A PRELIMINARY ASSESSMENT OF HALOGENATED ORGANIC COMPOUNDS IN MAN AND ENVIRONMENTAL MEDIA - PART I

by

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CONTENTS

FIGURES

TABLES

TABLES CONT'D.

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SECTION 1

INTRODUCTION

A general program concept was previously formulated which attempted to furnish a systematic approach that would relate man's potential exposure via environmental media and human body burden. A flow diagram depicting these relationships between environmental media, man's potential routes of exposure, and human body burden was described (1). Several prerequisite components were delineated that needed verification for such a potential relationship to exist between halocarbons (halogenated organic compounds) in the environment and human body burden. The concept was divided into two basic levels. The first level called for demonstrating human exposure to halocarbons via specific environmental media, i.e. air and drinking water (food was not included because analytical methods for the halocarbons selected for study had not been developed). The second level required establishing the presence and degree of body burden in man by making measurements for halocarbons in breath, blood, and urine. Although not a specific objective of this study, a third level which demonstrates human dosage could be envisioned. Thus, our objective was to test the hypothesis that a quantitative correlation existed between environmental media contaminated with halocarbons and the presence of these halocarbons in man.

Three basic elements were identified that needed to exist in order to test this hypothesis. These were: (1) that a source leading to contamination of the environment existed; (2) that a pathway existed by which a population might be exposed to the source(s) of pollution; and (3) that a plausible relationship occurred between environmental contamination and human activity patterns which permitted a correlation to human body burden. It was these essential ingredients that were incorporated in the model depicted in Figure 1.

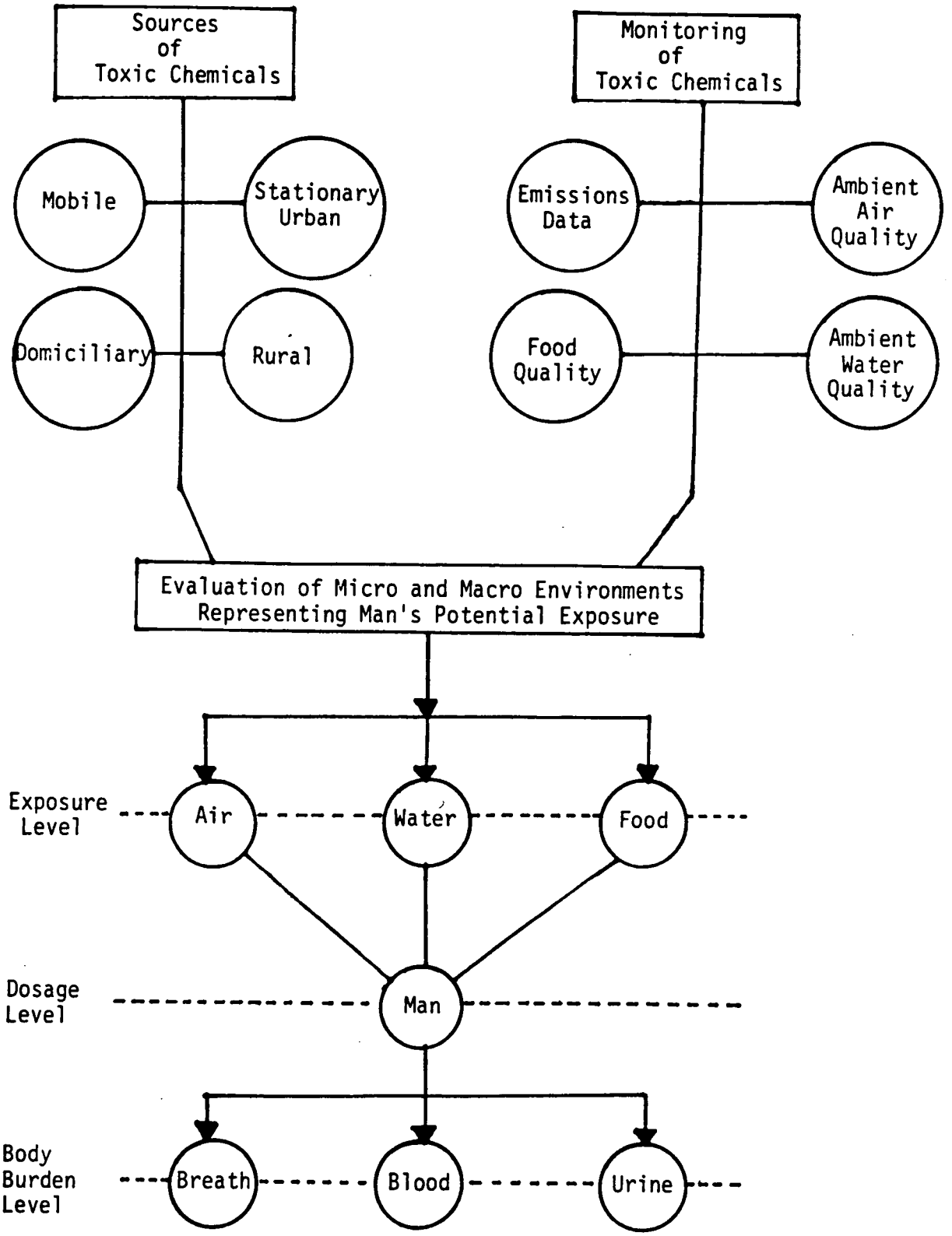

Figure 1. Relationships between macro- and micro-environmental pollution sources, exposure routes, and body burden.

The previously reported program concept also recognized a number of additional important factors necessary for successful testing of relationships between body burden and environmental exposure (1). These factors included: (1) for specific industrial processes, the existence of data which cite industrial activity (source) for a defined geographical area; (2) a means by which the pollutants are released from the sources and transported to the population as a whole (pathway); (3) stratification of the population based upon point sources; (4) the existence of a statistically significant number of exposed people in the geographical areas under study as compared to other areas and the ability to relate degrees of exposure to human activity; (5) the ability to perform measurements which document excessive levels of halocarbons in the area of interest [air and water] and the necessary time resolution to correlate these measurement processes to human activity; (6) the ability to demonstrate the presence of halocarbon substances in breath and biological fluids with the current technology; and (7) the existence of a quantitative relationship between macroenvironmental contamination [ambient environmental data on air and water] and man's microenvironment which constitutes exposure.

Initially, the various sources of exposures were examined in detail for a number of halocarbons emitted from stationary urban, domiciliary, rural, and mobile sources (1). The traditional stationary sources of pollution were deemed to be industrial activities producing, using, or storing halocarbons. Domestic sources included, for example, household and personal items that lead to individual exposure. All other nonpoint sources were considered to be mobile and rural activities that yield ubiquitous chemicals in the environment.

To adequately describe man's potential exposure to halocarbons, information on discharge sources was obtained (1). Also, to representatively analyze environmental matrices that serve as portals of entry to man, the hydrologic, meteorologic, and topographic characteristics in each geographical area under study were assessed (1). This information became the basis for a rational sampling design for collecting and analyzing environmental samples that represent both macroenvironments and microenvironments.

To assist in establishing an exposure-body burden relationship, demographic data were sought and a human sampling design was constructed which

adequately represents segments of the sampled population. To relate exposure levels to body burden, a tight experimental design was sought. The micro-environment surrounding each individual was monitored and the biological samples were acquired in a manner which attempted to link potential exposure and human activity. Thus, the program design called for the collection and analysis of samples of each individual's ambient breathing air and drinking water. Finally, biological samples (e.g., breath, blood) were obtained in a manner such that the measurement of halocarbons could be tied to a previous period of potential environmental (e.g., air, drinking water) exposure.

To assist in examining the relevance of fixed-site air monitoring (macroenvironment) to personal air monitoring of individual participants (microenvironment), both types of samples were collected and analyzed in each geographical area. The main objective was to establish whether a statistical correlation existed between halocarbon levels in environmental and human samples. This report discusses the results obtained in fulfillment of these objectives and the testing of the exposure-body burden concept.

SECTION 2

SUMMARY

A study was conducted to evaluate the exposure to selected halogenated compounds and subsequent body-burden in the general human population in Greensboro, NC, Baton Rouge/Geismar, LA, and Southeast Harris County, TX. A major component of this project was a statistical survey among populations potentially exposed to halocarbons from manufacturing, industrial users, or industrial storage facilities. Correlations between chemicals in the environment and in humans and the variation in exposure levels of halocarbons in air, water, breath, and blood were studied.

A statistical sample of the population was selected and individuals were recruited in each of the three study areas. The subjects collectively represented varying distances from both suspected and unsuspected potential emission sources. Subject selection was by stratified area sampling of a uniquely defined study population in each area which was geographically partitioned into high, medium, and low potentially exposed sites on the basis of possible emission sources and wind patterns. Because the purposive selection of the major areas precluded the valid extension of results to a State or national level, the usefulness of the results was enhanced by an unambiguous target population defined at each location. A probability sample was selected within each of those populations such that every "eligible" individual belonging to each population had a known nonzero chance of being selected for participation in the study (study eligibility was limited to persons 45-64 years of age with no occupational exposure during the prior year and who had resided in the study areas for at least 1 year).

Several criteria were used to define the study populations and for stratification. A site was required to have potentially major concentrations of the compounds being investigated and sufficient human population living within 1 or 2 kilometers of the potential point sources. Other considerations

were the prevailing wind patterns and the presence of nonstudy compounds that would prohibit isolation of effects of halogenated compounds. In the stratification step, atmospheric dispersion modeling and other mapping techniques such as aerial imagery were used to delineate the exposure area boundaries.

A two-stage stratified sampling design was employed that weighted statistical analysis to allow valid inferences to be made of the target population. Sample weights were computed for each stratum in each city and were assigned to all sample individuals. The first stage of the two-stage stratified design was intended to delineate the exact locations of all known potentially major point sources of halogenated hydrocarbons under study. These locations were mapped onto scaled maps of the purposively selected sites. Prevailing wind direction information (wind roses) for each region under study was used to define the exposure emission strata in the industrial areas. In each stratum, primary sampling units (PSU's) were created to completely cover without overlap the land area represented by the strata.

After the first-stage stratification specifications were determined, the PSU's for each site were stratified according to their distance from potential point sources and based on wind pattern information. As part of the second stage of the two-stage sampling, each PSU was screened for age eligibles. Noncompact clusters were employed in those PSU's that were too large for all households to be economically screened. This two-stage stratified design was used in Louisiana where both the zones and the PSU's with end zones were constructed on a block record level. For Geismar, the zones were constructed using enumeration district data and rough counts obtained by the cruise count. Baton Rouge was stratified into a high stratum that contained seven PSU's and another stratum that had five PSU's. The second- stage sampling was selected by the negative hypergeometric method. Geismar was defined as an all-high area.

The Greensboro site was divided into three strata defined as high, medium, and low income to provide geographic dispersion of the sample. Each stratum was listed and divided into five zones.

In Harris County, TX, 18 segments of PSU's were divided equally among three strata representing varying levels of presumed potential exposure. Sampling methodology for the Texas site differed slightly from that for

Greensboro and Baton Rouge sites. Like those sites, stratification in the areas of presumed high exposure level was achieved by direct stratification based on site variables and by implicit stratification based on wind velocity variables.

Weights for each site were computed according to prescribed formulas. At the second stage the selection probability for any eligible person was equal within a PSU. The second-stage weight component was then the inverse of the number of sample participants divided by the number of eligible persons in the PSU. The final-stage unadjusted weights were created by multiplying the first- and second-stage weight components for each subject. Adjustment for nonresponse at the individual or final-stage unit level was not required when all screened eligibles within the PSU were approached to obtain the desired sample size. This was the case in most of the PSU's in all three sites studied.

The initial step in the field survey activities was the creation of an accurate listing of housing units in each sample segment. Sample segments were selected and maps and preliminary sketches were provided to the field survey team that went to each segment to determine exact boundaries. Following specific procedures used by the all-field staff, a count and listing of all potential sampling housing units were made. After the evaluation of all segments in the area were completed, the results were then examined by a sampling statistician who determined sampling rates and start numbers for the household screening process.

After each segment was listed, a sampling rate was determined based on the number of listed units and a start number. Based on this information, a sample of listed units was created for screening, and household rosters were created for those who were eligible to participate in this halocarbon study. A screening questionnaire was completed for each housing unit in the sample. Any resident of the household who was at least 16 years of age and who was physically and mentally capable of responding provided the information for the form. After all segments were screened and the materials examined by sampling statisticians, the sample of the eligible respondents was selected to be contacted and asked to participate in this halocarbon study. In each area, a sample was selected and fielded. Each interviewer contacted a specific person, explained fully the study, and requested that the respondent participate; if

the respondent agreed, the interviewer administered the study questionnaire and established a sampling appointment. If a respondent agreed to participate, the interviewer obtained a signed consent form, completed the household screener, and established appointments for sampling the environmental and biological media.

The listed selected volatile halocarbons was sought in each of the three study site areas. Samples of air, drinking water, blood, and breath were collected from each of the study respondents as follows. Sampling began with a visit to the household in the evening between 7:30 and 9:30 o'clock. At this time, fixed-site and personal air monitors were initiated for the first of two sampling periods (10-12 h), and containers for collecting drinking water samples were provided to the study participants. During a second visit on the following morning between 7:00 and 8:30, the air collection devices that were exposed during the first sampling period were picked up, and the second air sampling period was initiated. The final visit was made in the afternoon of the same day between 4:30 and 6:30 at which time breath and blood samples were obtained from the study participants, and all of the drinking water samples that were acquired by the study participants were also picked up.

A quality control and assurance program was maintained for the sampling and analysis procedures employed. For Tenax GC® sampling cartridges (for ambient air and breath collections) and water samples, laboratory and field cartridge blanks were maintained. Laboratory and field controls were also incorporated into the analytical scheme for each batch of sampling devices. Controls for each of the sampling devices consisted of devices spiked with target halocarbons. Replicate samples of air, drinking water, and blood were collected at a frequency to represent a minimum of 10 percent of the total number of samples. Internal audit procedures were employed to assure that the operations of the collection and analysis systems functioned properly. A chain-of-custody procedure was maintained for each sample, blank cannister or cartridge, and control throughout the period of sampling and analysis of the environmental and biological media.

In summarizing the data from the halocarbon study, several statistical techniques were employed. The first statistic computed was the percent of the

compound detected by media, area, and stratum within the area. When computing this statistic, the percent exceeding the maximum quantifiable limit (MQL) was calculated. After examining the percent detected statistic, it was possible to eliminate a number of the compounds under study for further analysis since they were not detected or were almost never detected. This reduced the number of halocarbons to approximately 13 for calculating summary statistics by media and geographical area. The median and mean were both computed since the distribution of the compound levels was generally highly skewed and the sample mean tended to be highly sensitive to a few large values. In computing both the percent detected and the summary statistics, weighted population estimates were employed.

Relationships between media and selected halocarbons were then examined by first computing correlations between media. This indicated which media and compounds appeared to have some relationship with each other. In general, Spearman rank correlations were used since the assumption of normality was certainly not met for many of the distributions under investigation.

In addition to correlations, scatter plots between media for compounds which appeared to have some relationship with each other were plotted. These plots were useful in determining if a real relationship between media was apparent or a high correlation was simply due to one or two large values.

Finally, two-by-two percent detected tables were computed to indicate the particular compound detected in one medium which was also being detected in another medium. This type of statistic was used, for example, to answer questions as to whether or not breath and personal air samples tend to agree on a detected or not-detected basis more than breath and fixed-air samples.

SECTION 3

CONCLUSIONS

The data available for chemical analysis consisted of approximately 29 respondents in Greensboro, NC; 72 respondents in east Baton Rouge/Geismar, LA; and 45 respondents in Southeast Harris County, TX. Media analyzed included breath, fixed air (A.M. and P.M.), personal air (A.M. and P.M.), blood, and water. In Greensboro, chemical analysis was done for 36 compounds; in Baton Rouge and Harris, only a subset of these 36 were analyzed (see Table 5).

Initially, weighted percent detected statistics were computed by compound, medium, and exposure stratum within the three study site areas. The data shows that in general the percent detected for many compounds was zero or very small. This was particularly true for blood where all percentage detected values were less than 27 percent. In general, the principal compounds detected by medium were the following:

PRINCIPAL COMPOUNDS DETECTED BY MEDIA BY PERCENT

	Breath	Blood	Fixed Air	Personal Air	Water
Chloroform	31-52[a]	0-11	10-100	18-100	21-100
1,2-Dichloroethane			0-86	9-86	
1,1,1-Trichloroethane	34-55		44-100	11-100	0-9
Carbon tetrachloride			9-94	33-100	10-54
1,2-Dichloropropane			0-43	6-34	
Trichloroethylene			9-93	38-97	0-53
Bromodichloromethane					90
Tetrachloroethylene	51-68	0-27	27-100	58-99	0-53

(continued)

	Breath	Blood	Fixed Air	Personal Air	Water
Chlorobenzene				0-15	
Dichlorobenzene isomers	15-60	0-8	0-9	35-90	0-8
Trichlorobenzene isomers				33	

[a]Range of percent detected across the three study site areas (i.e., for chloroform in breath the percent detected was 49 percent in Greensboro, 52 percent in Baton Rouge, and 31 percent in Harris County.

Furthermore, in all three study areas, in at least one medium the following compounds were found: chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and dichlorobenzenes.

In addition: Baton Rouge/Geismar had 1,2-dichloropropane and vinylidene chloride in air samples; Greensboro had bromodichloromethane in air and water samples, and chlorobenzene and trichlorobenzene isomers in air samples; and Southeast Harris County had chlorobenzenes and dichloroethylene in air samples.

Summary statistics (e.g., mean, median, standard deviation) were then computed for 13 of the principal compounds detected in the three study areas (Tables 59-72). Examination of these summary statistics indicated that compared to the maximum quantifiable limit (MQL) the following eight compounds had elevated levels in various study sites:

COMPOUNDS WITH ELEVATED LEVEL BY MEDIA FOR THE STUDY SITES*

	Breath	Blood	Fixed Air	Personal Air	Water
Chloroform	BR[a]		H[b]	G[c],H	G,BR,H
1,2-Dichloroethane			BR,H	BR	
1,1,1-Trichloroethane	G,BR,H		G,BR,H	G,BR,H	
Carbon tetrachloride			BR,H	BR,H	H

(continued)

	Breath	Blood	Fixed Air	Personal Air	Water
Trichloroethylene			H	BR,H	
Bromodichloromethane					G
Tetrachloroethylene	G,BR,H		G,H	G,BR,H	
Dichlorobenzenes	H			G,BR,H	

*BR = Baton Rouge/Geismar, LA; G = Greensboro, NC; H = Southeast Harris County, TX.

[a]In breath samples, chloroform levels were elevated above the MQL in Baton Rouge/Geismar.

[b]In fixed-air samples, chloroform levels were elevated above the MQL in Southeast Harris County.

[c]In personal air samples chloroform levels were elevated above the MQL in Greensboro.

Compounds with relatively low levels in all media and study areas were vinylidene chloride, chloroprene, dichloroethylene, 1,2-dichloropropane and chlorobenzene.

Examination of the summary statistics also indicated that Harris County had particularly high levels of chloroform in water and air samples, relatively high levels of carbon tetrachloride in air and water samples, and relatively high levels of trichloroethylene in air samples. On the other hand, Greensboro had high levels of bromodichloromethane in water samples and Baton Rouge had elevated air levels of 1,2-dichloroethane and elevated breath levels of chloroform.

Finally, relationships between media were examined for 13 compounds. This examination involved computing correlation coefficients by compound (Tables 74 and 75); drawing several scatter plots (Figures 40-44 and Appendix C) and computing two-by-two percent detected tables (Table 76). The results of these calculations were the following:

1. Correlations
   a. Breath
      (1) In general, breath levels were not positively correlated with water levels.

(2) Breath levels did appear to be correlated with both fixed-site and personal air levels for selected compounds. In general, the correlations between personal air and breath were higher than between fixed-site air and breath.

(3) In particular, breath and personal air have relatively high correlations for 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and dichlorobenzenes.

(4) Breath and blood levels were relatively well correlated for dichlorobenzenes in Baton Rouge/Geismar.

(5) The magnitudes of the breath correlations were almost always less than 0.60.

b. Air

(1) Many of the air samples were correlated with each other, particularly personal air A.M. versus personal air P.M.

(2) Air and water sample levels were not highly correlated (an exception was chloroform air and water levels in Harris County).

(3) Fixed and personal air levels had relatively high corelations for (a) chloroform [Harris], (b) 1,2-dichloroethane [Baton Rouge], (c) carbon tetrachloride and tetrachloroethylene [all three areas], and (d) trichloroethylene and dichlorobenzenes [Greensboro].

(4) The magnitude of the air correlations was almost always less than 0.70.

2. Scatter Plots

In general, the plots that are presented show a positive trend as the levels in the two media increase, although it is clear that the trend is not always linear. Also, there is considerable scatter in the various plots. This is particularly true when there are low levels in one of the media (near the quantifiable limit). In this case, it is not uncommon to have nonmeasurable values in one medium and relatively high levels in the other medium. It often appears that there is no relationship between the media until a certain level is reached in both media. Certainly, it would be difficult to accurately predict levels of one medium from another for the compound levels found in the three geographical areas.

3. Two-by-Two Tables

The table (Table 76) was presented for breath versus personal and fixed air for five compounds. The table give the estimated percent detected in four categories (breath and air both measurable, breath measurable air not detected, breath not detected air measurable, breath and air both not detected). Results indicated that in many cases the personal air samples had better percent agreement with breath samples than did fixed air samples.

SECTION 4

RECOMMENDATIONS

When assessing the outcome of this survey design in regard to preparing for future work, one should concentrate the most effort on these aspects: improving response rates, and reducing unequal weighting effects. Suggestions for improving response rates are discussed in Section 6. Unequal weighting effects are influenced by response rate and the sizes of strata or segments. Defining all segments or strata to be more nearly equal in population size would have reduced the unequal weighting effects in this study, especially for Harris County, Texas, where the weights were most unequal.

The use of double sampling to discover eligibles worked fairly well in this study. The hypergeometric sampling procedure, which results in a probability sample when carefully executed, also worked well in Greensboro, North Carolina, and Baton Rouge/Geismar, Louisiana. It was not used in Harris County, Texas. This hypergeometric technique does require rigorous attention to detail by the field interviewers and field supervisors, so it should not be used if inexperienced interviewers must be employed.

As a result of the experience gained during the conduct of the field aspects of this study, the following recommendations should be considered:

(1) Continue to use the standard techniques described in this report for counting and listing sample segments and for screening selected housing units. Questionnaire specifications should be based on the screening variables being used.

(2) Modify the process of selecting the actual respondent to include the selection of an early sample to test for response rate, and the selection of a final "hold" sample, based on the early sample, to provide a final sample of the size required.

(3) Continue to use independent subcontractors, paid on a piecework basis, to collect invasive samples, such as blood collected by venipuncture.

(4) Investigate ways to increase response rate, including increased incentive, better prepublicity in the sample areas, and the provision of more positive study benefit to all respondents.

Additional analysis of data obtained from this study is also recommended to resolve a number of unanswered questions. These questions relate to three broad areas such as (1) statistical sampling design, (2) chemicals and media, and (3) statistical data analysis.

The following questions and issues regarding the statistical sampling design should be addressed:

(1) what sample sizes are needed for these chemicals and media in future monitoring studies?

(2) what were the design effects in this study?

(3) what was the effectiveness of the stratification variables?

(4) what should the cluster sizes be in future studies of this nature?

(5) what measures can be taken to improve participant response rates?

(6) what were the measurement errors and their effect on sample size in the bias of results.

Questions remaining on chemicals and media are:

(1) what should be the threshold of measurement (detection and quantification) of halocarbons in various environmental and biological media and which chemicals should be or not be monitored by currently available methodology?

(2) what is the relationship between personal and fixed-site sampling in representing human exposure, is one superior and should it be employed exclusively?

(3) which media best reflect human exposure and body burden for the halocarbons studied here?

Finally, there are a few questions relating to statistical analysis of data:

(1) Are there techniques for addressing data containing non-measurable values (nondetected) for a chemical in a medium and calculating

summary statistics and percent detection (with varying limits of detection)?

(2) What models can be constructed for future similar studies in other geographical areas?

(3) What are the trends or relationships, if any, between demographic data and chemical levels in different media?

SECTION 5

EXPERIMENTAL PROCEDURES

STUDY POPULATION AND SURVEY DESIGN

The purpose of this investigation was to evaluate the exposure to and body burden of selected halogenated compounds in the human populations living in areas of relatively high and low concentrations of these compounds. Higher concentrations were expected in areas immediately surrounding point sources; lower concentrations were expected in outlying residential and rural areas, and areas with no known point sources. Both site-specific and ubiquitous compounds were selected for inclusion in the study. One study objective was to investigate possible correlations between chemical levels in the environment and in members of the above mentioned populations at risk by testing for variations in exposure levels in air, water, blood, and breath.

Site Selection

The sample survey design for the Halogenated Organic Compounds Study was a three-site stratified sample, involving two sample selection stages. The three sites studied were Baton Rouge/Geismar, Louisiana; Harris County, Texas; and Greensboro, North Carolina. These geographical areas were purposively selected on the basis of several criteria. The primary criterion for selecting the first two of these areas was that they were areas where halogenated organic levels in the environment (e.g., air) were high enough to be measurable; this expectation was based on available exposure and emission information (1). This ability to measure halogenated organic compounds was essential to the study because the primary goal of the study was to examine relationships between environmental levels and body burdens. The first two sites were also required to have sufficient human population living within 1 or 2 kilometers of the potential point sources. Other considerations included prevailing wind patterns (1) and the presence of nonstudy compounds that would complicate isolation of the effects of halogenated compounds.

The third site, Greensboro, North Carolina, was selected as a comparison site because of its presumed absence of major emissions from point sources (Fig. 2). Any halogenated organics found in the Greensboro samples were assumed to be ubiquitous to the local environment. Thus it was not necessary to consider the prevailing wind patterns in Greensboro, though the presence of interfering compounds and sufficient population in the study area were considerations in the selection of Greensboro as a comparison site.

Exposure Stratification

Study areas in Louisiana and Texas were geographically partitioned on the basis of emission sources and wind patterns, forming exposure strata at each site. To compensate for meterological variability, the strata radiated in all directions from the potential emission sources. Strata immediately adjacent to point sources were designated "high exposure" areas.

In each of the exposure sites, at least one of the population segments was sufficiently large to investigate some individuals that did not reside immediately adjacent to suspected point sources. The strata not immediately adjacent to point sources were presumed to have little or no exposure and were designated as "low exposure" areas. This allows cause-effect type analysis and exposure/body burden comparisons for at least one point source in each area. However, not every point source had sufficient population density for both "high" and "low" exposure areas, so only estimates of ubiquitous levels in nearby communi- For example, the levels of exposure in Geismar, Louisiana, will need to be compared to reference individuals in Baton Rouge or with those in Greensboro, North Carolina. Observed differences based on such comparisons are of limited use and will be so qualified when released. Greensboro, North Carolina, was presumed to have uniformly low exposure, and geographic partitioning was achieved by stratification on income information. Within each stratum, subunits were established based on city blocks and other physical features. Since some of the strata were suburban and rural, detailed Census mapping was not available for the total target population. Hence, aerial photography, street maps, and mapping by RTI field staff were used to supplement Census materials.

Household interviewers were assigned specific segments to screen. Up to three visits were made to each dwelling in each sample segment to obtain information about eligibility, and the screening information was returned to RTI for

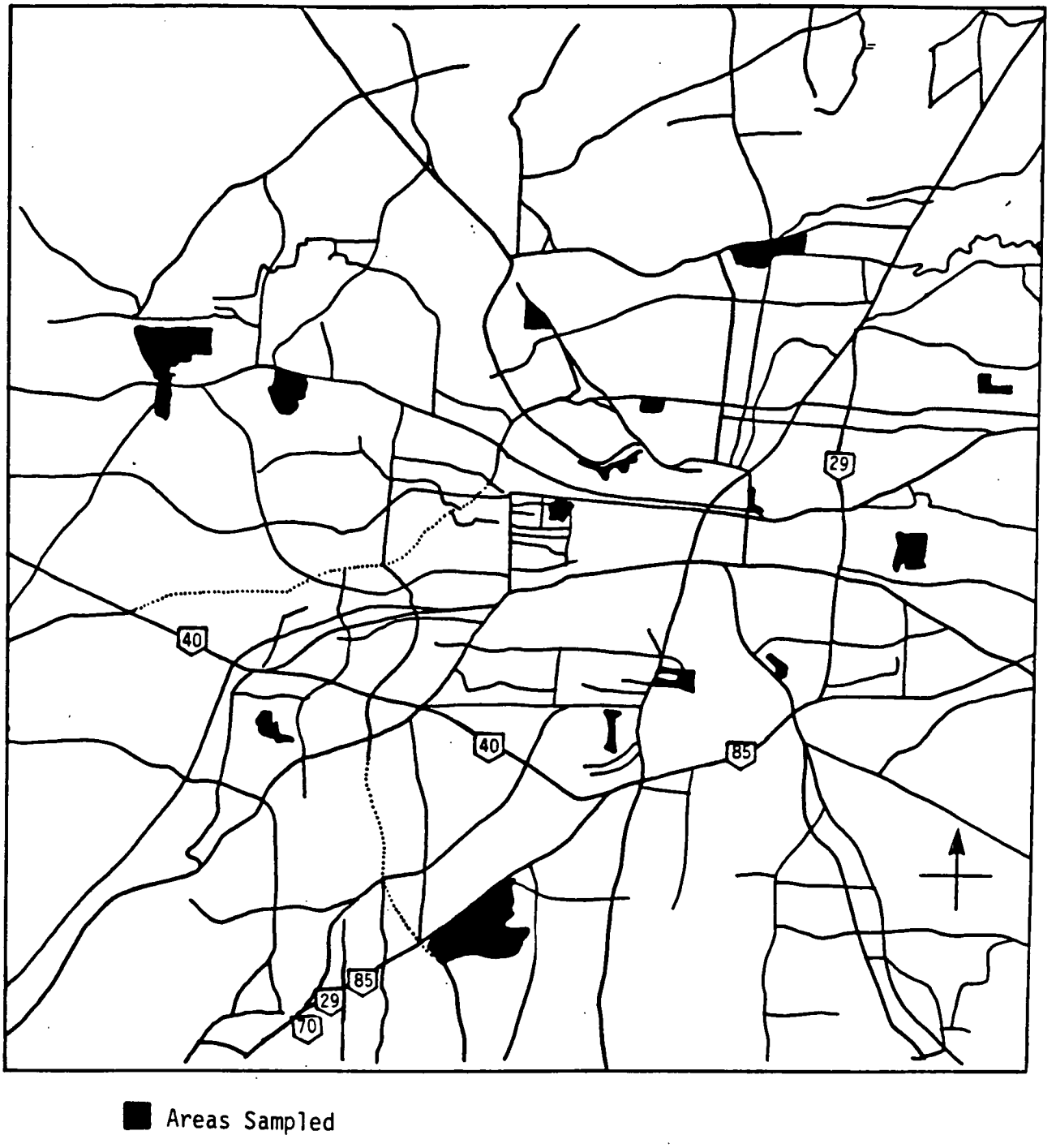

Figure 2. Sampling site and locations in the Greensboro, NC, area.

selection of the sample. Subjects were selected by probability sampling within each stratum, independent of other strata. Listings of sample individuals were then returned to the field staff for use in subsequent activities. A record of all household contacts was made; nonrespondents (including those not able to be contacted and refusals) were recorded for each interviewer and at each site. These records can be used to assess the potential of bias in the final results. To reduce the nonparticipation rate, and to reimburse the subject for time spent on the study, volunteers were offered a $10.00 incentive for participating.

A questionnaire was administered to each participant to obtain information on demographic variables, residential histories, and special potential exposure situations. For each individual, an air specimen measuring exposure near their residence was collected just prior to blood (10 mL) and breath sampling (representing absorption or body burden); tap water and soil specimens (probability point samples) were collected at each residence. All specimens were analyzed by gas chromatography/mass spectrometry/data system (GC/MS/DS).

Target Population

The purposive (nonrandom) selection of the major sites precludes the validity of generalizing results to a state or national level. To enhance the usefulness of the results within that constraint, however, an unambiguous target population was defined at each location. The target population was defined with the objective of studying a reasonably meaningful population, a portion of which resides in potentially high-exposure areas. A probability sample was selected within each of those populations, such that every "eligible" individual belonging to each population had a known nonzero chance of being selected for participation. The target populations were defined as persons 45-64 years of age with no occupational exposure during the prior year and who had resided in the study areas for at least one year.

These target populations, while well defined, are somewhat arbitrary. One might, for instance, select the sample from Harris County, from Houston City, or from all individuals residing within 1 kilometer of a specific point (suspected source). The main advantage of any of these options over purposive selection of a panel of participants is threefold: (1) the randomness of the probability sample protects against studying a totally atypical mix of individuals or a biased group, (2) the population to which the study relates can be characterized

on the basis of Census data and other extant information, and (3) the results can be presented in a meaningful context to a known reference population rather than simply presenting statistics and leaving the designation of an inference population up to the user. The target populations are defined and sample sizes are noted in Tables 1-3.

Stratification and Sampling Weights

Introduction--

The two-stage stratified sampling design that was employed in this study requires that weighted statistical analyses be performed in order to make valid inferences to the target population. Sampling weights were computed for each stratum in each city and were assigned to all sample individuals.

The criteria for stratifying and for mapping all geographic sites varied slightly from site to site, although the basic two-stage stratified design was the same. The following is an outline of the general stratification procedures, followed by a description of the specific site-by-site designs.

Basic Two-Stage Stratified Design--

First Stage--The exact locations of all known potentially major point sources of the halogenated hydrocarbons under study were mapped onto scale maps of the purposively selected sites. This information was then combined with prevailing wind direction information (wind roses) for each region for each season under study, and used to define the exposure/emission strata in the industrial areas. The general rule of thumb used in forming exposure strata was to include all areas within 1.5 km of at least one potential point source as "high exposure" areas. At each site with "high exposure" strata, areas falling outside of the "high exposure" strata but still within political boundaries were designated as "low exposure" strata. In Greensboro, the comparison site, wind patterns were not considered since no major potential point sources were known.

Once first stage stratification boundaries were determined, the desired PSU (primary sampling unit) size was calculated. Each PSU would be expected to contain at least 25 age-eligible (45-64 years of age) individuals. This count was estimated using the specific county's age distribution, and 1970 population counts (when available--these data are not available from the Census for all study areas). The choice of 25 age-eligibles per PSU was based on the following

TABLE 1. HOUSTON, TEXAS, AREA: A STRATIFIED RANDOM SAMPLE OF 45 INDIVIDUALS WAS SELECTED FROM THE STUDY POPULATION COMPRISING PASADENA, DEER PARK, AND ADJACENT COMMUNITY LOCATIONS WITHIN HOUSTON WITH A COMBINED POPULATION OF 114,000

Sample Matrix[a]

	Deer Park	S.E. Houston	Pasadena	
Sample	High-Exposure Area	High-Exposure Area	Low-Exposure Area	Total
Design	20	20	20	60
Actual	14	23	8	45

[a]The table presents the number of sample individuals according to the design and the number that actually participated in the study.

TABLE 2. BATON ROUGE, LOUISIANA, AREA: A STRATIFIED RANDOM SAMPLE OF 75 INDIVIDUALS WAS SELECTED FROM THE STUDY POPULATION COMPRISING THE CITY OF BATON ROUGE AND 1.5 km RADIUS AREAS IN THE NEARBY CITY OF GEISMAR WITH POPULATION OF 165,000

Sample Matrix[a]

	Baton Rouge		Geismar	
Sample	High-Exposure Area	High-Exposure Area	High-Exposure Area	Total
Design	30	20	25	75
Actual	30	20	25	75

[a]The table presents the number of sample individuals according to the design and the number that actually participated in the study.

TABLE 3. GREENSBORO, NORTH CAROLINA, AREA: A STRATIFIED RANDOM SAMPLE OF 29 INDIVIDUALS SELECTED FROM THE STUDY POPULATION COMPRISING GREENSBORO WITH A POPULATION OF 144,000

Sample Matrix[a]

	Greensboro			
Season	Low Income	Middle Income	High Income	Total
Design	9	10	10	29
Actual	10	10	10	30

[a]The table presents the number of sample individuals according to the design and the number that actually participated in the study.

assumptions and specifications, which were modified from site to site depending on the size of the target population and the desired sample size.

Assumptions:

1. It is desired to select an average of four and an approximately equal number of "eligibles" per PSU. To compensate for variations in the proportion of eligibles in PSUs, an expected PSU size of eight eligibles was used.
2. Given that each individual is age-eligible, assumptions were that
   - 10 percent were occupationally exposed, i.e., could come into contact with selected halocarbons;
   - 10 percent had inadequate residency (less than 1 year); and
   - 20 percent would refuse to participate.

   Therefore, 65 percent of age-eligibles would be possible study participants.
3. An average of 12.5 age-eligibles would be necessary in order to obtain the desired PSU size (8/.65 = 12.5). (Note: a double estimate of 25 was used to accommodate the possibility of a second-round study.)

PSUs consisted of combined Block level records and were created to completely cover, without overlap, the land area represented by each stratum.

PSUs were geographically ordered for selection within strata to provide geographical dispersion of the PSUs and thus control for differential wind exposure. Within each stratum, the frame PSUs were ordered in a serpentine fashion. Serpentining based on wind direction is somewhat time consuming to implement, and in some sites was replaced by merely ordering segments in a circular fashion within each stratum, if wind directions for the season of interest seemed reasonably uniform. Approximately equal-sized substrata were then formed on the ordered frames. One PSU per substratum was independently selected using probabilities proportional to the estimated number of age-eligibles.

Second-Stage--(Screening and Sample Person Selection). Each PSU was screened for age-eligibles. Clusters of non-contiguous households were selected for screening in those PSUs that were too large for all households to be economically screened. PSUs were ultimately constructed of at least 50 HUs (housing

units). All screening forms were returned to RTI, and a decision was made for each age-eligible as to that individual's study eligibility.

All eligibles were included in a randomly ordered list (second-stage frame), whether or not they had indicated willingness at screening to participate further. Person-identifiers were used that permitted interviewers to establish correspondence between first-stage unit, housing unit, and person on the household roster (screening form) in order to locate the appropriate individual. Person identifiers were listed for each sample PSU and a 4-digit random number was associated with every eligible on the list. The use of a 4-digit number was to avoid any "ties" (random number duplication). The random numbers were ranked from low to high, carrying along the person identifier. This resulted in a randomly ordered list of person identifiers. The number, m(i), of eligibles to be selected from each PSU was computed separately, based on the following definitions:

- $s(i)$ = the size of the PSU (i);
- $S(i)$ = the size of the substratum from which that PSU was selected;
- $N(i)$ = total number of housing units in the PSU (i);
- $n(i)$ = number of housing units in the PSU (i) designated for screening;
- $n(i)^*$ = number of housing units successfully screened[1];
- $M(i,j)$ = total number of eligibles identified in housing unit (j) in PSU (i) (i.e., screening result codes = 0 and 4 and 8); and
- $m(i)$ = number of sample eligibles selected from PSU (i).

The number of sample eligibles, m(i), to be selected from PSU (i) was computed:

$$m(i) = f \left[\frac{S(i)N(i)}{s(i)n(i)^*} \sum M(i,j) \right], \text{ where f is the stratum sampling rate for eligibles.}$$

[1] n(i)* is the number of households having screening results codes =
0 (eligible and willing)
3 (ineligible)
4 (eligible, but refused further participation)
5 (vacant)
6 (business office)
7 (nonexistent)
8 (other)
Excluded are codes = 1 (not at home); (2) refused screening)

The quantity m(i) was constrained such that

$2 \leq m(i) \leq M(i,j)$, where M(i,j) is the total number of eligibles identified in housing unit (j) in PSU (i).

After randomly ordering the eligibles in each PSU and determining the value m(i) for each PSU, the first m(i) people were selected as the sample persons. Individuals were contacted until [m(i) + 1] eligibles willing to participate were identified. The last person identified was not interviewed; merely their willingness to cooperate was established.

The negative hypergeometric procedure differs from simple random sampling by the [m(i) + 1] additional selection. This procedure allows the estimation of the potential number of respondents in the PSU. The sequential procedure used to select sample individuals in the second-stage sample selection introduces a potential for increasing nonresponse rates and, hence, nonresponse bias. This potential made it absolutely necessary that lists of replacement persons were not made available to field interviewers until every means of converting refusals had been exhausted. It is doubtful that any substitution/replacement scheme can be made operational without some potential for increasing nonresponse rates and related bias.

Baton Rouge and Geismar, Louisiana

The two-stage stratified design that was outlined above was used in Baton Rouge, Louisiana (Fig. 3). Substrata were constructed on the Block record level, and PSUs within substrata were also Block level constructions (Fig. 4). Baton Rouge was stratified into a "high exposure" stratum that contained seven PSUs and a "low exposure" stratum that had five PSUs. The second-stage sampling was selected by the negative hypergeometric method described above.

The sampling frames for Geismar were constructed using Enumeration District data and rough counts obtained by cruising in an automobile. Geismar was all "high exposure" area and contained insufficient population to implement the negative hypergeometric sample selection at the second-stage. Simple random sampling of eligibles was used for the two study areas of interest in Geismar. Specifically, in segment 7101, only 4 individuals were eligible, and a proportional sampling of 7101 and 7102 would give 23 from 7102 and only 2 from 7101. Because 7101 was the area of primary interest due to location and prevailing wind patterns, it was not desirable to subsample or exclude it. Note that with

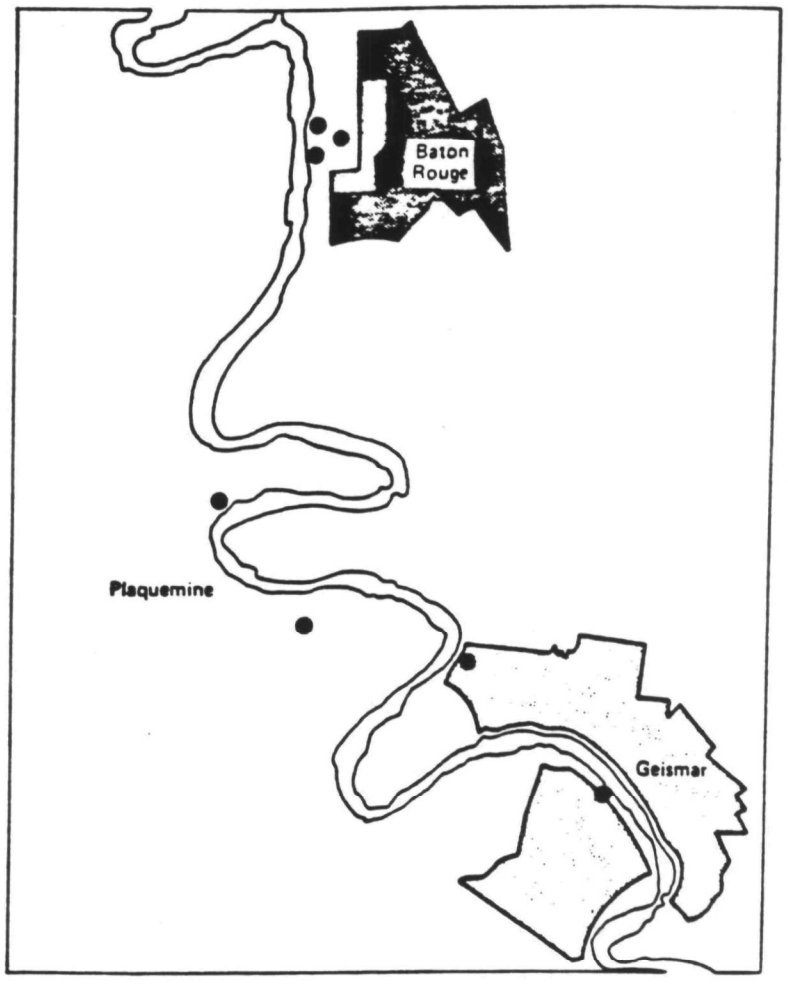

Figure 3. Stratified populations in Baton Rouge and Geismar, LA. Solid circles = potential sources, light and dark areas represent potentially high- and low-exposure areas (distance between sites not to scale).

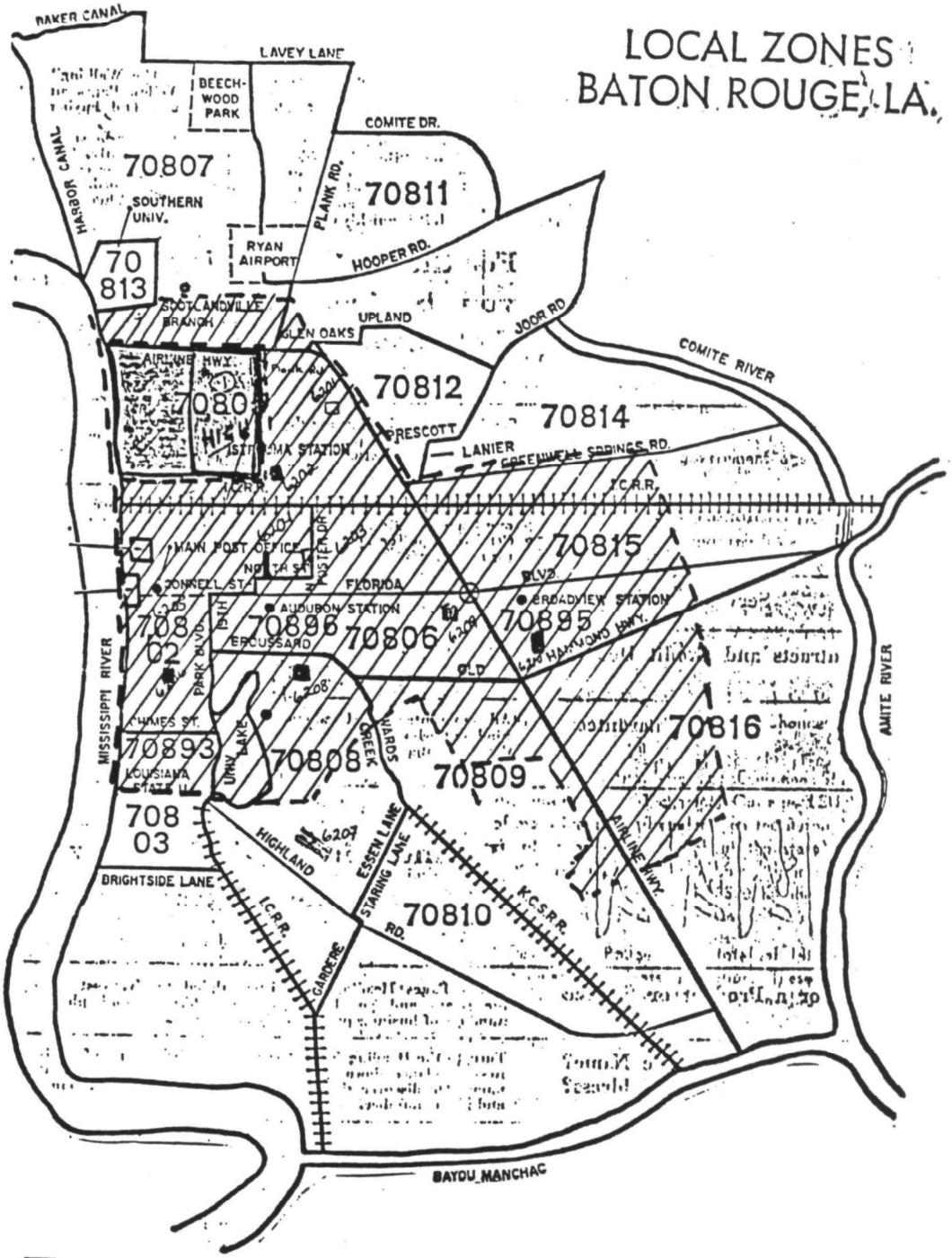

Figure 4. Sampling site and locations in east Baton Rouge.

the Mississippi River separating the two segments, it was hardly worthwhile to take only two persons from 7101. As a result, all four eligibles from 7101 were selected for the primary sample, and 21 from 7102, with all substitutions from 7102.

Greensboro, North Carolina

Greensboro, the comparison site, was divided into three strata, defined as high-, medium-, and low-income (at Census tract level). This was to gain estimation precision and to provide geographic dispersion of the sample (Fig. 2). Estimation precision can be gained by stratification on variables related to the parameters under study; income and environmental exposure are often related. Each stratum was listed and divided into five substrata. One PSU was selected per substratum with probability proportional to size. The sample allocation of 30 to the three first-stage strata was fixed and equal, resulting in 10 participants allocated to each stratum. While sample allocation within first-stage strata was calculated to provide a self-weighting sample, individual sample members will only be approximately self-weighting, as the sample allocation was forced to be two persons per PSU in Greensboro.

Harris County, Texas

In Harris County, Texas, 18 PSUs were divided equally among the strata representing varying levels (six high, six medium, and six low) of presumed exposure (Fig. 5).

Sampling methodology for the Texas sites differed slightly from that for the Greensboro and Baton Rouge sites. Like those sites, stratification in the areas of presumed high-exposure levels was achieved by stratification based on site and substratification based on wind velocity variables. List order of the sample area PSUs was used to control for differential wind exposures. In the presumed lower exposure areas, implicit substratification was based on two variables:

- distance from the nearest point source; and
- list order causing geographical dispersion to control for differential wind exposures in the sample area at the Census Tract level rather than at the Block level.

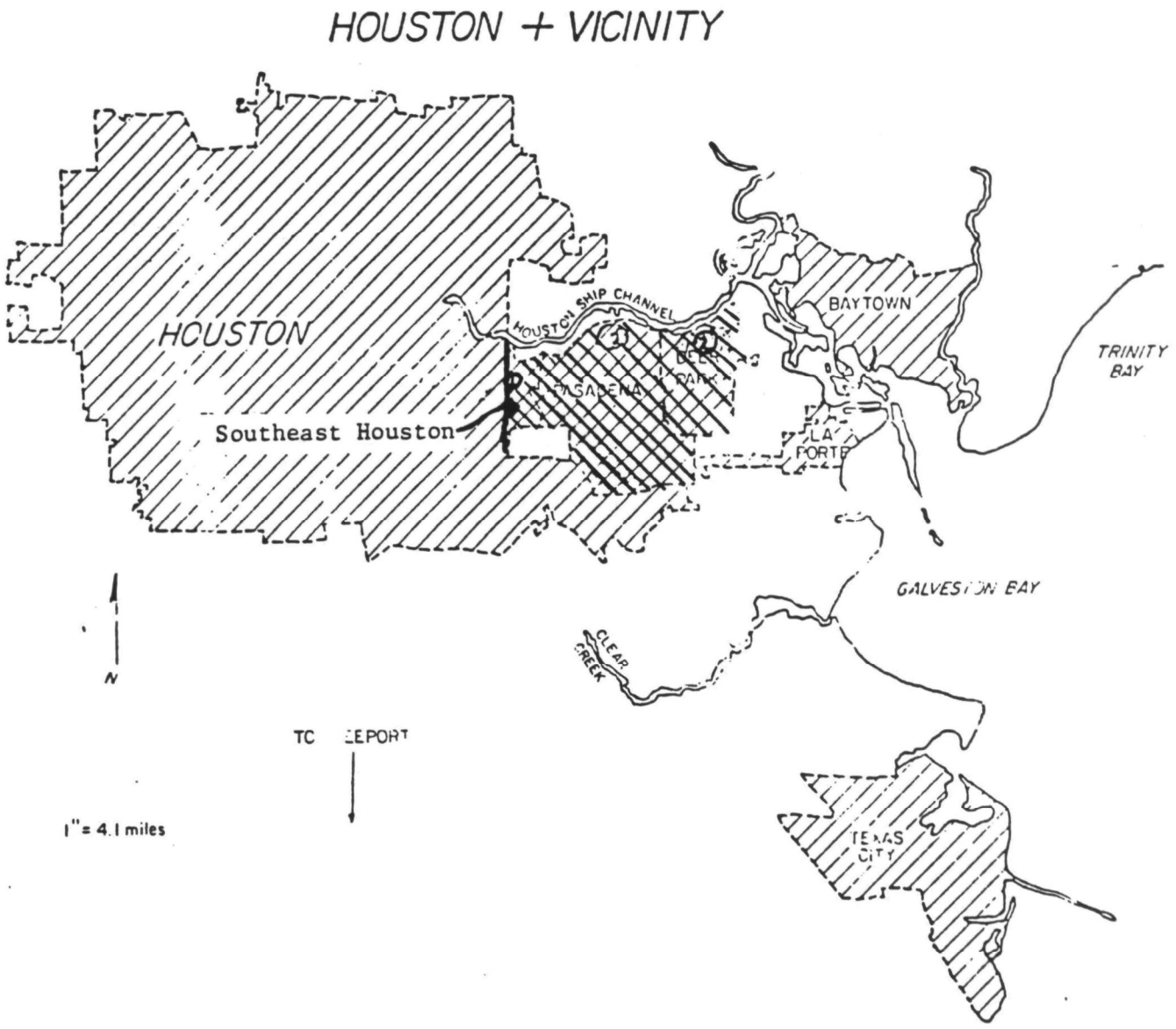

Figure 5. Sampling site and locations in the southeast Harris County, Texas, area.

Within each stratum, approximately equal-sized substrata were formed on the ordered frames. One PSU per substratum was selected independently using probabilities proportional to the estimated number of age-eligible individuals.

Weight Calculation

Weights for each site were computed according to the equations given below.

$$\text{PSU-level weight component (first-stage)} = W_{hij} = \left[\frac{K_h S_{hi}}{S_h} \right]^{-1}$$

where K_h = the number of PSUs selected per substratum. In this case, $K_h = 1$, and

$$W_{hij} = \left[\frac{S_{hi}}{S_h} \right]^{-1}$$

for those PSUs in which a noncompact cluster was used while screening for eligibles before second-stage selection

$$W_{hij} = \left[\frac{S_{hi}}{S_h} \cdot \frac{1}{\text{HU sampling rate}} \right]^{-1} .$$

At the second stage, the selection probability for any eligible person was equal within a PSU. The second-stage weight component was then the inverse of the number of sample participants divided by the number of eligible persons in the PSU, M(o), or

$$W_{ijk} = \left[\frac{m(i)}{M(o)} \right]^{-1}$$

The final-stage unadjusted weights, W_{hijk}, are

$$W_{hijk} = W_{hij} \cdot W_{ijk}$$

for each participating individual. The final-stage unadjusted weights were created by multiplying the first- and second-stage weight components for each person. In cases where the number of participating persons, m(i), was one or less, PSUs were combined across adjacent substrata within primary strata and

the weights were recalculated to reflect the combined substrata population. Adjustment for nonresponse at the individual or final-stage unit level was not required when all screened eligibles within the PSU were approached to obtain the desired sample size m(i). This was the case in most of the PSUs in all three sites studied.

SURVEY ACTIVITIES

Activities at each site (Greensboro, Baton Rouge, and Harris County) were undertaken as detailed in the Office of Management and Budget (OMB) Submission Package and as reviewed in the following sections. Each phase of the study will be discussed in general terms and site-specific differences pointed out as appropriate. The three phases of activities at each site included the initial count and list of the segments, the household screening, and the recruitment and interviewing of selected respondents.

Count and List of Segments

The initial step in the field activities was the creation of an accurate listing of the housing units in each sample PSU. Only sample PSUs were selected with maps and preliminary sketches being provided to the field survey team. Field interviewers, hired locally at the PSUs, were trained to accomplish the tasks. They went to each PSU, determined exact boundaries, became familiar with the area, and then, following specific procedures used by all RTI field staff personnel, proceeded to count and then list all potential sample housing units. After all the PSUs in an area were completed, the results were returned to RTI so that the sampling statisticians could determine sampling rates and start numbers for the household screening process. Table 4 presents the results of the count and list operation in each site by providing a count of the number of segments selected and the number of field interviewers who worked the area.

Interviewers at each site were hired to participate in all activities but were trained for only one activity at a time. Interviewers were located by using RTI's National Interviewer File and network of field supervisors. After the interviewers in each area were identified by, and discussed with, the staff for whom they had previously worked, they were contacted by phone. The study was explained and, if interest and availability were expressed, the interviewer's position was offered. All training was done on-site by the SOC task leader, who, after training was complete, directly supervised the first few days of

TABLE 4. RESULTS OF COUNT AND LIST OPERATION

Parameter	Greensboro	Baton Rouge	Harris County
Number of Field Interviewers	2	3	3
Number of Segments	15	14	18
Total Households Listed	1599	982	1263
Number of Households Screened	374	721	660
Number of Households Containing at least One Eligible	101	190	148
Number of Eligible and Willing Respondents	112	208	72

each field activity. No interviewer failed to complete the activities for which they were retained.

Household Screening

After each PSU was listed, statisticians determined a sampling rate, dependent on number of listed units, and a start number. Based on this information, a sample of listed units was created for screening. The purpose of the screening was to create household rosters and to determine those members of the household who were eligible to participate in the study. A screening questionnaire (Fig. A1) was completed for each housing unit in the sample. Any resident of the household who was at least 16 years of age and who was physically and mentally capable of responding was allowed to provide the information for the form. The interviewers were instructed to make a minimum of three visits to each housing unit in order to complete the forms. If after three visits, on different days and at different times of the day, no contact had been made, the interviewer was to discuss the case with the Survey Operations Center (SOC) task leader during the regular (twice-a-week) reporting call, or with the designated lead interviewer at the site. In all PSUs, more than three calls were made before finalizing cases as 'No Contacts'. Neighbors were contacted to verify that the house was occupied and to determine when residents were generally at home. After all units in a PSU were finalized, the interviewer completed a second edit of all forms and mailed them to RTI. After receiving the forms, they were logged in, scan-edited for completeness, and transferred to the statistician for selection of eligible respondents. Table 4 continues by displaying the total number of households listed and then screened. It also displays the number of households with at least one eligible person, and the total number of eligibles found who expressed a willingness to participate.

In general, each interviewer returned to the PSUs that he/she had originally counted and listed. The interviewers were also assigned work for the interview sample phase in the same PSUs. Assignments were made to distribute the number of PSUs evenly. The single exception to an even division of PSUs was at the Baton Rouge site. The two PSUs in Geismar required additional driving time. Therefore, the interviewer who did the screening in those PSUs was assigned a reduced load in Baton Rouge.

Two changes in procedure became apparent for the screening phase of the study. When the roster of the household residents was created, no names were collected. While this helped assure the respondents of their anonymity, it made contacting specific individuals very difficult. Collection of first names will assist in determining the selected respondent while not compromising respondent confidentiality. Subsequent experience has shown that few housing unit respondents refuse to participate due to this change. The second area for modification of procedures is to drop the question asking about the willingness of presumed eligibles to participate. If an eligible person expresses an unwillingness to participate, but is selected to be a respondent, he or she can easily say, "I already told you 'no'". This happened, quite frequently, with a poor chance of converting the refusal. Subsequent experience with a similar screening process minus the willingness question yielded a better response.

Respondent Interviews and Sampling

After all PSUs were screened and the materials sent to sampling statisticians, a sample of the eligible respondents was selected to be contacted and asked to participate. Eligibility was determined by age (45-64 years at time of screening), residence in area (at least 1 year), nonoccupational exposure to the chemicals of interest, and not currently smoking. In each area, a sample was selected and fielded. The interviewer contacted the specific person, fully explained the study, requested that the respondent participate, and, if the respondent agreed, administered the Study Questionnaire (Fig. A2) and established a sampling appointment. If a respondent refused and could not be converted, a replacement potential respondent was provided from an ordered list selected by sampling statisticians and maintained by the lead interviewer. This system of replacement on a one-by-one basis was cumbersome and was not effective since the interviewers quickly realized that a list of replacements was available and they were more likely to accept refusals after fewer attempts to convert them. The need to use the initially selected respondent was stressed during training. This system also increased field time and associated costs since replacements were given out one-at-a-time causing inefficient repeat visits to PSUs.

Once a respondent agreed to participate, the interviewer obtained a signed Consent Form, completed the Study Questionnaire, and established appointments for sampling. The Study Questionnaire was designed to collect basic

demographic data about the respondents as well as data which might be used as explanatory variables in the analysis of the relationships between the various environmental and biological samples collected. For example, one section of questions collected information on occupation and looked for chance contact with hydrocarbons either through miscellaneous contact or because of the respondent's work site location relative to known sources. Questions on general health, current respiratory disease, and any medications were asked to determine any possible influences on metabolism and excretion of the chemical being studied. Food and water sources were also examined for the same reason. Household influences were examined for presence of the chemicals due to hobbies, or other residents carrying the chemicals on their clothes. Ventilation of the house was also recorded.

Sampling was explained and conducted by analytical chemists. Sampling appointments were established to permit maximum numbers of cases to be scheduled in minimum time. Sampling started in the early evening with the placement of monitors and sampling jars. A morning visit was used to exchange monitors, to collect the first morning void urine, and to collect water samples. A late afternoon sample visit was used to retrieve air monitors, to collect the blood sample, to pay the incentive, and to obtain the Incentive Receipt. Blood samples were collected by trained personnel (recommended by the local health department) using vacutainers with brachial venipuncture. In Greensboro and Harris County, health department nurses were used, while trained venereal disease fieldworkers were used in Baton Rouge. All personnel worked on a paid-by-the-case basis on their own time. This independent subcontractor arrangement was very effective, allowing direct control and supervision of approved personnel.

Post-Field Activities

After the interviewer completed the Study Questionnaire, he/she left it, with the RTI copy of the Consent Form attached, with the respondent. The analytical chemists retrieved these forms during the first visit with the respondent. As documents were picked up, study numbers were assigned, using preprinted labels that were attached to all forms and samples collected. They attached the signed Incentive Receipt and returned all forms to survey specialists upon their return to RTI. All documents for all respondents were accounted

for during a log-in procedure. The Consent Form and Incentive Receipt were separated from the Study Questionnaire and placed in a secure storage. All documents remained linked by study number only. All Study Questionnaires were edited and coded completely by survey specialist personnel and sent in batches to Data Entry for conversion to data files for analysis. All data entry was 100 percent key-verified for quality control. The data entry programs also contained range checks and internal logic to assure quality data for analysis. The results of the questionnaire data are discussed in Section 6.

Chemical Sampling and Analysis

As described earlier, the three study areas were Greensboro, NC, Baton Rouge/Geismar, LA, and Harris County, TX. Figures 1 through 4 depict the study areas from which the participants's were selected.

The selection of volatile halocarbons and the respective study areas was previously discussed (1). The basis for the selection of chemicals for monitoring and those chemicals which are site-specific and ubiquitous was also delineated (1). Table 5 presents the halocarbons monitored in air and breath of the study areas. All halocarbons were monitored in the Greensboro, NC, area; the listing was essentially a composite of halocarbons previously found in the other areas that were to be studied (1). Thus, a subset of the chemicals listed for monitoring in Greensboro were monitored in Baton Rouge/Geismar, LA, or Harris County, TX.

The volatile halocarbons selected for measurement in drinking water and blood are given in Table 6. Again, the list for Greensboro is a composite from several study areas which contained both ubiquitous and site-specific chemicals (1).

The overall sampling strategy applied to each study participant is given in Table 7. Personal and fixed-site air samples were collected over two sampling periods (an overnight and a daytime period) for each participant. Each period was approximately 11-12 h long. The personal and fixed-site air samples were collected concurrently. A fewer number of fixed-site air sampling locations were, used however, since a fixed-site station was located to represent several households.

The sampling generally began with a visit to the household in the evenings between 7:30 and 9:30 o'clock. At this time, fixed-site and personal air

Table 5. VOLATILE HALOCARBONS SELECTED FOR MONITORING IN AIR AND BREATH OF STUDY AREAS

Volatile Halocarbons	Greensboro, NC	Baton Rouge/ Geismar, LA	Harris County, TX
vinylidene chloride	√	√	
chloroform	√	√	√
chloroprene	√		√
1,2-dichloroethylene	√	√	√
1,2-dichloroethane	√	√	√
1,1,1-trichloroethane	√	√	√
carbon tetrachloride	√	√	√
1,2-dichloropropane	√	√	
trichloroethylene	√	√	√
bromodichloromethane	√		
dichlorobutane isomer	√	√	√
1,1,2-trichloroethane	√	√	√
chlorodibromomethane	√	√	
trichlorobutane isomer	√		
tetrachloroethylene	√	√	√
bromodichloroethane	√		
chlorobenzene	√		√
bromoform	√		
1,1,2,2-tetrachloroethane	√	√	
bromobenzene	√		
chlorotoluene isomers	√		
dichlorobenzene isomers	√	√	√
hexachloroethane	√		
trichloropentane isomer	√		
bis-(chloroisopropyl)ether	√		
chloronitrobenzene	√		
trichlorohexane isomer	√		
dichlorotoluene isomers	√		
trichlorobenzene isomers	√		

(continued)

Table 5 (cont'd.)

Volatile Halocarbons	Greensboro, NC	Baton Rouge/ Geismar, LA	Harris County, TX
1,3-hexachlorobutadiene	√		
trichlorotoluene isomers	√		
tetrachlorobenzene isomers	√		

Table 6. VOLATILE HALOCARBONS SELECTED FOR MONITORING IN DRINKING WATER AND BLOOD OF STUDY AREAS

Volatile Halocarbons	Greensboro, NC	Baton Rouge/ Geismar, LA	Harris County, TX
vinylidene chloride	√	√	√
chloroform	√	√	
chloroprene	√		
1,2-dichloroethylene	√	√	√
1,2-dichloroethane	√	√	√
1,1,1-trichloroethane	√	√	√
carbon tetrachloride	√	√	√
1,2-dichloropropane	√	√	
trichloroethylene	√	√	√
bromodichloromethane	√		
dichlorobutane isomer	√	√	√
1,1,2-trichloroethane	√	√	
chlorodibromomethane	√	√	
trichlorobutane isomer	√		√
tetrachloroethylene	√	√	√
bromodichloroethane	√		
chlorobenzene	√		√
bromoform	√		
1,1,2,2-tetrachloroethane	√	√	
bromobenzene	√	√	
chlorotoluene isomers	√		
dichlorobenzene isomers	√	√	√
hexachloroethane	√	√	
trichloropentane isomer	√		√
bis-(chloroisopropyl)ether	√		√
chloronitrobenzene	√		
trichlorohexane isomer	√		√
dichlorotoluene isomers	√		
trichlorobenzene isomers	√		

(continued)

Table 6 (cont'd.)

Volatile Halocarbons	Greensboro, NC	Baton Rouge/ Geismar, LA	Harris County, TX
1,3-hexachlorobutadiene	√		
trichlorotoluene isomers	√		
tetrachlorobenzene isomers	√		

Table 7. OVERALL SAMPLING STRATEGY APPLIED TO EACH STUDY PARTICIPANT

Sampling Period	Fixed-Site Air	Personal Air	Breath	Blood	Drinking Water
7:30 PM-7:30 AM	X	X	-	-	-
7:30 AM-6:00 PM	X	X	X[a]	X[a]	X[b]

[a]Samples taken at the end of monitoring period.

[b]Samples from tap were generally acquired during one of the three visits made to the household.

monitors were initiated for the first sampling period. Containers for the collection of drinking water samples were also provided to the study participants. A second visit was made during the following morning between 7:00 and 8:30. At this time, the air collection devices which were exposed during the first sampling period were picked up and the second air sampling period was initiated. The second sampling period ran from 7:30 AM to 6:00 PM on that same day. The final visit was made in the afternoon between 4:30 and 6:30. At this time, breath and blood samples were also obtained from the study participants. All drinking water samples which had been acquired from the study participants and the air samples were also picked up. Generally, a sampling team of two individuals were able to attend to three study participants per day.

To collect personal air samples, the volunteer wore a vest equipped with a collection system as shown in Figure 6. The sampling train was a Tenax GC® sampling cartridge (2) preceded by a glass fiber filter (for removing particulate) and a small personal air pump (DuPont Model No. P125 or MSA C-200). The fixed-site air sampler was identical to the personal air sampler (Fig. 7) except that it was placed outside the home in the participant's yard. A fixed-site sampler represented a cluster of participants (1 to 3). However, it always matched a personal air sample for at least one participant in each cluster. A nominal sampling rate of 30-35 mL/min was used. Approximately 20-25 liters of air were sampled during each time period.

The specific details for collecting environmental and biological samples have been previously described (3). Sampling was conducted during the months of October and November, 1980, in Greensboro, NC; January and February, 1981, in Baton Rouge/Geismar, LA; and June and July, 1981, in Harris County, TX. Tables 8-10 list the samples collected, analyzed, and the degree of completeness of analysis. The number of samples collected both for single and duplicate analysis, field cartridge of cannister blanks, controls, and laboratory blanks and controls are listed. The total number of samples collected and analyzed are also given (Tables 8-10).

The analysis of air (fixed-site and personal), breath, blood, and water has been previously described (3).

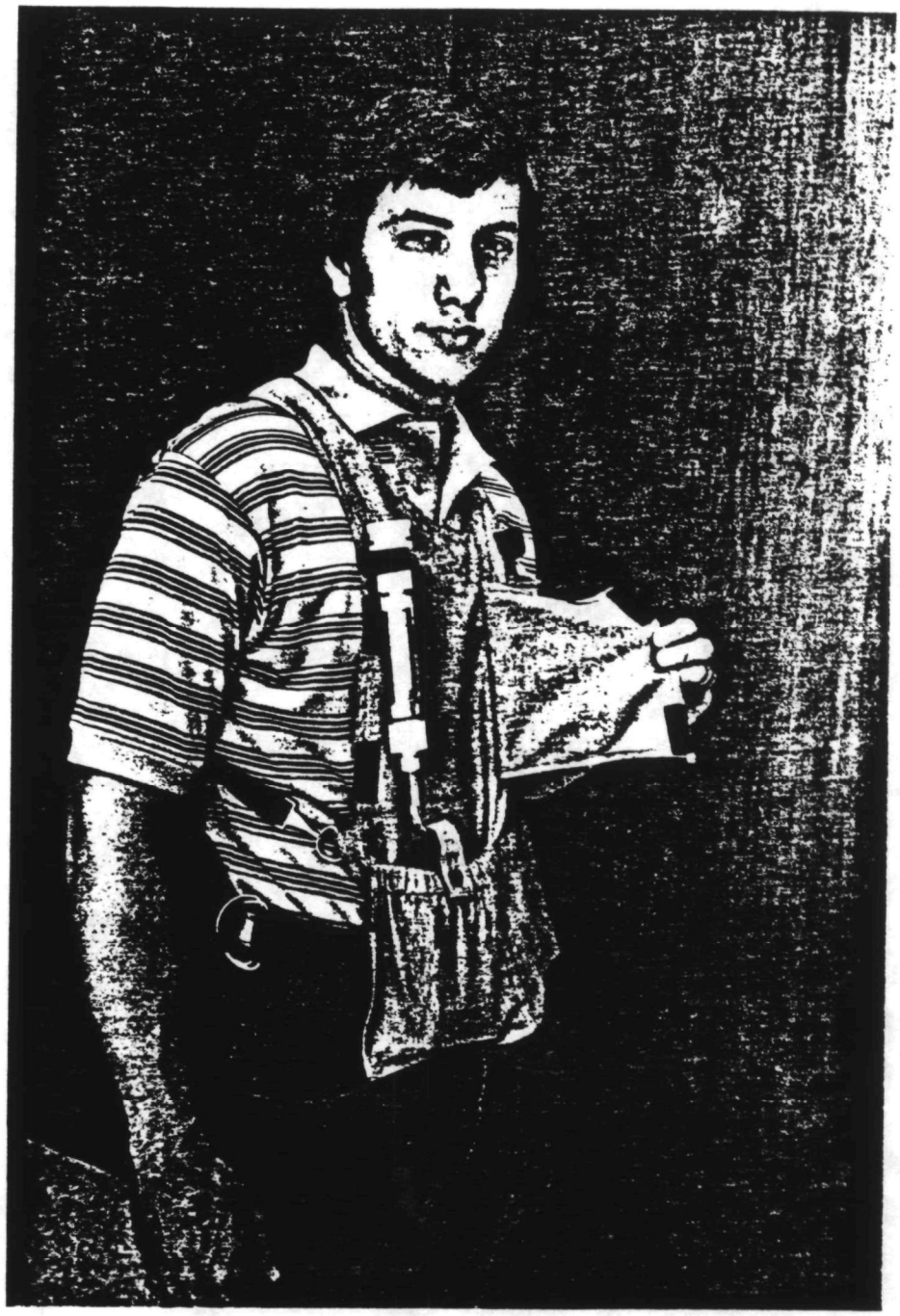

Figure 6. Vest equipped with Tenax GC® sampling cartridge, prefilter for particulate, and personal pump (in pocket) for collecting vapor-phase halocarbons in personal air.

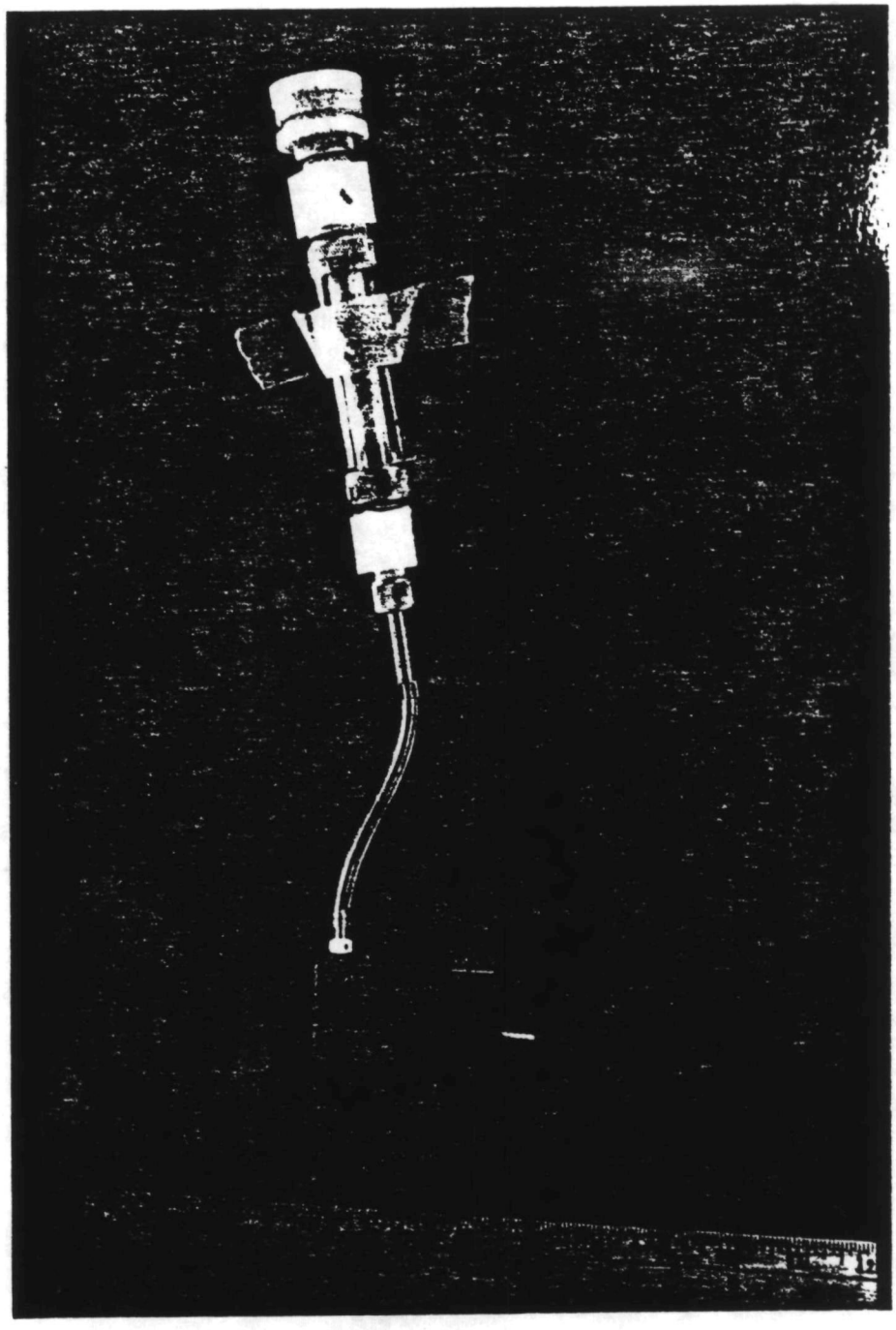

Figure 7. Sampling system depicting filter, Tenax GC® cartridge, and pump for collecting fixed-site air samples.

Table 8. SAMPLES COLLECTED, ANALYZED, AND COMPLETENESS FOR GREENSBORO, NC, STUDY AREA (NUMBER OF PARTICIPANTS = 29)[a]

	VF	VP	BR	BH	WH
Samples Collected (F)	41	58	28	29	29
Duplicates Collected (D)	34	6	28	8	11
Field Blanks (FB)	3	4	6	4	3
Field Controls (FC)	4	6	5	4	3
Lab Blanks (LB)	3	4	5	4	3
Lab Controls (LC)	4	6	5	4	3
Total Samples	89	84	77	53	52
Total Analyzed	89	84	77	53	52
Percent Completeness	100	100	100	100	100

[a]VF = fixed-site air, VP = personal air, BR = breath, BH = blood, WH = water.

D. Tetrachloroethylene--In all three areas, personal samples have better agreement with breath than fixed-site samples. Relatively high agreement occurred in Greensboro. Again, fixed-site samples in Harris have relatively poor agreement.

E. Dichlorobenzenes--In Greensboro and Harris County, agreement with breath samples is relatively high for both fixed-site and personal-air samples. In Baton Rouge/Geismar, the personal air samples have much better agreement than do the fixed samples.

predict levels of one medium from another for the compound levels present in the three geographical areas.

Two-by-Two Tables--

In addition to the correlations and scatter plots, Table A59 presents by area two-by-two percent-detected tables for breath versus personal and fixed- air samples for the five compounds: chloroform; 1,1,1-trichloroethane; carbon tetrachloride; tetrachloroethylene; and dichlorobenzenes. The tables present weighted estimates (i.e., population estimates) for the three areas. The two-by-two tables give the estimated percent detected in the four categories (i.e., breath and air both measurable, breath measurable air not detected ...) as well as percent agreement between the two media and the sample sizes that the population estimates are based upon.

In general, the tables indicate that in many cases the personal-air samples have better percent agreement with the breath samples than do the fixed-air samples. In addition, in most cases the A.M. and P.M. percent agreement is approximately the same within fixed-site and personal samples for each compound. In examining the tables, the reader is cautioned that the sample sizes for fixed-site samples in Harris County are quite small. Specifically:

A. Chloroform--In Greensboro, the agreement between personal-air and breath samples is relatively high (80%) compared to fixed-site air samples. For Baton Rouge/Geismar and Harris County, the agreement between the samples is relatively modest particularly for fixed-site air in Harris (again note the small sample sizes for fixed-site air samples in Harris).

B. 1,1,1-Trichloroethane--In Greensboro and Harris County, the agreement between personal-air and breath samples is higher than for fixed-site samples with the Greensboro agreement being relatively high (85%).

C. Carbon Tetrachloride--Greensboro and Baton Rouge/Geismar have relatively high agreement for both fixed-site and personal-air samples. Harris County on the other hand has relatively low agreement between the various samples.

In general, the plots presented are for the following pairs of media:

1. breath and personal air P.M.;
2. fixed air A.M. and personal air A.M.;
3. fixed air P.M. and personal air P.M.;
4. personal air A.M. and personal air P.M.; and
5. breath and blood.

Figures A30 through A34 presented one plot from each of these groups. In addition, plots are also presented between water and air samples for chloroform (Appendix B).

To further aid in interpreting the various plots, Figures A30 through A34 and selected plots in the appendixes also include the median of values on the vertical axis for intervals indicated on the horizontal axis (the medians are indicated by boxes with the box at the median of the vertical axis points within the horizontal interval).

In general, the plots that are presented show a positive trend as the levels increase, and many of the Spearman correlations between the two media are significantly different from zero. The medians given on Figures A30 through A34 clearly show this positive trend, although it is clear that the trend is not always linear. However, there is considerable scatter in the various plots. This is particularly noticeable in the lower left-hand corner of the plots where the nonmeasurable values are plotted (i.e., the X's). Here the nonmeasurable values in one medium may have relatively high values in the other media (e.g., Figure A33, Appendix C Figure C1, etc.). In fact, in many cases it appears that until a certain level of both media is reached that there is no relationship between the media. Then as levels increase, a trend does begin to emerge (e.g., Figs. A30, A33, and A34).

In general, the personal-air a.m. versus personal-air p.m. plots (Figure A33 and Appendix C Figures C1 through C12) appear to have the strongest positive trends for the various groups plotted.

To summarize, the plots between media show considerable scatter, but positive trends are evident after the media reach certain levels. The medians presented on selected plots clearly show the positive trends. Certainly, from the data presented, it would be difficult to accurately

To further examine correlations between media, Table A58 presents unweighted Spearman correlations based only upon measurable values for breath, air, and water samples for the eight compounds and areas that showed the highest correlations in Table A57. That is, values below the quantifiable limit in either media have been eliminated in computing these correlations. The reader is cautioned that the correlations in this table are based on very small sample sizes; however, as the footnote indicates, all correlations presented in the table are based on at least five measurable values. Undoubtedly, many of the negative correlations noted in the table are due to the small sample sizes.

Table A58 indicates the following for measurable values for the eight compounds:

A. For breath:
   1. Again, personal-air levels are more highly correlated with breath levels than are fixed-site air levels.
   2. The results for breath versus water levels indicate approximately as many negative correlations as positive correlations.

B. For air:
   1. Personal a.m. and p.m. air samples are very well correlated.
   2. In general, air and water samples do not appear to be well correlated with many of these correlations being negative. One noticeable exception is for chloroform levels in Houston.

Scatter Plots--

To further examine relationships between media, Figures A30 through A34 and Appendix C Figures C1 through C37 present several scatter plots between the various media. The plots were usually selected to examine relatively high correlations and should not be considered as a sample of the relationships being examined. Note the plots are on the log scale and that an X indicates that one or both of the media being examined were below the quantifiable limit while a 0 indicates both media were measurable. The plots also indicate the maximum quantifiable limit (across areas) for each medium and give the Spearman correlation coefficient [r(all)] for all observations as well as for measurable values only [r(meas. only)].

Table A57 indicates for the 13 compounds examined that:

A. Chloroprene and 1,2-dichloroethylene had no correlations and/or sample sizes that met the criterion for entry into the tables (i.e., correlation > 0.2 and at least two measurable values in both media being examined).

B. For breath:

   1. In general, breath levels are not positively correlated with water levels.
   2. Breath levels do appear to be correlated with both fixed-site and personal-air levels for certain compounds. The correlations between personal air and breath appear to be higher than between fixed-site air and breath. In particular, breath and personal air have relatively high correlations for 1,1,1-trichloroethane; trichloroethylene (this compound had limited data above the MQL); tetrachloroethylene; and dichlorobenzenes.
   3. Breath levels and blood levels were relatively well correlated for dichlorobenzenes in Baton Rouge/Geismar.

C. For air:

   1. Many of the air samples are correlated with each other. This is particularly true for personal air A.M. versus personal air P.M.
   2. In general, as might be expected, the air and water sample levels do not appear to be highly correlated with one another. In fact, many of the correlations are negative between the two media (exceptions are the personal air and water levels for chloroform in Houston).
   3. Compounds and areas that have several relatively high correlations between the two types of air samples are:
      (a) chloroform (Houston);
      (b) 1,2-dichloroethane (in Baton Rouge/Geismar);
      (c) carbon tetrachloride (all three areas);
      (d) trichloroethylene (Greensboro);
      (e) tetrachloroethylene (all three areas); and
      (f) dichlorobenzenes (Greensboro).

(8) Dichlorobenzenes levels were elevated in breath samples in Deer Park, Texas. For personal air samples, levels were elevated in all the strata examined--particularly in Geismar, LA, and the Texas strata.

Relationships Between Media

Correlations--

To examine the relationships between the various media, unweighted Spearman correlations were first computed for the 13 compounds examined in Tables A43-A56 for areas where these compounds were measured. The correlations were computed between breath, blood, fixed air (A.M. and P.M.), personal air (A.M. and P.M.), and water. Table A57 presents these Spearman correlations between breath, air, and water samples (blood samples had very few values over the maximum quantifiable limit; therefore, their correlations are only presented for breath and blood). Before examining the table, the reader is cautioned that the sample sizes for many of the correlations are quite small (see footnote 5 for the table) and, in addition, that many of the correlations are based on several values which are below the maximum quantifiable limit (see Tables A38-A42). To help emphasize this, correlations in the table are underlined which are based on a medium that has less than 5 percent of its sample values greater than the maximum quantifiable limit (MQL). In addition, correlations based on less than two measurable values in both media were eliminated from the table as were correlations between -.2 and +.2.

As an example of the caution that should be taken in interpreting the correlations, Figure A30 gives a plot of fixed-air P.M. levels versus personal-air P.M. levels for trichloroethylene in Greensboro. Even though the Spearman correlation is 0.49, the plot shows very little relationship between the two media. In addition, except for one value, the levels for fixed air (shown on the log scale) are all below the maximum quantifiable limit. (The MQL is indicated by a + mark on the figure). Note also that the correlation between measurable values only (indicated by 0's on the plot) is very small. Thus, even though many of the correlations in Table A57 are significantly different from zero, plots similar to Figure A30 of the relationships between media (shown later) indicate a large amount of variation in these relationships.

Table 17 (cont'd.)

Compound	Media						
			Fixed Air		Personal Air		
	Breath	Blood	A.M.	P.M.	A.M.	P.M.	Water
Tetrachloroethylene	Greens. BR/G Harris	low	Greens. Harris	Greens. Harris	Greens. BR/G Harris	Greens. BR/G Harris	low
Chlorobenzene	low						
Dichlorobenzenes	Harris	low	low	low	BR/G Harris	Greens. BR/G Harris	low

[a]Low = relatively low levels compared with maximum quantifiable limit.

[b]east Baton Rouge/Geismar (BR/G) has relatively high levels in at least one exposure stratum.

[c]Southeast Harris County, TX (Harris) has relatively high levels in at least one exposure stratum.

[d]Greensboro (Greens.) had relatively high levels.

Table 17. SUMMARY OF THE MAGNITUDE OF COMPOUND LEVELS COMPARED TO THE MAXIMUM QUANTIFIABLE LIMIT OVER THE THREE SITES, BY COMPOUND AND MEDIA

Compound	Media						
			Fixed Air		Personal Air		
	Breath	Blood	A.M.	P.M.	A.M.	P.M.	Water
Vinylidene chloride	low[a]	←					→
Chloroform	BR/G[b]	low	Harris[c]	Harris	Greens.[d] Harris	Greens. Harris	Greens. BR/G Harris
Chloroprene	low	←					→
Dichloroethylene	low	←					→
1,2-Dichloroethane	low	low	BR/G Harris	BR/G Harris	BR/G	BR/G	low
1,1,1-Trichloroethane	Greens. BR/G Harris	low	Greens. BR/G Harris	Greens. Harris	Greens. BR/G Harris	Greens. BR/G Harris	low
Carbon tetrachloride	low	low	Harris	BR/G Harris	BR/G Harris	Harris	Harris
1,2-Dichloropropane	low	←					→
Trichloroethylene	low	low	Harris	low	Harris	BR/G Harris	low
Bromodichloromethane	low	←					→ Greens.

(continued)

1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, bromodichloromethane, tetrachloroethylene, and dichlorobenzenes. Table 17 presents a summary of the results of comparing compound levels with the maximum quantifiable limits. Of particular interest are the following observations by compound:

(1) Chloroform had elevated levels in all media except blood. These elevated levels were particularly noticeable in water in Southeast Houston and Pasadena, TX (e.g., the median water level in Pasadena was 410 ng/mL). Elevated levels in water were also noted in Geismar, LA, and Greensboro, NC. Air levels of chloroform were elevated in all three exposure strata in Texas--particularly in Southeast Houston and Pasadena for personal air. In breath, only the high stratum in Baton Rouge indicated elevated levels.

(2) 1,2-Dichloroethane had elevated air levels in the three Baton Rouge/Geismar exposure strata.

(3) 1,1,1-Trichloroethane had elevated levels in air and breath. For breath, Greensboro had the highest values: median = 3.3 $\mu g/m^3$, range = 0.060-1,048 $\mu g/m^3$ and sample mean = 50.59 $\mu g/m^3$. Personal air levels were generally higher in Greensboro and Harris County.

(4) Carbon tetrachloride had elevated levels in the Texas exposure strata for air and water samples. In addition, for personal air (p.m.) samples in Greensboro, the sample mean and the range were relatively large (i.e., 48.5 $\mu g/m^3$ and 0.025-1,300 $\mu g/m^3$, respectively.

(5) Trichloroethylene air levels were relatively high in the three strata in Texas.

(6) Bromodichloromethane levels were relatively high in only one medium, water, in Greensboro. The range in Greensboro was 0.050-98 ng/mL.

(7) Tetrachloroethylene levels were elevated in breath and air samples in all three sites. For the air samples, the median levels were highest in the Texas exposure strata. For blood samples, the range was 0.225-38 ng/mL in Greensboro.

(3) For breath, Harris County was relatively high for dichlorobenzenes of the three areas.

(4) Because of the relatively low percentages, the tests for blood were usually not significant.

(5) With the exception of water, the percentages for the three strata in Southeast Harris County, TX, were usually not significantly different.

(6) For water (a) Harris County had relatively high percentages for the three areas for trichloroethylene and tetrachloroethylene; (b) for the three strata in Louisiana, Geismar had high percentages for chloroform and 1,2-dichloroethane; (c) for the three strata in Harris County, Houston and Pasadena had high percentages for chloroform, carbon tetrachloride, trichloroethylene, and tetrachloroethylene.

Summary Statistics

After examining the percentages in Tables A36-A42, 13 halocarbons were selected on which to compute additional statistics. The compounds were selected because they were the principal compounds detected in at least one of the three areas. Tables A43-A49 present summary statistics (i.e., percent over maximum QL, means, standard errors, medians, and ranges) in Greensboro, east Baton Rouge/Geismar, and Southeast Harris County, TX, for these 13 principal compounds. In computing the statistics, values below the limit of detection (LOD) were set equal to 1/2 x LOD, and values at trace were set equal to 5/8 the quantifiable limit (QL). Again, the statistics in the table are weighted estimates and thus give population estimates for the three areas. Because the population sample sizes are much larger in the "other" exposure strata in east Baton Rouge and the "low" exposure strata in Southeast Harris County, TX, these strata dominate the population estimates for the areas. This can be seen clearly in Tables A50 through A56 which present estimated population medians by exposure strata for the various areas.

Tables A43 through A56 indicate that eight of the 13 compounds examined have elevated levels over the maximum quantifiable limit in at least one medium over the three areas examined. These were chloroform, 1,2-dichloroethane,

Table 16. SUMMARY OF THE RESULTS OF TESTS OF SIGNIFICANCE ON PERCENT OVER THE MAXIMUM QUANTIFIABLE LIMIT

	Breath	Blood	Fixed Air	Personal Air	Water
3 Areas	(1) dichlorobenzenes in Harris[a]	(1) tetrachloroethylene in Greensboro	(1) chloroform in Harris (2) 1,2-dichloroethane in Baton Rouge (3) 1,1,1-trichloroethane in Harris (4) carbon tetrachloride in Harris (5) trichloroethane in Harris (a.m. only) (6) tetrachloroethylene in Harris	(1) chloroform in Harris (p.m.) (2) 1,2-dichloroethane in Baton Rouge (3) 1,1,1-trichloroethane in Greensboro and (4) carbon tetrachloride in Harris (5) 1,2-dichloroethane in Baton Rouge (p.m.) (6) trichloroethylene in Harris (7) tetrachloroethylene in Greensboro and Harris (p.m.) (8) dichlorobenzenes in Harris	(1) chloroform in Greensboro and Harris (2) trichloroethane in Harris (3) tetrachloroethylene in Harris
Strata in East Baton Rouge/Geismar	(1) vinylidene chloride in High B.R. and Geismar[b] (2) chloroform in High B.R. (3) 1,1,1-trichloroethane in High B.R. (4) tetrachloroethylene in High and other (5) dichlorobenzenes in Geismar	(1) tetrachloroethylene in Greensboro	(1) 1,2-dichloropropane in Geismar and other B.R. (a.m. only)	(1) 1,2-dichloroethane in other B.R. (p.m.) (2) 1,1,1-trichloroethane in other B.R. (3) carbon tetrachloride in other B.R. (p.m.) (4) 1,2-dichloropropane in other B.R. (p.m.) (5) trichloroethane in other B.R. (p.m.) (6) tetrachloroethylene in other B.R.	(1) chloroform in Geismar (2) 1,2-dichloroethane in Geismar (3) carbon tetrachloride in other B.R. and Geismar
Strata in Southeast Harris County, TX	(1) 1,1,1-trichloroethane in Houston		(1) 1,2-dichloroethane in Houston (a.m. only)		(1) chloroform in Houston and Pasadena (2) carbon tetrachloride in Houston and Pasadena (3) trichloroethane in Houston and Pasadena (4) tetrachloroethylene in Houston and Pasadena

[a] Southeast Harris County, TX, had the highest percent over the maximum quantifiable limit (MQL) of the three areas studied for dichlorobenzenes (for dichlorobenzenes, at least one of the three pairwise tests was significant at the .05 level).

[b] For the 3 strata in east Baton Rouge/Geismar, the high exposure strata in Baton Rouge and Geismar had the highest percent over MQL for vinylidene chloride.

Table 15. PRINCIPAL COMPOUNDS[a] DETECTED BY AREA AND MEDIA

Area	Breath	Blood	Fixed Air	Personal Air	Water
Greensboro	chloroform 1,2-dichloroethane 1,1,1-trichloroethane tetrachloroethylene dichlorobenzenes	tetrachloroethylene 1,3-hexachlorobutadiene	chloroform 1,2-dichloroethane 1,1,1-trichloroethane tetrachloroethylene	chloroform 1,2-dichloroethane 1,1,1-trichloroethane carbon tetrachloride trichloroethylene bromodichloromethane tetrachloroethylene chlorobenzene dichlorobenzene trichlorobenzene isomers	chloroform carbon tetrachloride bromodichloromethane
East Baton Rouge	chloroform 1,2-dichloroethane 1,1,1-trichloroethane tetrachloroethylene dichlorobenzenes		vinylidene chloride chloroform 1,2-dichloroethane 1,1,1-trichloroethane carbon tetrachloride 1,2-dichloropropane trichloroethylene tetrachloroethylene	vinylidene chloride chloroform 1,2-dichloroethane 1,1,1-trichloroethane carbon tetrachloride 1,2-dichloropropane trichloroethylene tetrachloroethylene dichlorobenzenes	chloroform carbon tetrachloride
Southeast Harris County	chloroform 1,1,1-trichloroethane tetrachloroethylene dichlorobenzenes	chloroform	chloroform 1,2-dichloroethane 1,1,1-trichloroethane carbon tetrachloride trichloroethylene tetrachloroethylene	chloroform dichloroethylene 1,2-dichloroethane 1,1,1-trichloroethane carbon tetrachloride trichloroethylene tetrachloroethylene chlorobenzene dichlorobenzenes	chloroform carbon tetrachloride trichloroethylene tetrachloroethylene

[a]Greater than 10% detected.

(2) Blood: (a) chloroform; (b) tetrachloroethylene; (c) dichlorobenzenes; (d) 1,3-hexachlorobutadiene;

(3) Fixed Air: (a) vinylidene chloride; (b) chloroform; (c) 1,2-dichloroethane; (d) 1,1,1-trichloroethane; (e) carbon tetrachloride; (f) 1,2-dichloropropane; (g) trichloroethylene; (h) tetrachloroethylene; (i) dichlorobenzenes;

(4) Personal Air: same as fixed air plus chlorobenzene and trichlorobenzene isomers;

(5) Water: (a) chloroform; (b) 1,1,1-trichloroethane; (c) carbon tetrachloroide; (d) trichloroethylene; (e) bromodichloromethane; (f) tetrachloroethylene; (g) 1,1,2,2-tetrachloroethane; (h) dichlorobenzenes.

It is important to note here, in general, that the percent detected for many compounds was zero or very small. This is particularly true for blood where all percent-detected values were less than 27 percent. Thus, care must be taken not to over emphasize the importance of summary statistics or correlations between media for the current data.

In addition to Table 14, Table 15 presents the principal compounds detected by area and media.

Finally, Tables A36 through A42 also indicate the results of pairwise tests of significance between the weighted percentages. An asterisk is shown if any of the three pairwise tests between the percentages was significant. (The table does not indicate exactly which pairwise test was significant). Table 14 summarizes the tests by indicating which area was highest for compounds that had at least one pairwise test significant.

The results in Table 16 indicate that:

(1) Southeast Harris County had relatively high percentages in fixed-site and personal air for several compounds including chloroform; 1,1,1-trichloroethane; carbon tetrachloride; 1,1,1-trichloroethane; and tetrachloroethylene.

(2) Baton Rouge/Geismar had relatively high percentages of 1,2-dichloroethane and 1,2-dichloropropane in fixed-site and personal air samples.

1. Percent-detected statistics are presented first to indicate which compounds were present in the various areas.
2. Summary statistics are then presented for those compounds that had sufficient percent detected available for analysis. These statistics include the mean, standard deviation, median, and the range.
3. Relationships between media are then presented for those compounds which had sufficient percent detected which include correlations and two-by-two percent-detection tables (e.g., breath versus personal air).

In computing the various statistics, the percent detected, the summary statistics, and the two-by-two percent-detection tables are weighted estimates (i.e., weighted by the sampling weights since the sample respondents were selected under a probability sampling framework).

Finally, the percent detected the percent over the maximum quantifiable limit (MQL) (defined as the highest limit of quantification across all samples for that chemical in a medium) is presented. The reason for the use of the MQL was also discussed above.

Percent Detected

Recall that Figures 1-4 presented maps of the areas sampled for the present study in Greensboro, NC; east Baton Rouge/Geismar, LA; and Southeast Harris County, TX. In particular, Figure 3 indicates the exposure strata sampled in east Baton Rouge, and Figure 4 shows the exposure strata in Southeast Harris County.

Tables A36-A42 summarize the weighted percentage of measurable values over the maximum quantifiable limit of halogenated hydrocarbons in the three areas by media, area, and exposure stratum within area. The maximum quantifiable limit for each medium and compound is also given in the tables, and the percentages are the proportion of sample values over this maximum.

Table 14 indicates the compounds detected in the three areas by media as indicated in Tables A36-A42. Tables A36-A42 indicated that the principal compounds detected were:

(1) Breath: (a) chloroform; (b) 1,2-dichloroethane; (c) 1,1,1-trichloroethane; (d) tetrachloroethylene; and (e) dichlorobenzenes;

Table 14. COMPOUNDS DETECTED BY MEDIA IN THE THREE AREAS

Compound	Media						
	Breath	Blood	Fixed Air (a.m.)	Fixed Air (p.m.)	Personal Air (a.m.)	Personal Air (p.m.)	Water
Vinylidene chloride[a]	1		1	1	1,3	1	
Chloroform	A	1,2	A	A	A	A	A
Chloroprene[a]	2		2	2	2	2	
Dichloroethane	2		1,3	1	2	2	
1,2-Dichloroethane	1,3		A	1,2	A	A	1
1,1,1-Trichloroethane	A	1	A	A	A	A	1,2
Carbon tetrachloride	A		A	A	A	A	A
1,2-Dichloropropane[a]	3		1	1	1,3	1,3	
Trichloroethylene	1,2		A	2,3	A	A	2
Bromodichloromethane[a]					3	3	3
Tetrachloroethylene	A	1,3	A	A	A	A	2,3
Chlorobenzene[a]	2		2,3	2	2,3	2,3	
1,1,2,2-Tetrachloroethane[a]	3		1	1	1	1,3	3
Dichlorobenzenes	A	1,2	1,2	1,2	A	A	1,2
Trichlorobenzene isomers[a]	3	3		3	3	3	
1,3-Hexachlorobutadiene[a]		3		3	3		

A = compound present at all three areas.
1 = east Baton Rouge/Geismar.
2 = Southeast Harris County.
3 = Greensboro.

[a]Note, not all halocarbons were chemically analyzed for in Southeast Harris County and east Baton Rouge/Geismar. See Tables 5 and 6.

at the 0.05 level (*) is also indicated. In general, the plots show considerable scatter about the 45° line. However, the majority of points are within ±25% of the 45° line. The relationship for 1,1,1-trichloroethane (which has a large dynamic range) shows the highest linear trend of the compounds plotted.

Similarly, Figures A14-A20 depict log-log plots for carbon tetrachloride, chloroform, 1,2-dichloroethane, trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, and chlorobenzene, respectively, in fixed-site air samples. Again, there is scatter about the 45° line, but the majority of values are within ±25 percent. A comparison of the correlation coefficients for halocarbons in personal air and fixed-site air sampling and analysis reveals that similar magnitudes were obtained.

Figures A21-A27 are log-log plots for carbon tetrachloride, chloroform, trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, dichlorobenzenes, and chlorobenzene, respectively, in breath samples. In several cases (carbon tetrachloride, chloroform, trichloroethylene, and chlorobenzene), the data were near or below the maximum quantifiable limit. However, when a large dynamic range in concentration was observed, the correlations were high.

Plots for chloroform and carbon tetrachloride in water are shown in Figures A28 and A29. Only a few measurements for carbon tetrachloride were above the maximum quantifiable level.

Thus, in general the plots demonstrate a good linear relationship when the dynamic range of the data is relatively large. However, when the range is small, the linear relationships are not so apparent. Also, larger relative discrepancies occur between field and duplicates when the magnitude of the data is near or below the quantifiable limit.

STATISTICAL ANALYSIS OF FIELD DATA

Introduction

As discussed earlier, this section of the report presents statistics by compound and media for the three areas sampled. These statistics were computed after averaging the field and duplicate sample values for an individual. The organization of the section is as follows:

Initially, replicate field samples for personal and fixed-site air for selected compounds in Greensboro and Baton Rouge were plotted (Figs. A3-A6). Only field duplicate samples that yielded measurable values in both samples were included. For many chemicals, insufficient data were available from a single area for performing linear regression analysis. Figure A3 depicts the replicates for tetrachloroethylene measured in Greensboro samples. The data were plotted on a log-log scale. Linear regression analysis revealed rather contrasting correlations (r) when using Pearson and Spearman computation methods for fixed-site air samples (Fig. A3). This example underlines the importance of plotting the data to examine the relative distribution of measured data, since each correlation technique emphasizes slightly different weighting to the data over a concentration range. In this case, the Pearson method computed a high correlation which was significantly different from zero at the 0.05 level. A similar example of this case is depicted in Figure A4. In contrast, the data for replicate samples for the halocarbon, 1,2-dichloroethane, in Baton Rouge samples exhibited similar Pearson and Spearman correlations.

Another factor which is important when computing the regression correlations is the dynamic range of concentrations in the data. For Figures A3-A5, the dynamic ranges were approximately 40, 100, and 100, respectively. However, the range is only 4 for carbon tetrachloride (Fig. 15) and does not lend itself to good correlations, even though the scatter in the data is comparable to the previous Figures (note that the axes in each plot have different scaling factors).

In order to gain more insight into the comparability of replicate field sample analyses, plots of a sample versus its duplicate results were prepared for data over all study areas. Again, only data that were obtained when both replicates yielded measurable values were used for constructing the plots. Figures A7-A13 show log-log plots for carbon tetrachloride, chloroform, 1,2-dichloroethane, trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, and dichlorobenzenes, respectively, in personal air samples. The Pearson and Spearman correlations (r_p and r_s, respectively), number of observations, maximum quantifiable limit, and the 45° line with $\pm$ 25% limits are given on the graphs. The significance of the correlation coefficients

vinylidene chloride, 1,2-dichloroethane, carbon tetrachloride, trichloroethylene, and tetrachloroethylene.

Finally, it is important to note here that relatively few pairs of duplicate and field samples had both values measurable (e.g., for personal air, the sample size ranged from 11 to 20 over sites for the compounds examined). Therefore, only limited analysis was possible on these measurable pairs.

Table A34 presents summary statistics for the coefficients of variation (CV) between the field-duplicate pairs. In particular, a coefficient of variation was computed for each measurable field-duplicate pair as follows.

$$CV = \frac{\sqrt{(F-D)^2/2}}{\frac{F+D}{2}} \times 100$$

where F = field value; D = duplicate value.

The table presents the median, minimum, and maximum CV by compound and medium for the matched pairs of samples. Table A34 indicates overall that the median CV is usually less than 50 percent with the average median over compounds for each medium being water = 32.14%, breath = 32.92%, fixed-site air = 50.79%, and personal air = 26.67%. For the three media--breath, fixed-site air, and personal air--the median CVs for chloroform and 1,2-dichloroethane were somewhat larger than for the other compounds examined. There is no real evidence from the data to support the hypothesis that a particular medium has smaller CVs than another medium although fixed-site air does appear to have somewhat higher CV's.

Pearson and Spearman correlations between duplicate and field samples (measurable values only) were determined for data within and overall study areas (Table A35). Correlations based on less than five measurable pairs were not included in these calculations. Chloroform had relatively low correlations; however, caution must be exercised in the interpretation of these data, since the measurable levels were near or below the maximum quantifiable limit. For this reason, the data were plotted to provide a better perspective of the dynamic range of concentrations which were measured, and the number of observations distributed near the quantifiable limit of the technique.

matched duplicate and field samples were available for analysis. These sample sizes make it very difficult to compute meaningful statistics within each of the study areas.

First, a subset of the compounds under study was selected which had a sufficient number of sample values above the quantifiable limit for meaningful analysis. Then the percent agreement (above and below the quantifiable limit) between the field and duplicate samples was computed for these compounds. These results are given in Table A32 (blood was not included since it had so few measurable values). The table presents over sites the percent of samples where (1) both field and duplicate samples were measurable, (2) both field and duplicate samples were below the quantifiable limit, and (3) the field sample and the duplicate sample did not agree on measurability. The table indicates that in most cases the percent agreement (both measurable or both nonmeasurable) is greater than 80 percent. The largest discrepancies (usually between 20 to 30 percent) occurred for 1,1,1-trichloroethane and carbon tetrachloride in fixed air; chloroform, trichloroethylene, and bromodichloromethane in breath; and carbon tetrachloride and tetrachloroethylene in water.

To further investigate these discrepancies, Table A33 presents a listing comparing the field and duplicate samples when there was a disagreement as to whether or not the compound was measurable. The table gives the field sample value, the duplicate value, and the difference between the two sample values. In addition, the maximum quantifiable limit (MQL) over the three study areas is given to give an indication of how the magnitude of the values compares with this limit. The asterisks in the table indicate cases where one of the samples is greater than twice the MQL and the other sample is not measurable (this may be used to identify the percent of relatively large disagreements between field samples and duplicates). In most cases, the disagreements are relatively minor. The percents of large disagreements for breath across compounds are almost all less than 2 percent; for fixed air, these percentages are usually less than 5 percent. Compounds and media that have a relatively large percentage of large disagreements include breath--chloroform; fixed air--1,1,1-trichloroethane; and personal air--

not available. Thus, laboratory and field blanks were compared to determine whether contamination might have occurred during transportation of samples. As indicated by the results, major contamination of the "blanks" did not appear to occur. (Similarly to reagent water "blanks", blood "blanks" were used to calculate recovery information in spiked control samples.) Data for other study areas were similar to Tables A18 and A19.

Recovery of Halocarbons From Control Samples--

The recoveries of selected halocarbons (those generally yielding measurable values in field samples) from control air and breath Tenax GC® sampling cartridges for the three study areas are given in Tables A20-A23. The data are mean recoveries and percent relative standard deviation for each halocarbon (which represents the entire period from their preparation to analysis). In some cases, the storage period reached 5 weeks. None of the field sample data were corrected for bias, if any.

Tables A24-A26 give representative percent recovery of selected halocarbons from spiked water samples for the three study areas. None of the field sample data were corrected for recoveries.

The results of laboratory and field control data for blood are given in Tables A27-A30. Although the recoveries were acceptable for all three study areas, very few measurable values were found in field samples (see below).

The recovery results for laboratory and field urine controls (urine spiked with volatile halocarbons) from the Greensboro study presented some important questions regarding the methodology for storage, transfer, and purging. Because low and highly variable recoveries were observed, the methodology was considered unsuitable for further use in this program. This problem was traced to the headspace over the urine sample (a situation occurring with the collection method employed) which led to volatility losses during sample processing. For this reason, the collection and analysis of urine for volatile halocarbons were dropped.

Measurement Error--

In this section, an analysis is presented of matching field and duplicate samples collected in the three areas under study. Table A31 presents the number of duplicate samples available for this analysis by media and area. The table indicates that relatively few blood, water, and personal air

measurable levels in field samples, and thus the other halocarbons are not included. Table A13 presents the RMR values for a number of the halocarbons (for which there were measurable values in the samples) that were determined on the CH-7 GC/MS/DS. The mean RMR and the relative standard deviation are indicated for a set of standards prepared by different individuals and analyzed as batches to create the historical data bank. The overall mean RMR which was used in calculating the concentrations in the samples represents the total of 16 replicate determinations.

Stability of Permeation Tubes--

Table A14 presents a historical record of the permeation rates for the halocarbons that were employed in calibrating instruments in this program. The one chemical that was particularly troublesome was chloroprene which had a propensity to polymerize in the permeation tube and thus the permeation rate was very erratic. Evidence of this erratic permeation rate is indicated by the high relative standard deviation of its permeation rate. For the most part, however, permeation rates of halocarbons were acceptable as indicated by their relative standard deviation over time.

Blanks Associated With Sampling Devices--

Representative examples of background observed on Tenax GC® sampling cartridge blanks employed for fixed-site and personal air sampling are shown in Tables A15 and A16. These data were representative of all areas. In general, the background that was observed was very low or nondetectable. Any measurable background on sampling devices from a batch was systematically subtracted when calculating the quantity of halocarbon in the field sample. Thus, all data were corrected for background, if any.

Example results for laboratory "reagent" water field "blanks" are given in Table A17. The preparation of water free of these halocarbons was not sought; however, water for these samples was also used for preparing controls. Thus, these data were used for correcting the measured amounts in laboratory and field controls to calculate percent recoveries. Volatility losses due to transportation and storage were thus monitored in spiked water samples.

Tables A18 and A19 give the results for unspiked laboratory and field blood "blanks". A source of blood that did not contain any halocarbons was

These changes will help reduce ambiguity in questions, collect better, more useful data, and reduce burden by shortening the interview.

QUALITY CONTROL AND QUALITY ASSURANCE

Chemical Analysis

Precision and Accuracy of Preparing RMR Cartridges for Instrument Calibration--

The molar response factors determined by GC/FID for PFB and PFT which were the external standards used in quantification by mass spectrometry are given in Table A1. Cartridges were prepared at various times over approximately a 4-month period. The relative standard deviation was 20.8 and 11.7 for PFB and PFT, respectively. The RMR parameters and values for a number of halocarbons which could be analyzed by GC/FID are also given in Tables A2-A12. These halocarbons were selected also because they were found in measurable amounts (1).

The procedure that was employed to monitor the RMR standards was prone to uncertainties at several points. Uncertainties on analyses and quantification were impossible to truly isolate those associated with the loading of the standards themselves. There are, however, two conclusions one can reach from these results. The first is that with the exception of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane, the relative standard deviation (precision) was <20%. The second conclusion is that compounds loaded by the flash vaporization system had on the whole better precision than those loaded via the permeation system. It should also be noted though that the duration of monitoring of compounds loaded by the flash vaporization system was also shorter. Precision appears to be better over shorter periods of storage time. Nevertheless, the relative standard deviation appeared to be acceptable over the approximately 6-month period that a number of these determinations was made.

The poor precision for 1,1,2,2-tetrachloroethane may have been attributed to fluctuating permeation rates from the tube over the latter 3 months.

Unfortunately, other compounds of interest such as carbon tetrachloride, chloroform, and 1,1,1-trichloroethane either coeluted or appeared as a shoulder and could not be evaluated by this GC/FID study. The halocarbons selected for this study were basically those which were in fact found at

smokers were reported by 65 (43.6%) of the respondents. Other occupational exposure came from 1 painter, 10 chemical plant workers, 3 petroleum plant workers, 1 furniture repairman, 1 plastics worker, and 1 textile mill worker. Hobby-related exposures were reported for 10 painters, 4 furniture restorers, and 30 gardeners in the homes of respondents.

Question Utility

Several items became apparent after reviewing the questionnaire, the interviewer experiences, and the tabulated data. Several questions need further refinement and development if these forms are to be used again in a similar study. As was mentioned in Section 5, the question concerning willingness of eligible respondents to participate should be dropped from the screening questionnaire and would be the only deletion.

While all of the topics covered in the Study Questionnaire remain appropriate, some individual items need to be changed. These are some examples:

A. Employment questions could be refined to reduce apparent redundancies concerning length of employment, student status could be removed from the "not employed" question, and away from home could be redefined in question 9.

B. The smoking questions could be simplified. Since only nonsmokers are eligible for the study, questions 18, 19, and 20 could be combined to ask how long a former smoker did smoke.

C. The dietary questions could be revised to obtain data on food items consumed, e.g., provide the average number of servings for any food item consumed daily from a foodstuff list that reflects FDA food groupings. The dietary questions produced information, in some cases, which was of little value (e.g., meals eaten at home, meals eaten elsewhere). The special diet questions evoked no response for organic or vegetarian diets and these could be removed, with responses being captured under "Other."

D. Water source questions might be revised to determine if any nontap municipal supply water is used at the residence and, if so, for what purpose. Water source information was strongly weighted to the municipal tapwater supply.

working at or in a chemical plant. These were the only reported exposures. Previous smoking (a total of at least 5 packs of cigarettes) was reported by 101 (67.8%) respondents.

The amount of time spent outside each day ranged from 0 to 14 hours with a median of 2 and a mode of 2 hours. Incidental exposure from self-service gas stations was reported by 91 respondents; while 8 respondents had been in a dry cleaning establishment during the past 24 hours, but only 2 did their own dry cleaning. Exposure from hobbies was reported by 8 furniture refinishers, 12 painters, 1 model builder, and 59 gardeners. Contacts with insecticides, pesticides, or herbicides were reported by 53 respondents.

Self-reported levels of health status included 29 excellent, 73 good, 30 fair, and 17 poor. Seventy respondents reported currently taking prescription medications, with 45 different medicines reported. In addition, 49 respondents reported taking a nonprescription medication within the past 48 hours, with 16 different medicines reported. Current doctor's care was reported by 69 (46.3%) of the respondents, with 24 diseases or illnesses reported. Respiratory problems were reported by 49 (33.8%) respondents. The incidence of specific diseases included 19 with anemia, 3 with liver disease, and 18 with kidney disease.

The distribution of frequencies of consumption of food types was relatively uniform. In all cases but one, each reported food item was eaten, by the majority of respondents, more than three times per week, but less often than daily. Only fish differed and was reported, by most people, to be eaten only once per week.

Length of residence in the area ranged from 1 to 63 years with a median of 24 years and a mode of 30 years, while residence at the current address ranged from 1 to 57 years with a median of 15 years and a mode of 10 years.

Drinking water was obtained overwhelmingly from municipal suppliers by 135 (90.6%) of the respondents, from private wells by 8, from and bottled water by 1, and from other unspecified sources by 2. Cooking water was similarly distributed as to source.

Other potential sources of the chemicals under investigation included the activities of other residents of the housing units. Other household

Table 13 (cont'd.)

Data Item	All Sites	Greensboro	east Baton Rouge/Geismar	Southeast Harris County
Other Hobby Exposure:				
Painting	10	3	3	4
Furniture	4	3	1	0
Gardening	30	5	5	20
N of Sample	149	29	75	45

Table 13. SELECTED QUESTIONNAIRE DATA BY SITE

Data Item	All Sites	Greensboro	east Baton Rouge/Geismar	Southeast Harris County
Sex: Male/Female	54/95	8/21	24/46	17/28
Race: Wh/Bk/Hisp.	105/38/2	22/7/0	40/31/0	43/0/2
Age: Median/Mode	33/55	50/47	54/55	52/55
Employed	79	19	37	23
Ever Smoked	101	19	50	32
Average Time Outside: Median/Mode	2/2	2/2	1/2	2/2
Pump Own Gas	91	19	43	29
Hobbies:				
Furniture	8	0	5	3
Painting	12	2	4	6
Model Building	1	0	0	1
Gardening	59	9	26	24
Use of Pesticides, etc.	53	12	25	16
Health Status:				
Excellent	29	6	13	10
Good	73	16	32	25
Fair	30	5	18	7
Poor	17	2	12	3
Current R_x Meds.	70	14	33	23
Under Doctor's Care	69	13	36	20
Years in Area: Median/Mode	24/30	15/10	32/30	22/30
Other Smokers in HU	65	11	35	19
Other Occupational Exposure:				
Painting	1	0	1	0
Chemical/Pet. Plant	13	0	8	5
Plastic	1	0	0	0
Textile	1	1	0	0

(continued)

statisticians worked independently of each other in calculating the analysis weights from census data, original field counts, household screening results, and sample individual response status results. As part of the weight calculations, the execution of the design and all field results were checked, the weights computed, and results compared, with discrepancies resolved by the senior statistician who developed the original design. After this check, the distribution of the weights was examined for excessive variability, which can contribute to unequal weighting effects (see TIPS report, for a comprehensive discussion of this problem, ref. 6). It was necessary to adjust weights in only one stratum, stratum 2, in Houston, Texas. Here the zone weight for three PSU's was truncated (made smaller) and the remaining stratum weights smoothed or adjusted to compensate for the reduction of the largest stratum weight. This is a widely used method to reduce unequal weighting effect. Fortunately, the distributions of weights in the other Texas strata and in the North Carolina and Louisiana sites were within adequate analysis limits without any truncation being necessary.

QUESTIONNAIRE DATA

Demographic Data and Other Questionnaire Items

After all documents from the three sites were received at RTI and processed through the data entry procedure, 149 sets of data were available for analysis. This section discusses the population of respondents in terms of some of the questionnaire data collected. Statistics for the entire population are presented in the text, while Table 13 displays, for selected variables, both the overall data and the individual site data.

The overall population sampled contained 54 (36.2%) males and 95 (63.8%) females and was divided racially into 105 (72.4%) white persons, 38 (26.2%) black persons, and 2 (1.4%) Hispanic persons. The ages of the respondents ranged from 45 to 64 with a median age of 53 and the distribution mode at 55. Employment in any status was claimed by 79 (53%) members of the population, of whom 67 (84.1%) stated that they worked away from the home. Of the remaining unemployed population, 45 (65.2%) were housewives, 4 (5.8%) were unemployed, 11 (15.9%) were retired, and 9 (13.0%) were disabled.

Question 16 asked if the respondents had worked at or in any potential source industries during the previous week. Three respondents reported

SECTION 6

RESULTS AND DISCUSSION

SURVEY DESIGN

The survey design was constructed to maximize information about specific target groups in each site. These groups included employed people between 45 and 64 years of age, who were presumed to have varied exposure to the chemicals under study and to have some potential for bioaccumulation over time from their jobs or residences.

Targeting to these specific age groups, while advantageous in terms of increasing the potential for discovering possible chemical levels in body fluids of sampled individuals, had one major disadvantage from a quality assurance standpoint. It was not possible to check sampling weights in each site by standard quality control procedures. Usually, when the target population is a subsample of the total population of a site, the analysis weights of the sampled individuals sum to the total population of the site, as measured or estimated by national or local census. Since subsampling was done on an age-specific group of employed people in each site, accurate estimates of the total population of that description in each site were difficult to compute. Consequently, the resulting analysis weights could not be checked exactly. Other aspects of the survey design were subject to standard RTI quality control procedures during the design phase and during the interface between statistical sampling and survey operations/field data collection. This included the two-person, independent verification of occupation and age eligibility of screened respondents at each site, double checks of sample individual selection prior to release to field staff, site visitation by a sampling statistician to Baton Rouge and Geismar, the study site with the most challenging physical characteristics, and independent calculation of analysis weights by two statisticians. This last step was the major component of the quality assurance procedure. The two

Relationships between media for selected compounds were then examined by first computing correlations between media. This indicated which media and compounds appeared to have some relationship with each other. In general, Spearman rank correlations were used since the assumption of normality was certainly not met for many of the distributions under investigation.

After examining the correlations, scatter plots between media for compounds which appeared to have some relationship with each other were plotted. These plots are very helpful in determining if a real relationship between media is apparent or a high correlation is simply due to one or two large values. The plots also emphasize the range of the data and may indicate that a low correlation is simply due to the fact that the data have a small range near the quantifiable limit (i.e., the relationship between media for a compound was really not tested in this study because of relatively low levels of the compound).

Finally, two-by-two percent detected tables were computed to indicate whether a particular compound that is detected in one medium was also detected in another media. This type of statistic can be used to answer questions as to whether breath and personal air samples tend to agree on detected or not detected more than breath and fixed air samples.

The maximum quantifiable limit was used so that comparisons between areas or strata within areas could reasonably be compared since the quantifiable limit for each sample varies due to such factors as sampling volume, temperature, etc. More specifically, the sample values available for analysis from each sample respondent were (a) not detected (i.e., below the limit of detection, LOD); (b) trace (i.e., between the LOD and the quantifiable limit, QL); or (c) measurable. To obtain the maximum quantifiable limit for a particular compound and medium, all samples considered to be below the limit of detection (LOD) had their LOD values multiplied by 4 and then the maximum quantifiable limit or 4 × LOD value for the compound and medium were computed over all three areas under investigation. In computing the
percentages, field samples and duplicate samples were first averaged for each individual participant and then this average value was compared with the maximum quantifiable limit. [Note, in computing averages, values below the LOD were set equal to 1/2 (LOD) and values at trace were set equal to 5/8 QL; 5/8 QL is the midpoint between the LOD and the QL.]

After examining the percent detected statistics, it was then possible to drop several of the compounds under study from further analysis since they were not detected or were almost never detected. This reduced the number of compounds to 13. For these 13 compounds, summary statistics by medium and area were then computed (means, standard deviations, medians, and ranges). The median and mean were both computed since the distributions of the compound levels are highly skewed and the sample mean tends to be highly sensitive to a few large values.

In computing both the percent detected and the summary statistics, weighted population estimates are presented (i.e., weighted by the sampling weights since the sample respondents were selected under a probability sampling framework). Thus, for example the percent detected estimates given are estimates of population percentages (i.e., for Greensboro, east Baton Rouge/Geismar, and southeast Harris County, Texas, or for a given stratum within these areas). Recall that the study population in each area comprises persons 45-64 years of age with no occupational exposure during the prior year who have resided in the area for at least 1 year.

The method of calculating RMR was as follows:

$$RMR_{unknown/standard} = \frac{A_{unk}/Moles_{unk}}{A_{std}/Moles_{std}}$$

$$RMR_{unk/std} = \frac{A_{unk}/(g_{unk}/GMW_{unk})}{A_{std}/(g_{std}/GMW_{std})}$$

where A = peak response of a selection ion,
g = number of grams present, and
GMW = gram molecular weight.

The area A was determined by normalizing all peaks at an attenuation of 1.28×10^{-10} and a chart speed of 1 cm/min and then by multiplying the peak height by the peak width (at one-half peak height). Although it is more desirable to determine the RMR of a unknown relative to a standard (PFB or PFT) on the same cartridge, this procedure was not possible using GC/FID since several compounds coeluted with PFB or PFT and it was not possible to distinguish the separate areas with a detector such as FID. Thus, RMR's were determined relative to another cartridge which had only PFB or PFT loaded onto it. When this was not possible for a particular RMR cartridge, the average response factor for PFB and PFT was used for the quantitation.

Calibration of Permeation Tubes--Permeation tubes that were employed for the purpose of calibrating instruments were also themselves calibrated twice weekly when in use by gravimetric procedures. Every 2 weeks, the permeation tubes were weighed and the weight-loss calculated and the mean average of five determinations was derived for calculating the permeation rate.

STATISTICAL METHODS

In summarizing the data from the halocarbon study, several statistical techniques were employed. The first statistic computed was the percent detected by media, compound, area, and stratum within area. In computing this statistic, the percent values over the maximum quantifiable limit (MQL) (defined as the highest limit of quantification across all samples for that compound in a medium) was presented.

GC® cartridge by a permeation system. The RMR values of these standards were calculated and the system tested for acceptability.

Estimates of precision for the GC/MS air, breath, and water analysis were based on a historical RMR (± standard deviation) for each analyte on each analytical system. These reference values were calculated from the analysis of at least seven RMR determinations.

Determination of Loading Precision for GC/MS Calibration Standards--A series of GC/MS calibration standard cartridges (RMR cartridges) prepared over several months was monitored by GC/FID. The purpose of this study was to determine the accuracy and precision for preparing GC/MS calibration standards and to examine the methods of loading the compounds onto these cartridges. The long-range goal of the study was to develop a reference to the precision for RMRs which may be used for future studies involving large quantities of samples to be analyzed by GC/MS.

Calibration cartridges were loaded with halocarbons by one of two methods, permeation of flash evaporation. Permeation of various compounds was effected with permeation tubes with gravimetrically determined permeation rates. The cartridges were then placed on line with these permeation tubes for a known amount of time. Flash evaporization involved the instantaneous vaporization of a known volume of standard methanol spiking solution (2). The vaporized compounds were then flushed onto the cartridge using helium gas.

The PFB and PFT external standards were loaded by injecting a known volume of gas which contained a known concentration of PFB and PFT provided by permeation tubes onto the cartridge.

From each batch of RMR cartridges delivered for analysis by GC/MS, one or two cartridges were analyzed by GC/FID. During the latter portion of the study, a cartridge loaded with external standards perfluorobenzene (PFB) and perfluorotoluene (PFT) were also run on GC/FID for quantitation purposes.

Analyses were performed by thermal desorption with capillary GC/FID. The column was a 60-m WCOT glass capillary coated with SE-30. The cartridges were desored for 8 min. The trapped samples were then injected onto the capillary column (2). The oven program was 30°C for 5 min, 40°C for 5 min, and programmed to 100°C @ 2°C/min and finally to 200°C @ 4°C/min.

previously described protocols (3). After their collection, the blood samples were immediately placed on ice and stored at 4°C until ready for analysis.

Urine Sampling--A 24-h urine void sample was obtained from each participant the morning after the first air monitoring period had been initiated. Urine samples were returned to the central receiving area and immediately chilled and stored until ready for analysis.

Chemical Analysis--

Air/Breath--The determination of halocarbons on Tenax GC® sampling cartridges was carried out by capillary column GC/MS/DS as previously described (2,3). The cartridge containing the components of either an air or breath sample was placed in the desorption chamber and the target compounds thermally desorbed and subsequently introduced onto the GC column.

All Tenax GC® cartridges submitted for analysis were loaded with perfluorobenzene (PFB) and perfluorotoluene (PFT). PFB was used as a reference standard in the calculation of relative molar response (RMR) factors for the GC/MS/DS while PFT was used to assess the tune of the analytical system.

A comprehensive quality control program was instituted during the air, breath, and water analyses.

Column Performance--At the start of each analytical assay Tenax GC® cartridge loaded with selected compounds was analyzed by capillary GC/MS/COMP to define system performance. A measure of column resolution was based on the chromatographic behavior of ethylbenzene/p-xylene. Peak asymmetry factors were determined for 1-octanol, 2-nonanone, and acetophenone. Acceptability criteria were defined for each of the above parameters.

The PFT mass spectrum was scanned and peak intensities at m/z 69, 79, 93, 117, 167, 186, and 236 calculated relative to the base peak at m/z 217. Each ratio was required to fall within a predetermined range (±15 percent).

All of the above information was recorded on report forms and stored as raw analytical data.

The column performance cartridge was utilized for another purpose. Target compounds for which permeation tubes did not exist were added to this cartridge by a flash evaporation technique (2). The GC/MS molar response of these standards was referenced to PFB and the system tested for acceptable performance. The remaining target compounds were loaded onto a second Tenax

participant burden (Fig. 6). The pump was calibrated with a bubble meter before and after the collection period and the average flow used in calculating the sample volume. Stationary (fixed-site) air samplers were placed outside one home in each primary sampling unit to provide an estimate of ambient pollutant levels for that primary sampling unit.

Water Sampling--The water which the participant used for drinking and cooking was sampled at two different times during the day, early morning and late afternoon.

A narrow mouth, clear, 250-mL glass bottle was used for sample collection. The bottles were precleaned and the action of chlorine was prevented by adding 100 μL of a 5% sodium thiosulfate solution. The sample was collected from a cold water tap after allowing the water to run at a moderate rate for 30 seconds. The bottle was filled to capacity such that closure with a Teflon-lined screw cap produced no headspace. The sample bottle was immediately placed in a cooler and returned to the central workroom and stored in a 4°-7°C refrigerator.

Breath Sampling--Breath samples from each participant were obtained at the end of the second air collection period.

The samples were collected by means of a spirometer. A bubbler filled with distilled/deionized water was used to humidify the air before filling the Tedlar® inhale bag for breathing. The participant was seated in front of the device and asked to breathe normally through the spirometer mouthpiece. In this manner, the inhale bag air was inspired and exhaled into the breath collection bag. To prevent inhalation of ambient air, the participant was asked to wear a noseclip during this period. When the breath collection was finished, the contents of the exhaled bag were split between two Tenax GC® sampling cartridges using calibrated (flow rate and total volume register) Nutech model 221 pumps. In cases where a single breath sample was scheduled for collection, only one precleaned Tenax GC® sampling cartridge was placed in the manifold assembly. Two cartridges were positioned in the manifold when the duplicate sample collections were scheduled (3).

Blood Sampling--Samples of blood for the analysis of volatiles and the CEA assay were collected from the participants at the end of the second collection period. Two individual samples were collected according to the

Date (Initial)_____

Sample Code _____

Volume/cartridge ____L

Point Sources:

0 No Pt. Source
1 Strongly Upwind
2 Weakly Upwind
3 Weakly Downwind
4 Strongly Downwind
5 Crosswind
6 Variable/Inteterminate

Study No: (_ _ _ _ _ _) Site: (_ _)
Sample: (_ _ _ _ _ _) Trip: (_ _)

AIR SAMPLING

Model _____ Serial No.: _____ Fixed _____
Personal _____
HiVol _____

Time (initial) _____ (final)_____

Flow Rate (initial)_____ (final)_____ (Avg.) _____

Counts (initial) _____ (final)_____ Calibration _____

METEOROLOGICAL DATA

Time (initial)_____ (final):_____

Temp. (initial)_____ (final):_____

Relative Hum. (Initial)_____ (final):_____

Wet _____ Dry _____ Wet _____ Dry _____

Wind Dir/Speed (initial)____/____ (final):_____

Odor (initial)_____ (final):_____

BREATH SAMPLING

Time:_____ Temp._____°F

Meter Reading (initial)_____ (final):_____

Total Volume _____(liters) (28.3 liters = 1 cubic foot)

Duration of Exhalation_____

Rate of Exhalation _____

WATER, BLOOD, URINE, TISSUE, AND SOIL SAMPLING

Time:_____

Amount Collected _____

Water Source: Well_____ City _____ Other (specify)_____

Soil Conditions: Wet_____ Dry _____

Vegetation: (heavy)_____ (light)_____ (none)_____

Point Source Water Runoff:

Remarks:_____

_____

_____

Figure 9. 1568 Field Sampling Protocol Sheet - HHC study.

(Fig. 9) which was needed to compute levels of halocarbon, in particular. In some cases, a descriptive nature of the sample was recorded (Appendix A).

Sampling Quality Control--

After the collection of approximately every tenth sample, a field blank and control were exposed to the sampling conditions at the site. These quality control materials were prepared at RTI. The field blanks (deionized water or precleaned Tenax cartridge) were designed to identify contamination situations, and the field controls (known amounts of target compounds or precleaned Tenax® or in deionized water) were intended to provide an estimate of analyte losses during the sampling operation. The field blanks/controls were transported to and from the site with the sampling containers/cartridges and according to a predetermined schedule. One blank and control (a QC set) were taken to the sampling location and returned to the sample storage area (-20°C).

The source and fate of every sample whether collected at the site or used as a field blank/control were documented on a chain-of-custody sheet (Fig. A1). This form (or a copy) accompanied the sample until analysis and data reduction were completed. Breath and air volumes which were recorded on the reverse side of this sheet were checked for accuracy by coworkers in the field (Fig. A2).

To eliminate subjective judgments on the part of the sample collector, the sampling schedule specified when quality control samples were to be exposed and when a duplicate was to be collected.

Sample Collection--

Sample collection was carried out by personnel working in teams of two. The more experienced individual was designated as the team leader. One team leader was assigned the position of site administrator. He/she was responsible for maintaining a liaison with the field interviewer staff, coordinating sampling assignments with other teams, sample shipment to RTI, and overall performance at the sampling site.

Air Sampling--Personal air collections were sampled over two 11-12 h periods, early evening to the next morning, and then to later that afternoon.

The air samples were collected on Tenax GC® cartridges. Personal monitoring pumps drawing 30-35 mL/min were used to pass a total of ~20-25 ℓ of air through the sampling device. The pump was placed in a vest designed to minimize

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SAMPLE CODE:	Sample Type:	Volume Collected:
	No. of Containers:	Volume Analyzed:

Relinquished By:	Received By:	Time	Date	Operation Performed (aliquot, std. conc., remarks, etc.)

Figure 8. Chain of Custody record.

Table 12. QUALITY CONTROL SAMPLES

Matrix	Compound Class	Control and Blanks Matrix	Volume, mL	Amount of Each Std. Loaded (ng/sample)
Air	Volatiles	Tenax	-	100-600
Water	Volatiles	Distilled water	100	100-600
Breath	Volatiles	Tenax	-	100-600
Blood	Volatiles	Distilled water	10	100-600
Urine	Volatiles	Distilled water	25	100-600

Table 11. QUALITY CONTROL/QUALITY ASSURANCE

- Tenax GC® Cartridges and Water Sampling Containers
  - * laboratory blanks
  - * field blanks
  - * laboratory controls (spiked with target halocarbons)
  - * field controls (spiked with target halocarbons)
- Replicate Samples
- Audit of Sampling and Analytical Systems
  - * pump flow rates
  - * battery charge
  - * GC/MS performance specifications and control charts

QUALITY CONTROL AND QUALITY ASSURANCE PROCEDURES

Chemical Sampling and Analysis

Introduction to Overall Strategy--

A quality control and assurance program (QC/QA) was maintained for the sampling and analysis procedures employed in this program. Table 11 gives the major categories of the QC/QA program. For Tenax GC® sampling cartridges (ambient air and breath) and water samples, laboratory and field cartridge blanks were maintained. The Tenax GC® sampling cartridges were selected from a batch preparation (∿30-50) of cartridges to demonstrate the potential background, if any, that might develop during the period of sampling and analysis. Field blanks were sampling cartridges and drinking water containers which were transported to the field and returned to the laboratory unused, while laboratory blanks were stored during the entire period prior to sample analysis. Thus, some indication of the potential for sample contamination which might occur for a batch of sampling devices and/or from the influence of transportation was assessed.

Laboratory and field controls were also incorporated into the analytical scheme for each batch of Tenax GC® cartridges and water sampling containers used. Controls were sampling devices spiked with a list of target halocarbons. A listing of the matrices, compound classes, and the amounts of each of the standards loaded as quality control samples are given in Table 12. Quality control samples prepared as indicated above were used during field sampling at all three geographical areas.

Replicate samples for air, breath, drinking water, blood, and urine were collected to represent a minimum of 10 percent of the total samples.

Each sampling train for air and breath was internally audited before, during, and after a participant in each geographical area. Flow rates were checked with a bubble meter to record the proper rates attained. Battery charge was verified on personal samplers to insure that the flow rates were maintained throughout the entire sampling period. Recharging was instituted after each sampling period.

A chain-of-custody record (see Fig. 8 and Appendix B for examples of each matrix) was maintained for each sample, blank, and control throughout the period of sampling and analysis. Information on each sample was also maintained

Table 10. SAMPLES COLLECTED, ANALYZED, AND COMPLETENESS FOR HARRIS COUNTY, TX, STUDY AREA (NUMBER OF PARTICIPANTS = 45)[a]

	VF	VP	BR	BH	WH
Samples Collected (F)	23	87	44	44	45
Duplicates Collected (D)	9	8	5	5	5
Field Blanks (FB)	5	8	5	5	5
Field Controls (FC)	5	8	5	5	5
Lab Blanks (LB)	5	8	5	5	5
Lab Controls (LC)	5	8	5	5	5
Total Samples	52	127	94	72	69
Total Analyzed	52	115	94	72	69
Percent Completeness	100	90	100	100	100

[a]VF = fixed-site air, VP = personal air, BR = breath, BH = blood, WH = water.

Table 9. SAMPLES COLLECTED, ANALYZED, AND COMPLETENESS FOR BATON ROUGE/GEISMAR, LA, STUDY AREA (NUMBER OF PARTICIPANTS = 75)[a]

	VF	VP	BR	BH	WH
Samples Collected (F)	84	150	74	74	75
Duplicates Collected (D)	16	22	74	9	7
Field Blanks (FB)	8	8	13	8	8
Field Controls (FC)	8	8	13	8	8
Lab Blanks (LB)	8	8	13	8	8
Lab Controls (LC)	8	8	13	8	7
Total Samples	132	204	200	115	113
Total Analyzed	132	204	200	111	113
Percent Completeness	100	100	100	96	100

[a]VF = fixed-site air, VP = personal air, BR = breath, BH = blood, WH = water.