	20	Off (Groves)	Worked in pohto-lab developing (9/78-12/78); father refinery worker
B	F	W	21	Off (Port Neches)	Used pesticides in yard
C	F	W	21	Off (Beaumont)	Ex-smoker; household includes smoker, chemical plant worker
D	F	W	21	Dorm	Family members work at petroleum plant; pesticides sprayed in garden; Raid; Lysol; liquid starch
E	F	B	22	Off (Beaumont)	Uses liquid paper
F	M	W	18	Dorm	Swims regularly; expo[illegible] smokers
G	M	W	24	Dorm	Sprayed with diesel fuel (30 min) prev. week; painted house four months previously
H	M	W	29	Dorm	None
I	M	W	21	Dorm	Swins regularly; dorm neighbors painted indoors recently; dry cleaning job over Christmas
J	M	W	21	Dorm	Swims regularly; worked at chemical plant 5/79-8/79; exposed to smokers
K	M	W	23	Dorm	Pumped gas in last 24 hours; uses hair spray twice a week

Table 20. DEMOGRAPHIC CHARACTERISTICS OF UNC VOLUNTEERS

Participant Code	Sex	Race	Age	Residence	Possible Exposure Activities
U	M	W	21	Off (Carrboro)	Swims regularly; lifequard; swam within last 24 hours; taking cortisone.
V	M	W	20	Off (Chapel Hill)	Swims regularly; was employed (dishwasher) in Dept. of Anesthesiology for 4 months; mother works in antibody screening room at Red Cross; uses bleach when mopping floors at night.
W	M	W	19	Off (Carrboro)	Swims regularly; used pesticide in last 72 hours; uses spray starch, deodorant; smokers at home.
X	M	W	19	On	Lifeguard; swam in last 24 hours; pumped gas in last 72 hours; uses spray deodorant.
Y	M	W	22	Off	Inhaled Methyl chloride for another EPA experiment; used liquid paper in last 24 hours.
Z	M	W	19	On	Cook; swims regularly; swam in last 24 hours; uses spray deodorant; smokers in household.

benzene, chloroform, trichlorothylene, tetrachloroethylene, 1,1,1-trichloroethane, and dichlorobenzene isomer; and four others in more than 50% of the samples: vinylidene chloride, ethylene dichloride, bromodichloromethane and o-dichlorobenzene (Tables 21 and 22).

Six of these 10 compounds showed high variability, ranging over 2-3 orders of magnitude: trichloroethylene, tetrachloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, dichlorobenzene isomer, and vinylidene chloride.

Geometric means for one compound--1,1,1-trichloroethane--exceeded 50 ug/m^3 in each student group. Geometric means for seven other compounds generally fell between 1 and 10 ug/m^3 for each group (Fig. 5). No significant difference in concentration was noted between the two student groups for any compound.

Breath. Results of the breath sampling are displayed in Tables 23 and 24. Five compounds were found in 100% of the samples; benzene, chloroform, tetrachloroethylene, 1,1,1-trichloroethane, and dichlorobenzene isomer ; two others were found in more than 50% of the samples: trichloroethylene and vinylidene chloride.

Five of these seven compounds showed highly variable levels trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, m-dichlorobenzene, and vinylidene chloride. Two showed low variability: benzene and chloroform. Geometric means for these seven compounds ranged from about 1-15 ug/m^3. Significant differences were noted between the two student groups in breath concentrations for three of the seven compounds: chloroform, vinylidene chloride, and 1,1,1-trichloroethane. In all three cases, UNC geometric means were higher.

Table 21. ESTIMATED LEVELS OF SELECTED VAPOR-PHASE ORGANICS IN AMBIENT AIR ASSOCIATED WITH HUMAN PARTICIPANTS--LAMAR UNIVERSITY STUDENT STUDY ($\mu g/m^3$)

	Participant No.												
Compound	30001	30002	30003	30004	30005	30011	30012	30013	30014	30015	30016	LOD[a]	QL[b]
Benzene	9.5	2.5	11	2.9	3.6	4.8	5.8	8.3	3.2	5.3	386	0.08	0.40
Chloroform	1.4	1.5	3.8	8.3	5.2	4.0	4.8	6.0	3.2	1.9	4.8	0.08	0.40
Vinylidene chloride	416	1.4	76	1.0	1.1	-	7.0	5.7	2.1	4.6	-	0.12	0.60
1,1-Dichloroethane	1.8	-	0.93	-	-	-	-	-	-	-	-	0.12	0.60
1,2-Dichloroethane	11	0.49	-	0.32	0.52	1.0	0.94	0.95	0.72	0.71	13	0.12	0.60
1,1,1-Trichloroethane	592	22	1,069	8.5	8.3	31	62	72	12	67	40	0.16	0.80
Trichloroethylene	19	7.5	26	1.6	0.90	3.8	2.0	63	0.99	2.4	3.7	0.16	0.80
1,2-Dichloropropane	-	-	-	-	-	-	-	-	-	-	-	0.20	1.00
Tetrachloroethylene	174	162	7.2	5.4	5.6	5.0	30	718	4.5	172	9.3	0.24	1.20
Bromodichloromethane	1.6	1.5	-	3.2	1.0	-	1.1	3.7	0.84	-	-	0.24	1.20
Dibromochloromethane	-	-	-	-	-	-	-	-	-	-	-	0.24	1.20
Ethylene dibromide	-	-	-	-	-	-	-	-	-	-	-	0.28	1.40
Chlorobenzene	-	-	-	-	0.47	-	-	-	-	-	2.1	0.16	0.80
Dichlorobenzene isomer	8.4	73	8.0	6.9	2.5	6.4	3.0	23	1.8	4.3	33	0.20	1.00
o-Dichlorobenzene	-	-	-	2.4	0.38	-	0.20	-	-	-	-	0.20	1.00

[a]Limit of Detection (LOD) was defined as S/N = 4 for m/z ion selected for quantification, all values in $\mu g/m^3$.

[b]Quantifiable Limit (QL) was defined as 5 × LOD or S/N = 20, all values in $\mu g/m^3$.

Table 22. ESTIMATED LEVELS OF VAPOR-PHASE ORGANICS IN AMBIENT AIR FOR SEVERAL HUMAN SUBJECTS--UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL STUDY ($\mu g/m^3$)

	Participant Number					
Compound	40001	40002	40003	40011	40012	40013
Benzene	14	7.5	3.8	3.2	4.2	3.0
Chloroform	7.8	5.1	3.7	3.2	17	2.2
Vinylidene chloride	14	27	9.8	3.5	5.7	7.0
1,1-Dichloroethane	-[a]	-	-	-	-	-
1,2-Dichloroethane	-	-	1.1	0.42	0.45	0.63
1,1,1-Trichloroethane	165	194	93	14	70	57
Trichloroethylene	9.7	2.2	10.8	4.6	2.2	183
1,2-Dichloropropane	-	-	-	-	-	-
Tetrachloroethylene	2.5	2.6	2.1	1.2	4.3	127
Bromodichloromethane	-	-	-	-	4.3	-
Dibromochloromethane	-	-	-	-	-	-
Ethylene dibromide	-	-	-	-	-	-
Chlorobenzene	-	-	-	0.17	0.18	-
Dichlorobenzene isomer	35	0.58	0.46	0.29	15	0.63
o-Dichlorobenzene	1.5	0.32	-	-	0.27	0.14

[a]- = not detected.

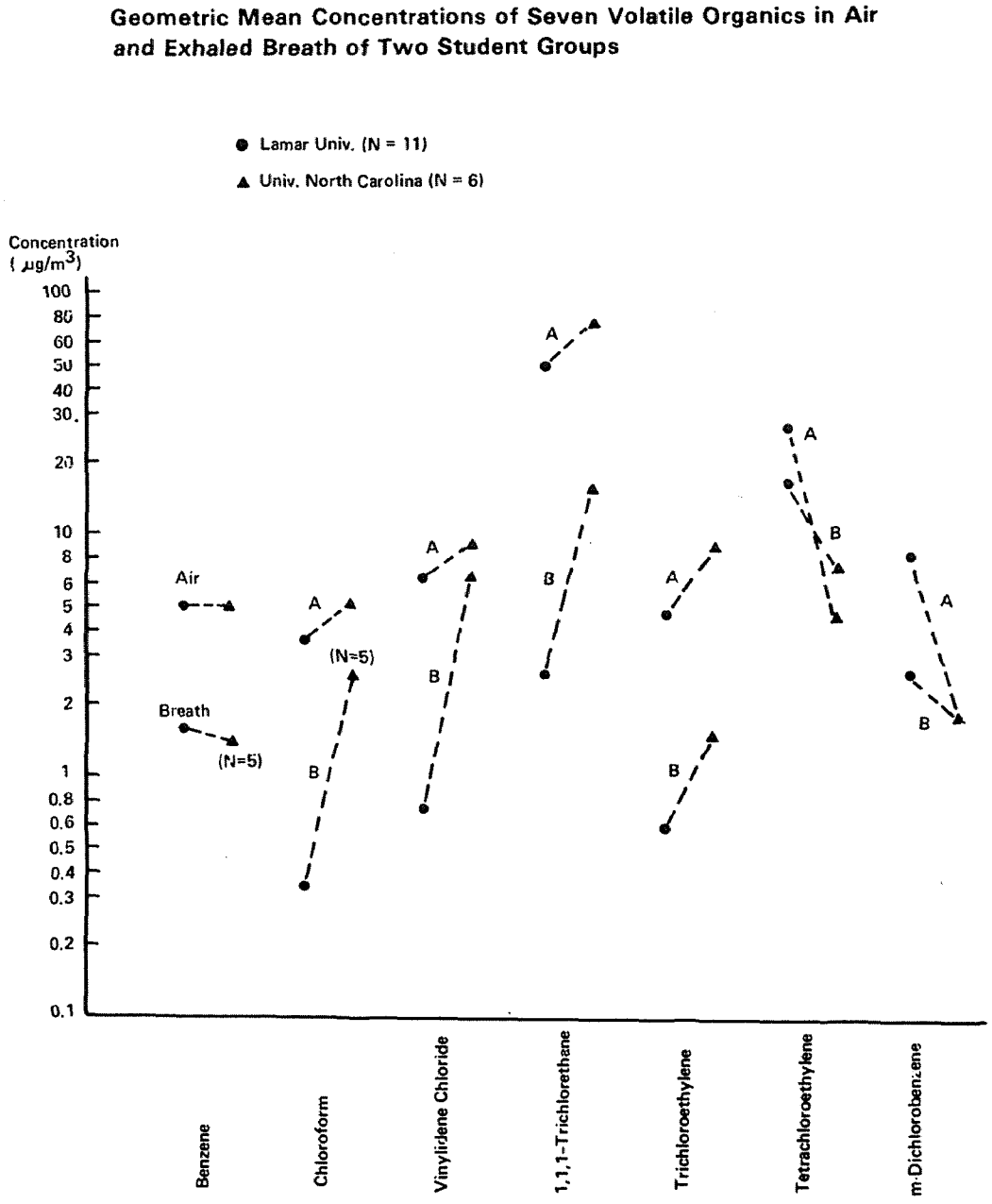

Figure 5. Geometric mean concentrations of seven volatile organics in air and exhaled breath of two student groups.

Table 23. ESTIMATED LEVELS OF SELECTED VAPOR PHASE ORGANICS IN BREATH--LAMAR UNIVERSITY STUDENT STUDY ($\mu g/m^3$)

Compound	Participant Number											LOD	QL
	30001	30002	30003	30004	30005	30011	30012	30013	30014	30015	30016		
Benzene	2.9 ± 1.1	1.4 ± 0.2	0.7 ± 0.0	1.71 ± 0.28	0.99 ± 0.33	1.8 ± 0.13	2.2	1.7 ± 0.15	1.1 ± 0.15	1.9 ± 0.20	1.3 ± 0.52	0.11	0.55
Chloroform	T[a]	T	T	T	T	T	2.48	T	T	T	T	0.11	0.55
Vinylidene chloride	15 ± 2.8	0.08	26 ± 8.0	0.08	2.9	0.08	0.08	0.5 T	5.8 ± 1.6	3.8 ± 1.2	0.08	0.16	0.82
1,1-Dichloroethane	-[b]	-	-	-	-	-	-	-	-	-	-	0.16	0.82
1,2-Dichloroethane	-	-	-	-	-	-	-	T	-	T	-	0.16	0.82
1,1,1-Trichloroethane	161 ± 16	0.66 ± 0.16	93 ± 21	T	T	T	2.5	T	1.7 ± 0.46	6.5 ± 0.75	T	0.22	1.10
Trichloroethylene	-	1.11 ± 0.04	T	T	-	T	T	1.45 ± 0.10	T	1.07 ± 0.04	T	0.2	1.10
1,2-Dichloropropane	-	-	-	-	-	-	-	-	-	-	-	0.27	1.37
Tetrachloroethylene	69 ± 5.4	96 ± 0.20	9.8 ± 1.0	13 ± 1.5	13 ± 0.71	T	24	161 ± 31	1.0	176 ± 0.91	T	0.33	1.65
Bromodichloromethane	-	-	-	-	-	-	-	-	-	-	-	0.33	1.65
Dibromochloromethane	-	-	-	-	-	-	-	-	-	-	-	0.33	1.65
Ethylene dibromide	-	-	-	-	-	-	-	-	-	-	-	0.38	1.92
Chlorobenzene	-	-	-	-	-	-	-	-	-	-	-	0.22	1.10
Dichlorobenzene isomer	T	31 ± 2.5	T	T	T	T	1.3 ±	20 ± 6.2	6.1 ±	23 ± 3.0	T	0.27	1.37
o-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	0.27	1.37

[a]T = trace amount.

[b]- = not detected.

Table 24. ESTIMATED LEVELS OF VAPOR PHASE ORGANICS IN BREATH OF HUMAN SUBJECTS--UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL STUDY ($\mu g/m^3$)

Compound	Participant Number					
	40001	40002	40003	40011	40012	40013
Benzene	1.0 ± 0.05	1.4 ± 0.23	1.4 ± 0.18	1.1 ± 0	NC[a]	1.5 ± .41
Chloroform	2.8 ± 1.5	3.0 ± 0.16	5.1 ± 2.8	1.8 ± 0.28	NC	1.7 ± 0.41
Vinylidene chloride	4.5 ± 0.39	14 ± 1.3	5.5 ± 1.3	3.9 ± 0.09	7.7 ± 0.05	7.9 ± 0.65
1,1-Dichloroethane	-[b]	-	-	-	-	-
1,2-Dichloroethane	-	-	-	-	0.37	0.48
1,1,1-Trichloroethane	23 ± 3.6	48 ± 11	19 ± 5.7	6.1 ± 0.04	8.5 ± 1.8	13 ± 0.34
Trichloroethylene	1.1 ± 0.12	0.55 ± 0.19	1.2 ± 0.36	0.65 ± .05	0.49 ± 0.11	32 ± 0.70
1,2-Dichloropropane	-	-	-	-	-	-
Tetrachloroethylene	3.4 ± 0.44	3.3 ± 0.19	4.3 ± 0.76	8.8 ± 1.1	7.5 ± 0.68	48 ± 5.5
Bromodichloromethane	-	-	-	-	-	-
Dibromochloromethane	-	-	-	-	-	-
Ethylene dibromide	-	-	-	-	-	-
Chlorobenzene	-	-	0.27	-	0.11[c]	-
Dichlorobenzene Isomer	0.54 ± .03	4.5 ± 0	2.2 ± 0.56	0.92 ± 0	5.3 ± 0.71	1.1 ± 0.36
o-Dichlorobenzene	-	-	-	-	-	-

[a]NC = missing values.

[b]- = not detected.

[c]Given value is below the limit of detection.

Water. Ten VOC were measured in tap water (Tables 25 and 26). UNC tap water showed consistently higher mean chloroform values than the Lamar University sources (220 ppb to 150 ppb), except for the one water sample at the Port Neches home of one of the Lamar University students. (This was the only sample not taken from the Beaumont water supply). Tetrachloroethylene values were also higher in the UNC supplies. Bromodichloromethane values were similar in the two supplies (20 ppb at Lamar; 17 ppb at UNC). Total trihalomethanes exceeded the standard of 100 ppb in all 38 water samples from the two areas.

All of the tap water samples contained chloroform and bromodichloromethane. Some samples contained small amounts of tetrachloroethylene, chlorobenzene and either trichloroethylene or 1,1,2-trichloroethane. No benzene, carbon tetrachloride, 1,2-dichloroethane, vinylidene chloride, or 1,1,1-trichloroethane was detected.

Blood and Urine. Because of the quality control difficulties discussed above, the analytical results of the blood and urine tests will not be listed or discussed.

Table 25. QUANTITIES OF TARGET COMPOUNDS FOUND IN TAP WATER (ng/mL), LAMAR UNIVERSITY

Number	Chloroform	1,2-Dichloroethane	1,1,1-Trichloroethane	Carbon Tetrachloride and/or Bromodichloromethane	Trichloroethylene and/or 1,1,2-Trichloroethane	Tetrachloroethylene	Chlorobenzene
1-30001	110	-[a]	-	16	NC[b]	-	-
1-30002	260	-	-	18	NC	-	-
2-30002	130	-	-	23	NC	-	-
1-30003	550	-	-	44	NC	T[c]	-
1-30004	160	-	-	25	NC	-	-
2-30004	99	-	-	18	NC	-	-
1-30005	140	-	-	25	NC	-	-
2-30005	120	-	-	22	NC	-	-
1-30011	120	-	-	20	NC	-	-
2-30011	120	-	-	18	NC	0.2	0.2[d]
3-30011	110	-	-	23	NC	-	-
1-30012	120	-	-	22	NC	-	-
2-30012	170	-	-	26	NC	-	-
3-30012	110	-	-	17	NC	-	-
1-30013	140	-	-	18	NC	-	-
2-39913	160	-	-	22	NC	0.1[d]	-
3-30013	130	-	-	18	NC	-	-
1-30014	160	-	-	20	NC	-	-
2-30014	130	-	-	18	NC	-	-
3-30014	110	-	-	13	NC	-	-
1-30015	110	-	-	7.4	NC	0.2[d]	0.2[d]
2-30015	140	-	-	18	NC	-	-
1-30016	120	-	-	13	NC	-	-
2-30016	120	-	-	13	NC	-	-
3-30016	120	-	-	14	NC	0.1[d]	-
LOD	1.0	0.6	0.2	0.4	1.3	1.1	0.6

[a]- = not detected.

[b]NC = missing data.

[c]T = trace amount.

[d]Given value is below limit of detection.

Table 26. QUANTITIES OF TARGET COMPOUNDS FOUND IN TAP WATER (CHAPEL HILL) (ng/mL)

Sample	Chloro-form	1,2-Dichloro-ethane	1,1,1-Trichloro-ethane	Bromodichloro-methane	Trichloro-ethylene	Tetrachloro-ethylene	Chloro-benzene
40001-1	260	ND	ND[a]	20	2.8	3.8	ND
40001-2	260	ND	ND	19	3.0	3.8	ND
40002-1	220	ND	ND	17	ND	1.8	ND
40002-3	250	ND	ND	18	ND	1.8	ND
40003-1	200	ND	ND	18	ND	1.8	1.4
40003-2	230	ND	ND	18	ND	1.8	ND
40011-1	200	ND	ND	17	ND	1.7	ND
40011-2	210	ND	ND	16	ND	1.8	ND
40011-3	220	ND	ND	17	ND	1.8	1.5
40012-1	210	ND	ND	17	ND	1.8	ND
40012-2	210	ND	ND	16	ND	1.8	ND
40013-1	180	ND	ND	15	ND	1.3	1.5
40013-2	200	ND	ND	15	1.3	1.3	ND
Mean[b]	220	-	-	17	0.6	2.0	0.4
SD	23	-	-	2	1	0.8	0.6
CV (%)	10	-	-	12	170	40	150
Median	220	-	-	17	ND	1.8	ND
LOD[c]	0.05	0.06	0.1	0.1	0.05	0.05	ND

[a]Not detected.

[b]Mean of all values (ND - 1/2 LOD).

[c]Limit of detection (S/N = 3).

SECTION 7

DISCUSSION

SUMMARY STATISTICS: AIR AND BREATH

The air and breath data are summarized in Tables 27 and 28. Each statistic was computed using the measurements for all subjects. For those compounds not detected, values were estimated as 1/2 LOD. Those compounds detected as trace levels were estimated as 1/2 (QL+LOD). The numbers displayed as (,) indicate how many of the samples were below the limit of detection and at trace levels, respectively. The median, as well as the arithmetic mean, is provided because of the skewness of the data. The standard deviations, minumum and maximum values suggest large variation in the data for most compounds. In most cases, the standard deviations are larger than the means and the magnitude of this relationship is reflected in the coefficients of variation:

$$(CV = \frac{\text{Standard deviation}}{\text{mean}} \times 100\%)$$

The concentrations of some chemicals reached unexpectedly high levels, both in air and in human breath, compared to recent studies (1,7,9) of ambient levels. These levels are far below the workplace standards set by the Occupational Safety and Health Administration; however, their chronic effects are unknown and could be of significant public health concern.

The great variability exhibited by seven of the 10 most prevalent

Table 27. SUMMARY STATISTICS FOR ESTIMATED LEVELS OF SELECTED VAPOR-PHASE ORGANICS--LAMAR UNIVERSITY

		% Detected[a]	% at Trace	Mean[b]	Std. Dev.	Median	Range	% ≥ 10 μg/m³
Benzene	Air	100	0	40.30	118.87	5.16	2.46-386.56	18
	Breath	100	0	1.61	0.62	1.70	0.72-2.95	0
Chloroform	Air	100	0	4.00	2.13	4.04	1.39-8.33	0
	Breath	100	91	0.42	0.68	0.22	0.22-2.48	0
Vinylidene chloride	Air	82	0	46.84	124.43	2.14	0.06-416.07	18
	Breath	55	9	4.88	8.19	0.33	0.08-25.17	18
1,1-Dichloroethane	Air	18	0	0.30	0.57	0.06	0.06-1.83	0
	Breath	0	0	0.08	0.00	0.08	0.08-0.08	0
1,2-Dichloroethane	Air	91	9	2.72	4.66	0.72	0.06-12.80	18
	Breath	18	18	0.12	0.10	0.08	0.08-0.33	0
1,1,1-Trichloroethane	Air	100	0	180.35	339.47	40.00	8.27-1,069.04	82
	Breath	100	45	24.37	53.14	0.66	0.44-161.50	18
Trichloroethylene	Air	100	0	11.88	18.90	3.67	0.90-63.39	27
	Breath	82	54	0.59	0.43	0.44	0.11-1.45	0
1,2-Dichloropropane	Air	0	0	0.10	0.00	0.10	0.10-0.10	0
	Breath	0	0	0.13	0.00	0.13	0.13-0.13	0

(continued)

Table 27. (continued)

		%[a] Detected	% at Trace	Mean[b]	Std. Dev.	Median	Range	% ≥ 10 μg/m³
Tetrachloroethylene	Air	100	0	117.63	212.38	9.26	4.54-718.20	45
	Breath	100	18	51.36	65.61	13.25	0.66-176.32	64
Bromodichloromethane	Air	64	0	1.23	1.24	1.00	0.12-3.71	0
	Breath	0	0	0.16	0.00	0.16	0.16-0.16	0
Dibromochloromethane	Air	0	0	0.12	0.00	0.12	0.12-0.12	0
	Breath	0	0	0.16	0.00	0.16	0.16-0.16	0
Ethylene Dibromide	Air	0	0	0.14	0.00	0.14	0.14-0.14	0
	Breath	0	0	0.19	0.00	0.19	0.19-0.19	0
Chlorobenzene	Air	18	0	0.30	0.08	0.61	0.08-2.12	0
	Breath	0	0	0.11	0.00	0.11	0.11-0.11	0
Dichlorobenzene Isomer	Air	100	0	15.56	21.52	6.95	1.83-73.47	27
	Breath	100	54	7.73	11.31	0.56	0.55-30.67	27
o-Dichlorobenzene	Air	27	0	0.34	0.67	0.10	0.10-2.40	0
	Breath	0	0	0.13	0.00	0.13	0.13-0.13	0

[a] n = 11.

[b] All compounds measured in μg/m³.

Table 28. SUMMARY STATISTICS FOR ESTIMATED LEVELS OF SELECTED VAPOR PHASE ORGANICS UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL STUDY

		%[a] Detected	% at Trace	Mean[b]	Std. Dev.	Median	Range	% ≥ 10 μg/m³
Benzene	Air	100	0	5.89	4.14	4.00	2.95-13.65	17
	Breath	100	0	1.29	0.22	1.38	1.00-1.51	0
Chloroform	Air	100	0	6.59	5.66	4.41	2.25-17.46	17
	Breath	10 (n=5)	0	2.86	1.36	2.84	1.70-5.06	0
Vinylidene chloride	Air	100	0	11.21	8.66	8.40	3.53-27.29	33
	Breath	100	0	7.28	3.73	6.59	3.94-14.12	17
1,1-Dichloroethane	Air	0	0	0.06	0.00	0.06	0.06-0.06	0
	Breath	0	0	0.08	0.00	0.08	0.08-0.08	0
1,2-Dichloroethane	Air	67	0	0.45	0.39	0.43	0.06-1.09	0
	Breath	33	0	0.19	0.18	0.08	0.08-0.48	0
1,1,1-Trichloroethane	Air	100	0	99.07	68.06	81.81	14.45-193.77	100
	Breath	100	0	19.47	15.14	15.97	6.10-47.63	67
Trichloroethylene	Air	100	0	35.33	72.16	7.13	2.17-182.43	33
	Breath	100	0	5.94	12.60	0.86	0.49-31.66	17
1,2-Dichloropropane	Air	0	0	0.10	0.00	0.10	0.10-0.10	0
	Breath	0	0	0.13	0.00	0.13	0.13-0.13	0

(continued)

Table 28. (continued)

		%[a] Detected	% at Trace	Mean[b]	Std. Dev.	Median	Range	% ≥ 10 μg/m³
Tetrachloroethylene	Air	100	0	23.34	50.94	2.56	1.22-127.30	17
	Breath	100	0	12.52	17.40	5.92	3.30-47.74	17
Bromodichloromethane	Air	17	0	0.83	1.73	0.12	0.12-4.36	0
	Breath	17	0	0.29	0.30	0.16	0.16-0.91	0
Dibromochloromethane	Air	0	0	0.12	0.00	0.12	0.12-0.12	0
	Breath	0	0	0.16	0.00	0.16	0.16-0.16	0
Ethylene Dibromide	Air	0	0	0.14	0.00	0.14	0.14-0.14	0
	Breath	0	0	0.19	0.00	0.19	0.19-0.19	0
Chlorobenzene	Air	33	0	0.11	0.05	0.08	0.08-0.18	0
	Breath	17	0	0.14	0.0	0.11	0.11-0.27	0
Dichlorobenzene Isomer	Air	100	0	8.66	14.14	0.61	0.29-34.96	33
	Breath	100	0	2.42	2.01	1.53	0.54-5.30	0
o-Dichlorobenzene	Air	50	0	0.40	0.55	0.18	0.10-1.52	0
	Breath	0	0	0.13	0.00	0.13	0.13-0.13	0

[a] n=6 unless otherwise noted.

[b] All compounds are measured in μg/m³.

compounds indicates that human exposures to many VOC may vary so widely even in a very small geographical area that it is not generally possible to characterize a geographical cohort with unifrom exposures. If this preliminary conclusion is validated by future studies, it would have serious implications for epidemiological studies, which have traditionally assigned similar exposure histories to residents of a given region.

At Lamar University, four of the five students with the highest air exposures and breath levels lived off-campus. The reason for this result is unknown.

Table 29 shows the relative contribution of each of 12 volatile organics to the air exposure of each of the 17 subjects. In both study areas, 1,1,1-trichloroethane is the main contributor, supplying over half the total intake at UNC, and more than a third at Lamar. The relative importance of benzene, chloroform, and vinylidene chloride was also very similar at each location, ranging between 4% and 8%. However, tetrachloroethylene was far more important at Lamar University than at UNC (35% to 7%), while trichloroethylene was relatively more important at UNC (13% to 4%). Dichlorobenzenes also seemed more common at Lamar than at UNC.

Bromodichloromethane, chlorobenzene and 1,1-dichloroethane contributed less than 2% to total air exposure at Lamar, and even less at UNC.

CORRELATIONS BETWEEN AIR AND BREATH SAMPLES

Spearman correlation coefficients were computed between the Lamar air and breath samples for all compounds (Table 30). Of particular interest are the correlations between air and breath for a given compound, shown in the highlighted diagonal of the correlation matrix. Three of

Table 29. PERCENT OF INDIVIDUAL AIR EXPOSURE SUPPLIED BY SELECTED VAPOR-PHASE ORGANICS--BOTH GROUPS

Participant	Benzene	Chloroform	Vinylidene chloride	1,1-Dichloroethane	1,2-Dichloroethane	1,1,1-Trichloroethane	Trichloroethylene	Tetrachloroethylene	Bromodichloromethane	Chlorobenzene	m-Dichlorobenzene	o-Dichlorobenzene
Lamar University												
30001	0.76	0.11	34	0.14	0.88	48	1.5	14	0.13	-	0.67	-
30002	0.86	0.51	0.48	-	0.17	8.0	2.6	59	0.52	-	27	-
30003	0.86	0.30	6.0	0.07	-	85	2.1	0.57	-	-	0.63	-
30004	7.1	20	2.4	-	0.73	21	3.9	13	7.8	-	17	5.9
30005	8.8	13	27	-	1.2	20	2.2	14	2.4	1.2	6.0	1.0
30011	8.6	7.1	-	-	1.8	55	6.8	87	-	-	11	-
30012	4.7	3.9	5.7	-	0.7	51	1.6	25	0.90	-	2.5	0.17
30013	0.93	0.67	0.67	-	0.11	8.0	7.0	80	0.40	-	2.5	-
30014	11.0	11.0	7.2	-	2.4	41	3.4	16	2.8	-	6.2	-
30015	2.0	0.7	1.7	-	0.26	25	0.9	67	-	-	1.6	-
30016	*	6.1	-	-	16	51	4.7	12	-	2.7	42	-
Mean	4.7	5.8	7.8	-	2.2	38	3.5	35	1.4	-	11	0.6
Standard Deviation	3.8	±6.2	±11.0	-	±4.4	±22	±2.0	±30	±2.3	-	±12	-
UNC												
40001	5.6	3.1	5.6	-	-	66	3.9	1	-	-	14	0.6
40002	3.1	2.1	11	-	-	81	0.9	1.1	-	-	0.2	0.1
40003	3.0	3.0	7.8	-	0.88	74	8.8	1.7	-	-	0.4	0.1
40011	11	11	12	-	1.3	47	15	4.0	-	0.7	1.0	0.3
40012	2.4	9.6	3.2	-	0.23	40	1.2	2.4	2.5	0.1	8.5	0.2
40013	0.8	0.6	1.8	-	0.16	15	48	34	-	-	0.16	0.03
Mean	4.3	4.9	6.9	-	0.43	54	13	7.4	0.4	0.1	4.0	0.2
Standard Deviation	±3.3	±3.9	±3.8	-	±0.49	±23	±16	±12	-	-	±5.3	±0.2

*Outlier--not included in calculations.

Table 30. CORRELATIONS[a] BETWEEN AIR AND BREATH FOR ESTIMATED LEVELS OF SELECTED VAPOR-PHASE ORGANICS--LAMAR UNIVERSITY

	Breath														
Air	Benzene	Chloroform	Vinylidene Chloride	1,1-Dichloroethane	1,2-Dichloroethane	1,1,1-Trichloroethane	Trichloroethylene	1,2-Dichloropropane	Tetrachloroethylene	Bromodichloromethane	Dibromochloromethane	Ethylene Dibromide	Chlorobenzene	m-Dichlorobenzene	o-Dichlorobenzene
Benzene	.04	.10	.31	0	.15	.29	-.15	0	-.12	0	0	0	0	-.36	0
Chloroform	-.16	.20	-.46	0	.07	-.74 **	.01	0	-.19	0	0	0	0	-.25	0
Vinylidene Chloride	.24	.30	.67 *	0	.22	.82 **	-.02	0	.53	0	0	0	0	.20	0
1,1-Dichloroethane	.07	-.15	.69 *	0	-.22	.71 *	-.43	0	.03	0	0	0	0	-.40	0
1,2-Dichloroethane	.44	.10	-.18	0	.07	-.12	-.14	0	-.17	0	0	0	0	-.14	0
1,1,1-Trichloroethane	.27	.10	.47	0	.37	.63 *	.18	0	.30	0	0	0	0	.04	0
Trichloroethylene	.12	-.20	.18	0	.30	.25	.41	0	.25	0	0	0	0	.11	0
1,2-Dichloropropane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tetrachloroethylene	.4	.10	.11	0	.60	.32	.39	0	.80 **	0	0	0	0	.43	0
Bromodichloromethane	.29	.10	-.15	0	.11	-.14	.12	0	.49	0	0	0	0	.19	0
Dibromochloromethane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ethylene Dibromide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Chlorobenzene	-.43	-.14	-.18	0	-.22	-.47	-.37	0	-.36	0	0	0	0	-.40	0
Dichlorobenzene Isomer	.03	-.30	-.24	0	.07	-.08	.40	0	.16	0	0	0	0	.08	0
o-Dichlorobenzene	.03	.38	-.33	0	-.28	-.32	-.38	0	-.02	0	0	0	0	-.32	0

[a]Spearman correlation coefficient.

n = 11 for each coefficient.

* = $p < .05$; ** = $p < .01$.

the five compounds found at Lamar in sufficient numbers above trace levels to allow meaningful correlations were significantly correlated (p, the probility of a chance correlation, is less than 0.05). Correlations significantly different from zero are denoted by * ($p<.05$) and ** ($p<.01$).

Spearman correlation coefficients were also computed between air and breath samples for the UNC students (Table 31). Although the number of samples was exceedingly small (N=6), two correlations were significant at $p<0.01$. One of the compounds (1,1,1-trichloroethane; $\underline{r}=0.94$), was also significant at Lamar ($\underline{r}=0.63$).

Since no significant differences were observed between the two student groups with respect to air concentrations, they were combined into a single group (N=17) and studied further for correlations between chemicals in air and breath (Table 32). Four of the five chemicals prevalent in the breath samples showed significant correlations with their concentrations in air; only benzene showed little correlation between breathing-level exposure and breath clearance.

Breath/Air Relationships.

Regressions were run for several compounds relating breath levels to air levels. Logarithms were employed because of the wide range of concentrations. To determine the effect of assigning different numerical values to the "Trace" and "Non-Detect" (ND) categories, two approaches were used:

1) The "Standard" approach of assigning the Non-detectable (ND) category a value of 1/2 the Limit of Detection (LOD) and the "Trace" category a value halfway between the LOD and the Quantifiable Limit (QL);

Table 31. SPEARMAN CORRELATION COEFFICIENTS BETWEEN AIR AND BREATH FOR ESTIMATED LEVELS OF SELECTED VAPOR PHASE ORGANICS--BOTH GROUPS

	n		$r_{Air-Breath}$	
	UNC	Lamar	UNC	Lamar
Benzene	5	11	.70	.04
Chloroform	5	11	.60	.20
Vinylidene chloride	6	11	.48	.67*
1,1-Dichloroethane	6	11	.00	.00
1,2-Dichloroethane	6	11	.44	.07
1,1,1-Trichloroethane	6	11	.94**	.63*
Trichloroethylene	6	11	.94**	.41
1,2-Dichloropropane	6	11	.00	.00
Tetrachloroethylene	6	11	.20	.80**
Bromodichloromethane	6	11	.20	.00
Dibromochloromethane	6	11	.00	.00
Ethylene dibromide	6	11	.00	.00
Chlorobenzene	6	11	.31	.00
Dichlorobenzene isomer	6	11	.03	.08
o-Dichlorobenzene	6	11	.00	.00

* $p < .01$

** $p < .05$

Table 32. SIGNIFICANT SPEARMAN CORRELATION COEFFICIENTS FOR VOLATILE ORGANIC COMPOUNDS OBSERVED IN BREATHING-ZONE AIR AND IN EXHALED BREATH OF 17 STUDENTS AT LAMAR UNIVERSITY AND UNIVERSITY OF NORTH CAROLINA

	Breath				
Air	Benzene	Methyl Chloroform	Tetrachloro-ethylene	Trichloro-ethylene	Vinylidene Chloride
Benzene					
1,1,1-Trichloroethane		.74			.62
Tetrachloroethylene	.54		.73		
Trichloroethylene				.53	
Vinylidene Chloride		.88			.77
1,2-Dichloroethane	.54				

2) The "Maximum" approach of setting ND values equal to the LOD and Trace values equal to the QL. (No "Minimum" approach was used since setting an ND value equal to 0 would give a logarithm of negative infinity.) The results of these approaches are compared in Table 33.

The table indicates that little difference occurs in the regression parameters as a result of the two approaches. For all three chemicals 50% or more of the variance in breath levels was explained by the preceding air exposures. The F values are all above the 99% level.

The simple log-linear model appears capable of predicting breath levels to within a factor of 3 or 4, given the air exposures for the preceding eight hours.

Tetrachloroethylene: $C_B=10^{.23}\ C_A^{\ .72\pm.13}$

1,1,1-Trichloroethane: $C_B=10^{-.98}\ C_A^{\ .91\pm.23}$

Vinylidene chloride: $C_B=10^{-.24}\ C_A^{\ .71\pm.17}$

A linear relationship between the logarithms of air exposures and breath concentrations of several compounds is suggested in Figures 6-8. If this preliminary observation is confirmed by future studies, an exposure-dose relationship could be established for some compounds. This would allow exposures to be estimated from a single non-invasive test lasting just 15 minutes.

Correlations Within Air and Breath Media

Of the 15 chemicals sought in air and breath, eight in air and five in breath were above trace levels often enough to include in a study of correlations within and between media. Spearman rank correlations were determined for all possible pairs of these chemicals in air, in breath,

Table 33. COMPARISON OF BREATH-AIR REGRESSIONS USING DIFFERENT CONVENTIONS FOR ASSIGNING VALUES TO "TRACE" AND "NON-DETECTABLE" CATEGORIES

Approach	A[a]	B[a]	F	R^2	S.E.	S.E. (B)
			Tetrachloroethylene			
Standard[b]	.23	.72	31	.68	.44	.13
Maximum[c]	.27	.71	39	.72	.38	.11
			1,1,1-Trichloroethane			
Standard	-.98	.91	16	.52	.54	.23
Maximum	-.77	.84	17	.73	.48	.20
			Vinylidene Chloride			
Standard	-.23	.71	17	.53	.67	.17
Maximum	-.13	.67	18	.55	.56	.16

[a]Log (Concentration in Breath) = A + B log (Concentration in Air).

[b]Standard Approach: ND = 1/2 LOD; Trace = 1/2 (LOD + QL).

[c]Maximum Approach: ND = LOD; Trace = QL.

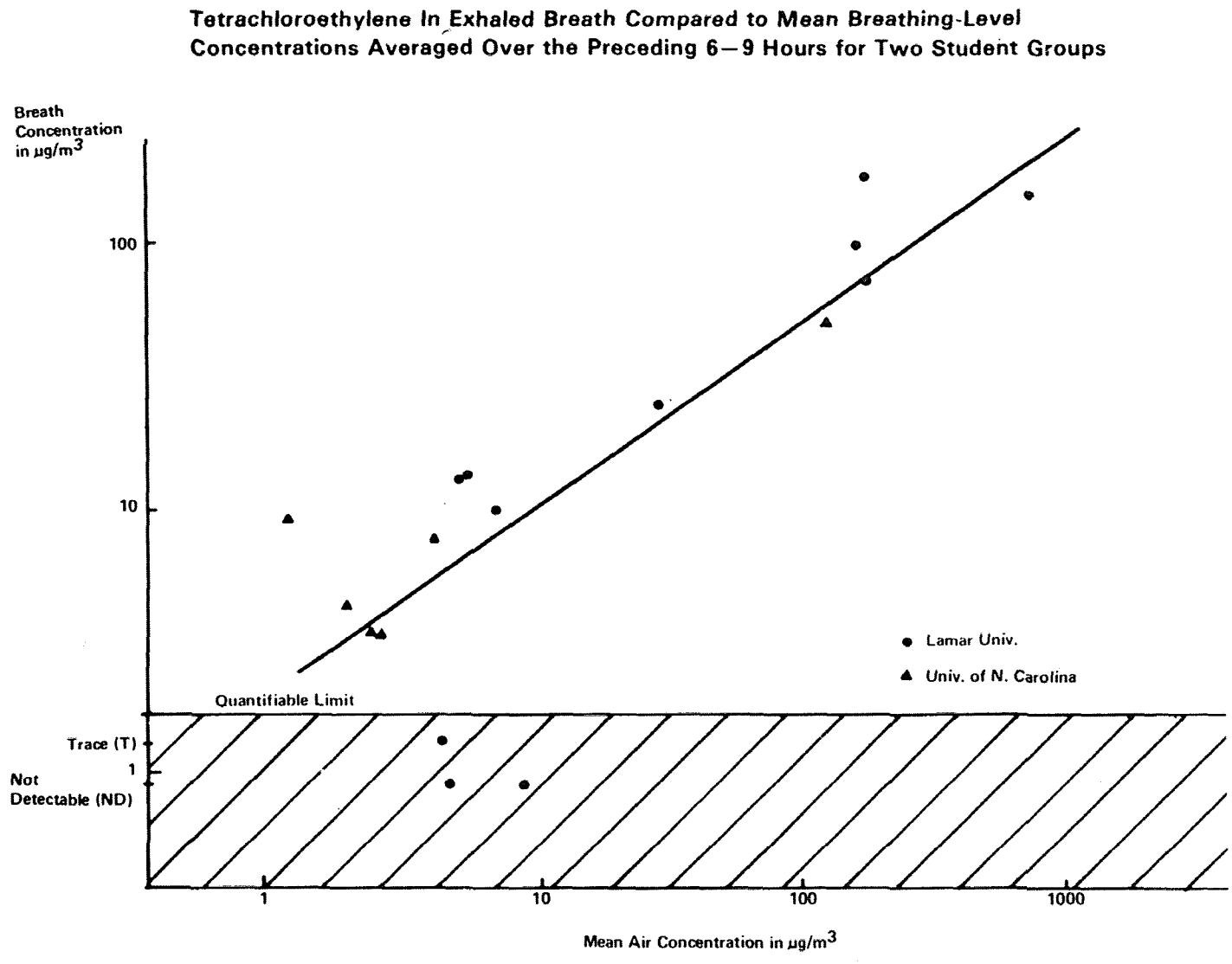

Figure 6. Tetrachloroethylene in exhaled breath compared to mean breathing-level concentrations.

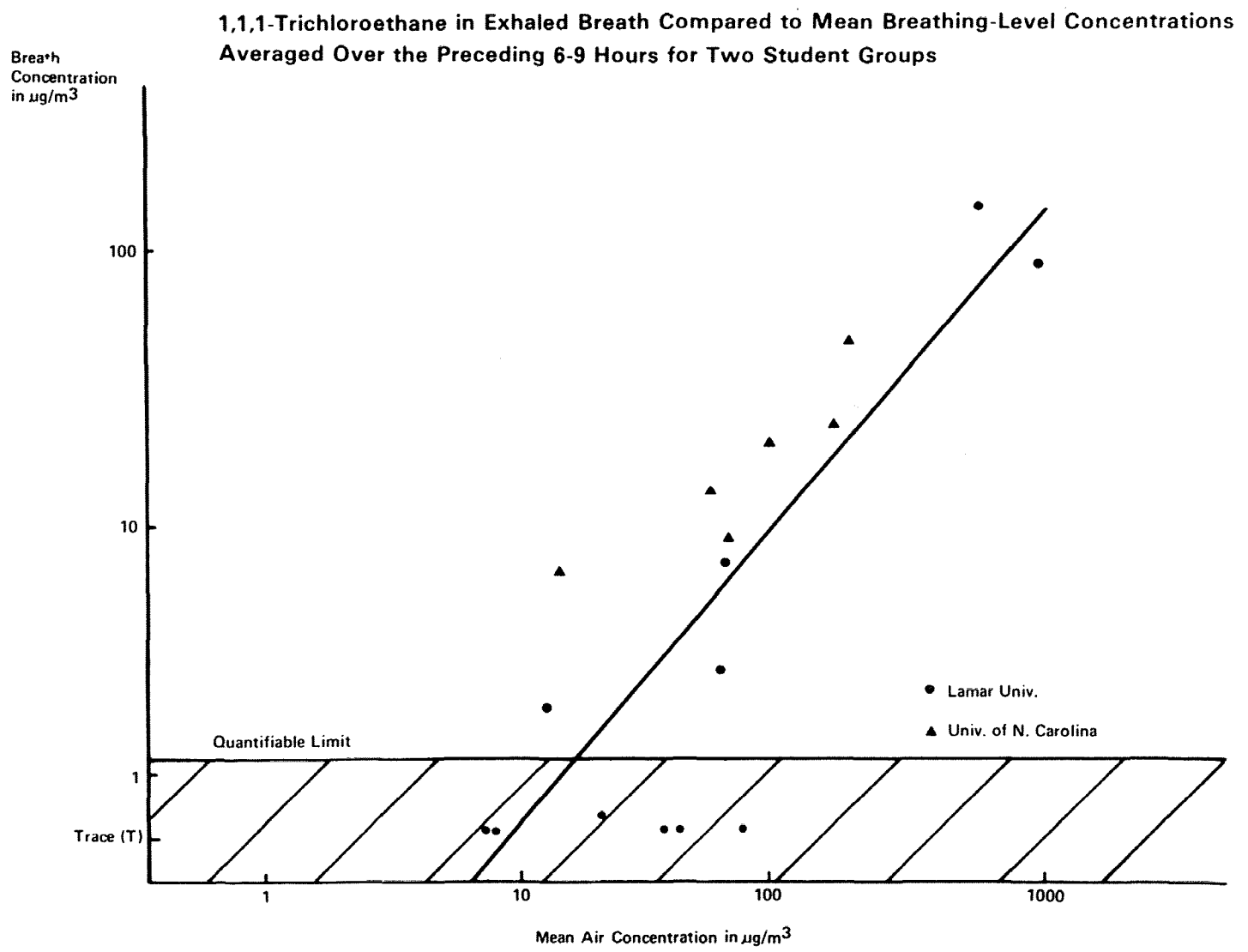

Figure 7. 1,1,1-Trichloroethane in exhaled breath compared to mean breathing-level concentrations.

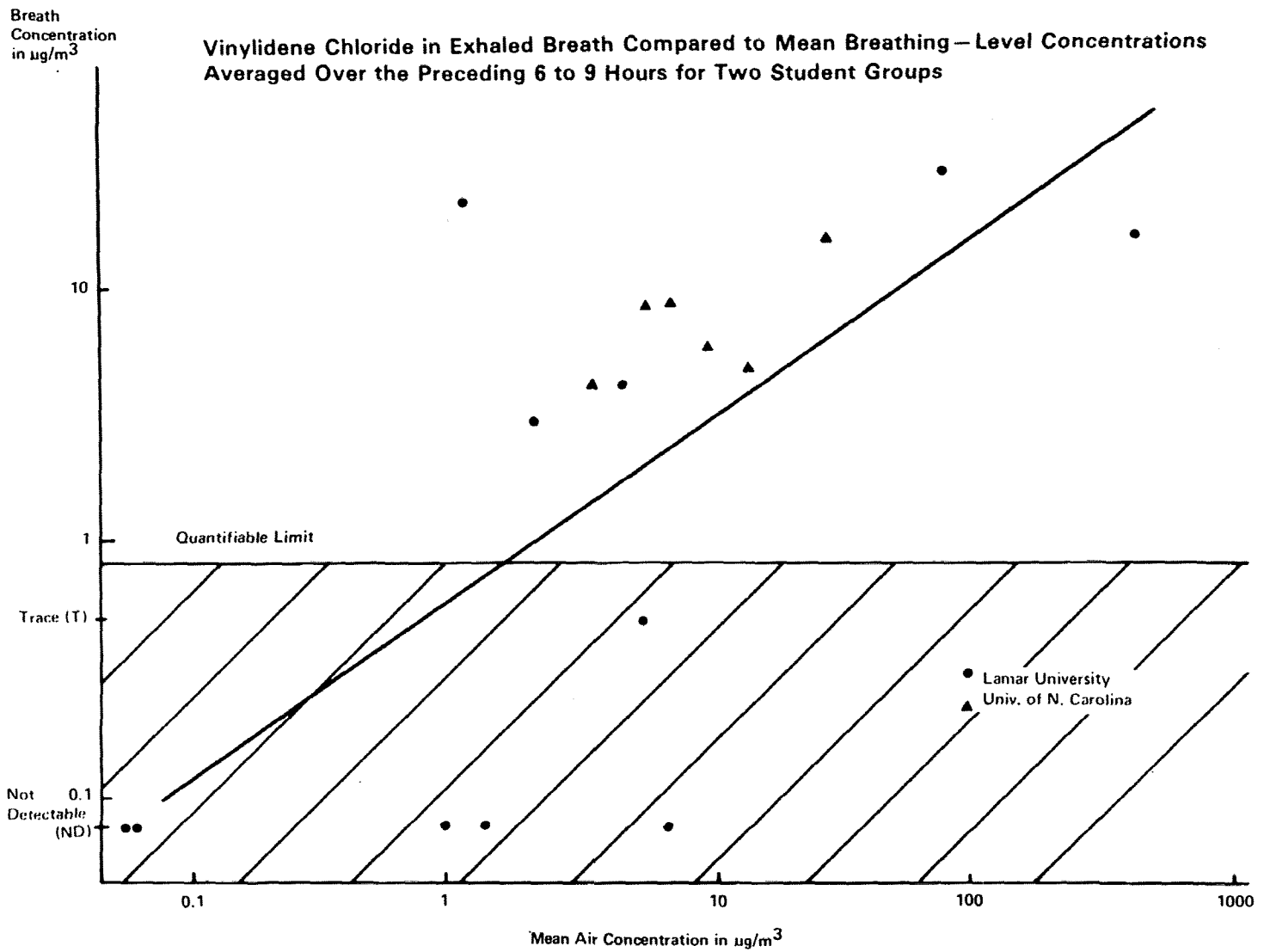

Figure 8. Vinylidene chloride in exhaled breath compared to mean breathing-level concentrations.

and between air and breath for each group separately and for both groups combined (Tables 34, 35, 36). For the combined groups, 16 of the 78 possible correlations were significant at the $p < .05$ level, a result obtainable by chance less than once in 10^{52} tries. A striking result was the relation between vinylidene chloride and 1,1,1-trichloroethane, which displayed the strongest correlations in air, in breath, and also between air and breath. These chemicals occur together in the manufacture of vinylidene chloride, and so might be expected to correlate in a manufacturing area. However, they also correlated in the nonmanufacturing area. Hence an atmospheric chemistry relationship may also exist.

As a check on the Spearman calculations and also on the suitability of employing the logarithms of the observed chemical concentrations in air and breath, Pearson correlation coefficients were calculated for the logarithms of the concentrations. Fifteen of the 16 significant Spearman correlations were also significant when calculated by the Pearson method (Table 37).

Breath-Air Ratios

The concentrations of seven VOC in air were compared to their concentrations in exhaled breath for the two student groups (Table 38). Assuming constant concentrations in air and breath, and no additional exposures through water or food, the breath-to-air ratio of a compound is simply the additive inverse of the absorption factor for that compound. (That is, if one breathes out 30% of what he breathes in, then 70% of the quantity has been absorbed).

Breath-air ratios are similar between the two student groups for benzene (0.3), vinylidene chloride (0.8) and trichloroethylene (0.2).

Table 34. SPEARMAN CORRELATION COEFFICIENTS FOR SELECTED VAPOR-PHASE ORGANICS IN AIR AND BREATH: LAMAR UNIVERSITY

	Air	vs.	Air	Spearman Rank Correlation	N	P
*1.	1,1,1-Trichloroethane		Benzene	.88	10	.0008
2.	Vinylidene chloride		Benzene	.79	10	.006
3.	1,1,1-Trichloroethane		Trichloroethylene	.79	11	.004
4.	m-Dichlorobenzene		Trichloroethylene	.79	11	.008
*5.	1,1,1-Trichloroethane		Vinylidene chloride	.72	11	.012
6.	1,1,1-Trichloroethane		Tetrachloroethylene	.64	11	.035
7.	Trichloroethylene		Tetrachloroethylene	.61	11	.047
	Breath	vs.	Breath			
8.	n-Dichlorobenzene		Trichloroethylene	.79	11	.004
9.	1,1,1-Trichloroethane		Vinylidene chloride	.67	11	.024
10.	m-Dichlorobenzene		Tetrachloroethylene	.67	11	.025
	Air	vs.	Breath			
11.	Tetrachloroethylene		Tetrachloroethylene	.80	11	.003
*12.	Vinylidene chloride		1,1,1-Trichloroethane	.82	11	.002
13.	Vinylidene chloride		Vinylidene chloride	.67	11	.024
*14.	1,1,1-Trichloroethane		1,1,1-Trichloroethane	.63	11	.038

*Also significant ($p < 0.05$) at University of North Carolina.

Table 35. SPEARMAN CORRELATION COEFFICIENTS FR SELECTED VAPOR-PHASE ORGANICS IN AIR AND BREATH: UNIVERSITY OF NORTH CAROLINA

	Air	vs.	Air	Spearman Rank Correlation	N	P
*1.	1,1,1-Trichloroethane		Vinylidene chloride	.94	6	.005
*2.	1,1,1-Trichloroethane		Benzene	.83	6	.042
3.	Chloroform		Benzene	.83	6	.042
	Breath	vs.	Breath			
4.	Tetrachloroethylene		1,1,1-Trichloroethane	-.83	6	.042
	Air	vs.	Breath			
*5.	Vinylidene chloride		1,1,1-Trichloroethane	1.0	6	.000
6.	Trichloroethylene		Trichloroethylene	1.0	6	.000
*7.	1,1,1-Trichloroethane		1,1,1-Trichloroethane	0.94	6	.005
8.	1,1,1-Trichloroethane		Tetrachloroethylene	0.94	6	.005
9.	Benzene		Tetrachloroethylene	0.89	6	.014
10.	Vinylidene chloride		Tetrachloroethylene	0.83	6	.042

*Also significant ($p < 0.05$) at Lamar University.

Table 36. SPEARMAN CORRELATION COEFFICIENTS FOR SELECTED VAPOR-PHASE ORGANICS IN AIR AND BREATH: BOTH GROUPS

	Air	vs.	Air	Spearman Rank Correlation	N	P
1.	Vinylidene chloride		1,1,1-Trichloroethane	.86	17	.001
2.	Benzene		1,1,1-Trichloroethane	.81	16	.001
3.	Benzene		Vinylidene chloride	.69	16	.002
4.	Trichloroethylene		1,1,1-Trichloroethane	.57	17	.008
5.	Trichloroethylene		Vinylidene chloride	.49	17	.024
	Breath	vs.	Breath			
6.	Vinylidene chloride		1,1,1-Trichloroethane	.81	17	.001
7.	Benzene		Tetrachloroethylene	.44	16	.045
	Air	vs.	Breath			
8.	Vinylidene chloride		1,1,1-Trichloroethane	.88	17	.001
9.	Vinylidene chloride		Vinylidene chloride	.77	17	.001
10.	1,1,1-Trichloroethane		1,1,1-Trichloroethane	.74	17	.001
11.	Tetrachloroethylene		Tetrachloroethylene	.73	17	.001
12.	1,1,1-Trichloroethane		Vinylidene chloride	.62	17	.004
13.	Trichloroethylene		Trichloroethylene	.53	17	.013
14.	Tetrachloroethylene		Benzene	.54	16	.015
15.	Ethylene dichloride		Benzene	.54	16	.016
16.	Benzene		1,1,1-Trichloroethane	.46	16	.038

Table 37. COMPARISON OF SPEARMAN AND PEARSON CORRELATION COEFFICIENT FOR AIR AND BREATH VALUES--BOTH GROUPS

	Correlation	Correlation Coefficient r		Probability due to Chance p	
		Spearman	Pearson*	Spearman	Pearson
1.	Vinylidene chloride (air) vs. 1,1,1-Trichloroethane (breath)	.88	.82	.001	<.0005
2.	Vinylidene chloride (air) vs. 1,1,1-Trichloroethane (air)	.86	.73	.001	<.0005
3.	Vinylidene chloride (breath) vs. 1,1,1-Trichloroethane (breath)	.81	.81	.001	<.0005
4.	Benzene (air) vs. 1,1,1-Trichloroethane (air)	.81	.70	.001	.001
5.	Vinylidene chloride (air) vs. Vinylidene chloride (breath)	.77	.73	.001	<.0005
6.	1,1,1-Trichloroethane (air) vs. 1,1,1-Trichloroethane (breath)	.74	.72	.001	.001
7.	Tetrachloroethylene (air) vs. Tetrachloroethylene (breath)	.73	.82	.001	<.0005
8.	Vinylidene chloride (air) vs. Benzene (air)	.69	.72	.002	.001
9.	Vinylidene chloride (breath) vs. 1,1,1-Trichloroethane (air)	.62	.52	.004	.016
10.	Trichloroethylene (air) vs. 1,1,1-Trichloroethane (air)	.57	.50	.008	.020
11.	1,2-Dichloroethane (air) vs. Benzene (breath)	.54	.59	.016	.006
12.	Tetrachloroethylene (air) vs. Benzene (breath)	.54	.56	.015	.009
13.	Trichloroethylene (air) vs. Trichloroethylene (breath)	.53	.61	.013	.004
14.	Vinylidene chloride (air) vs. Trichloroethylene (air)	.49	NS**	.024	NS**
15.	Benzene (air) vs. 1,1,1-Trichloroethane (breath)	.46	.54	.038	.012
16.	Benzene (breath) vs. Tetrachloroethylene (breath)	.44	.42	.045	.048

* Calculated using logarithms of observed concentrations

**Not Significant (p > .05)

Table 38. BREATH/AIR RATIOS[a] FOR SELECTED VOLATILE ORGANICS FOR STUDENT VOLUNTEERS FROM TWO GEOGRAPHICAL AREAS

Participant Number	Benzene	Chloroform	Vinylidene Chloride	1,1,1-Trichloro-ethane	Trichloro-ethylene	Tetrachloro-ethylene	m-Dichloro-benzene
Lamar University							
1	0.3	0.2	0.04	0.3	0.01[c]	0.4	0.1[b]
2	0.6	0.2[b]	0.06[c]	0.03	0.2	0.6	0.4
3	0.07	0.1[b]	0.3	0.09	0.03[b]	1.4	0.1[b]
4	0.6	0.04[b]	0.08[c]	0.07[b]	0.4[b]	2.4	0.1[b]
5	0.3	0.06[b]	2.5	0.07[b]	0.1[c]	2.4	0.3[b]
6	0.4	0.08[b]	-	0.02[b]	0.2[b]	0.2[b]	0.1[b]
7	0.4	0.5	0.01[c]	0.04	0.3[b]	0.8	0.4
8	0.2	0.05[b]	0.09[b]	0.01[b]	0.02	0.2	0.8
9	0.3	0.1[b]	2.7	0.1	0.7[b]	0.2	3.3
10	0.4	0.2[b]	0.8	0.1	0.4	1.0	5.4
11	-	0.07[b]	-	0.02[b]	0.2[b]	0.1[b]	0.03[b]
UNC							
1	0.07	0.4	0.3	0.1	0.1	1.4	0.02[b]
2	0.2	0.6	0.5	0.2	0.2	1.2	7.8
3	0.4	1.4	0.6	0.2	0.1	2.1	4.7
4	0.3	0.6	1.1	0.4	0.1	7.2	3.1[b]
5	-	-	1.4	0.1	0.2	1.7	3.5
6	0.5	0.8	1.1	0.2	0.2	0.4	1.7[b]
Arithmetic Mean (± Standard Deviation)							
Lamar University	0.31 ± .18	0.15 ± .14	0.74 ± 1.1	0.08 ± .07	0.23 ± .21	0.88 ± .83	1.0 ± 1.7
UNC	0.30 ± .17	0.72 ± .38	0.83 ± .42	0.23 ± .11	0.17 ± .06	2.4 ± 2.5	3.5 ± 2.6
Combined	0.31 ± .17	0.33 ± .35	0.78 ± .86	0.13 ± .11	0.21 ± .17	1.4 ± 1.7	1.9 ± 2.4

[a]Calculated using T - 1/2 (LOD + QL); ND - 1/2 LOD.

[b]Breath value - trace or below quantifiable limit.

[c]Breath value below limit of detection.

For three other compounds, however, (1,1,1-trichloroethane, tetrachloroethylene, and dichlorobenzene isomer) the UNC mean breath-air ratios are several times greater than those of Lamar. Moreover, for two of these compounds (tetrachloroethylene and dichlorobenzene isomer) the UNC breath-air ratio is greater than 1. This anomaly is most likely a result of the high variance and small number of subjects (N=6) at UNC.

Comparison of Lamar University Participants with University of North Carolina Participants--Air and Breath

Differences between the Lamar and UNC geometric means for each of the 15 compounds in both air and breath were examined for significance by performing a t-test on the natural logs of the data. No significant differences were found between the two study groups for any of the compounds in air. However, among breath samples chloroform was higher in the UNC group ($t = 6.34$, degrees of freedom (df) = 14, $p<.00001$). This considerable difference between UNC and Lamar breath levels is readily explainable as the result of the higher chloroform levels in UNC drinking water. Other compounds with higher mean values in the UNC group were vinylidene chloride ($t=3.01$, $df=11.4$, $p<.05$) and 1,1,1-trichloroethane ($t = 2.71$, $df = 13.4$, $p <.05$). Caution must be exercised in evaluating these results because of the small sample sizes and the high variability and skewed nature of these sample distributions. For example, the mean value of the Lamar 1,1,1-trichloroethane breath concentrations is actually larger than the corresponding UNC mean (Lamar = 24.4 mg/m^3, UNC = 19.5), due to the occurrence of two extremely large concentrations in the Lamar group.

Table 39. SUMMARY STATISTICS FOR ESTIMATED LEVELS OF SELECTED VAPOR PHASE ORGANICS IN TAP WATER--LAMAR UNIVERSITY STUDENT STUDY

	% Detected	% at Trace	Mean[a]	Standard Deviation	Median	Range
Chloroform	100	0	172.38	126.56	130.00	117.00-550.00
1,2-Dichloroethane	0	0	0.30	0	0.30	0.30-0.30
1,1,1-Trichloroethane	0	0	0.10	0	0.10	0.10-0.10
Bromodichloromethane and/or Carbon Tetrachloride	100	0	21.21	8.38	20.33	13.33-44.00
Trichloroethylene and/or 1,1,2-Trichloroethane	-	-	-	-	-	-
Tetrachloroethylene	9	9	0.95	1.33	0.55	0.55-4.95
Chlorobenzene	0	0	0.30	0	0.30	0.30-0.30

[a]All compounds are measured in ng/mL.

Table 40. SUMMARY STATISTICS FOR ESTIMATED LEVELS OF SELECTED ORGANICS IN TAP WATER--CHAPEL HILL

	% Detected	% at Trace	Mean[a,b]	Standard Deviation	Median	Range
Chloroform	100	0	220	23	220	180-260
1,2-Dichloroethane	0	0	-	-	-	ND
1,1,1-Trichloroethane	0	0	-	-	-	ND
Bromodichloromethane	100	0	17	2	17	15-20
Trichloroethylene	23	0	0.6	1	ND	ND-3.0
Tetrachloroethylene	100	0	2.0	0.8	1.8	1.3-3.8
Chlorobenzene	23	0	0.4	0.6	ND	ND-1.5

[a]All compounds are measured in ng/ml.

[b]Mean of all values (ND = 2.00).

Summary Statistics -- Drinking Water

Summary statistics for the Lamar and UNC drinking water data are given in Tables 39 and 40. For each participant with more than one water sample, mean values were calculated for each compound and replace the raw values. Each statistic is computed using the actual or estimated values for all participants except where data are missing. The "percent detected" column indicates the percentage of measurements greater than the limit of detection (including trace amount). The medium and the arithmetic mean are provided as measures of central tendency. In general, the sample distributions for water show much less variability and skewness than for air and breath.

Spearman coefficients were computed for the air-water and water-breath concentrations of the target compounds; no significant correlations were observed.

Estimated Total Daily Intake. Only two of the compounds measured in tap water samples contributed significantly to the total daily intake from air and drinking water of the volunteers (Table 41). Assuming daily intakes of 10 cubic meters of air and one liter of water, drinking water accounted for 79 percent of the chloroform intake and 76 percent of the bromodichloromethane intake. By contrast, drinking water contributed only 7 percent of the daily intake of tetrachloroethylene for the UNC students, and even less for the Lamar students.

The estimated daily intake of all volatile organic compounds from air and drinking water is listed in Table 42 for each subject. The air values range from 0.3-12.4 mg/day, with a geometric mean of about 1.6

Table 41. ESTIMATED DAILY INTAKE* OF SELECTED COMPOUNDS FROM WATER COMPARED TO AIR (ug/day)

	Chloroform			Bromodichloromethane			Tetrachloroethylene		
Subject	Air	Water	Percent Intake from Air	Air	Water	Percent Intake from Air	Air	Water	Percent Intake from Air
1	13.9	185	7	16.3	17	49	1,750	ND***	100
2	15.2	130	10	15.2	23	40	1,620	ND	100
3	28.3	550	5	ND**	44	<3	72.1	T	95
4	83.3	130	39	32.1	22	59	54.1	ND	>98
5	52.2	130	29	10.0	24	29	56.5	ND	>98
6	40.4	117	26	ND	20	<6	49.8	0.07	100
7	48.4	133	27	11.4	22	34	301	ND	100
8	60.2	143	29	37.1	19	66	7,180	0.03	100
9	31.7	133	19	8.4	17	33	>45.4	ND	>98
10	18.6	125	13	ND	13	<9	1,720	0.01	100
11	48.2	120	29	ND	13	<9	92.6	0.03	100
12	78.1	255	23	ND	20	<6	24.8	3.8	86
13	50.9	235	18	ND	18	<7	26.5	1.8	94
14	37.4	215	15	ND	18	<7	20.6	1.8	92
15	31.9	210	13	ND	17	<7	12.2	1.8	87
16	175	210	45	43.6	16	73	43.2	1.8	96
17	22.5	190	11	ND	15	<8	1,270	1.3	100

* Assuming 10 m^3/day respiration rate and 1 l/day ingestion rate

** ND = < 1.2 ug/10m^3

***ND = < 1.1 ug/l

Table 42. ESTIMATED DAILY INTAKE* OF 10 VOLATILE ORGANIC COMPOUNDS THROUGH AIR AND WATER FOR 17 SUBJECTS

Subject	Air ug/day	Water	Total	Percent from Air
30001	12,400	200	12,600	98
30002	2,700	150	2,850	95
30003	12,000	600	12,600	95
30004	400	150	550	73
30005	300	150	450	67
30011	550	140	690	80
30012	1,250	160	1,410	89
30013	9,000	160	9,160	98
30014	300	150	450	67
30015	2,600	140	2,740	95
30016	1,140**	130	1,270	90
40001	2,470	280	2,750	90
40002	2,390	260	2,650	90
40003	1,250	240	1,490	84
40011	300	240	540	56
40012	1,240	230	1,470	84
40013	3,800	210	4,010	95

*Assuming 10 m^3/day and 1 liter/day intake rates for air and water.

**Omitting one outlier.

mg/day and a geometric standard deviation of about 3.5. The corresponding geometric mean for the water intake is 0.2 mg/day. Thus air is the major contributor to total daily intake of the volatile organics measured.

Summary.

This report documents the first field effort of a continuing exposure monitoring program at the United States Environmental Protection Agency. Sampling equipment and analytical protocols were tested on 17 subjects at two universities. The sampling equipment (personal monitors and a specially designed spirometer) and the analytical protocols worked well for the air, breath, and tap water samples. However, difficulties were encountered with the purge and trap analytical protocol for blood and urine. These difficulties are being investigated further.

The results for air, breath, and tap water indicate that the concept of making direct measurement of individual human exposure to a significant number of volatile organic compounds is feasible. This first effort has resulted in a number of findings, including particularly the wide range of exposures among a homogenous group of subjects, and the apparent direct relationship between the logarithms of the amounts of certain compounds inhaled and exhaled. These findings could not have been made using standard approaches of ambient monitoring.

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11. Recovery efficiencies are tabulated in Pellizzari (note 7 above).

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APPENDIX

DATA COLLECTION INSTRUMENTS USED AT LAMAR UNIVERSITY

LAMAR UNIVERSITY

BLOOD TEST QUESTIONNAIRE

DATE: _____

NAME _____

NUMBER OF YEARS YOU HAVE LIVED IN THE BEAUMONT AREA _____

AGE _____ DATE OF BIRTH _____

RACE _____ SEX _____

DO YOU LIVE ON THE UNIVERSITY CAMPUS? _____

IF YES, HOW LONG? _____

IF YOU DO NOT LIVE ON THE UNIVERSITY CAMPUS, GIVE YOUR HOME ADDRESS

_____

DO YOU CONSIDER YOURSELF ATHLETIC? _____

IF YES, WHAT SPORT ACTIVITY? _____

HOW FREQUENTLY DO YOU WORKOUT? _____

DO YOU WORK WITH CHEMICALS? _____

AROUND AIRCRAFTS? _____

AROUND DRY CLEANERS? _____

AROUND DEGREASING SOLVENTS (AS IN AUTO SHOP)? _____

DO YOU DRINK DECAFFEINATED COFFEE REGULARLY? _____

Date of Form: 2/21/80

UNIVERSITY OF MIAMI
MIAMI, FLORIDA 33177

DEPARTMENT OF EPIDEMIOLOGY
AND PUBLIC HEALTH
SCHOOL OF MEDICINE

DIVISION OF CHEMICAL EPIDEMIOLOGY
15655 S.W. 127th AVENUE
MIAMI, FLORIDA 33177
(305) 255-3300

INFORMED CONSENT - DRINKING WATER STUDY

All water contains a number of chemicals. Most chemicals appear by nature depending on the geographical location of the water source. Others are introduced as a result of various water purification and treatment methods.

The University of Miami School of Medicine's Department of Epidemiology and Public Health is conducting a study to determine if the chemicals which are present in Dade County's water are also present in the blood of the residents of the county who drink that water.

You can help in this research study by allowing us to draw a small amount of blood (20 cc., the amount usually collected for other blood tests) which will be analyzed for its chemical content.

There is no adverse effect on the body and the only discomfort which you might feel is the needle prick. Occassionally a small bruise mark may be noted which will disappear in a short time. The blood will be drawn by qualified personnel using sterile equipment.

We will be glad to answer any questions you may have regarding this research project.

To participate, please sign the form below:

I, _____(Name)

_____

_____(Address)

agree to participate in the University of Miami Drinking Water Research Project and authorize _____to withdraw approximately 20 cc. of blood for chemical analysis.

_____ _____
(Witness) (Date)

Date of Form - 7/20/79

RECEIPT

I have received a payment of $10.00 (cash) for participating in the University of Miami's Drinking Water Research Project (EPA Grant No. R806833-01).

_____ NAME

_____ ADDRESS

_____ SOCIAL SEC. NO.

_____ DATE _____ PAYEE

A private, independent, international university
An equal opportunity/affirmative action employer

DRINKING WATER QUESTIONNAIRE

I.D.# Card #

Interview Date [ ][ ] Mo. 12-13 [ ][ ] Day 14-15 [ ][ ] Year 16-17 Class [ ] 1 [ ][ ][ ][ ] 2 3 4 5 [0][1] 6 7

Control I.D.#

Interviewer_____ [ ][ ][ ][ ] 8 9 10 11

[ ] 18 Information obtained from 1. personal
2. relative or friend only
3. records only
4. both other person, records

[ ] 19 Name_____19. Sex 1. M._____2.F_____

[ ][ ] 20-21 Age:

[ ] 22 Marital Status 1.S_____2.M_____3.W_____4.D_____5.Sep._____

[ ][ ] 23 24 Total Number in Household: _____ Age:_____ Age:_____ Age:_____ Age:_____ Age:_____ Age:_____

[ ] 25 Race: 1.White:____2. Black:____3. Hispanic:____4.Oriental:____
5.Other:_____ (Specify)_____

[ ] 26 Education:
1. 0-6:____2. 7-9:____3. 10-12:____4. College: 1-2:____
5. 3-4:____ 6. Graduate School:____years 9. Unknown____

Estimate Family Income:

[ ] 27 Number of contributors:____

[ ] 28 1.Under $5,000:_____ 2.$5,000 - $9,999:____3. $10,000 - $14,999____
4.$15,000 - $19,999:____ 5. $20,000 or above:____ 9. Unknown____

Addresses: (Present and last 5 years)

Location	City, State	From Mo.	From Yr.	To Mo.	To Yr.
1.					
2.					
3.					
4.					
5.					

[ ] 29 Residence in Water area: 1. Less than 5 years____
2. 5 or more years_____

Code for 30-34:
(1) None, (2) Less than half, (3) Half or more, (4) All, (9) Unknown

Source of water supply used in drinking and cooking:

[ ] 30 Municipal Supply:____ Name:_____
Address:_____

[ ] 31 Well Water:____ Address:_____

[ ] 32 Bottle Water:____ Name (supplier):_____
Address:_____

[ ] 33 Other (specify):____ Address:_____
_____

[ ] 34 Do you use any method of water treatment?
Type: 1. Water softener:____2. Filters:____3. Other:____
4. None____
Comments:_____

Any comments on tapwater: (clarity, taste, odor, color, sediment, pressure)
_____

[ ] 35 Do you have a pool?
(1) yes, swim regularly (2) yes, don't use pool much (3) no, but use other pools regularly (4) no, but occasional pool use, (5) no pool, rarely use others (9) no information

[ ] 36 Do you use a pest-control service on a regular basis?
(1) never, (2) in yard only, (3) in house only, (4) in both yard and house, (9) unknown
Name and address of service:_____

Eating Habits:

How many meals do you eat each day? At home [ ] 37. Elsewhere [ ] 38

Fluid Intake: (Approximate daily amounts in ounces)

Type of Fluid	Amount (oz)	Amount (oz) in Last 24 Hours	Comments
1. Tap Water			
2. Coffee			
3. Tea			
4. Soft Drinks			
5. Milk (Cocoa)			
6. Soups, broths, etc.			
7. Juices (Fruit, vegetable)			
8. Bottled or Boiled Water			
9. Beer			
10. Wine			
11. Spirits			
Approximate total Daily Fluid Intake	[ ][ ][ ] 39 40 41	[ ][ ][ ] 42 43 44	

Do you drink decaffeinated coffee regularly? 1=yes, 2=no [ ] 45

Smoking Habits:

Have you used:

Code:

1 = use now
2 = formerly, not now
3 = never

		How long (years)	If not now, when (last year)
Cigarettes:	[ ] 48	[ ][ ] 49 50	[ ][ ] 51 52
Cigars:	[ ] 53	[ ][ ] 54 55	[ ][ ] 56 57
Pipe:	[ ] 58	[ ][ ] 59 60	[ ][ ] 61 62
Chewing Tobacco:	[ ] 63	[ ][ ] 64 65	[ ][ ] 66 67
Snuff:	[ ] 68	[ ][ ] 69 70	[ ][ ] 71 72

Cigarette Frequency: [ ] 73

(1) Never, (2) Less than 1/2 pack/day (3) More than 1/2 pack per day, no more than 1 pack (4) Between 1 and 2 packs, (5) More than 2 packs (6) Smoker, no information on frequency (9) no information

Occupational History:

Employer Address	Position Type of Work	From Mo. Yr.	To Mo. Yr.
SELF:			
Present:			
1.			
Past Occupations:			
2.			
3.			
4.			
5.			
SPOUSE:			
Present:			
1.			
Past Occupations:			
2.			
3.			
4.			
5.			

Chemical exposure: (occupation)

[ ] 74 (1) self presently occupationally exposed (2) previously (3) never (9) unknown

[ ] 75 (1) spouse or other family member presently occupationally exposed (2) previously, (3) never (9) unknown

DRINKING WATER QUESTIONNAIRE

ID# [ ] 1 [ ][ ][ ][ ] 2 3 4 5 Card # [0][2] 6 7

Exposure to Chemicals:

Ever been exposed to:
1 = yes
2 = no
3 = doesn't know

Type Code:
1 = acute
2 = chronic
3 = sporadic

Time Code:
1 = within last 24 hours
2 = within last 72 hours

[ ] 8	chloroform	[ ] 9	[ ] 10
[ ] 11	carbontetrachloride	[ ] 12	[ ] 13
[ ] 14	trichloroethylene	[ ] 15	[ ] 16
[ ] 17	tetrachloroethylene	[ ] 18	[ ] 19
[ ] 20	dry-cleaning solvents	[ ] 21	[ ] 22
[ ] 23	other volatile halocarbons _____	[ ] 24	[ ] 25
[ ] 26	halothane	[ ] 27	[ ] 28
[ ] 29	other anesthetic _____	[ ] 30	[ ] 31
[ ] 32	ethylene dichloride	[ ] 33	[ ] 34
[ ] 35	pesticides and sprays	[ ] 36	[ ] 37
[ ] 38	paint thinners _____	[ ] 39	[ ] 40
[ ] 41	degreasers _____	[ ] 42	[ ] 43

Exposure to Chemicals:

Ever been exposed to: 1 = yes 2 = no 3 = doesn't know		Type Code: 1 = acute 2 = chronic 3 = sporadic	Time Code: 1 = within last 24 hours 2 = within last 72 hours
☐ 44	gasoline, naphtha	☐ 45	☐ 46
☐ 47	chlorox, purex bleach	☐ 48	☐ 49
☐ 50	other chlorine-containing bleaches	☐ 51	☐ 52
☐ 53	chlorine pool chemicals, HCl	☐ 54	☐ 55
☐ 56	cyanuric acid (Duochlorin)	☐ 57	☐ 58
☐ 59	fingernail polish	☐ 60	☐ 61
☐ 62	fingernail polish remover	☐ 63	☐ 64
☐ 65	hair spray	☐ 66	☐ 67
☐ 68	other aerosols	☐ 69	☐ 70
☐ 71	liquid paper	☐ 72	☐ 73
☐ 74	cough syrup	☐ 75	☐ 76
☐ 77	toothpaste	☐ 78	☐ 79
☐ 80	other	☐ 81	☐ 82

[ ] 1 ID # [ ][ ][ ][ ] 2 3 4 5 Card# [0][3] 6 7

Health History:

(put circled number in box)

[ ] 8 Present Health Status: 1. excellent - no health problems 2. Generally good - no complaints 3. generally good - acute problem (surgery) 4. poor health 5. autopsy

Height: [ ][ ] 9 10 in. Present weight: [ ][ ][ ] 11 12 13 lbs.

[ ][ ][ ] 14 15 16 Recent (last 6 months) weight change:

Gain (amount)_____ Loss (amount)_____

[ ] 17 Reason: (1) illness (2) planned (exercise, special diet) (3) unplanned

[ ] 18 Are you presently taking any medications? yes(1)_____No(2)_____

If yes, please complete:

	Kind (Name, if known)	Prescribed	Condition	Amount per day, week, etc.
1.				
2.				
3.				
4.				
5.				
6.				

Past Health History: (please put number in box)

[ ] 19 19. When did you see a physician last? (1) less than a week ago (2) 1-4 weeks (3) 1-5 months (4) 6-17 months (5) at least 18 months (9) unknown

[ ] 20 20. Reason: (1) acute problem, current (2) acute problem, past (3) chronic problem (4) physical exam, immunizations, etc. (9) unknown

[ ] 21 21. Have you been hospitalized? (1) Yes_____(2) No_____ (9) unknown

If Yes, reason: _____ when (year) _____

Have you ever required a doctor's care for the following?

Condition	Code: (1) yes (2) no (9) Unknown	When (yr.)	Duration of Illness (days)
22. Eyes	☐	_____	_____
23. Ears, Nose, Throat	☐	_____	_____
24. Upper Respiratory	☐	_____	_____
25. Gastro-intestinal	☐	_____	_____
26. Hypertension	☐	_____	_____
27. Circulatory Problem	☐	_____	_____
28. Heart Condition	☐	_____	_____
29. Stroke	☐	_____	_____
30. Endocrine (Diabetes, etc).	☐	_____	_____
31. Muscular-skeletal problem	☐	_____	_____
32. Genito-urinary	☐	_____	_____
33. (Females) Obstetrical	☐	_____	_____
34 Gynecological	☐	_____	_____
35. Neurological	☐	_____	_____
36. Nervousness; Emotional	☐	_____	_____
37. Tumors, Growths	☐	_____	_____
38. Allergies	☐	_____	_____
39. Skin problems (dermatitis)	☐	_____	_____
40. Dental problems	☐	_____	_____
41. Liver (hepatic) problems	☐	_____	_____

Comments: _____

Serum Chloroform Level ☐☐☐☐
42 43 4445

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