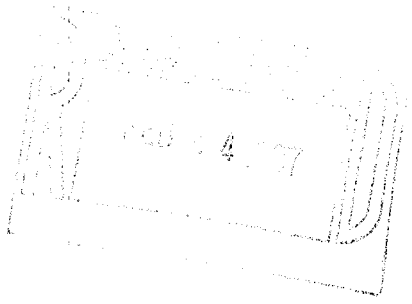
# LOVE CANAL EMERGENCY DECLARATION AREA HABITABILITY STUDY NIAGARA FALLS, NEW YORK
**EPA REGION II**

# PILOT STUDY FOR LOVE CANAL EDA HABITABILITY STUDY VOLUME I



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February 1987

# PREFACE

This report is Volume I of a two-volume series. Volume I describes the basis for and results of the air and soil pilot studies conducted pursuant to planning the full-scale Love Canal habitability study, and recommends an approach for the conduct of the air aspects of the habitability study. Volume II presents the sampling design proposed for the soil aspects of the habitability study.

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# 1.0 INTRODUCTION

The New York State Department of Health (DOH) and the United States Department of Health and Human Services/Centers for Disease Control (DHHS/CDC) have proposed criteria for determining whether or not the Love Canal Emergency Declaration Area (EDA) is now habitable. The habitability criteria report (DOH/CDC, December 1986) recommended that pilot studies involving air and soil sampling be conducted before a full-scale habitability study is undertaken.

This document is a report of the recommended air and soil sampling pilot studies. It is in two volumes: Volume I describes the basis for and results of the air and soil pilot studies; Volume II (under separate cover) presents the sampling design proposed for the full-scale habitability study.

Section 1.1 below reviews the history of contamination and remediation efforts at the Love Canal site. Section 1.2 reviews development of the habitability criteria. Section 1.3 sets out the objectives and scope of the pilot studies.

Section 2.0 discusses the goals, statistical design, sampling and analytical methods, and results of both the air and soil pilot studies. Section 3.0 presents the conclusions and recommendations of the pilot studies.

The appendixes contain the technical discussions and bases for the information presented in the main body of the report. Appendixes A and B present detailed discussions of the sampling and analytical methods used in the air and soil pilot studies, respectively. Appendix C describes the approach to and results of the review and validation of the soil laboratory data results. Appendix D contains the soil chemistry laboratory audit report prepared by the EPA Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (EMSL-LV). Appendix E develops a "method detection limit" for the chemical protocol developed for the soil Love Canal indicator chemicals (LCICs).

## 1.1 BACKGROUND

Most of the following history of the Love Canal hazardous waste site is a condensed version of Appendix I of Love Canal Emergency Declaration Area Proposed Habitability Criteria (DOH/CDC, December 1986) (the habitability criteria report).

The former Love Canal landfill is a rectangular, 16-acre tract of land located in the southeast end of the City of Niagara Falls in Niagara County on the western edge of New York State (see Figure 1). The landfill takes its name from William T. Love, whose plan in the 1890s was to dig a power canal between the upper and lower Niagara River to provide cheap hydroelectric power for a proposed model industrial city. The model city project and the partially dug canal were abandoned before the turn of the century.

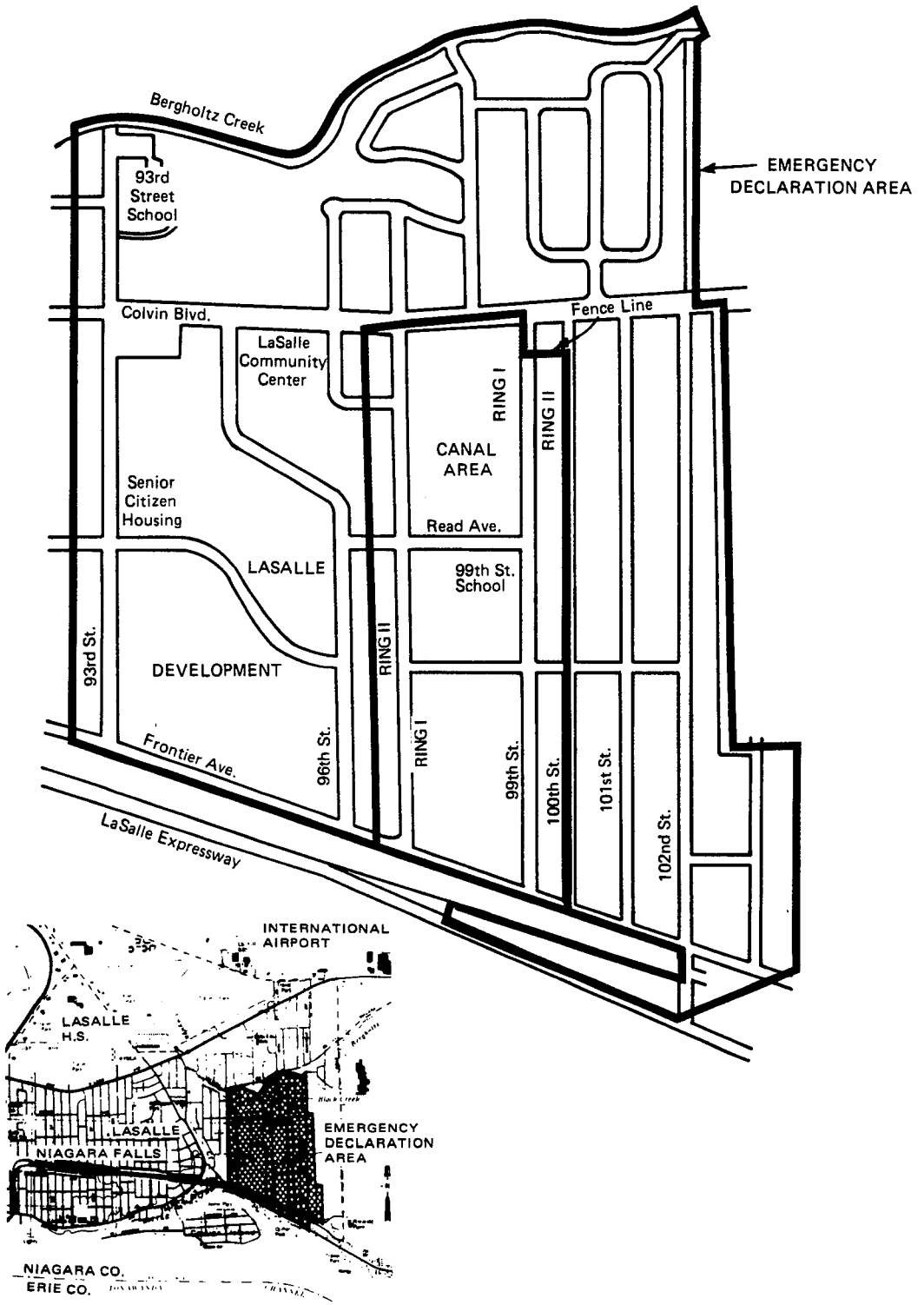
Aerial photography from 1938 depicts the canal as being about 3,000 feet long and almost 100 feet wide, extending in a north-south axis, with the southern end approximately 1,500 feet from the Niagara River. Much of the canal bed contained impounded water and there was no visible evidence of waste disposal. The Hooker Electric Chemical Company, now the Occidental Chemical Corporation, admitted to dumping at least 21,800 tons of chemical wastes in the canal between 1942 and 1953. These wastes, some drummed, some not, included chlorinated hydrocarbon residues, processed sludges, fly ash, and other materials. The City of Niagara Falls also used the site for disposal of municipal wastes for a number of years until 1953.

In 1953, the site was sold by Hooker to the Board of Education of the City of Niagara Falls. Beginning in 1950, home building accelerated along the streets adjacent to the canal and the existing residential neighborhood grew (several homes had been built in the 1930s and '40s). In 1954, a public elementary school was built on the middle third of the Love Canal property (see Figure 1).

During the years that followed, chemical odors from the landfill were cited by residents in complaints to local officials. There were also persistent reports of chemicals breaking through the topsoil, spontaneous fires, and children and pets injured by chemicals while playing at the canal site. As early as the mid-1970s, it became increasingly apparent that rainwater and melting snow had seeped into the canal and had forced waste chemicals to the surface of the site, contributing to the lateral spread of chemicals into yards and basements of adjoining homes.

In 1977, DOH analyses of sump samples and U.S. Environmental Protection Agency (EPA) analyses of air samples taken from several homes abutting the canal revealed significant contamination. In April 1978, the DOH declared the area a threat to human health and welfare and ordered that access to the landfill site be restricted.

During the spring and summer of 1978, a remedial action plan was developed, environmental sampling and analyses continued, and epidemiological studies were initiated. On




Adapted from: Environmental Monitoring at Love Canal, Volume III.

Figure 1
**LOVE CANAL STUDY AREA**

August 2, 1978, DOH declared a state of emergency at Love Canal and issued a second order recommending relocation of pregnant women and children under age two residing in dwellings adjacent to the canal, as well as closure of the 99th Street School. On August 3, 1978, the Governor of New York directed the formation of an interagency Love Canal Task Force to relocate affected families, construct a drainage system to prevent further migration of toxic chemical waste from the landfill, and continue environmental testing and toxicological and epidemiological studies.

In August 1978, the President of the United States declared an emergency and authorized actions necessary to protect human health and property at Love Canal. The Governor expanded the State's relocation effort, authorizing permanent evacuation of all persons in homes in Rings I and II immediately adjacent to the canal (see Figure 1). During the same period, plans were finalized to contain the migration of chemicals from the canal site, and environmental testing and epidemiological studies continued. In February 1979, DOH issued a supplemental order recommending temporary relocation of all pregnant women and children under age two residing between 97th Street and 103rd Street and from Frontier Avenue North to Colvin Boulevard. The Governor modified the order to apply to entire families with pregnant women or young children and to include residents of the LaSalle Development west of the Love Canal. In June 1979, the State Supreme Court ordered temporary relocation at State expense for area residents who claimed to be suffering illness or breathing difficulties associated with site remediation work.

By mid-October 1979, three relocation programs were in progress at the Love Canal, with the following status:

- Permanent Relocation Program for Rings I and II: Of the 239 families eligible, 237 closings on property parcels had been completed.

- Temporary Relocation Program for Families with Pregnant Women or Young Children: Of the 49 eligible families, 33 sought and had been placed in apartments or other longer term housing.

- Temporary Relocation Based on Illness Associated with Remedial Construction Work: 91 families were being maintained in temporary accommodations.

On November 5, 1979, the last of the deep excavations at the construction site was completed and the temporary relocation program ordered by the State Supreme Court was terminated.

Although increased levels of chemicals related to the canal site were detected on the site itself, in storm sewers and

creeks draining the area, and in certain homes in the first two rings, no official report was issued documenting either the extent of chemical migration or the probability of health risk attendant upon it. The decision to relocate residents from Rings I and II has been characterized as a pragmatic one, based on limited data demonstrating beyond any reasonable doubt that toxic chemical waste products had been identified in and/or on the property of some specific homeowners living adjacent to the canal. These findings and the reactions of homeowners to it suggested the relocation of all residents living on the streets immediately surrounding the canal as the most prudent course of action.

On May 17, 1980, results of an EPA study were released showing that some residents of the Love Canal area may have suffered chromosome damage from exposure to toxic chemicals buried at the landfill. On May 21, 1980, then-Governor Carey requested President Carter to declare an emergency in the Love Canal area. On May 22, President Carter declared a Federal Emergency in the area and offered federal funds for temporary relocation. In June, the Governor requested further federal assistance for the purchase of Love Canal homes. The resulting Emergency Declaration Area (EDA) established by the New York State Legislature included the neighborhoods adjacent to and surrounding the inactive landfill site, but did not include the canal itself nor the area formerly occupied by the two rows of demolished homes immediately east and west of the site. In July, Congress approved emergency appropriations resulting in a $7.5 million federal grant in October and a $7.5 million advance to New York State for the acquisition of Love Canal properties. To date, approximately 480 of the 550 eligible EDA homes have been purchased by the Love Canal Area Revitalization Agency (LCARA), which was established by an act of the state legislature to revitalize and stabilize the EDA.

In the summer of 1982, the EPA released an assessment of the extent of contamination of air, water, and soil in the EDA as a basis for forming recommendations regarding future use of the area (USEPA, May 1982). Later, the Department of Health and Human Services/Centers for Disease Control (DHHS/CDC) became responsible for deciding, on the basis of the EPA study and other data, whether the EDA was habitable. In July, after considering comments by the National Bureau of Standards on the procedures the EPA used, and after further consultation with the EPA, DHHS/CDC affirmed its earlier provisional decision that the EDA was as habitable as the control areas to which it was compared. This decision was contingent on the provision that the storm sewers and their drainage tracts be cleaned and that special plans be made to perpetually safeguard against future leakage from the canal.

In December 1982, the Congressional Office of Technology Assessment (OTA) was requested to examine the technical basis for and validity of the habitability decision for the EDA and to evaluate the current and planned Love Canal monitoring and cleanup activities directed by the New York State Department of Environmental Conservation (DEC), which included a drain around the canal, a clay cap, and a leachate treatment plant. In June 1983, the OTA reported that, with the information available, it was not possible to conclude whether or not unsafe levels of toxic contamination existed in the EDA, and that the analysis of available data did not support the DHHS/CDC decision that the EDA was as habitable as the control areas with which it was compared. The OTA had three major criticisms of the study:

- The 1982 study was not designed for a comparison approach; therefore, the choice of a comparison area was not necessarily appropriate nor were sufficient samples obtained from the comparison area to conduct a comparison.

- The number of samples with nondetectable concentrations made a statistical comparison of the EDA with a background comparison area difficult.

- Ambiguity in the detection limits for nondetectable concentrations made assessment of public health implications impossible.

OTA pointed out that one of the major shortcomings of the 1982 study on habitability was that specific criteria for determining habitability were not developed prior to implementing the study (OTA, 1983). Consequently, OTA indicated the need to demonstrate more unequivocally that the EDA was safe both immediately and over the long-term; otherwise it might be necessary, OTA suggested, to accept the original presumption that the area is not habitable.

In August 1983, in response to the OTA report, the EPA established a Technical Review Committee (TRC) composed of the EPA, DHHS/CDC, DOH, and DEC to provide coordination and oversight of the habitability and remedial programs at Love Canal. The member agencies of the TRC asked DHHS/CDC and DOH to develop criteria that would be considered by the New York State Commissioner of Health in his determination of whether or not the EDA is habitable.

The two health agencies selected ten scientists to advise the TRC on the EDA habitability criteria. These scientists met seven times over a 2-year period in a public forum to discuss what they felt were appropriate criteria to determine the habitability of the EDA. The advice of the scientists became the cornerstone of the habitability criteria

document (DOH/CDC, December 1986). This document also reflects concerns and advice presented by an independent group of peer review scientists (ICAIR, 1986) and the public. The peer review scientists met in Niagara Falls in March 1986 to critique the document in an open public forum. Section 1.2 below further describes the habitability criteria and study.

Meanwhile, additional remedial efforts at Love Canal have included plugging and abandonment of sewers within Rings I and II immediately adjacent to the site, repairs to the leachate collection system, construction of an improved and expanded cap, including installation of a synthetic membrane, and cleaning of 65,000 linear feet of storm and sanitary sewers in the EDA.

More recent and ongoing efforts include continued remediation of area sewers and creeks, construction of a remedial program administration building, study and design of an aboveground interim containment facility for the storage of sediments to be removed from the creeks and for the hazardous wastes generated by some of the site's other remedial programs, testing of a mobile plasma arc unit to destroy the liquid wastes from the leachate treatment unit that are stored onsite, and design and installation of a long-term groundwater monitoring and perimeter survey.

## 1.2 HABITABILITY CRITERIA AND STUDY

The habitability criteria formed the basis of the pilot study design described in Section 2 of this report. The purpose of the habitability criteria is to

> ...yield information necessary to answer this question: Does the Love Canal hazardous waste disposal site (in its present state of remediation and with the guarantees of EPA and NYSDEC for continuous monitoring and containment) have a measurable impact on the environment of the Emergency Declaration Area (EDA) which in the judgment of the New York State Commissioner of Health renders the entire Emergency Declaration Area or neighborhoods in the EDA not habitable from a public health standpoint? This document recommends additional environmental testing to determine whether differences in frequency of occurrence and/or levels of Love Canal Indicator Chemicals (LCIC) can be demonstrated in soils, ambient air, and indoor air between neighborhoods in the EDA and comparison neighborhoods. The comparison neighborhoods must be like the EDA except that the comparison neighborhoods must not be impacted by a hazardous waste disposal site. Additional testing of

> residential soil in the EDA is also to be conducted to determine whether the 1 part per billion level of concern for TCDD (2,3,7,8 tetrachlorodibenzo-p-dioxin)[a] is exceeded. (DOH/CDC, December, 1986, p. 3)

The present report addresses the recommended soil and air comparisons. The dioxin-related habitability criteria are addressed in a separate study (USEPA, November 3, 1986). The habitability criteria require that the air in each residence in the EDA be sampled for certain airborne LCICs, which were selected based on criteria described in Appendix 9 of the draft habitability criteria document. The chosen airborne LCICs are chlorobenzene, 2-chlorotoluene, and 4-chlorotoluene. They are intended to represent chemicals that could be found in indoor air, originate from the Love Canal, and are not common household contaminants. The concentrations of these chemicals in occupied EDA residences will be compared to concentrations of the LCICs in indoor air of the comparison area homes. Any occupied EDA residences that are found to have LCIC concentrations significantly greater than the chosen aggregate concentration of the LCICs in the comparison areas will be retested and, if appropriate, remediated. The concentrations of LCICs in unoccupied EDA residences will be compared to EDA ambient air LCIC concentrations. Unoccupied EDA residences with air LCIC concentrations significantly greater than the chosen aggregate LCIC concentration of the EDA ambient air will be retested and, if appropriate, remediated.

The soil comparisons are intended to determine whether or not the entire EDA or neighborhoods of the EDA have soil LCIC concentrations that are significantly different from those of the comparison areas. The soil LCICs also were chosen based on criteria given in Appendix 9 of the draft habitability criteria document and are intended to represent chemicals that, if found in the EDA soils, could have originated from Love Canal. These LCICs were selected to be non-ubiquitous. The selected soil LCICs are chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, 2-chloronaphthalene, beta-BHC (B-BHC) and gamma-BHC (G-BHC).

The habitability criteria further state that the design of the soil comparison study should be based on detecting an order-of-magnitude difference between the EDA and the comparison areas for each LCIC, with a 5 percent overall significance for all comparisons and 90 percent power. These comparisons are to take into account individual (univariate)

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[a]Also known as dioxin.

and collective (multivariate) properties of LCICs. Variations in the reliability of data with changing concentrations should be considered in the comparisons.

A two-part pilot study of soil and air in the EDA and comparison areas was conducted to obtain information needed to implement the habitability criteria. The soil pilot study is complete and is described in this report. The air pilot study consists in turn of two phases, a field-intensive phase and a time-variant phase. The field-intensive phase is complete and is discussed in this report, while the time-variant phase is ongoing.

To date, the following steps have been accomplished in implementing the habitability criteria.

- The comparison areas have been selected by the DOH and consist of neighborhoods in Tonawanda, located north of Buffalo, and Cheektowaga, located near the Buffalo airport.
- 65,000 linear feet of sewers in the EDA have been cleaned under the remedial program.
- The habitability criteria document has successfully undergone a formal peer review.
- The pilot study, which is the subject of this report, has been completed for soil and is partially completed for air.
- The sampling of EDA soils for dioxin is 75 percent complete and the samples are undergoing chemical analysis.

## 1.3 OBJECTIVES AND SCOPE OF PILOT STUDY

In general, the Love Canal air and soil pilot studies were conducted to demonstrate the feasibility of implementing the habitability criteria as proposed. Specific objectives were to:

- Test the sampling and analytical methods proposed for the full habitability study
- Provide preliminary data on the levels and statistical distribution of indicator contaminant concentrations
- Provide a basis for determining the number of samples that need to be taken to produce statistically valid results in the full-scale habitability study

This volume discusses the results of the air and soil pilot studies and recommends an approach for the conduct of the air portion of the habitability study. The second volume presents the design considerations for the soil comparison portion of the habitability study.

# 2.0 PILOT SAMPLING AND ANALYSIS PROGRAM

This section provides a summary of the goals, statistical design, sampling and analytical methods, and results of the air and soil pilot studies.

## 2.1 GOALS

### 2.1.1 AIR PILOT STUDY GOALS

The overall goals of the air pilot study are to reduce the uncertainties and assumptions involved in the collection and analysis of air samples, and to obtain information on the characteristics of the data that are likely to be collected during the habitability study. This information will be used to conduct the air sampling portion of the full habitability study as required by the habitability criteria document.

The air sampling program for the pilot study consists of two parts, the field intensive study and the time variant study. The field intensive study is a relatively short-term sampling program that assumes that the variability of chlorobenzene, 2-chlorotoluene, and 4-chlorotoluene, the three LCICs selected for study, will be small during the short time period in which the sampling is conducted. The time variant study is intended to reveal the variations of LCICs over a longer period of time. The field intensive part of the program has been conducted and will be the main subject of this report.

The field intensive study was designed to provide information on the percentage and level of detects of LCICs in the EDA, and if airborne LCICs are present, whether the canal is contributing to them. A mobile mass spectrometer, the trace atmospheric gas analyzer (TAGA), was also tested during the field intensive study to determine its future role as a field instrument for sample analysis.

Specific objectives of the field intensive study are to collect adequate information on the:

- Expected levels of LCICs in the indoor and outdoor air of the EDA and comparison areas
- Expected frequency of detectable levels of LCICs in the air of the EDA and comparison areas
- Performance and potential role of the TAGA in future field applications

- Contribution of the canal to detected LCIC levels through air emission, if LCICs are present in the outdoor atmosphere

The air pilot study is also intended to test three major hypotheses:

- That the presence of detectable levels of airborne LCICs is specific to the site, rather than ubiquitous, and that such presence indicates contamination from Love Canal

- That the methods and techniques used for sampling and analysis are appropriate

- That sufficient numbers of comparison area homeowners will agree to sampling to allow the habitability criteria to be implemented

Appendix A contains additional information on the air pilot study goals.

### 2.1.2 SOIL PILOT STUDY GOALS

The overall objective of the analytical phase of the soil pilot study was to determine what levels of selected volatile and semivolatile LCICs in soil can be detected in the EDA and comparison areas. The concentrations of LCICs that can be detected reliably are more than 100 times lower than those detected in previous efforts in the EDA.

The specific analytical objectives of the soil pilot study included:

- Test specially developed soil sampling and sample preparation techniques to determine if these methods affect analytical results.

- Develop and evaluate a new analytical procedure for measuring low-level (i.e., 1 to 10 ug/kg) concentrations of selected volatile and semivolatile LCICs.

- Generate information on the distribution of concentrations of selected volatile and semivolatile LCICs found in the EDA and comparison areas.

- Generate information on the sources of intralaboratory and interlaboratory variability in the analytical data.

- Develop methods for estimating LCIC detection limits for the GC/MS/SIM analytical method.

The data resulting from this sampling and analysis activity are being used in the design and preparation of the sample collection and analysis plan for performing the soil part of the full-scale habitability study. Appendix B discusses the soil pilot study goals in further detail.

## 2.2 DESIGN

### 2.2.1 AIR PILOT STUDY DESIGN

In the 1980 study, approximately 90 percent of air measurements resulted in nondetectable concentrations of LCICs. The analytical techniques used for the air pilot study were considerably more precise than the earlier techniques, but they were not more sensitive; therefore, the same percentage of nondetectable concentrations was expected in the air sampling for the pilot study.

Assuming this percentage of nondetects and assuming the categories of detect/nondetect are binomially distributed, it can be calculated that approximately 90 percent of any group of 30 samples can be expected to have at least one detectable concentration. Therefore, the target sample size was set at 30 houses in each of the EDA occupied, EDA unoccupied, and comparison area occupied strata. Ambient air was monitored at each area during sampling of selected houses.

The TAGA was used in the field for initial analysis of samples. The precision of the TAGA was evaluated using duplicate analysis of field samples and the check samples sent by the EPA Environmental Monitoring Systems Laboratory at Research Triangle Park (EMSL-RTP). The accuracy of the TAGA was estimated by comparing the analyses done by the TAGA and Battelle laboratory in Columbus, Ohio (Battelle-Columbus), on the same check samples.

All the air samples taken during the field study were analyzed for LCICs by the TAGA. Since a large number of nondetect samples was expected, 10 percent of the samples with nondetectable LCIC concentrations were sent to the Battelle-Columbus GC/MS laboratory for confirmatory analysis. In addition, all detectable concentrations, duplicate pairs, check samples, and blank samples were sent to the laboratory for analysis after screening analysis in the field by the TAGA.

### 2.2.2 SOIL PILOT STUDY DESIGN

The soil sampling plan was designed to estimate the sources of variability in the LCIC concentration values and to estimate the statistical distribution of these values. These estimates are needed to aid in the design of the sampling

plan for the full-scale habitability study, which will be discussed in Volume II.

The importance of knowing the source and magnitude of variability in the data stems from the influence variability has on the sample sizes required for the habitability study. The more variable the data is, the more uncertain are the estimates of the statistics derived from the data. Clearly, then, to obtain an uncertainty in the estimate of a mean no greater than a desired level (for example, to compare the mean of the EDA concentrations of an LCIC with the mean of concentrations from the comparison area) more samples will be needed as the variability increases. The variability of concentration estimates can be reduced if its sources can be identified and controlled.

Three sources of variability were thought to be important in the concentration estimates: spatial, interlaboratory, and intralaboratory. The main sampling scheme was to carefully randomize both the location of each sample within an area and the other factors, such as order of collection, that might influence the results obtained. Each lab received equal numbers of samples from each area from each day of sampling. An analysis of variance was to be used with this scheme to estimate the magnitude of the three variability components.

Within this main sampling scheme an additional sampling scheme was included. The second scheme was to split all samples so that an additional estimate of intra- and interlaboratory variability could be obtained independent of spatial variability. For one-third of the split samples, both splits of each sample went to the same laboratory, while for the remaining two-thirds of the split samples, the two splits of each sample went to two different laboratories.

Estimates of the variability obtained from the 1980 EPA study led to 45 samples being taken from both the EDA and the comparison areas.

Inherent in the overall design of the soil sampling study was testing of a new analytical protocol designed to lower the detection limits of the LCICs by a factor of 100 from the 1982 EPA study. A special study was conducted to determine the method detection limit.

## 2.3 METHODS

### 2.3.1 AIR PILOT STUDY METHODS

#### Sample Collection

The air sampling protocol assigned a sequence of sites to the sampling teams. An ambient site was assigned between every two indoor sites so that the ambient sample would be equally representative of the ambient conditions for both indoor samples.

The designated indoor location for sampling was at the bottom of a basement stairway. For homes without a basement, the sample was taken in the living room at the corner closest to the middle of the entire house. Ambient outdoor samples were always taken at a predetermined location.

All air samples were collected in SUMMA polished 6-liter stainless steel canisters equipped with a needle valve for controlling the air flow. Each canister was fitted with a stainless steel, fixed frit particle filter at the inlet end to keep particles from clogging the sampling flow.

The canisters were kept at high vacuum with the valves tightly closed prior to sample collection. Sample air was drawn into the canister by the vacuum inside when the valve was open. The canisters were open for 2 or more minutes, sufficient time to allow filling to atmospheric pressure.

In addition to collecting samples, each two-member sampling team was required to complete a field notebook, sampling activity log, and, for indoor samples, a resident questionnaire. Each team returned the canister and associated documentation to a canister control center.

The holding time of collected samples in the canisters was kept to a minimum. During the pilot study, the samples were sent within 24 hours from the field to the laboratory, where they were all analyzed within 12 days from the time they were collected.

Appendix A presents more information on the air sampling methods used in the field intensive part of the air pilot study.

#### Sample Analysis

All collected samples as well as the quality assurance samples (duplicates, controls, and blanks) and check samples were analyzed in the field for LCICs with a mobile mass spectrometer (TAGA). All samples determined by the TAGA as detect were sent to the laboratory. All duplicate sample

pairs and blanks were also sent to the laboratory after field analysis. Since all duplicate samples were randomly selected on a daily basis during the field sampling period, and they were all nondetect as determined by the TAGA, the duplicate sample in each of the pairs also represented the control sample sent to the laboratory for the confirmation of nondetect results obtained in the field.

The field analytical instrument was the TAGA Model 6000E by Sciex, a mobile mass spectrometer (MS/MS) unit capable of performing quick analysis of air samples in the field with low ppb level of detection limits. Because it lacks a gas chromatographic unit, the TAGA cannot distinguish individual isomers, particularly 2-chlorotoluene and 4-chlorotoluene, and can only report the total concentration of the isomers. A description of TAGA's analysis procedure is included in Attachment 1 to Appendix A. Canister samples that were at atmospheric pressure when collected were pressurized with ultra high purity air (zero air) to provide positive internal pressure to feed the sample air for TAGA analysis. Sample air pressure inside a canister was measured before and after pressurization to correct for sample dilutions in calculating sample concentrations.

The detection limit for the TAGA is affected by ambient atmospheric conditions, particularly humidity, because ambient air is used for instrument calibration (see Attachment 1 in Appendix A for further explanation).

For samples sent to the laboratory for further GC/MS analysis, the laboratory measured the air pressure inside each canister as it was received to determine if the sample to be analyzed was still under positive gauge pressure. The sample air was drawn through a cryogenic preconcentration unit before reaching the GC/MS for detailed analysis. The GC/MS identified all LCICs and quantified detectable levels.

Appendix A contains more details on the air pilot study analytical methods.

### 2.3.2 SOIL PILOT STUDY METHODS

#### Sample Collection and Preparation

The soil pilot study samples were collected with a hydraulic Porta-Sampler that drove a 2-inch-diameter Shelby tube approximately 13 inches into the soil. The Shelby tube was capped and shipped to the sample preparation laboratory, where the soil was extruded from the Shelby tube. After extrusion, the soil was mixed immediately, and a portion was placed in the volatile shipping container; the remainder of the sample was further mixed and placed in the semivolatile shipping container. Both containers were then shipped to an

analytical laboratory. Two sampling splits, each consisting of a volatile and semivolatile portion, were obtained from each Shelby tube. For one-third of the split samples, both splits of each sample were sent to the same laboratory, while for the remaining two-thirds of the split samples, the two splits of each sample went to two different laboratories. Appropriate quality control samples were sent to the laboratories with the soil samples. A detailed discussion of the soil sample collection and preparation procedures is given in Appendix B.

Sample Analysis

It was decided to use a more sensitive technique for soil LCIC analysis because the numbers of nondetectable concentrations, and the detection limit itself, are important factors in the habitability decisionmaking process. To measure the LCIC concentration in soil samples at the 1 ppb level, a new analytical method had to be developed.

The final analytical method chosen to meet the soil pilot study objectives was the GC/MS/SIM technique. The isotope dilution GC/MS technique for LCIC analysis was also discussed. Although there are certain advantages to using the isotope dilution GC/MS technique, it was decided that the next best technique, GC/MS/SIM, should be used because the stable-labeled isotopes required by the isotope dilution technique for all the compounds of interest were not available. The following paragraphs summarize the sample preparation and analysis procedures used in the soil pilot study.

For semivolatile analysis, a 20-gram portion of soil was extracted with methylene chloride/acetone, and the combined extract went through extensive cleanup techniques. An aliquot of the final concentrated extract was analyzed by capillary-column GC/MS operating in the SIM mode. For volatile analysis, inert helium gas was bubbled at 40 ml/min for 12 minutes through a mixture of a 5.0-gram soil sample and 10 ml of reagent water in an specially designed purging chamber at 40°C. After purging was completed, the sorbent column where the volatile LCICs were trapped was heated at 180°C to desorb the volatile LCICs onto packed-column GC/MS operating in the SIM mode.

Because of the importance of laboratory results in determining a practical course of action that may be followed in the future EDA habitability study, a QA/QC program as shown in Section 3.0 of Appendix C was implemented for all the participating laboratories. The criteria specified in the QA/QC program were used to monitor laboratory performance, improve the reliability of the chemical data, and determine how well the new analytical method performed. In addition,

a new method detection limit procedure as shown in Appendix D was implemented to support the validity for the measurement of the LCIC concentration at 1 ppb level.

## 2.4 RESULTS

### 2.4.1 AIR PILOT STUDY RESULTS

The field intensive part of the pilot study has identified a total of only two samples with detected levels of LCICs. Both of the detects were trace levels of chlorotoluenes in occupied homes, one in the EDA (out of 30 sampled) and one in the comparison area (out of 30 sampled). No chlorobenzene was detected in any of the indoor samples, and all ambient outdoor samples as well as unoccupied EDA houses were found to be nondetect for the LCICs as analyzed by either the TAGA or both the TAGA and the GC/MS.

The percentage of detects was approximately 3 percent for the EDA occupied homes, 0 percent for the EDA unoccupied homes, and approximately 1.7 percent overall for the EDA indoor samples. For the comparison areas, Tonawanda and Cheektowaga, the total percentage of detects was approximately 3 percent for the indoor air samples.

Because of the few detects and the lack of quantitative information on the presence of chlorotoluenes in the indoor environment documented in the literature, statistical analysis of the detected concentration values was not practical.

The analysis results from the TAGA and laboratory were generally consistent. Check sample concentrations correlated very closely between the two analytical instruments. All the duplicate samples and blanks results were consistent between the two analytical instruments. The determination of detect and nondetect samples using the TAGA analysis results was in excellent agreement with the laboratory GC/MS results.

Sufficient numbers of residents of both the EDA and comparison areas granted permission for entry and sampling. Of the total of 60 occupied homes, only 4 residents were absent at the scheduled sampling time, and alternative homes were found to satisfy the requirements of the pilot study.

Using evacuated stainless steel canisters for the collection and preservation of samples was successful. Field recycling of the canisters provided clean canisters for reuse throughout the field study. The overall sample collection procedure successfully preserved the air samples for both field analysis and further laboratory analysis.

The field intensive study also has provided information on the capability and consistency of performance for the TAGA. Laboratory GC/MS analysis is in general more specific in identifying LCIC isomers and more accurate in quantifying the detected levels. However, using the TAGA, sample concentrations can be detected at low parts per billion levels with very short turnaround time in the field. In addition, based on the sample analysis, the inability of the TAGA to distinguish the chlorotoluene isomers did not seem to be a handicap for identifying detectable samples. However, since the TAGA is calibrated using ambient air and can be sensitive to changes in humidity, the effective detection limit may vary within a small range from day to day.

The sampling results have revealed relatively low percentage of detects for both the EDA and comparison areas. The design of the pilot study was stratified by occupied/unoccupied house and by EDA/comparison area. The study can only be interpreted in terms of this stratification. That is, the detection rate is 1/30 for both the EDA occupied homes and the comparison area occupied homes.

Although the number of detects is too limited for statistical analysis, the LCIC concentrations detected in the pilot samples have provided some idea of the LCIC levels likely be found indoors and outdoors in the EDA and comparison areas.

Samples collected and analyzed for the field intensive study have not suggested that either off gases from the canal or trace levels in outdoor ambient air contribute to the detected indoor LCIC levels. Because of the low percentage of detects found in the EDA and comparison areas, the data were insufficient to determine the sources of the LCICs. Review of the home questionnaires and activity logs also was inconclusive in terms of correlating the LCICs detected with any indoor activities involving volatile chemicals. The DOH is currently conducting a followup survey of the homes with detectable LCIC concentrations in an attempt to determine whether any household products might have contributed to the detected LCICs.

Appendix A discusses the air pilot study results in more detail.

### 2.4.2 SOIL PILOT STUDY RESULTS

#### Analytical Results

Table 1 (Table B-1 of Appendix B) presents a summary of the soil pilot study percent detects and maximum concentrations for each of the eight LCIC analytes in the EDA as a whole versus the comparison areas taken together. Other tables summarize the sampling data (numbers of sites and samples)

Table 1
(Table B-1)
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS
PERCENT DETECTS AND MAXIMUM CONCENTRATIONS FOR
LCICS IN THE EDA AND COMPARISON AREAS

| LCIC Analyzed | Percent Detects (>1.0 ppb) | | Maximum Concentration (ppb) | |
|---|---|---|---|---|
| | EDA | CAs | EDA | CAs |
| Chlorobenzene | 0 | 0 | n/d[a] | n/d |
| 1,2-Dichlorobenzene (VOA) | 0 | 0 | n/d | n/d |
| 1,2-Dichlorobenzene (SV) | 16.3 | 11.7 | 8.6 | 3.2 |
| 1,2,4-Trichlorobenzene | 31.7 | 1.1 | 71.0 | 1.4 |
| 1,2,3,4-Tetrachlorobenzene | 34.6 | 0 | 181.0 | n/d |
| 2-chloronaphthalene | 1.0 | 0 | 1.1 | n/d |
| Beta-BHC | 3.8 | 0 | 250.0 | n/d |
| Gamma-BHC | 2.9 | 0 | 18.9 | n/d |

[a] n/d = nondetect.

and analytical results (numbers of nondetects and detects and maximum concentrations) for each of the six EDA sampling sections (see Figure 2) and each of the two comparison areas (Cheektowaga and Tonawanda).

The highest percent detects occurred for tri- and tetrachlorobenzene overall in the EDA, with 32 to 35 percent detects, respectively, for each of these two chemicals. Semivolatile analysis of 1,2-dichlorobenzene resulted in 11 percent total detects in the EDA and 12 percent total detects in the CAs. Volatile analysis of 1,2-dichlorobenzene, however, resulted in zero percent total detects in both the EDA and CAs. The difference of 1,2-dichlorobenzene detection between semivolatile and volatile analysis is due to contamination of the laboratory blanks in the semivolatile analysis. The results should be interpreted accordingly. A detailed discussion of this laboratory blank contamination can be found in Appendix C. B-BHC and G-BHC, although not detected in significant percentages over the EDA as a whole, were detected in 50 percent of the E5 samples. Chlorobenzene and 1,2-dichlorobenzene from volatile analysis and 2-chloronaphthalene from semivolatile analysis did not show many detects in the EDA as a whole or in any individual sampling section.

1,2-dichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4,-tetrachlorobenzene, B-BHC, and G-BHC were detected at maximum concentrations of 8.6 ppb, 71.0 ppb, 181 ppb, 250 ppb, and 18.9 ppb, respectively, in section E-5. The concentrations for these compounds were the highest of all the concentrations reported for the samples collected in the EDA. Possible reasons for this high contamination have not yet been determined. Chlorobenzene and 1,2-dichlorobenzene from volatile analysis and 2-chloronaphthalene from semivolatile analysis did not show any significant concentrations in the EDA as a whole or in any individual sampling section. Eleven samples from the two comparison areas had 1,2-dichlorobenzene concentrations from semivolatile analysis higher than 1.0 ppb. The concentration range of 1,2-dichlorobenzene is between 1.1 ppb and 3.2 ppb. Except one sample, all of these samples were reported by MGM. This is because MGM reported higher blank values for 1,2-dichlorobenzene than the other two laboratories. The results of 1,2-dichlorobenzene reported by MGM should be interpreted as having a significant blank contribution. One sample, LC2276, from the Cheektowaga area had 1,2,3,4-tetrachlorobenzene, 2-chloronaphthalene, B-BHC, and G-BHC concentrations at greater than 1 ppb. Split samples of LC2276, however, did not detect any of those compounds. The difference in the results may be due to sample heterogeneity. This is possible because LC2276 was a contingency sample obtained from a different Shelby tube.

Appendix B presents the soil pilot study results in full.

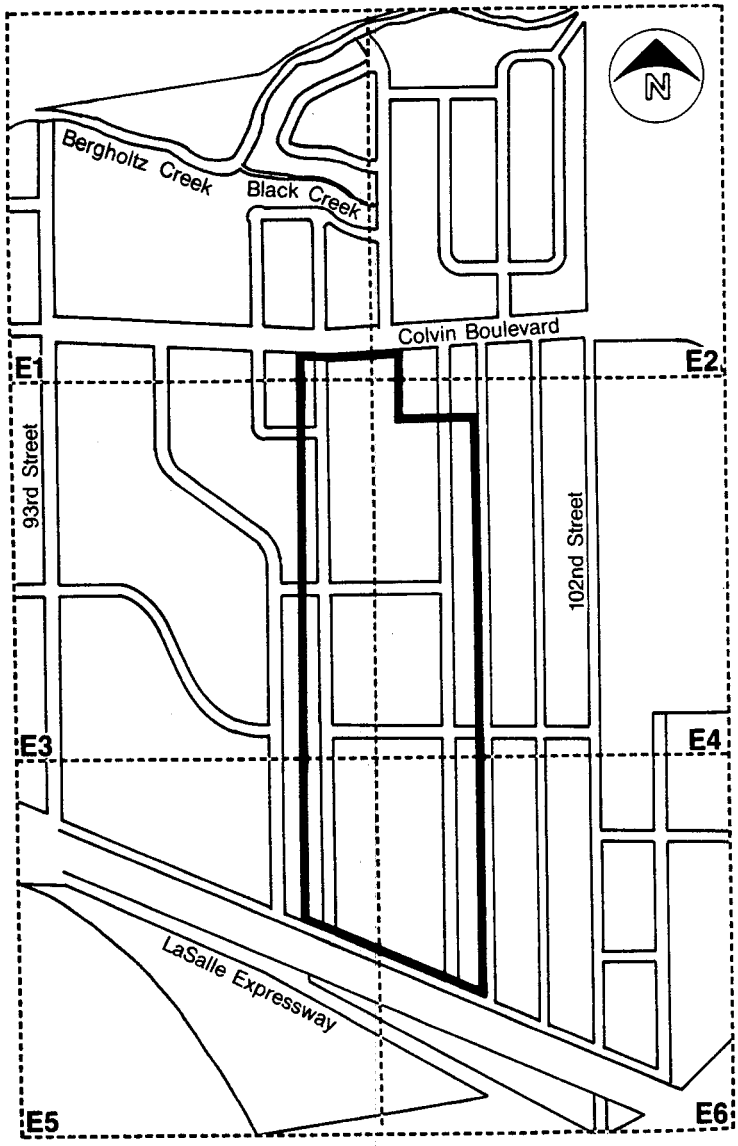


Figure 2
**EMERGENCY DECLARATION AREA (EDA) STUDY SECTIONS**

## QA/QC Results

It was found that the QA/QC program design for the soil pilot study was effective in monitoring methods and laboratory performance. One indication of its effectiveness was that the data from the QC sample analyses met the 95 percent data completeness goal. Another indication was the fact that no samples with concentrations greater than 1 ppb were invalidated retroactively by EMSL/LV during its review of the data (discussed in Appendix D). The high percentage of data completeness and validated samples was due to the fact that the participating laboratories adhered to the required QA/QC procedures. The performance of the method was acceptable with the following minor exceptions.

- The semivolatile sample extraction procedure introduced variability and bias to the 1,2-dichlorobenzene concentrations.

- Contamination of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene was found in the semivolatile method/holding blank analysis.

Detailed discussions and recommendations for these two problems can be found in Appendix C.

A high percentage of soil samples showed LCICs at concentrations of less than 1 ppb. The reliability of measurements of concentrations at less than 1 ppb is low because the interferences present in the sample preclude the reliable identification and quantification of the LCICs. Those samples with concentrations of less than 1 ppb were not considered reliable because of the variability of the data at this level. A detailed assessment and explanation of this decision is given in Appendix E.

## Results of Detection Limit Study

Environmental studies such as the Love Canal habitability study require a careful definition and evaluation of the detection limit associated with the chemical analysis. This is especially necessary when a large number of analyses are expected to produce nondetectable results.

During the pilot study, a preliminary estimator was developed for the method detection limit of the quantitative aspects of the analytic process. This estimator provides a value for analyte concentration which, if present in a sample, should be detected with high probability. It does not, however, provide any guidance as to whether a particular sample's concentration is at a detectable level.

The detection limits were estimated using a modified Hubaux and Vos method (Hubaux and Vos, 1968) that involves spiking Love Canal soil with predetermined levels of LCICs and regressing the instrument response against the known concentration. Table 2 summarizes the estimated method detection limits.

Table 2
ESTIMATED METHOD DETECTION LIMITS

| LCIC | Average Method Detection Limit for CAA[a] and MGM[b] Laboratories in ppb |
|---|---|
| Chlorobenzene | 0.15 |
| 1,2-Dichlorobenzene (volatile analysis) | 0.47 |
| 1,2-Dichlorobenzene (semivolatile analysis) | 1.5 |
| 1,2,4-Trichlorobenzene | 1.0 |
| 2-Chloronaphthalene | 0.5 |
| 1,2,3,4-Tetrachlorobenzene | 1.1 |
| B-BHC | 2.5 |
| G-BHC | 2.2 |

[a]Cambridge Analytical Associates, Cambridge, Massachusetts.

[b]CH2M HILL laboratory in Montgomery, Alabama.

These method detection limits are all in the same range as the analytical design target of 1 ppb. Note that the sensitivity of the volatile analysis appears to be greater than for the semivolatile analysis. This is apparently an artifact of the different extraction efficiencies of the two methods on spiked versus in situ analytes. Preliminary indications are that the semivolatile method is relatively constant while the volatile method has higher extraction efficiencies for spiked samples in which the analyte is only in contact with the soil for a short time. This aspect of the chemical analysis is under investigation.

Appendix E presents the results of the method detection limits study.

# 3.0 RECOMMENDATIONS

## 3.1 AIR PILOT STUDY RECOMMENDATIONS

### 3.1.1 GENERAL RECOMMENDATIONS

The general recommendations based on the experience of the field intensive part of the air pilot study are:

- For the purpose of extensive indoor air sampling at multiple locations over a large number of houses, it is recommended that a long sample transport tube be utilized to draw air samples for direct sample analysis by the TAGA. A method development study is currently being conducted to substantiate the application and limitations of a heated transport tube used with the TAGA.

- The sample air should be analyzed directly without being diluted using ultra high purity air. This would avoid compromising the instrument detection limit by applying dilution factors to all of the analysis results.

- Consistent with the TAGA's capability, it is recommended that total chlorotoluene be allowed to replace 2-chlorotoluene and 4-chlorotoluene as an LCIC for the purpose of field screening analysis using the TAGA.

- The data quality objectives for the future air studies, including both the time variant part of the air pilot study and the full-scale habitability study, should be defined. To meet these requirements, specific laboratory standard operating procedures should be developed, and a specific quality assurance project plan addressing the data quality objectives should be designed and implemented.

### 3.1.2 TIME VARIANT STUDY RECOMMENDATIONS

A basic question remaining from the field intensive study is the following: Are LCIC concentrations always at nondetectable levels or is there a time component to the variability in concentrations such that LCICs are more likely to be detected at some times rather than others?

Since this question is difficult to answer with nondetectable concentrations, a first task of the time variant study is to identify additional houses with detectable levels of LCICs. These can then be monitored over several days (for

diurnal patterns) and seasons (for seasonal patterns). The recommended course for the time variant study is the following:

- Prior to the time variant study, perform a screening analysis, i.e., air sampling at multiple locations inside each house studied, and select target houses, preferably houses with detectable LCIC concentrations, for the time variance study.

- During the time variant study itself, perform detailed air sampling in each of the houses with detectable LCIC concentrations to determine whether any indoor activities or sources may have contributed to the detected LCICs.

- Develop a protocol for air sampling inside houses to monitor changes in the detected LCIC concentrations during a diurnal cycle at the same locations.

- Conduct future indoor sampling at the same locations inside the same group of houses selected for diurnal LCIC monitoring during consecutive winter, spring, and summer seasons.

### 3.1.3 HABITABILITY STUDY RECOMMENDATIONS

Since the field intensive study results showed approximately 97 percent nondetects for EDA occupied houses and 100 percent nondetects for the EDA unoccupied houses, the expected total number of detect houses in the EDA would be very few. It is, therefore, recommended that the houses in which LCICs have been detected during either the field intensive or time variant parts of the air pilot study be resampled during the habitability study and thoroughly investigated to identify any source location.

## 3.2 SOIL PILOT STUDY RECOMMENDATIONS

The conclusions of the soil pilot study and recommendations based on these conclusions are given in this section. More thorough discussions can be found in Appendixes B, C, D, and E.

### 3.2.1 SAMPLE COLLECTION AND PREPARATION RECOMMENDATIONS

The sample collection method worked very well in obtaining a relatively undisturbed soil sample. Some difficulties were encountered in obtaining a full 13-inch deep sample due to sampling in fill and rubble. The 13-inch depth was originally based on the requirements of the GC/ECD analytical method and standard shovel length. However, the GC/MS/SIM

analytical method ultimately selected requires less soil. It should be decided, therefore, whether a sample depth of 13 inches is needed for the habitability study or if the more easily obtained depth of 6 to 7 inches would be sufficient. If 13 inches are required, protocols will be developed for cases when less than 13 inches are collected.

During sample preparation it was observed that the initial volatile mixing did not include as much of the lower and more densely packed portion of the soil sample as the semivolatile sample did. This observation combined with the observed differences in the volatile and semivolatile dichlorobenzene concentrations has raised concerns about the adequacy of the mixing protocol. Tests are currently being conducted to determine if the mixing protocol is the source of the differences in the dichlorobenzene concentrations.

### 3.2.2 SAMPLE ANALYSIS RECOMMENDATIONS

The analytical results of the soil samples and their associated quality control results indicate that the analytical method was able to reliably identify and quantify LCIC concentrations at the 1 ppb level. With the exception of tri- and tetrachlorobenzene, most LCICs in the EDA were less than 1 ppb. Most of the LCICs in the comparison area were generally less than 1 ppb. All chlorobenzene concentrations in both the EDA and comparison areas were less than 1 ppb.

The quality control data indicate that the data quality objectives were met and that the analytical method performed very well. The reliability of the laboratories positively identifying the LCICs was very high, indicating that multiple laboratory use of the analytical method produces about the same results. Some problems were encountered in low level contamination of laboratory blank samples. The contamination was within the quality control guidelines but may result in difficulty of statistical interpretation of the data. The analytical method should be revised to avoid as much as possible any sources of laboratory contamination.

Variability in the results of some of the quality control data suggests that the semivolatile sample extraction procedures may need minor modifications and that the laboratories should be trained to obtain a more uniform application of the extraction procedure. The extraction protocol changes and laboratory training should be completed prior to sample collection for the habitability study.

The data quality validation and review resulted in the determination of 1 ppb as the level at which the LCICs could be reliably identified and quantified. If it is desirable to lower this detection level, the identification criteria

for the LCIC should be further defined to maintain comparable results between laboratories.

It was noted that 1,2-dichlorobenzene exhibited poor chromatographic performance for the volatile analysis and that the semivolatile analysis had higher concentrations. This difference is currently under investigation. These problems with the volatile dichlorobenzene analysis and the fact that there were no samples with chlorobenzene concentrations greater than 1 ppb have led to a recommendation that the volatile analysis not be included in the habitability study.

Overall, the soil pilot analytical results are very reliable and are suitable for use in the design of the soil comparison habitability study. Volume II discusses the soil sample design for the full-scale habitability study.

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# APPENDIX A
## Love Canal Air Pilot Study

# Appendix A

# LOVE CANAL AIR PILOT STUDY

CH2M HILL

February 1987

CONTENTS

TABLES



FIGURES

## 2.0 FIELD INTENSIVE STUDY

The field intensive part of the air sampling pilot study provides preliminary data on and understanding of Love Canal conditions and tests the sampling methodologies and analytical techniques to be used in the habitability study.

### 2.1 Sampling Period

During a 4-day period, July 28 through July 31, 1986, samples were collected in the EDA and comparison areas. Field teams used two 90-minute sampling windows each day, 9:30 a.m. to 11:00 a.m. and 1:30 p.m. to 3:00 p.m., to collect all required samples under comparable conditions.

### 2.2 Sampling Locations

Thirty occupied and 33 unoccupied houses in the EDA and 15 occupied houses in each of the two comparison areas of Cheektowaga and Tonawanda, New York, were sampled. Horizon Systems Corporation set up a random sampling schedule to select sampling locations in the EDA and the comparison areas. DOH coordinated and scheduled homeowner permission for sampling crews to enter their properties at the scheduled times. When no one was home during the assigned sampling time, the NYSDOH was notified and alternate houses selected.

The following criteria provided the basis for selection of ambient air sample sites: representativeness of the area, ease of access, and absence of obstructions, buildings, or vegetation. EDA sites both upwind and downwind of the Canal were included to sample possible canal emissions. Three EDA ambient sites were selected, and one in each of the two comparison areas. Although it would have been desirable to collect samples simultaneously at all indoor and outdoor locations, it was impractical. The program sampled a portion of the indoor locations from each stratum and all five of the outdoor ambient locations within a designated sampling time window.

To illustrate the sampling site locations, the EDA and the comparison areas were divided into the subareas shown in Figure A-1. Table A-1 presents the location distributions.

### 2.3 Types of Samples and Sampling Schedules

Teams sampled each ambient site location two times each day during the 4-day study to collect 24 EDA ambient air samples and a total of 16 ambient air samples from the two comparison areas. During the 4-day sampling period, 32 supposedly occupied EDA houses were sampled; however, two proved vacant and were counted as unoccupied houses. Thirty-one known EDA

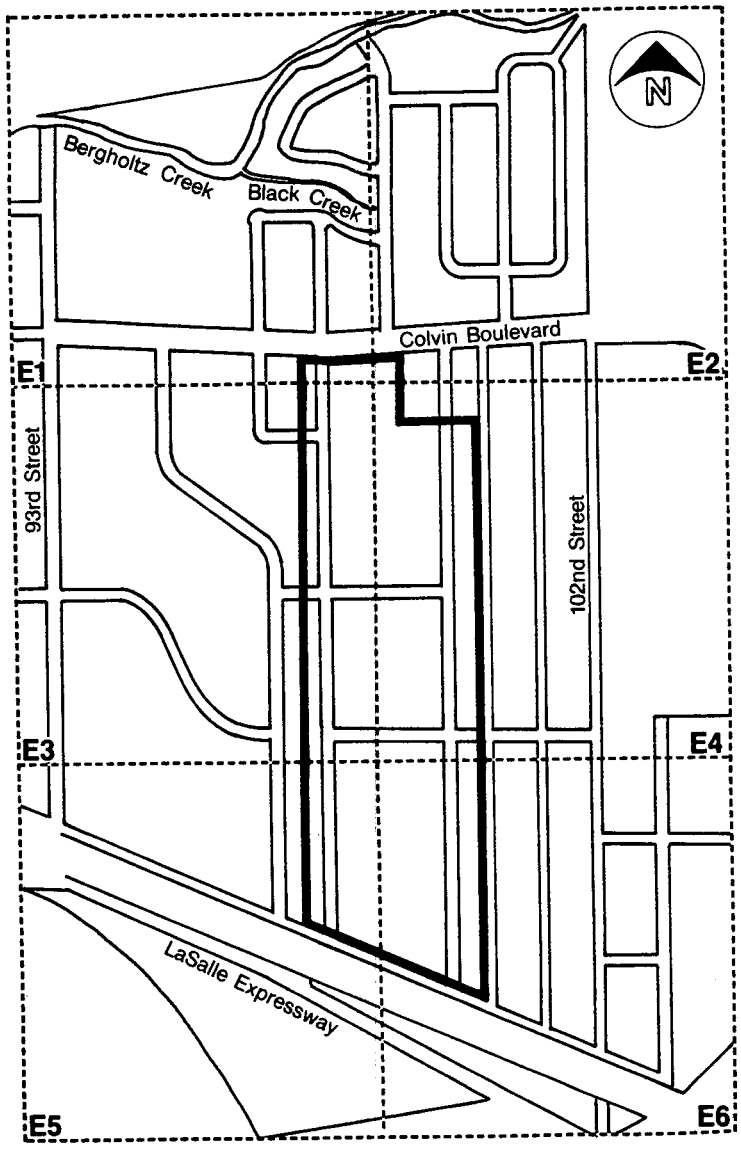



Figure A-1
**EMERGENCY DECLARATION AREA (EDA) STUDY SECTIONS**

Table A-1
DISTRIBUTION OF SAMPLED HOUSES

| Areas | Number of Houses |
|---|---|
| EDA Unoccupied* | |
| E1 | 3 |
| E2 | 19 |
| E3 | 2 |
| E4 | 4 |
| E5 | 0 |
| Total | 5 |
| | 33 |
| EDA Occupied* | |
| E1 | 9 |
| E2 | 7 |
| E3 | 5 |
| E4 | 2 |
| E5 | 0 |
| E6 | 7 |
| Total | 30 |
| Comparison Areas | |
| Total | 31 |

Note: *Refer to Figure A-1 key map for subareas.

unoccupied houses were also sampled totaling 33 unoccupied houses sampled. Air samples were also obtained from 16 occupied houses in Cheektowaga and 15 occupied houses in Tonawanda to total 31 occupied comparison area houses sampled.

During the 4-day period, teams collected 134 different samples. A computerized random selection process picked 16 indoor and outdoor locations distributed through the different strata to be sampled in duplicate. Table A-2 presents the number of samples and duplicates collected from each stratum.

Table A-2
NUMBER OF COLLECTED SAMPLES

| Strata | Number of Samples | Number of Duplicates | Total Samples Collected |
|---|---|---|---|
| EDA Unoccupied | 33 | 3 | 36 |
| EDA Occupied | 30 | 3 | 33 |
| EDA Ambient | 24 | 3 | 27 |
| CA Occupied | 31 | 3 | 34 |
| CA Ambient | 16 | 4 | 20 |
| Total | 134 | 16 | 150 |

Five check sample canisters and five blank canisters that were first analyzed by both the TAGA and the GC/MS unit at Battelle-Columbus were sent with all duplicate samples and control samples (selected nondetects) back to Battelle-Columbus as blind samples.

## 2.4 Field Operations

Four units functioned onsite at Love Canal: the canister control center, the TAGA bus, the Battelle-Columbus canister recycling center, and six sample collection teams. Figure A-2 illustrates the routing of canisters through the operation system in the field. The canister control center, located in the field trailer with the field office, determined the routing of canisters and the disposition of canister samples.

During each half-day sampling period, the six sample collection teams received clean canisters, associated site and sample information, and necessary documentation. Canisters with both collected samples and quality control samples were sent in groups ranging from 17 to 23 to the TAGA unit for analysis. Following analysis, individual canisters were sent to the laboratory for GC/MS analysis or to the recy-

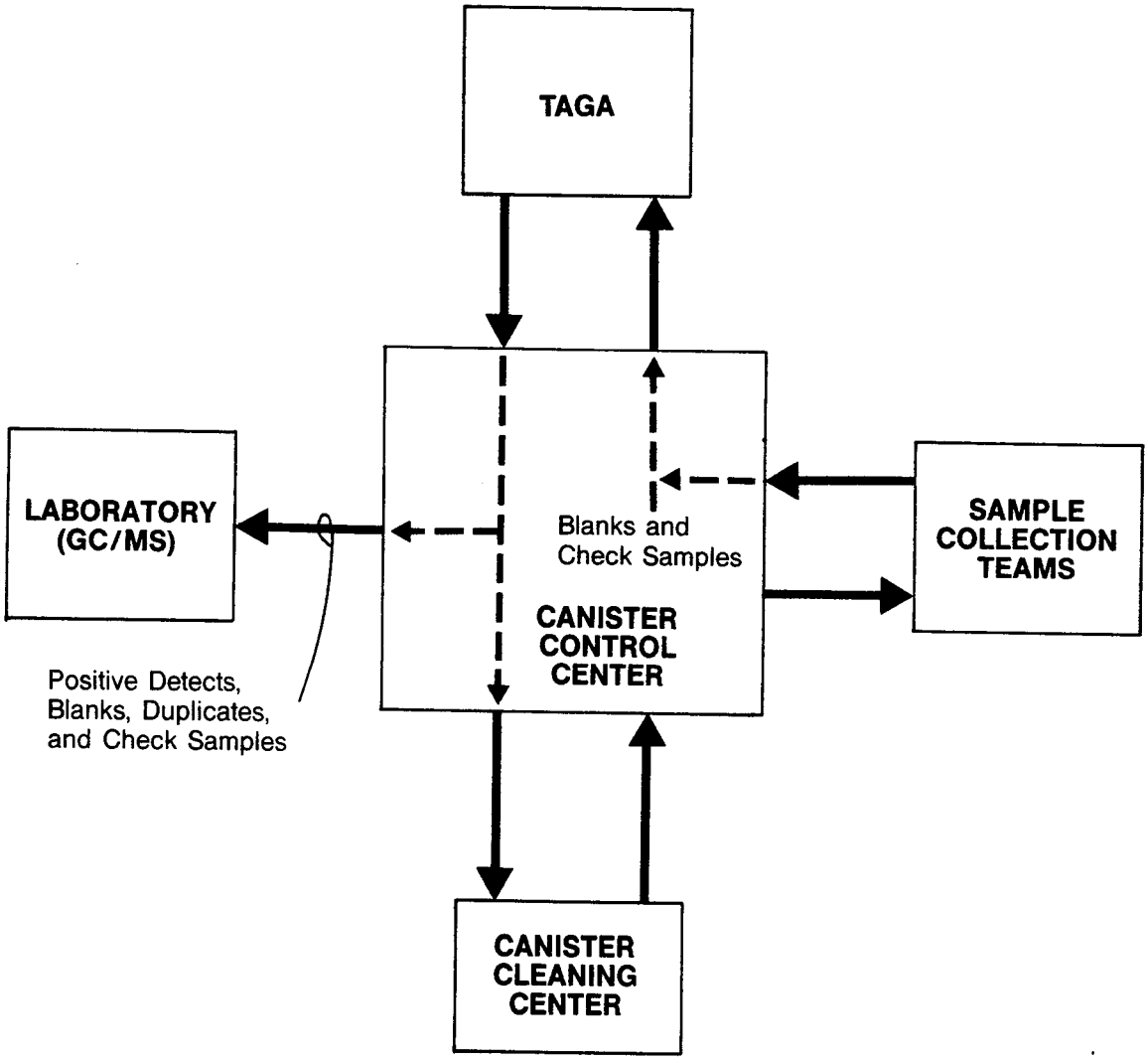



Figure A-2
**CANISTER SAMPLE ROUTES**

cling center for cleaning and reuse. Eighty canisters were used in the field to collect a total of 150 samples analyzed using TAGA. Forty of these samples were then sent to the laboratory for confirmational analysis with five blanks and five check samples.

## 2.5 Sample Collection

All air samples were collected in SUMMA polished 6-liter stainless steel canisters equipped with a needle valve for controlling the air flow. Each canister was fitted with a stainless steel, fixed-frit particle filter (Nupro type SS-4F-T7-2) at the inlet end to prevent particle clogging of the sampling flow. The canisters were kept at high vacuum with the valves tightly closed until scheduled for collection samples. When the valve was opened, the vacuum inside drew the sample air into the canister. The canisters were kept open for a minimum of 2 minutes to allow sufficient time to fill to atmospheric pressure. The valve was closed at the end of the sample collection and not reopened until the sample was analyzed. One sample was not collected when the valve handle slipped and did not open the valve. This sample was one of a duplicate sample pair. The other sample of the pair remained valid and another random duplicate pair was later selected to replace the lost duplicate sample.

Each sample collection team followed the assigned sequence of sampling sites, usually an ambient site assigned between two indoor sites to make the ambient sample equally representative of the ambient conditions for both indoor samples. The designated indoor location for sampling was at the bottom of the basement stairway or, in homes without basements, in the living room at the corner closest to the middle of the entire house. Ambient outdoor samples were taken at the exact location specified in the assignment.

Each two-member sampling team was required to complete the necessary documentation: a field notebook, sampling activity log, and, for indoor samples, a resident questionnaire. Each team returned the canisters and associated documentation to the canister control center. When the residents were not home, the collection team made a telephone call to one of the two mobile phones near the field office. A decision was then made at the field office to have the team delay the sampling at that site or arrange with the NYSDOH for an alternative site.

The collected sample holding time in the canisters was kept to a minimum. Studies establishing the integrity of samples containing parts per billion (ppb) levels of LCICs in 6-liter SUMMA polished stainless steel canisters vary from 7 days (Holdren et al., 1986), to 15 days (McClenney, 1986) or

30 days (Oliver et al., 1986). These studies found nondetectable or minimal change in concentrations during the study period. During the air sampling pilot study, the samples were sent the same day or the next day from the field to the laboratory and analyzed within 12 days of the time of collection.

## 2.6 Sample Analysis

All collected samples, the quality assurance samples (duplicates, controls, and blanks), and the check samples were analyzed in the field for LCICs. All samples determined by the TAGA as detect were sent to the laboratory with all duplicate sample pairs and blanks. Because all duplicate samples were randomly selected daily during the field sampling period and all were determined nondetect by the TAGA, the duplicate sample in each of the pairs also represented the control sample sent to the laboratory for the confirmation of nondetect results obtained in the field.

The field analytical instrument was TAGA Model 6000E by Sciex, a mobile Mass Spectrometer (MS/MS) unit capable of performing quick analysis of air samples in the field with low ppb level of detection limits. Because it lacks a gas chromatographic unit, the TAGA cannot distinguish individual isomers, particularly 2-chlorotoluene and 4-chlorotoluene, and will report only the total concentration of the isomers. (Refer to Attachment 1 for a description of TAGA's analysis procedure.) Canister samples collected at atmospheric pressure were pressurized with ultra high purity air (zero air), to provide positive internal pressure to feed sample air for the TAGA analysis. Sample air pressure inside a canister was measured before and after pressurization to calculate the degree of dilution to correct the sample analysis results.

The detection limit for the TAGA is generally affected by ambient atmospheric conditions, particularly humidity, because ambient air is used for instrument calibration. (See Attachment 1 for additional explanation.) The defined detection limit for the TAGA is three times the level of the standard deviation of the noise level at the time of analysis.

For samples sent to the laboratory for further GC/MS analysis, the laboratory measured the air pressure inside each canister on receipt to determine whether the sample to be analyzed was still under positive gauge pressure. The sample air was drawn through a cryogenic preconcentration unit before reaching the GC/MS for detailed analysis. The GC/MS identified all LCICs and quantified them when levels were detectable.

## 2.7 Field Canister Cleaning

The Battelle-Columbus mobile recycling center onsite recycled canisters for reuse in the field following the verified procedure described in the Battelle pilot study report (Holdren et al., 1986). During the 4-day study, 81 canisters were cleaned in groups of 5 to 10 canisters for reuse in the field.

Canisters were cleaned by cyclic filling with ultra high purity air and evacuating to vacuum (25-inch Hg) while baking at 50°C. The canisters were ready for sampling after the internal pressure was reduced to less than 100 millitorr and the valves closed. This cleaning technique and procedure was developed and tested before the air sampling pilot study began and was closely followed in the field to provide recycled canisters for sample collection. Details of the procedure are described in the QAPP. Five blank samples were analyzed over the 4-day field study period to verify periodically the cleanliness of the recycled canisters.

## 2.8 Ambient Conditions

The climatological conditions during the 4-day sampling period were recorded and measured onsite or, in the case of relative humidity, taken from the National Weather Station at Buffalo International Airport. Average conditions for the morning and afternoon of the four days are presented in Table A-3.

Table A-3
LOCAL AVERAGE CLIMATOLOGICAL CONDITIONS[a]

| Time Period | Wind Direction (from) | Wind Speed (mph) | Temperature (°F) | Barometric Pressure (in Hg) | Relative[b] Humidity (%) |
|---|---|---|---|---|---|
| 7/28/86 a.m. | SSW | 3 | 76° | 29.020 | 64 |
| 7/28/86 p.m. | SSW | 5 | 80° | 29.005 | 44 |
| 7/29/86 a.m. | NW | 5 | 70° | 29.025 | 83 |
| 7/29/86 p.m. | NW | 6 | 77° | 29.120 | 61 |
| 7/30/86 a.m. | NNW | 3 | 71° | 29.130 | 86 |
| 7/30/86 p.m. | NW | 4 | 73° | 29.135 | 76 |
| 7/31/86 a.m. | NNE | 2 | 70° | 29.140 | 80 |
| 7/31/86 p.m. | N | 2 | 75° | 29.150 | 69 |

[a] Measured in the EDA during the July 28-31, 1986, sampling period, except noted.

[b] Data from the National Weather Station at Buffalo, New York. Measurements are at 10:00 a.m. and 2:00 p.m.

# 1.0 INTRODUCTION

## 1.1 Goals

The overall goal of the air sampling pilot study described in the Quality Assurance Project Plan for Air Sampling Pilot Plan, Love Canal Habitability Study (USEPA, July 1986) (QAPP) is to reduce the uncertainties involved in the collection and analysis of air samples, and to obtain information on the characteristics of the data that are likely to be gathered during the full-scale habitability study. This information will be used to implement the air sampling study required by the habitability criteria document (DOH/CDC, December 1986) for the habitability study.

The objectives of the air sampling pilot study are to make preliminary investigation of:

- Expected indoor and outdoor levels of Love Canal indicator chemicals (LCICs) in the air of the Emergency Declaration Area (EDA) and comparison areas (Tonawanda and Cheektowaga, New York)
- Expected frequency of detectable levels of LCICs in the air of the EDA and comparison areas
- Performance and potential role of the Trace Atmospheric Gas Analyzer (TAGA) in future field application
- Whether the Love Canal is contributing through air emission to detected LCIC levels and whether LCICs are present in the outdoor atmosphere
- Temporal variation in LCIC levels in the outdoor ambient air

The air pilot study is also intended to test three major premises:

- That the presence of airborne LCICs at the detection limits achievable is specific to the site, not ubiquitous, and that it indicates contamination
- That the methods and techniques used for sampling and analysis are appropriate
- That sufficient numbers of comparison area homeowners will agree to sampling to allow the habitability criteria to be implemented

## 1.2 Approach

The air sampling program for the pilot study has two parts: the field intensive study and the time variance study. This appendix addresses the field intensive study. Issues pertaining to the time variance study will be discussed in a later document.

The field intensive study provides information on the percentage and level of detects of LCICs in the EDA, and whether the canal contributes to any potential outdoor LCIC levels. The use of the TAGA as a field instrument for sample analysis also was tested during the field intensive study to determine its future role in the time variance part of the pilot and habitability studies. Attachment 1 of this appendix summarizes the TAGA analysis procedures.

The field intensive study assumes that during a short-term sampling period the three LCICs (chlorobenzene, 2-chlorotoluene, and 4-chlorotoluene) selected for the study will vary relatively little. The time variance study to be conducted at a later date will examine LCIC variations over a longer time.

The strata considered in the field intensive study included indoor air sampling of occupied and unoccupied houses and outdoor ambient air samples in the EDA and comparison areas. A mobile TAGA collected and analyzed air samples in the field. Sample canisters containing TAGA-identified LCICs were sent to the analytical laboratory. Check samples (unconfirmed audit samples) provided by the U.S. Environmental Protection Agency (EPA) Environmental Monitoring Systems Laboratory at Research Triangle Park (EMSL-RTP) also were sent to the analytical laboratory following field analysis. The remaining samples were discarded and the containers cleaned in the field for reuse.

The EMSL-RTP Methods Development Branch of the EPA provided information and discussion to incorporate state-of-the-art sample collection and analysis technology in this part of the pilot study. The EPA Environmental Response Team, Edison, New Jersey, contributed the TAGA and the TAGA operating crew for the field canister sample analysis. Battelle (Columbus, Ohio, division), provided the confirmational Gas Chromatography/Mass Spectrometry (GC/MS) analysis, the initial checking and cleaning of the canisters, and the subsequent field canister cleaning facility and service. The New York State Department of Health (DOH), Office of Public Health, Health Liaison Program, facilitated community relations and scheduled and arranged for sample collection in the EDA and comparison areas. The QAPP presented more detailed design and procedures implemented in the field intensive study.

## 2.9 Field Audit

A field system audit was conducted by Northrup, Inc., a contractor to EMSL-RTP on July 29 and 30, 1986. CH2M HILL's internal audit team also visited the site during the sampling period to identify potential problems for the consideration and design of the full habitability study. The final audit report (Caviston et al., 1986) documented that the field intensive study was conducted by qualified personnel and that the sample documentation was adequate to track the sample flow in the field. The audit team made specific field study recommendations for the habitability study air sampling. The data collected by the audit team indicated that the TAGA has applicability for large-scale screening studies.

## 3.0 SAMPLE ANALYSIS RESULTS

Table A-4 presents the sample analysis results for all collected samples; Tables A-5 and A-6 show results for blanks and check samples. These results have been adjusted using the individual dilution factor for each sample. Dilution factors were calculated by taking the ratio of the pre- and post-dilution pressures measured inside the same canister. The calculated dilution factors for all the samples in the study are provided in Table A-7.

The detection limits for the TAGA as shown in Table A-4 (adjusted for dilution factor) range from 1.7 to 3.6 ppb for chlorobenzene and from 1.7 to 5.9 ppb for the chlorotoluenes. The TAGA detection limits (before adjustment for dilution factors) during the 4-day field intensive study are illustrated in Figure A-3. A definite and consistent trend of increased sensitivity and decrease in detection limit is shown during a 24-hour period for consecutive groups of sample analyses, and during the days for the last batch in a day. The principal suspected reason for this drift in sensitivity is instrument warmup. The progressive improvement of overall instrument operation during the sampling period may also partially account for the drift in sensitivity.

Sample results with concentrations of less than 0.05 ppb (not adjusted for dilution factor) were not reported by the GC/MS laboratory. Sample results with concentrations between 0.05 and 0.1 ppb were rounded up and reported as 0.1 ppb. The laboratory reported 2-chlorotoluene at a concentration of 0.1 ppb for samples SN006, SN066, SN099, SN172, and SN180 period. A 4-chlorotoluene was also reported at 0.1 ppb for sample SN066 and below the detection limit for the other four samples. Review of the GC/MS instrument records concluded that identification of 2-chlorotoluene and 4-chlorotoluene is questionable because of the absence of the testing ion for each target analyte. Although samples SN066 and SN099 were field duplicate samples, 4-chlorotoluene was detected at 0.1 ppb for sample SN066 but not for sample SN099, indicating that the variability of data at this level may be high; and, therefore, values at 0.1 ppb for the above samples are not reported.

Figure A-4 compares the TAGA and GC/MS results for the two collected samples with detectable levels of chlorotoluenes. The TAGA results are lower than the GC/MS results for both samples. Because of the scarcity of detects, there is no current explanation for the bias.

The GC/MS results for the chlorotoluene isomers were combined for comparison. There were no detects for chlorotoluene. The TAGA and GC/MS results for the check samples are compared

Table A-4 SAMPLE ANALYSIS RESULTS FOR COLLECTED SAMPLES

| Sample Number | Type | Site | TAGA (ppb) * | | Laboratory (ppb) ** | | |
|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | Total Chloro-toluene | Chloro-benzene | 2-Chloro-toluene | 4-Chloro-toluene |
| sn011 | sample | 027h | < 2.0 | < 2.4 | nd | nd | nd |
| sn016 | sample | 005h | < 1.8 | < 2.7 | nd | nd | nd |
| sn021 | sample | 021h | < 2.0 | < 3.0 | nd | nd | nd |
| sn023 | sample | 011h | < 2.2 | < 2.4 | nd | nd | nd |
| sn027 | sample | 018h | < 1.7 | < 2.9 | nd | nd | nd |
| sn033 | sample | 037h | < 1.9 | < 2.8 | nd | nd | nd |
| sn034 | sample | 016h | < 2.9 | < 5.0 | nd | nd | nd |
| sn055 | sample | 002h | < 2.2 | < 4.8 | nd | nd | nd |
| sn073 | sample | 022h | < 1.9 | 5.6 | nd | 18.0 | 1.5 |
| sn085 | sample | 025h | < 1.9 | < 2.3 | nd | nd | nd |
| sn098 | sample | 029h | < 1.9 | < 1.9 | nd | nd | nd |
| sn100 | sample | 032h | < 1.8 | < 1.8 | nd | nd | nd |
| sn102 | sample | 012h | < 2.1 | < 2.3 | nd | nd | nd |
| sn119 | sample | 007h | < 2.8 | < 4.2 | nd | nd | nd |
| sn120 | sample | 026h | < 2.0 | < 2.4 | nd | nd | nd |
| sn125 | sample | 009h | < 2.2 | < 2.4 | nd | nd | nd |
| sn128 | sample | 020h | < 1.9 | < 3.2 | nd | nd | nd |
| sn133 | sample | 017h | < 1.8 | < 3.1 | nd | nd | nd |
| sn142 | sample | 031h | < 1.9 | < 1.9 | nd | nd | nd |
| sn146 | sample | 030h | < 1.7 | < 1.7 | nd | nd | nd |
| sn078 | duplicate | 030h | < 1.8 | < 1.8 | nd | nd | nd |
| sn154 | sample | 004h | < 3.4 | < 5.6 | nd | nd | nd |
| sn166 | sample | 006h | < 3.0 | < 4.4 | nd | nd | nd |
| sn169 | sample | 010h | < 1.9 | < 2.1 | nd | nd | nd |
| sn170 | sample | 008h | < 3.1 | < 4.5 | nd | nd | nd |
| sn177 | sample | 019h | < 1.8 | < 3.1 | nd | nd | nd |
| sn181 | sample | 015h | < 2.5 | < 4.4 | nd | nd | nd |
| sn083 | duplicate | 015h | < 2.7 | < 4.6 | nd | nd | nd |
| sn183 | sample | 001h | < 3.3 | < 5.4 | nd | nd | nd |
| sn191 | sample | 023h | < 2.8 | < 4.2 | nd | nd | nd |
| sn194 | sample | 003h | < 3.6 | < 5.8 | nd | nd | nd |
| sn196 | sample | 028h | < 1.9 | < 2.3 | nd | nd | nd |
| sn190 | duplicate | 028h | < 1.9 | < 2.3 | nd | nd | nd |

* Those figures prefaced with '<' denote sample analysis results are below the TAGA detection limit.

** nd - not detected

Table A-4. SAMPLE ANALYSIS RESULTS FOR COLLECTED SAMPLES (continued)

| Sample Number | Type | Site | TAGA (ppb) * | | Laboratory (ppb) ** | | |
|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | Total Chloro-toluene | Chloro-benzene | 2-Chloro-toluene | 4-Chloro-toluene |
| sn003 | sample | 027u | < 1.9 | < 2.2 | nd | nd | nd |
| sn199 | duplicate | 027u | < 1.9 | < 2.3 | nd | nd | nd |
| sn005 | sample | 013u | < 3.1 | < 5.4 | nd | nd | nd |
| sn007 | sample | 026u | < 1.8 | < 2.2 | nd | nd | nd |
| sn008 | sample | 007u | < 3.5 | < 5.1 | nd | nd | nd |
| sn010 | sample | 031u | < 1.9 | < 1.9 | nd | nd | nd |
| sn019 | sample | 003u | < 2.4 | < 5.3 | nd | nd | nd |
| sn022 | sample | 005u | < 2.2 | < 2.4 | nd | nd | nd |
| sn182 | duplicate | 005u | < 2.3 | < 2.5 | nd | nd | nd |
| sn024 | sample | 015u | < 1.7 | < 2.9 | nd | nd | nd |
| sn026 | sample | 010u | < 2.9 | < 5.0 | nd | nd | nd |
| sn031 | sample | 001u | < 3.3 | < 4.9 | nd | nd | nd |
| sn032 | sample | 020u | < 1.9 | < 2.9 | nd | nd | nd |
| sn036 | sample | 017u | < 1.8 | < 3.0 | nd | nd | nd |
| sn050 | sample | 022u | < 1.9 | < 2.8 | nd | nd | nd |
| sn051 | sample | 002u | < 2.4 | < 5.2 | nd | nd | nd |
| sn074 | sample | 011u | < 3.3 | < 4.9 | nd | nd | nd |
| sn077 | sample | 008u | < 2.2 | < 2.4 | nd | nd | nd |
| sn082 | sample | 004u | < 2.1 | < 2.3 | nd | nd | nd |
| sn092 | sample | 009u | < 3.0 | < 4.3 | nd | nd | nd |
| sn094 | sample | 014h | < 2.7 | < 4.6 | nd | nd | nd |
| sn106 | sample | 024u | < 2.0 | < 2.5 | nd | nd | nd |
| sn114 | sample | 023u | < 1.8 | < 2.7 | nd | nd | nd |
| sn118 | sample | 019u | < 3.6 | < 5.9 | nd | nd | nd |
| sn123 | sample | 028u | < 2.9 | < 5.0 | nd | nd | nd |
| sn124 | sample | 018u | < 3.4 | < 5.5 | nd | nd | nd |
| sn130 | sample | 014u | < 2.0 | < 3.4 | nd | nd | nd |
| sn134 | sample | 012u | < 2.8 | < 4.9 | nd | nd | nd |
| sn137 | sample | 029u | < 1.9 | < 1.9 | nd | nd | nd |
| sn144 | sample | 006u | < 2.3 | < 2.4 | nd | nd | nd |
| sn175 | sample | 030u | < 1.8 | < 1.8 | nd | nd | nd |
| sn179 | sample | 025u | < 1.9 | < 2.3 | nd | nd | nd |
| sn184 | sample | 021u | < 1.9 | < 2.8 | nd | nd | nd |
| sn187 | sample | 016u | < 1.8 | < 3.1 | nd | nd | nd |
| sn138 | duplicate | 016u | < 1.9 | < 3.2 | nd | nd | nd |
| sn192 | sample | 013h | < 2.7 | < 4.7 | nd | nd | nd |

* Those figures prefaced with '<' denote sample analysis results are below the TAGA detection limit.

** nd - not detected

TABLE A-4. SAMPLE ANALYSIS RESULTS FOR COLLECTED SAMPLES (continued)

| Sample Number | Type | Site | TAGA (ppb) * | | Laboratory (ppb) ** | | |
|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | Total Chloro-toluene | Chloro-benzene | 2-Chloro-toluene | 4-Chloro-toluene |
| sn006 | sample | 006c | < 2.2 | < 2.4 | nd | nd | nd |
| sn015 | sample | 008c | < 2.7 | < 4.6 | nd | nd | nd |
| sn037 | sample | 004t | < 3.2 | < 4.7 | nd | nd | nd |
| sn043 | sample | 021t | < 3.2 | < 4.7 | nd | nd | nd |
| sn045 | sample | 002t | < 2.6 | < 5.7 | nd | nd | nd |
| sn047 | sample | 011c | < 1.9 | < 2.8 | nd | nd | nd |
| sn048 | sample | 016t | < 1.8 | < 1.8 | nd | nd | nd |
| sn058 | sample | 012t | < 1.8 | < 2.8 | nd | nd | nd |
| sn061 | sample | 001t | < 2.3 | < 5.1 | nd | nd | nd |
| sn069 | sample | 008t | < 2.8 | < 4.9 | nd | nd | nd |
| sn079 | sample | 005t | < 2.0 | < 2.2 | nd | nd | nd |
| sn088 | sample | 015c | < 1.8 | < 1.8 | nd | nd | nd |
| sn090 | sample | 004c | < 3.2 | < 4.7 | nd | nd | nd |
| sn096 | sample | 009c | < 1.9 | < 3.2 | nd | nd | nd |
| sn097 | sample | 006t | < 2.3 | < 2.5 | nd | nd | nd |
| sn099 | sample | 014t | < 2.0 | < 2.4 | nd | nd | nd |
| sn066 | duplicate | 014t | < 1.7 | < 2.1 | nd | nd | nd |
| sn103 | sample | 009t | < 1.7 | < 2.8 | nd | nd | nd |
| sn108 | sample | 011t | < 1.9 | < 2.8 | nd | nd | nd |
| sn115 | duplicate | 011t | < 1.9 | < 2.8 | nd | nd | nd |
| sn127 | sample | 010c | < 1.8 | 3.1 | nd | 5.0 | 0.6 |
| sn129 | sample | 013t | < 1.9 | < 2.3 | nd | nd | nd |
| sn131 | sample | 003c | < 3.2 | < 4.7 | nd | nd | nd |
| sn145 | sample | 002c | < 3.5 | < 5.8 | nd | nd | nd |
| sn147 | sample | 012c | < 1.8 | < 2.8 | nd | nd | nd |
| sn162 | sample | 015t | < 1.7 | < 1.7 | nd | nd | nd |
| sn165 | sample | 016c | < 1.8 | < 1.8 | nd | nd | nd |
| sn168 | sample | 007c | < 2.7 | < 4.7 | nd | nd | nd |
| sn171 | sample | 001c | < 3.4 | < 5.6 | nd | nd | nd |
| sn172 | sample | 005c | < 2.3 | < 2.5 | nd | nd | nd |
| sn180 | duplicate | 005c | < 2.2 | < 2.4 | nd | nd | nd |
| sn186 | sample | 013c | < 1.8 | < 2.2 | nd | nd | nd |
| sn193 | sample | 010t | < 1.9 | < 3.2 | nd | nd | nd |
| sn198 | sample | 014c | < 1.9 | < 2.2 | nd | nd | nd |

* Those figures prefaced with '<' denote sample analysis results are below the TAGA detection limit.

** nd - not detected

Table A-4. SAMPLE ANALYSIS RESULTS FOR DETECTED SAMPLES (continued)

| Sample Number | Type | Site | TAGA (ppb) * | | Laboratory (ppb) ** | | |
|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | Total Chloro-toluene | Chloro-benzene | 2-Chloro-toluene | 4-Chloro-toluene |
| sn004 | sample | 222m | < 3.1 | < 4.6 | nd | nd | nd |
| sn009 | sample | 222m | < 2.0 | < 2.4 | nd | nd | nd |
| sn159 | duplicate | 222m | < 2.0 | < 2.4 | nd | nd | nd |
| sn028 | sample | 333m | < 1.9 | < 2.2 | nd | nd | nd |
| sn030 | sample | 333m | < 1.8 | < 2.7 | nd | nd | nd |
| sn044 | duplicate | 333m | < 2.0 | < 3.0 | nd | nd | nd |
| sn035 | sample | 111m | < 1.9 | < 1.9 | nd | nd | nd |
| sn040 | sample | 111m | < 1.9 | < 2.3 | nd | nd | nd |
| sn041 | sample | 222m | < 2.0 | < 2.2 | nd | nd | nd |
| sn049 | sample | 333m | < 2.4 | < 5.2 | nd | nd | nd |
| sn062 | sample | 222m | < 2.3 | < 5.1 | nd | nd | nd |
| sn065 | sample | 111m | < 3.4 | < 5.0 | nd | nd | nd |
| sn075 | sample | 111m | < 2.9 | < 5.0 | nd | nd | nd |
| sn093 | sample | 333m | < 1.7 | < 2.9 | nd | nd | nd |
| sn095 | sample | 111m | < 1.8 | < 2.8 | nd | nd | nd |
| sn101 | sample | 222m | < 1.9 | < 3.3 | nd | nd | nd |
| sn109 | sample | 111m | < 3.0 | < 5.0 | nd | nd | nd |
| sn113 | sample | 222m | < 1.9 | < 1.9 | nd | nd | nd |
| sn135 | sample | 222m | < 2.7 | < 4.7 | nd | nd | nd |
| sn141 | sample | 333m | < 2.9 | < 4.2 | nd | nd | nd |
| sn143 | sample | 111m | < 2.2 | < 2.4 | nd | nd | nd |
| sn150 | sample | 333m | < 1.8 | < 1.8 | nd | nd | nd |
| sn156 | sample | 333m | < 2.8 | < 4.9 | nd | nd | nd |
| sn157 | sample | 111m | < 2.0 | < 3.4 | nd | nd | nd |
| sn167 | sample | 222m | < 1.8 | < 2.7 | nd | nd | nd |
| sn178 | sample | 333m | < 2.2 | < 2.4 | nd | nd | nd |
| sn136 | duplicate | 333m | < 2.1 | < 2.3 | nd | nd | nd |

* Those figures prefaced with '<' denote sample analysis results are below the TAGA detection limit.

** nd - not detected

Table A-4 SAMPLE ANALYSIS RESULTS FOR COLLECTED SAMPLES (continued)

| Sample Number | Type | Site | TAGA (ppb) * | | Laboratory (ppb) ** | | |
|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | Total Chloro-toluene | Chloro-benzene | 2-Chloro-toluene | 4-Chloro-toluene |
| sn001 | sample | 611m | < 1.9 | < 1.9 | nd | nd | nd |
| sn038 | duplicate | 611m | < 2.0 | < 2.0 | nd | nd | nd |
| sn014 | sample | 611m | < 2.8 | < 4.8 | nd | nd | nd |
| sn018 | sample | 611m | < 1.8 | < 2.7 | nd | nd | nd |
| sn025 | sample | 611m | < 1.8 | < 2.2 | nd | nd | nd |
| sn039 | sample | 511m | < 2.3 | < 2.4 | nd | nd | nd |
| sn056 | sample | 611m | < 2.2 | < 2.4 | nd | nd | nd |
| sn060 | sample | 511m | < 1.8 | < 1.8 | nd | nd | nd |
| sn081 | sample | 611m | < 2.3 | < 5.0 | nd | nd | nd |
| sn084 | sample | 611m | < 3.0 | < 4.4 | nd | nd | nd |
| sn089 | sample | 511m | < 1.9 | < 2.3 | nd | nd | nd |
| sn105 | sample | 511m | < 1.9 | < 3.3 | nd | nd | nd |
| sn112 | duplicate | 511m | < 1.9 | < 3.3 | nd | nd | nd |
| sn122 | sample | 511m | < 1.9 | < 2.8 | nd | nd | nd |
| sn076 | duplicate | 511m | < 1.9 | < 2.8 | nd | nd | nd |
| sn132 | sample | 611m | < 1.9 | < 3.3 | nd | nd | nd |
| sn158 | sample | 511m | < 3.0 | < 4.3 | nd | nd | nd |
| sn174 | sample | 511m | < 2.9 | < 5.0 | nd | nd | nd |
| sn173 | duplicate | 511m | < 2.8 | < 4.8 | nd | nd | nd |
| sn185 | sample | 511m | < 3.2 | < 5.2 | nd | nd | nd |

* Those figures prefaced with '<' denote sample analysis results are below the TAGA detection limit.

** nd - not detected

Table A-5
SAMPLE ANALYSIS RESULTS FOR BLANKS

| SAMPLE NO. | TYPE | SITE | DATE | CHLOROBENZENE (TAGA) (ppb) | CHLOROTOLUENES (TAGA) (ppb) | CHLOROBENZENE (LAB) (ppb) | 2-CHLOROTOLUENE (LAB) (ppb) | 4-CHLOROTOLUENE (LAB) (ppb) |
|---|---|---|---|---|---|---|---|---|
| SN020 | Blank | -- | 07/30/86 p.m. | <1.8 | <2.8 | nd | nd | nd |
| SN054 | Blank | -- | 07/30/86 p.m. | <1.9 | <2.8 | nd | nd | nd |
| SN063 | Blank | -- | 07/31/86 p.m. | <1.9 | <1.9 | nd | nd | nd |
| SN104 | Blank | -- | 07/29/86 p.m. | <2.7 | <4.6 | nd | nd | nd |
| SN195 | Blank | -- | 07/31/86 p.m. | <1.7 | <1.7 | nd | nd | nd |

Notes:
1. Those figures prefaced with "<" denote results below the detection limit of the TAGA.
2. nd - not detected

Table A-6
SAMPLE ANALYSIS RESULTS FOR CHECK SAMPLES

| SAMPLE NO. | TYPE | DATE | CHLOROBENZENE (TAGA) (ppb) | CHLOROTOLUENES (TAGA) (ppb) | CHLOROBENZENE (LAB) (ppb) | 2-CHLOROTOLUENE (LAB) (ppb) | 4-CHLOROTOLUENE (LAB) (ppb) |
|---|---|---|---|---|---|---|---|
| SN042 | Audit | 07/31/86 a.m. | 12.0 | 14.3 | 10.9 | 6.9 | 6.9 |
| SN057 | Audit | 07/31/86 p.m. | 31.0 | 37.8 | 32.6 | 21.1 | 20.2 |
| SN068 | Audit | 07/29/86 a.m. | 13.2 | 16.0 | 12.0 | 7.7 | 7.5 |
| SN164 | Audit | 07/30/86 a.m. | 28.2 | 35.9 | 30.1 | 18.0 | 16.6 |
| SN188 | Audit | 07/28/86 p.m. | 47.2 | 63.5 | 30.3 | 20.2 | 19.5 |

# Table A-7
# DILUTION FACTORS

| SAMPLE NUMBER | DILUTION FACTOR | SAMPLE NUMBER | DILUTION FACTOR | SAMPLE NUMBER | DILUTION FACTOR |
|---|---|---|---|---|---|
| SN001 | 1.94 | SN063 | 1.87 | SN132 | 1.94 |
| SN003 | 1.87 | SN065 | 1.98 | SN133 | 1.84 |
| SN004 | 1.84 | SN066 | 1.73 | SN134 | 1.87 |
| SN005 | 2.08 | SN068 | 1.88 | SN135 | 1.80 |
| SN006 | 1.84 | SN069 | 1.87 | SN136 | 1.77 |
| SN007 | 1.84 | SN073 | 1.87 | SN137 | 1.87 |
| SN008 | 2.03 | SN074 | 1.95 | SN138 | 1.87 |
| SN009 | 2.01 | SN075 | 1.94 | SN141 | 1.70 |
| SN010 | 1.94 | SN076 | 1.87 | SN142 | 1.94 |
| SN011 | 1.98 | SN077 | 1.81 | SN143 | 1.84 |
| SN014 | 1.84 | SN078 | 1.80 | SN144 | 1.88 |
| SN015 | 1.77 | SN079 | 1.67 | SN145 | 2.51 |
| SN016 | 1.80 | SN081 | 2.26 | SN146 | 1.73 |
| SN018 | 1.77 | SN082 | 1.77 | SN147 | 1.84 |
| SN019 | 2.40 | SN083 | 1.77 | SN150 | 1.80 |
| SN020 | 1.84 | SN084 | 1.75 | SN154 | 2.44 |
| SN021 | 2.01 | SN085 | 1.94 | SN156 | 1.87 |
| SN022 | 1.87 | SN088 | 1.78 | SN157 | 1.98 |
| SN023 | 1.81 | SN089 | 1.94 | SN158 | 1.74 |
| SN024 | 1.70 | SN090 | 1.88 | SN159 | 1.98 |
| SN025 | 1.84 | SN092 | 1.74 | SN162 | 1.70 |
| SN026 | 1.94 | SN093 | 1.73 | SN164 | 1.87 |
| SN027 | 1.73 | SN094 | 1.77 | SN165 | 1.84 |
| SN028 | 1.87 | SN095 | 1.84 | SN166 | 1.77 |
| SN030 | 1.77 | SN096 | 1.87 | SN167 | 1.80 |
| SN031 | 1.95 | SN097 | 1.95 | SN168 | 1.80 |
| SN032 | 1.91 | SN098 | 1.94 | SN169 | 1.60 |
| SN033 | 1.87 | SN099 | 2.01 | SN170 | 1.81 |
| SN034 | 1.94 | SN100 | 1.82 | SN171 | 2.44 |
| SN035 | 1.87 | SN101 | 1.94 | SN172 | 1.95 |
| SN036 | 1.77 | SN102 | 1.77 | SN173 | 1.84 |
| SN037 | 1.88 | SN103 | 1.66 | SN174 | 1.94 |
| SN038 | 2.01 | SN104 | 1.77 | SN175 | 1.84 |
| SN039 | 1.88 | SN105 | 1.94 | SN177 | 1.84 |
| SN040 | 1.91 | SN106 | 2.05 | SN178 | 1.84 |
| SN041 | 1.70 | SN108 | 1.87 | SN179 | 1.94 |
| SN042 | 1.91 | SN109 | 2.16 | SN180 | 1.81 |
| SN043 | 1.88 | SN112 | 1.94 | SN181 | 1.70 |
| SN044 | 1.98 | SN113 | 1.91 | SN182 | 1.91 |
| SN045 | 2.58 | SN114 | 1.80 | SN183 | 2.33 |
| SN047 | 1.87 | SN115 | 1.87 | SN184 | 1.87 |
| SN048 | 1.78 | SN118 | 2.58 | SN185 | 2.26 |
| SN049 | 2.37 | SN119 | 1.67 | SN186 | 1.84 |
| SN050 | 1.87 | SN120 | 1.98 | SN187 | 1.84 |
| SN051 | 2.37 | SN122 | 1.87 | SN188 | 1.74 |
| SN054 | 1.87 | SN123 | 1.91 | SN190 | 1.91 |
| SN055 | 2.16 | SN124 | 2.40 | SN191 | 1.67 |
| SN056 | 1.84 | SN125 | 1.84 | SN192 | 1.80 |
| SN057 | 1.80 | SN127 | 1.84 | SN193 | 1.91 |
| SN058 | 1.84 | SN128 | 1.87 | SN194 | 2.54 |
| SN060 | 1.80 | SN129 | 1.91 | SN195 | 1.66 |
| SN061 | 2.33 | SN130 | 1.98 | SN196 | 1.94 |
| SN062 | 2.33 | SN131 | 1.88 | SN198 | 1.87 |
| | | | | SN199 | 1.94 |

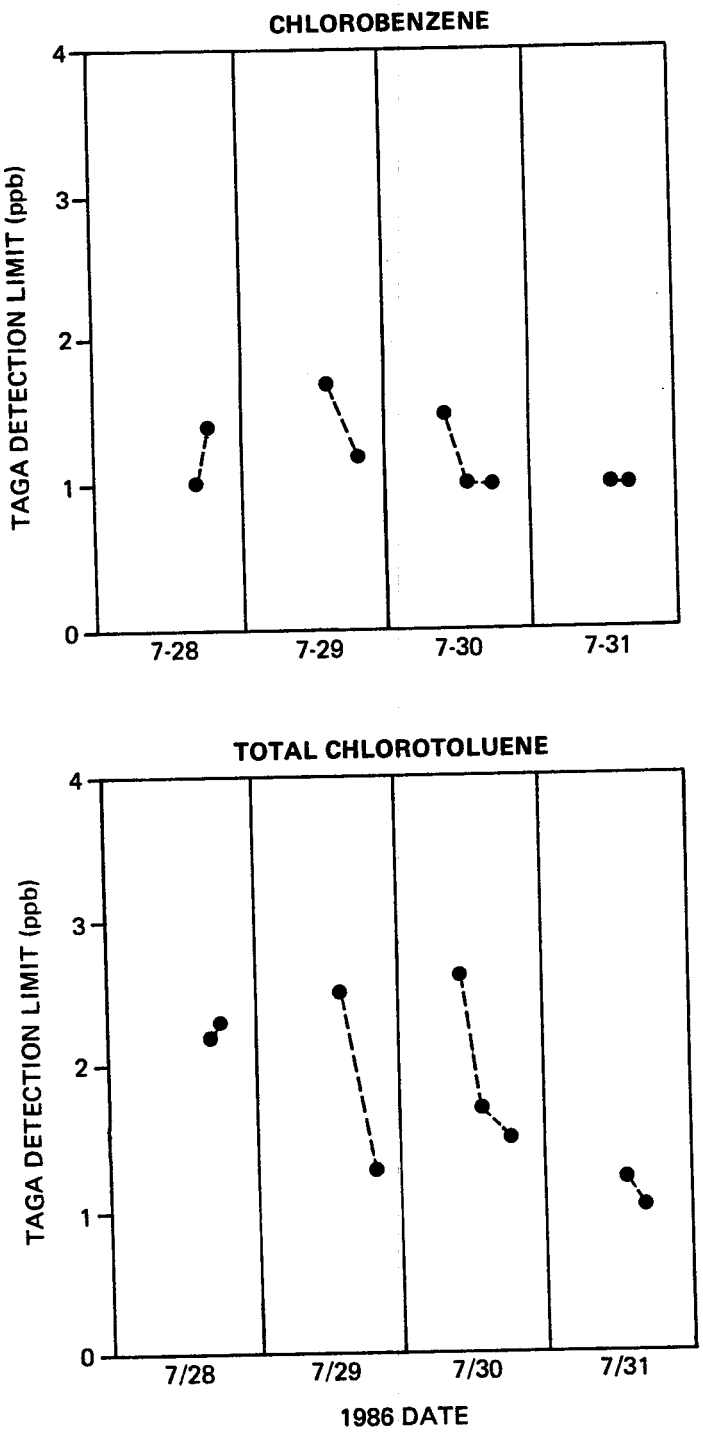



Figure A-3
**TAGA DETECTION LIMITS DURING THE FIELD INTENSIVE STUDY**

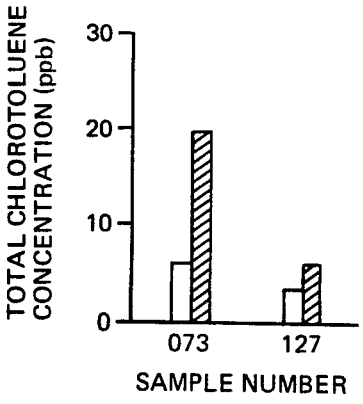



Figure A-4
**COMPARISON OF TAGA AND GC/MS RESULTS FOR DETECT SAMPLES (TOTAL CHLOROTOLUENE)**

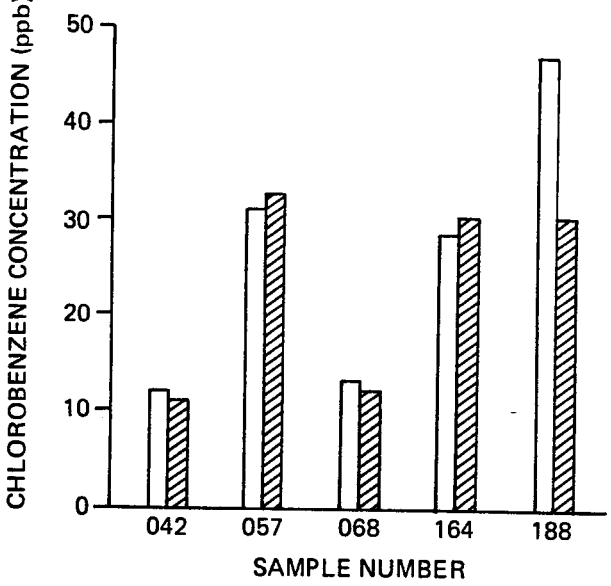
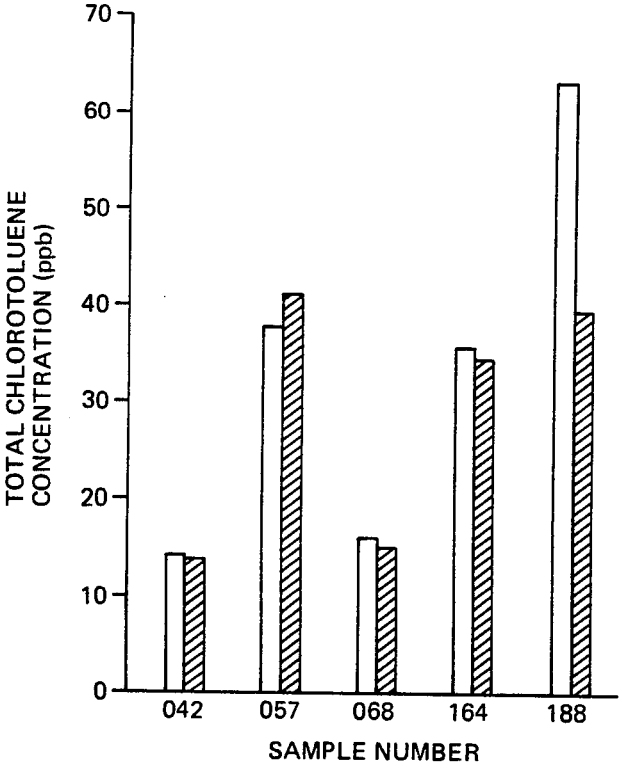



Figure A—5
**COMPARISON OF TAGA AND GC/MS RESULTS FOR CHECK SAMPLES (CHLOROBENZENE)**



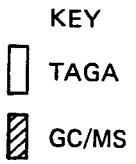




Figure A—6
**COMPARISON OF TAGA AND GC/MS RESULTS FOR CHECK SAMPLES (TOTAL CHLOROTOLUENE)**

in Figures A-5 and A-6 for chlorobenzene and chlorotoluene. Four of the five samples show concentration differences between the TAGA and GC/MS results of 1 of 4 ppb for both chlorobenzene and total chlorotoluene. Sample 188, however, shows a concentration difference of 17 ppb for chlorobenzene and 24 ppb for total chlorotoluene between the two instrument analyses.

Review of instrument records for TAGA analysis of sample 188 indicated that the TAGA ion source was turned off-and-on after the analysis of this sample and before the next routine calibration, making it impossible to quantify any sensitivity drift between the time of last calibration (less than 2 hours before) and the time sample 188 was analyzed. The possibility exists that the type of sensitivity drift (increase with time) shown in Figure A-3 occurred up to the time sample 188 was analyzed. Such an unnoticed increase in sensitivity would give a falsely high concentration reading.

A test for outliers has been performed on these five check samples results, comparing TAGA and GC/MS analysis. The test method followed the recommended procedure described in the Quality Assurance Handbook for Air Pollution Measurement Systems (USEPA, 1976). Test results implied that the measured differences in concentrations of either chlorobenzene or total chlorotoluene for sample 188 are questionable. No reasonable explanations are presently available.

Figures A-7 and A-8 correlate the TAGA and GC/MS results for chlorobenzene and chlorotoluenes. Figures A-7 and A-8 show close correlations for most check samples, except for check sample 188 and detect sample 073. The TAGA and GC/MS show close correlations for sample detect and nondetect.

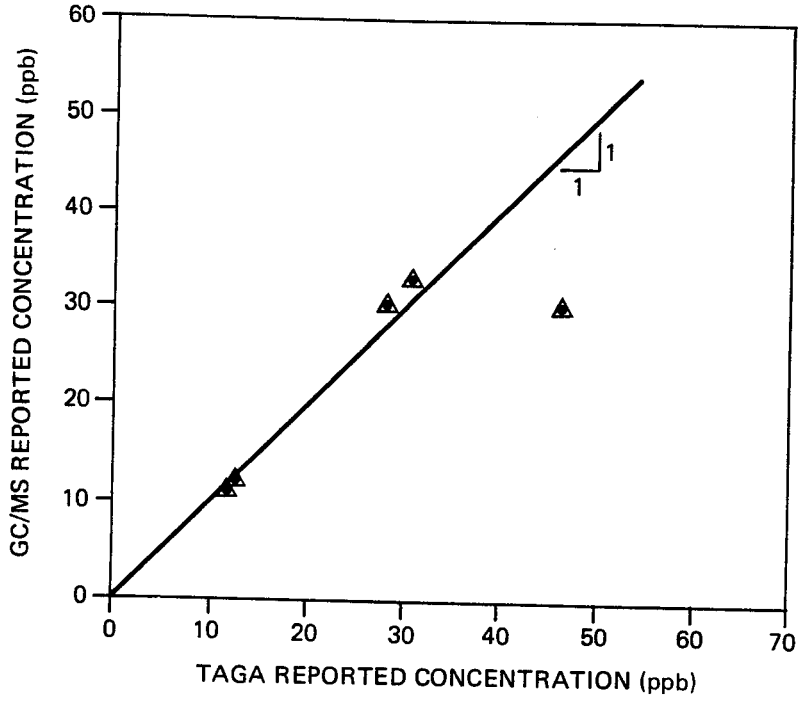



Figure A-7
**TAGA — GC/MS CORRELATION FOR CHLOROBENZENE**

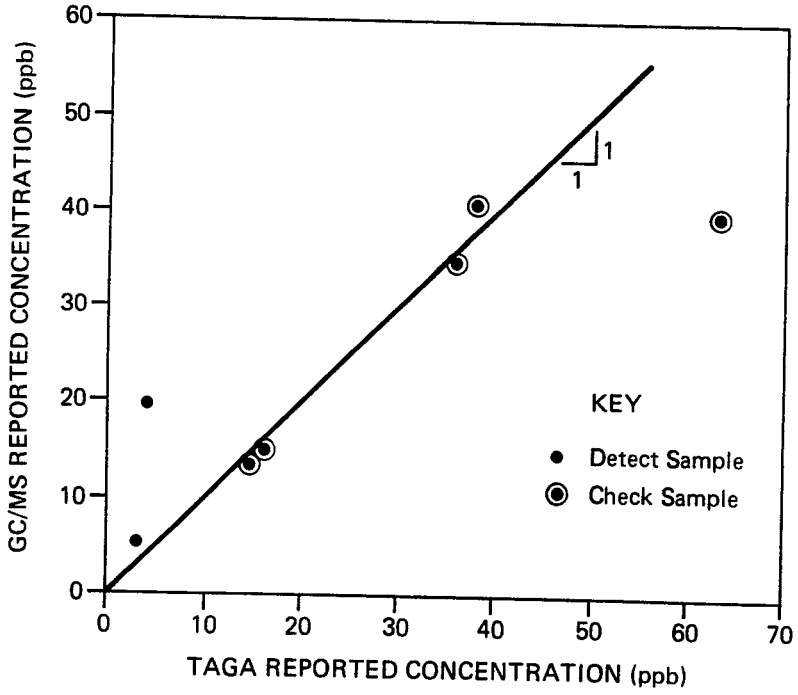



Figure A-8
**TAGA — GC/MS CORRELATION FOR CHLOROTOLUENE**

# 4.0 QUALITY ASSURANCE

This section provides an overview and describes the objectives, precision, accuracy and throughness necessary to obtain quality measurement data for the field intensive study.

## 4.1 Overview

Home survey questionnaires, indoor activity logs, and field notebooks were used to log and record activities. Field teams completed central sample control logs, chain-of-custody forms, and tracking and transmittal forms during the air sampling; and laboratories analyzed 134 samples, 16 duplicate samples, 5 check samples, and 5 blanks. Results obtained from the analysis of the duplicate samples were used to calculate precision, and the check sample results were used to calculate accuracy.

CH2M HILL and EPA quality assurance personnel reviewed quality assurance data from the TAGA and the analytical laboratory. The reviews provided a measure of confidence in the reported values and suggested quality assurance procedure modifications. The reviews also determined whether personnel followed QAPP procedures and protocols. The TAGA and the laboratory performed adequately with regard to chain-of-custody, calibrations, drift checks, and recordkeeping.

## 4.2 Objectives

The QAPP listed precision, accuracy, and completeness objectives as targets for the air sampling at Love Canal. Precision is calculated using the results obtained from the analysis of duplicate samples. Although duplicate pairs matched, the number of zero concentrations reported statistically invalidated precision calculations. Final confirmation of the check sample concentrations is not available at this time. Preliminary results based on comparison of GC/MS and TAGA results as well as the performance and system audit theoretical values indicate that the accuracy target was not met. The completeness objective was achieved with all samples accounted for. A detailed discussion of these objectives follows.

4.2.1 Precision. Precision for air quality measurements is calculated from the results obtained from the analysis of duplicate samples. Sixteen pairs of duplicate samples were collected and analyzed for the pilot study by both the TAGA and GC/MS units without prior knowledge of which samples were paired. Although the TAGA and GC/MS laboratory results were consistent in terms of detects and nondetects, precision cannot be calculated for results reported as "zero concentration."

4.2.2 Accuracy. Accuracy for air quality measurements is calculated from the results obtained from blind audit samples. Because no canister confirmatory analysis was performed by TAGA and GC/MS, the blind audit samples are called blind check samples. A discussion of check samples analyses based on theoretical values can be found on request in the Audit Report (Caviston et al., 1986) prepared for the performance and system audits for this task.

Target accuracies for chlorobenzene and both chlorotoluenes were ±20 percent. Assuming correct GC/MS analysis results, a preliminary calculation of accuracy based on the percent difference between the TAGA and the GC/MS results of each individual check sample was performed. The preliminary accuracy calculation for chlorobenzene resulted in an average percent difference of 12.9 with an upper 95 percent confidence limit of 44.2 percent and a lower 95 percent confidence limit of -18.4 percent.

Because the TAGA unit cannot distinguish the chlorotoluene isomers, the TAGA versus GC/MS accuracy calculation must be based on the results for total chlorotoluenes. This calculation results in an accuracy of 12.9 percent with an upper 95 percent confidence limit of 46.3 percent and a lower confidence limit of -20.5 percent.

The above comparisons, using the GC/MS results as the basis, indicate that the TAGA and GC/MS systems agree reasonably well. The target accuracy of ±20 percent was met for both chlorobenzene and total chlorotoluenes if the average percent difference is considered. The upper 95 percent confidence limit of 44.2 percent and 46.3 percent for the two components, respectively, do not meet the target accuracy. However, if sample 188 is considered as an outlier, the corresponding accuracy for chlorobenzene would be 2.2 percent with an upper 95 percent confidence limit of 14.9 percent and a lower 95 percent confidence limit of -10.5 percent. Similarly, the accuracy for total chlorotoluene would be 1.1 percent with an upper 95 percent confidence limit of 9.9 percent and a lower 95 percent confidence limit of -7.7 percent. For both components, the upper confidence limits meet the target accuracy of ±20 percent.

A comparison of TAGA and GC/MS results to the unconfirmed theoretical check sample concentrations (referred to in the Audit Report as "added" concentrations) may also be made. The calculation for GC/MS with respect to the theoretical concentrations results in an accuracy of 78.0 percent with 95 percent confidence limits of 88.4 (upper) and 67.6 (lower) percent for chlorobenzene, an accuracy of 33.8 percent with 95 percent confidence limits of 45.3 (upper) and 22.3 (lower) percent for 2-chlorotoluene, and an accuracy of 24.1 percent with 95 percent confidence limits of 36.3 (upper) and

11.9 (lower) percent for 4-chlorotoluene. The calculation for TAGA with respect to the theoretical concentrations results in an accuracy of 100.5 percent with 95 percent confidence limits of 153.8 (upper) and 47.2 (lower) percent for chlorobenzene, and an accuracy of 45.6 percent with 95 percent confidence limits of 92.7 (upper) and -1.5 (lower) percent for total chlorotoluenes.

Both sets of results indicate that there is a consistent positive bias with respect to theoretical values. The reason for this positive bias is presently undetermined; however, accuracy calculations based on unconfirmed theoretical concentrations do not meet the prescribed target objectives of ±20 percent for either GC/MS or TAGA. This positive bias, coupled with the extremely high percentage of zeroes reported, suggests that during the sampling period the concentrations of the indicator compounds present were below what should currently be considered as detection limits.

Accuracy calculations should be based on a comparison of reported results and results obtained by confirmatory analysis of the check samples; however, even with completed confirmatory analyses, results would remain questionable because of the long holding time for these samples prior to analysis.

In summary, final accuracy results are not available. Preliminary results indicate that the target objectives were not met when either TAGA or GC/MS is individually compared with the unconfirmed check sample concentrations; however, TAGA and GC/MS comparisons met the target objectives of ±20 percent, assuming the GC/MS analysis results are correct.

4.2.3 Completeness. Thirty samples were statistically required for each sampling stratum. Scheduling more than 30 indoor samples for each stratum achieved the completeness objective. Because two EDA houses originally identified as occupied were in fact unoccupied, two samples were redesignated as EDA unoccupied and additional occupied EDA homes were scheduled for sampling. A total of 30 occupied and 33 unoccupied EDA houses were sampled as well as 31 occupied houses in the comparison areas. Teams sampled five ambient air sites during eight sampling windows to total 40 ambient samples (24 in the EDA and 16 in the comparison areas).

## 5.0 DATA INTERPRETATION

The sample analysis results for the field intensive study identified two samples, both from occupied houses, one in the EDA and one in a comparison area, with detected levels of chlorotoluenes. None showed detected levels of chlorobenzene. Table A-8 summarizes the sample analysis results. The percentage of detect was approximately 3 percent for the EDA occupied homes and zero percent for the EDA unoccupied homes, approximating 1.7 percent overall for the EDA. In the comparison areas detects were 0 percent for Tonawanda and approximately 6.7 percent for Cheektowaga, approximating 3 percent overall. Earlier studies (USEPA, May 1982) at Love Canal found approximately 0.4 percent detect chlorobenzene and approximately 7 to 11 percent detect for chlorotoluenes among all indoor air samples in the EDA.

All ambient outdoor samples analyzed by TAGA or the GC/MS were nondetect for LCICs. The empirical censoring level for occupied houses in the pilot study is 29/30, or 96.66 percent.

Although no particular quantile is mentioned in the habitability criteria, an often discussed level of comparison is the 95th percentile. An individual estimated LCIC concentration from an EDA house would be compared with the 95th percentile of the distribution of estimated concentrations from comparison area houses. If the LCIC concentrations in an EDA home exceeded this criterion value, the source of the contamination would be sought by further sampling. Because 97 percent of the samples are nondetect, it will be difficult to uniquely estimate the 95th percentile, since any detectable concentration likely represents a value equal to or greater than the 97th percentile. This problem is discussed further in Section 7.0.

Although the absolute concentration levels obtained from the TAGA and GC/MS sample analyses differ, the two instruments are consistent in reporting detect and nondetect sample analysis results. Because the probable source for the detected levels was unclear, an attempt was made to identify indoor conditions and activities that might potentially contribute to or affect the LCIC concentrations. A review of the information in the questionnaires and the activity logs was inconclusive because the number of detects was inadequate for statistical analysis and the information available on the potential indoor or outdoor sources for the LCICs was insufficient. Because the detected chemical species were undetected in outdoor ambient samples, it is improbable that emissions from sources such as industrial facilities upwind of the sampling location or the canal contributed the detected levels.

Table A-8
SUMMARY SAMPLE ANALYSIS RESULTS

| Stratum | Number of Detect[a] | Number of Nondetects |
|---|---|---|
| EDA Unoccupied[b] | | |
| E1 | 0 | 3 |
| E2 | 0 | 19 |
| E3 | 0 | 2 |
| E4 | 0 | 4 |
| E5 | 0 | 0 |
| E6 | 0 | 5 |
| Total | 0 | 33 |
| EDA Occupied[b] | | |
| E1 | 0 | 9 |
| E2 | 0 | 7 |
| E3 | 0 | 5 |
| E4 | 0 | 2 |
| E5 | 0 | 0 |
| E6 | 1 | 6 |
| Total | 1 | 29 |
| EDA Ambient | 0 | 24 |
| Comparison Areas Occupied | 1 | 30 |
| Comparison Areas Ambient | 0 | 16 |

[a]Detected LCICs include 2-chlorotoluene and 4-chlorotoluene.

[b]Refer to Figure A-1 key map for subareas.

In November 1986 the DOH conducted a followup survey in houses with detected LCICs. The onsite inspection and information provided to the DOH by homeowners indicated the presence of several household products stored or used in the residences which may have contributed to the detection of chlorotoluenes in the indoor air. The DOH is contacting the manufacturers of these products to determine whether they contain either 2- or 4-chlorotoluene.

The three LCICs in question, chlorobenzene, 2-chlorotoluene, and 4-chlorotoluene, are rarely addressed in published air sampling studies. Moschandras et al., 1983 included chlorobenzene as one of the target compounds in a study for potential volatile compounds emissions associated with household gas appliances. A trace level (less than 0.2 ppb) of chlorobenzene was detected indoors; however, the source of the detected chlorobenzene was not specifically verified in the study. Bozzelli and Kebbekus (1983) of New Jersey Institute of Technology found variable outdoor ambient levels of LCICs in several New Jersey locations. The majority of the detected LCIC levels in their studies were below 1 ppb. Again the information was not conclusive in terms of source identification. Considering the difference in geographic location and chemical species studied, neither of these studies is appropriate to use for interpreting the pilot study results.

The pilot study results demonstrate the capability of the TAGA to detect LCICs at low parts per billion levels. The detection limit varies according to the amount of dilution of the samples and changes in ambient conditions. The reduction or elimination of the effects of these factors should improve the detection capability and consistency of the TAGA. The results of this pilot study apparently indicate that, with proper quality control procedures, the TAGA should be adequate at least for field screening analysis.

# 6.0 SUMMARY

## 6.1 Field Operation

A pilot air sampling study conducted in the EDA and comparison areas collected air samples using stainless steel canisters for field onsite analysis as well as laboratory confirmational analysis. Initial cleaning and leak checks showed no canister defects. The field canister recycling procedure was tested and shown to produce clean canisters for field reuse, and the sample collection technique using the cleaned, evacuated canisters proved feasible.

All scheduled occupied homes except four in the EDA were sampled. Owner absence necessitated selection of alternative houses to avoid sampling schedule delays. Only two homes in the comparison area were not sampled because of absent homeowners; one alternative sampling site was found and the other house was eliminated. There were no problems with access or collection of samples at the outdoor ambient sites. A canister sample routing control system designed for this study implemented sample collection, field sample analysis, canister cleaning, and additional confirmation and quantification with GC/MS analysis.

## 6.2 Sample Analysis

All field study canister samples were analyzed using the TAGA in the field to identify chlorobenzene and combined chlorotoluene isomers. Final field disposition of each canister sample was determined based on TAGA analysis results. All samples designated as detect and all duplicate sample pairs, blanks, and check samples were sent to the laboratory for GC/MS analysis. Ten duplicates and 10 control samples were required with controls defined as randomly selected TAGA nondetects. Because duplicate pairs were selected randomly on a daily basis and all the duplicate samples tested nondetect, one of each pair of duplicates also served as a control sample.

The GC/MS analysis provided confirmation and further quantification for the TAGA analysis of samples. The GC/MS results positively confirmed the identifications of LCICs by the TAGA. Further GC/MS quantifications correlated well with the TAGA results for most of the check samples analyzed when total chlorotoluene was considered.

## 6.3 Data Results

The results of the field intensive study revealed a low percentage of detects for LCICs in the EDA, and a comparable percentage for comparison areas. Check sample concentrations correlated closely between the two analytical instruments,

and all the duplicate samples and blanks results were consistent. The TAGA and GC/MS methods showed close agreement on detects and nondetects.

No chlorobenzene was detected in the collected samples. Both houses with detectable levels of LCICs in the EDA showed the presence of trace levels of chlorotoluenes. Because the detects were few and little information on the presence of chlorotoluenes in indoor environments was available in the literature, statistical analysis of the detected concentration values was not practical.

## 6.4 Objectives Met

The sampling results have revealed relatively low percentages of detects for both the EDA and comparison areas. The pilot study data were stratified by occupied/unoccupied house and by EDA/comparison area. The study can be interpreted only in terms of this stratification. That is, the detection rate is 1/30 for both the EDA occupied homes and the comparison area occupied homes.

Although the number of detects is too limited for statistical analysis, the LCIC concentrations detected in the pilot samples have provided some idea of the LCIC levels likely be found indoors and outdoors in the EDA and comparison areas.

The field intensive study also has provided information on the TAGA's capability and consistency. The TAGA can detect sample concentrations at low parts per billion levels with very short turnaround time in the field. The inability of the TAGA to distinguish the chlorotoluene isomers did not seem to be a handicap. However, since the TAGA is calibrated using ambient air and can be sensitive to changes in humidity, the effective detection limit may vary within a small range from day to day.

Samples collected and analyzed for the field intensive study have not suggested that either the offgases from the canal or the trace levels in outdoor ambient air contribute to the detected indoor LCIC levels. Without further detailed investigation, the sources for the LCICs that were detected indoors cannot be identified.

Because of the low percentage of detects found in the EDA and comparison areas, the data were insufficient to determine the sources of the LCICs. Review of the home questionnaires and activity logs also was inconclusive in terms of correlating the LCICs detected with any indoor activities involving volatile chemicals. The DOH is currently conducting a followup survey of the homes with detectable LCIC concentrations in an attempt to determine whether any household products may have contributed to the detected LCICs.

Using evacuated stainless steel canisters for the collection and preservation of samples was successful. Field recycling of the canisters provided clean canisters for reuse throughout the field study. The overall sample collection procedure successfully preserved the air samples for both field analysis and further laboratory analysis.

Laboratory GC/MS analysis is in general more specific than the TAGA in identifying LCIC isomers and more accurate in quantifying the detected levels. However, the TAGA was able to provide immediate onsite analysis for LCICs with reliable accuracy, as indicated by the correlation between the TAGA and the GC/MS analysis results.

Sufficient numbers of residents of both the EDA and comparison areas granted permission for entry and sampling. Of the total of 60 occupied homes, only 4 residents were absent at the scheduled sampling time, and alternative homes were found to satisfy the requirements of the pilot study.

# 7.0 RECOMMENDATIONS

## 7.1 General

The field study results show that the TAGA can provide prompt field analysis for LCICs with detection limits at low ppb levels and that stainless steel canisters used for air sampling provide a reliable method of collecting and preserving air samples containing LCICs for field and laboratory analyses. The field investigation analysis also indicates that the dilution factor introduced by adding pressurized ultra high purity air to the samples in the canisters compromises the instrument's detection limits.

On the one hand, it is more desirable to analyze the sample air directly as collected in order to achieve the lowest possible detection limits. This can be done by using the TAGA with a long sample transport tube to conduct sample air to the instrument sample port. This technique has been used in other indoor air studies for other target compounds, but not yet for LCICs. Flexible containers, such as air bags, also have been used in other sampling studies but have not been validated with respect to LCIC stability and container reliability. In order to implement either sampling approach for the habitability study, it would be essential first to establish the compatibility and stability of LCICs as measured by the TAGA direct sampling method. Concurrent with the preparation of this report, EPA's Environmental Response Team in Edison, New Jersey, has initiated a study to validate the TAGA's LCIC recovery in cold temperatures using a 200-foot heated sample transport tube, and to achieve more consistent and lower detection limits throughout the entire field study period.

On the other hand, since the TAGA can report only total isomer concentrations for the chlorotoluenes, even with a direct sampling technique it may still be necessary to quantify specific detected isomers using the laboratory GC/MS method. It would also be necessary, for the purpose of isomer separation, to develop a technique for parallel sampling (both directly with a long tube and with a canister) from the same source air simultaneously. Although preliminary information indicates that the laboratory GC/MS setup may be able to perform analysis with sample air drawn directly from the stainless steel canisters without pressurization using zero air, the analysis of canister samples would incur extra costs, and analysis results could only be obtained some days later.

Considering the analysis for chlorotoluenes using the TAGA, it is recommended to allow total chlorotoluene to replace 2- and 4-chlorotoluene as an LCIC. This change to addressing

total chlorotoluene should not cause any loss of information about either the presence of the respective isomers or the degree of quantification by TAGA. The available data on the detected 2- or 4-chlorotoluene in ambient air, such as the study in New Jersey by Bozzelli and Kebbekus (1983), indicated that the individual levels of these compounds if detected are at sub-parts-per-billion levels. The measurement of total chlorotoluene level as a sum of isomers using the TAGA yields a more quantifiable concentration level than individual isomers at low concentrations close to detection limits.

The data quality objectives for the habitability study will be specifically defined. To meet these requirements, the instrument tuning and calibration procedures, sample analysis procedures, identification and quantification criteria, and quality assurance/quality control procedures will be addressed in detail in the laboratory standard operating procedure. After this standard operating procedure is available, a specific quality assurance project plan addressing the data quality objectives will then be designed and implemented.

## 7.2 Time Variance Study

Since a very low percentage of detects was revealed in the field intensive study results, one of the primary tasks for the time variance study would be to locate a sufficient number of homes with detected LCICs for further evaluation of contamination. The field intensive study results indicate that the TAGA is an effective instrument for the screening analysis of homes. Since the TAGA is capable of providing "real-time" analysis results, multilocation sampling in a particular home is possible for the purpose of either identifying potential sources of contamination or selecting locations for temporal variation sampling. Diurnal changes in the indoor concentrations of LCICs also can be monitored by sequential sampling utilizing the TAGA, and seasonal variation can be studied through repeated sampling at the same location under different seasonal conditions.

Direct sample analysis using the TAGA would be the most efficient screening method. However, the canister sample collection method offers stable and secure air samples for repeated refined analysis. It is therefore desirable to include both techniques as alternatives before the TAGA validation study is completed.

Four sample collection and analysis alternatives may be considered for the time variance study:

- Use only the TAGA, with proper quality assurance and quality control procedures, for detecting LCIC

levels and tracing temporal variation of LCIC. It is recognized that, using the TAGA for sample analysis, the chlorotoluene isomers will have to be analyzed as total chlorotoluene.

- Use the TAGA and also collect a stainless steel canister air sample when a positive identification of LCIC occurs. This allows further confirmation and quantification of the LCIC.

- Use the TAGA, collect a canister sample for detects, and collect additional canister samples at randomly selected locations where no detectable levels of LCICs are found.

- Use only stainless steel canisters for sample collection and send all samples to the laboratory for GC/MS analysis. This alternative assumes that no TAGA analyses are to be performed. This alternative requires a large number of canisters, and it would be difficult to estimate the quantity needed.

Because of the low frequency of detects found in both indoor and outdoor air samples during the field intensive study, a primary task for the time variance study is to locate houses with detectable levels of LCICs for followup sampling and to provide nonzero concentrations data for statistical analysis if needed. The low frequency of detects also means that a large number of houses may need to be sampled before several detects can be found. Using the frequency for EDA occupied houses of 1 detect out of 30 sampled, to obtain three detected houses is expected to require screening 90 houses. No detects are expected to be found in unoccupied houses, based on the field intensive study results. Screening more EDA houses than were studied during the field intensive study would provide an estimate of expected percent of detects with more statistical confidence.

It seems clear that the TAGA, with its capability of performing "real time" analysis with detection limits at low ppb levels, would be the appropriate sample analysis instrument for screening a large number of houses. Of the four alternatives just proposed, the first is recommended, because any laboratory confirmatory analysis would generally delay the screening process. If appropriate quality assurance and quality control procedures can be developed for the TAGA, the confirmatory analysis may not be necessary.

The preliminary plan for the time variance study consists of: (1) the selection of four to six target houses through a screening search, (2) the detailed sampling in target houses with the attempt to identify and eliminate indoor source locations, if found, to establish "true" detect of

LCIC associated with the canal, (3) finalization of target houses, including nondetect houses if needed, (4) perform diurnal variation study, and (5) perform seasonal variation study. During the sampling period, the TAGA will be used to make traverse measurements of ambient air around the canal boundary periodically. This would provide information on any detectable LCIC contribution due to potential offgassing effect generally suspected for land disposal facilities.

The screening would consist of house-by-house sampling of each of four indoor locations: living room or den, kitchen, basement crawl space, and bedroom (preferably upstairs). Any detected levels found during screening will trigger a detailed sampling including more extensive room-by-room multi-location sampling with an attempt to locate and remove possible indoor emission sources for the LCIC detected. The houses with detected LCIC will be included as the target houses. If insufficient detects are found, randomly selected nondetect houses can be used to make up the four to six target houses. Detected houses during the field intensive study will be included as target houses if possible.

Diurnal sampling will be designed to monitor periodically the changes of LCIC concentrations, if detected, at a set of fixed indoor locations, preferably over a 24-hour cycle. Depending on the ease of access to the sampling location, modifications to monitor for less than 24-hour period may be considered. Sampling intervals will be approximately once every 2 hours at the same location.

Seasonal variation of the LCIC levels indoors is expected to be monitored during the sampling campaigns tentatively scheduled during March, May, and July.

## 7.3 Habitability Study

The habitability criteria specify that measurements of LCIC concentrations from each occupied house in the EDA would be compared to some aggregate measure of the distribution of concentrations in the comparison area. Although a particular quantile is not mentioned in the habitability criteria, an often discussed level of comparison is the 95th percentile. That is, an individual estimated concentration from a home in the EDA would be compared with the 95th percentile of the distribution of estimated concentrations from homes in the comparison area. If the EDA home exceeded this criterion value, the source of the contamination would be sought by further sampling.

Three sampling methods have been considered that would satisfy the intent of the criteria.

The first approach would be to select a sufficient number of homes in the comparison areas to estimate the 95th percentile and the 95th percent confidence limits on this percentile. Each estimate from a home in the EDA would then be compared with this estimated 95th percentile.

The major drawback to this approach is that the percentage of nondetects for the EDA occupied houses as estimated from the pilot study is 97 percent. This implies that the expected value of the 95th percentile is not detectable. One way around this would be to use a more conservative criterion such as the 99th percentile. Alternatively, if the detection limit of the analytical instrument could be lowered, more detects might result.

A second approach is to consider the 95 percent tolerance limit rather than an estimate of the 95th percentile. This approach is conceptually closer to the intent of the habitability criteria in that a nonparametric confidence level can be given that a given value is greater than 95 percent of the values obtained from the comparison areas. Specifically, if the largest estimated concentration from 90 samples taken from the comparison areas is used as the criterion, then there will be 99 percent confidence that this value is larger than 95 percent of all potential estimated concentrations of samples from this area. For 95 percent confidence in a concentration value being larger than 95 percent of estimated concentrations, 59 samples would be needed (see Conover, 1980, p. 119).

A third approach is recommended for the full study. This approach can be developed by examining the first two. For example, if there are about 90 occupied houses in the EDA and only three of them are expected to have detectable concentrations of an LCIC, then any criterion would be expected to affect about three houses. The zero detect frequency for the 33 randomly selected unoccupied houses in the EDA indicated that no detect house is expected statistically. If there are any, the number of houses should be very low. This being the case, it is a simpler and a more straightforward approach to resample any house in which an LCIC is detected to identify the source of LCIC rather than sample the comparison areas at all.

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Attachment 1

# SUMMARY OF TAGA ANALYSIS PROCEDURES

# FOR

# THE HABITABILITY STUDY AND THE REMAINDER OF THE PILOT STUDY

## GENERAL TAGA ANALYSIS PROCEDURE

The TAGA 6000E is a tandem mass spectrometer that samples ambient air for the trace levels of organic pollutants. The instrument has a low-pressure chemical ionization source that uses the sampled air as its chemical ionization reagent gas. The instrument draws samples from the outside air at a rate of 1.5 to 2 liters per second. From this sample stream approximately 10 milliliters per minute are pulled into the TAGA's source. This source uses the nitrogen, oxygen, and water vapor in the air to form various highly reactive charged species that then ionize the trace components with little or no fragmentation. The predominant parent ions formed by chlorobenzene in this process have masses of 112 and 114 atomic mass units (amu.), while those for chlorotoluene have masses of 126 and 128 amu. These parent ions are then isolated by the first filtering quadrupole and focused into a collision chamber, a nonfiltering quadrupole filled with sufficient argon gas to ensure that each parent ion will collide with an average of one argon molecule. The collisions cause the parent ions to fragment into smaller daughter ions, which are then separated by the second filtering quadrupole. When the two filtering quadrupoles are set to isolate the parent and daughter ions characteristic of a given compound, the ion current detected by the electron multiplier will be directly proportional to the concentration of that compound in the sampled air. When the ion signals for a group of such ion pairs are sequentially monitored with the above procedure, it is possible to analyze for several compounds on a semi-continuous mode while also reducing the risk of false positives by monitoring multiple fragmentation reactions for each compound (except for chlorobenzene, the parent of 112 amu. fragmenting to a daughter of 77 amu. and the parent of 114 amu. also fragmenting to a daughter of 77 amu.). The speed of the instrument allows a full set of measurements to be obtained every few seconds. Since preselected ion pairs are being monitored, it is not possible to obtain "spectra" while performing this type of analysis.

The selectivity of the instrument is compromised when two compounds, usually isomers, are present that form parent ions having the same mass and having daughter ions of equal mass but not always of equal intensities. Although no one compound interferes with all the monitored ion pairs for chlorobenzene, the ortho, meta, and para chlorotoluenes all share the same ion pairs. However, alpha-chlorotoluene forms a different parent ion from the parent ions of the other chlorotoluenes and therefore does not interfere with the quantification of the LCIC chlorotoluenes.

The instrument's high vacuum is maintained by a cryogenic pumping system that freezes the air pulled through the

source onto shells, called cryoshells, that are kept at temperatures ranging from 17° Kelvin at the beginning of the day to 19° Kelvin at the end of the day. Because the layers of frozen air insulate the shells from the sampled air, the shells must be thawed daily to boil off the trapped air. The thawing and recooling of the cryoshells, referred to as the instrument recycle, takes a minimum of 7 hours. Therefore, the instrument can be operated a maximum of 15 hours per day without affecting the time available for analyses the next day.

## SAMPLING PROCEDURES USED WITH THE TAGA

Because the TAGA can acquire a full set of concentration data every few seconds, several unique sampling methods will be used:

- Time-weighted average concentrations will be obtained at the center of selected rooms of each house sampled.
- Concentration versus location data will be obtained for houses in which the source of a LCIC is being determined.
- Ambient air concentrations versus location data will be obtained as the mobile laboratory is slowly driven around the canal itself.
- Time-weighted average ambient concentrations will be obtained outside each house analyzed and at upwind background locations.

Ambient air analyses are performed by pulling 1,500 to 2,000 ml/second of outside air through a glass sample port into a 7/8-inch Teflon tube connected by a glass tee to the instrument inlet probe. A 10 ml/minute aliquot is taken for analysis. One of the sample probes is extended through the laboratory roof and the other through the driver's side of the bus.

House air samples are taken by pulling the 1,500 to 2,000 ml/second sample through a Teflon-lined heated transfer tube that is maintained at 25°C to avoid any condensation of the LCICs on the tubing walls. Again a 10 ml/minute aliquot is pulled into the instrument for analysis. By using radio communications the sample crew will be able to tell the TAGA operator when the location of the inlet of the tube is moved, thus allowing the operator to place an appropriate flag in the data file. When the data are reduced the operator will be able to compare the flags with the sketches and notes in the sampling crew's logbook and thereby correlate the

concentration data to locations within the sampled house. For all houses analyzed, time-weighted average concentrations will be obtained for the center of the following rooms: the basement (or crawl space if no basement is present), the living room (or den, whichever is more heavily used), the kitchen, and one bedroom (preferably upstairs). Whenever an LCIC is detected, the concentrations will be monitored as the hose inlet is moved throughout the house in an attempt to isolate the source of the emissions.

## INSTRUMENT SETUP AND TUNING

At the start of each analysis day the instrument power is turned on and the high-voltage electronics are allowed to warm up for at least 30 minutes. While the electronics are warming up the heated sampling line will be turned on to allow it to come up to operating temperature. Also during this time, depending on the day, calibration checks will be performed on either the mass flow controller used in the cylinder calibrations or the transducer used to measure the flowrate of the sampled air. After the electronics have warmed up, a standard mixture of trichloroethylene and tetrachloroethylene is injected into the sample stream. The source conditions are then adjusted for any changes in humidity by maximizing the intensities of the parent ions formed by these two compounds. The source conditions are modified by changing the flow through the probe into the instrument, which in turn changes the source pressure, a key variable in determining the instrument's response. When this is completed the quadrupoles are tuned one at a time. Tuning a quadrupole initially consists of adjusting the resolution settings until all the preselected mass peaks have widths within the range of 0.6 to 0.8 atomic mass units and have acceptable peak shapes. The mass calibration of the quadrupole is then adjusted so that the quadrupole will filter the correct masses. This process is repeated for each quadrupole until no further adjustments are required. At this time the instrument is ready to be calibrated.

## CALIBRATION METHODS FOR THE TAGA

Since the TAGA uses the sample matrix to actually detect the trace contaminants, it is not possible to calibrate the TAGA by using gas standards that are fed directly into the instrument as would be done with more conventional air analysis equipment. Instead, all calibrations must be done by adding known concentrations of the vapors to the ambient air that is to be analyzed. By plotting the ion signals obtained at several different concentration spikes, it is possible to use a least-squares analysis to determine a slope that will be the proportionality constant that defines the instrument's

response per ppb of the compound present in that sample matrix. Individual response factors are determined for each pair: several ion pairs are monitored for each compound and the probability for a compound forming a given parent-daughter ion pair differ for each pair. The ratio of the response factors will equal the ratio of the probabilities. For example, the ratio of the 112/77 response factor to the 114/77 response factor should equal the ratio of the natural occurrences of the chlorine 35 isotope to the chlorine 37 isotope.

The calibration can be done in two ways: (1) by diluting a 25- to 50-ppm gas standard into the sample air stream and 2) by diluting air saturated with the compound's vapor into the sample stream. The first method has the advantage that the lowest concentration that can be realistically reached is a function of the original cylinder concentration, an easily changed variable. This method can be used to calibrate for several compounds simultaneously. Its disadvantages are that standard cylinders take several weeks to prepare and that the concentrations for some compounds do not remain stable over time, especially when the cylinder is being heavily used. Typical concentrations used for the cylinder calibrations for the LCICs range from 5 ppbv to 50 or 100 ppbv.

The second method uses a syringe drive to push into the sample stream air from a disposable syringe in which the air has been allowed to equilibrate with the vapor being emitted from several drops of the pure compound. The concentration in ppbv sampled will equal the vapor pressure of the compound divided by atmospheric pressure times the flowrate of air from the syringe barrel divided by the sample air flowrate. The vapor pressure of the compound is determined by measuring the temperature of the syringe barrel and then calculating a vapor pressure from the Antoine equation, a modified and more accurate version of the classical Clausius-Clapeyron equation. This method has the advantage that it can be used for any compound for which a database of vapor pressures versus temperatures exists. Its disadvantages are the fact that the lowest concentration used in the calibration is a function of the vapor pressure of the compound at room temperature and that errors in the vapor pressure determination can occur when the liquid has not reached the temperature of the syringe barrel. Typical concentrations used for the syringe drive calibrations are 12 to 55 ppb for chlorotoluenes and 25 to 100 ppbv for chlorobenzene.

## CALCULATIONS USED

The concentration of the analyte is determined by measuring the ion signals for a set of ion pairs supposedly unique for

that compound. Since the instrument is taking a set of ion pair measurements every few seconds, several measurements for each ion pair can be averaged for each reported ion pair signal. The average ion signals are then divided by the response factors for the appropriate ion pairs to generate a set of concentration values. These concentrations are then averaged to yield a better estimate of the concentration actually present in the air. By using the concentrations obtained from several ion pair measurements the slight effects of an interference to any concentration determination will be averaged out. Whenever an interference is major and therefore blatantly obvious, the concentration from the ion pair is not used in calculating the reported concentrations.

When the reported concentration is above the detection limit but below the quantification limit, the presence of the analyte is confirmed by the presence of positive signals for all of the monitored ion pairs. Once the reported concentration exceeds the quantification limit, the precision errors associated with measuring the individual ion pair signals become small enough to allow criteria to be applied to the individual concentration measurements versus the overall average concentration reported.

Detection limits are determined by monitoring the selected ion pairs while the instrument is sampling "clean" background air upwind of a potential source for several minutes and then determining the standard deviation in the signal obtained. If the background is truly clean, these signals will be equal to the background noise of the instrument. If the background is contaminated with a compound ubiquitous to the local environment, its concentration will remain essentially constant throughout the analysis. In either case the individual standard deviations in the ion pair signals are multiplied by three and then divided by the appropriate response factors. The individual 3 sigma values are then averaged to yield a detection limit for that compound. This approach is used because the decision of whether a compound is present or not is based upon the comparison of the average signal obtained for several ion pairs over several measurements against the average noise signal.

The quantification limits are calculated two ways. The first calculation involves multiplying the unrounded detection limits by 3.33 to obtain a 10 sigma value for the noise. While this method is quite appropriate for occasions in which definite signals are present in the background determinations, it tends to underestimate the uncertainty in the data when the sigma measurement is made for the electronic and random ion noise of the instrument. In these occasions the uncertainty in the low concentration measurement can be better approximated by using the theories of ion statistics, as initially derived by nuclear chemists measuring radiation,

to calculate a quantification limit from the response factors, the time taken to actually measure each ion signal, and the number of individual measurements used in obtaining an average concentration. This quantification limit is always compared against the 10 sigma limit and the larger of the two is used in processing the data.

## QUALITY CONTROL/QUALITY ASSURANCE

To avoid problems associated with potential drifts in the response factors caused by such factors as changes in the humidity, the response factors are remeasured throughout the day at predetermined intervals. The relative deviation of the response factors will be compared against the mean to determine if the instrument's sensitivity is stable or if it is starting to drift. Since each check of the response factors is a new calibration, whenever a drift is detected the new response factors will be loaded into the TAGA data acquisition programs. If the sensitivity is starting to drift, the percent drift between adjacent sets of calibration data will be monitored so that the drift stays within the criteria (based upon acceptable percent bias error levels) established in the QAPP. New detection limits will be calculated so that the sensitivity does not approach an unacceptable level.

As an additional quality assurance parameter, the percent accuracy and precision of the calibrations are calculated. The percent error due to the precision and accuracy of the calibrations is calculated from the standard deviations of the calibration data and a propagation-of-error analysis. The standard deviation is taken from the calibration curve itself (in particular the standard deviation of the actual concentrations from the curve concentrations at the same ion signal). The propagation-of-error analysis estimates the total error in the concentrations from the individual errors in the measurements used to calculate the concentrations. This latter term estimates the total effect that systematic individual errors in parameters such as the cylinder concentration and the sample air flow measurement could have on the accuracy of the calibration.

Additional quality control steps taken include:

- Checking the source pressure prior to each analysis to verify that it stays within 5 percent of the pressure used during the calibrations
- On alternate days checking the calibration of the mass flow controller used in the cylinder calibration to verify that it is within 10 percent

- On the other days checking the calibration of the transducer that measures the sample air flow to verify that it is also within 10 percent

- Periodically checking the transport efficiency of the heated sampling line to verify that it always greater than 90 percent

- Periodically checking the cylinder calibrations against the syringe drive calibrations to verify that the cylinder concentrations have not changed because of their heavy use

- Checking the calibration of the temperature probe prior to leaving the base lab. The temperature reading should be accurate within 5 percent. The syringe barrel temperature measured by the probe is required to compute a standard's vapor pressure.

- Checking the calibration of the syringe drive prior to mobilizing to verify that it is within 5 percent

# APPENDIX B
## Love Canal Soil Pilot Study

# Appendix B

# LOVE CANAL SOIL PILOT STUDY

CH2M HILL

February 1987

CONTENTS

TABLES



FIGURE

# INTRODUCTION

The Love Canal Emergency Declaration Area Proposed Habitability Criteria document (the habitability criteria document) (New York State Department of Health [DOH] and U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control [CDC], December 1986) describes the criteria that must be met in order for the Love Canal Emergency Declaration Area (EDA) to be considered habitable. One of the criteria is that the concentrations of certain chemicals in the EDA soil, called the Love Canal indicator chemicals (LCICs), should not be significantly different, individually or collectively, from the concentrations of these chemicals in the soils of two pre-selected comparison areas. The DOH selected the two comparison areas on the basis of criteria stated in the habitability document, one area in Cheektowaga and the other in Tonawanda. Both areas are in the vicinity of Buffalo and Niagara Falls, although neither is within the Niagara Falls metropolitan area.

The soil pilot study was designed to test sampling and analytical methods as a basis for implementing the soil LCIC comparison study, which is to be part of the habitability study called for in the habitability criteria document. This appendix describes the soil collection procedures and reports the analytical chemistry results. The pilot study provides information to reduce the uncertainties and assumptions surrounding the quality and characteristics of the data that will be obtained from the habitability study. Appendix C is a detailed discussion of the quality assurance and quality control aspects of the analytical chemistry method, and Appendix E is concerned with an in-depth look at the detection limits associated with the analytical chemistry method.

The soil pilot study was conducted by obtaining soil samples from the EDA and two comparison areas, splitting each sample, and sending the sample parts to two different analytical laboratories. The samples were collected and prepared using specially developed procedures. They were then subjected to an analytical technique 100 times more sensitive than techniques used in previous studies.

## OBJECTIVES

Specific objectives of the soil pilot study were to:

- Test specially developed soil sampling techniques to determine if these methods are suitable for use in the habitability study
- Test specially developed sample preparation techniques to determine if these methods are suitable for use in the habitability study
- Test new analytical procedures for measuring low-level (1-100 ppb) concentrations of the LCICs
- Determine the distribution of LCIC concentrations in the EDA and the comparison areas
- Identify sources of interlaboratory and intralaboratory variability in the analytical data
- Provide information needed to determine the number of samples needed for the habitability study

## SAMPLING DESIGN

The soil sampling plan was designed to estimate the sources of variability in the concentration values and to estimate the statistical distribution of these values. These estimates are needed to aid in the design of the sampling plan for the full habitability study which will be discussed in Volume II.

The importance of knowing the source and magnitude of variability in the data stems from the influence variability has on the sample sizes required for the habitability study. The more variable the data, the more uncertain are the estimates of the statistics derived from the data. For example, the uncertainty of the estimate of the mean value, assuming a normal distribution, is proportional to the intrinsic variability of the data (estimated by the standard deviation) divided by the square root of the number of samples.

More samples will be needed as the variability increases in order to obtain an uncertainty in the estimate of a mean no greater than a desired level (e.g., to compare the mean of the EDA concentrations of an LCIC with the mean of concentrations from the comparison area within a target resolution). The variability of concentration estimates can be reduced if the sources of variability can be identified and controlled.

Three sources of variability were thought to be important in the concentration estimates: spatial (sites), laboratories (interlaboratory), and analytical processes (intralaboratory). These were estimated by careful allocation of where the samples were taken in each area (EDA or comparison) and which labs analyzed each sample.

The main sampling scheme was to carefully randomize the location of each sample within an area and randomize other factors, such as order of collection, that might influence the results obtained. Each lab received equal numbers of samples from each area from each day of sampling. An analysis of variance was used with this scheme to estimate the magnitude of the three variability components.

Within this main sampling scheme an additional sampling scheme was included. The second scheme was to split all samples so that an additional estimate of intra- and interlaboratory variability could be obtained independent of spatial variability. One-third of the splits went to the same laboratory while the remaining two-thirds went to two different laboratories.

Estimates of the variability obtained from the 1980 EPA study led to 45 samples being taken from both the EDA and

the comparison areas. This sample size was based on a target of detecting a 16 percent difference in variance with 95 percent power and 95 percent confidence. The results of the chemical analysis of these samples and their splits are reported elsewhere in this report. The results of the statistical analysis will be reported in Volume II.

Inherent in the overall design of the soil pilot study was testing of a new analytical protocol designed to lower the detection limits of the LCICs by a factor of 100 from the 1980 EPA study. A special study was conducted to determine the method detection limit. At each sample site, a contingency sample was collected and was archived in the event that additional analysis was desired at a later date. Some of these were used after unsatisfactory attempts to analyze several of the original samples.

To select sampling locations, 120 potential sampling points were machine-generated on a Love Canal base map. If a point was outside of the EDA, in a river, in the middle of the roadway, or in some other unsuitable location, the point was not chosen as a sampling location. This method was followed until all 45 points were chosen. This procedure was repeated using maps of the comparison areas for selecting the 45 points in those areas.

Each of the 90 samples was divided into two parts. A balanced random allocation was used to assign the two parts of each original field sample to the three laboratories used for the soil pilot study. (These laboratories were Cambridge Analytical Associates of Boston, Massachusetts (CAA); the CH2M HILL laboratory in Montgomery, Alabama (MGM); and Environmental Monitoring Services in Thousand Oaks, California (EMS). More interlaboratory variance than intralaboratory variance was anticipated. Therefore, for two-thirds of the pairs of split samples, the two parts of each split sample were sent to different laboratories. For the remaining one-third of the pairs of split samples, both parts of each split sample were sent to the same laboratory.

## FIELD QUALITY CONTROL CHECKS

Interlaboratory and intralaboratory variances were measured by using quality control measures, which included preparation of:

- A replicate (split) of each regular sample
- Six replicates taken at one location in the EDA for measurement of precision of the collection procedure
- Field duplicates, representing at a minimum 10 percent of the number of samples collected, for measurement of any errors associated with the sample collection procedure
- Field handling blanks for measuring effects of sample handling in the field
- Preparation handling blanks for measuring the effects of sample handling in the sample preparation laboratory

In addition, at least 5 percent of the total number of containers (Shelby tubes, jars, and vials) cleaned were tested for contamination. No contamination was found, indicating that the samples were not contaminated during the cleaning process. Shipping and storage blanks and preparation shipping and storage blanks were also provided for analysis in case the field handling blanks indicated contamination. Finally, contingency storage blanks were used to measure any contamination from the contingency sample storage area and the shipment of samples to the storage area.

## SOIL SAMPLING PROCEDURE

The sample collection procedure consisted of these steps:

1. The area to be sampled was cleared of any surface debris (twigs, rocks, litter, snow, etc.) using a shovel.

2. The hydraulic Porta-Sampler was erected, anchored, and checked for operation.

3. The caps and shipping plug were removed from the Shelby tube. The head was wrapped in aluminum foil, dull side out, and attached to the Shelby tube.

4. The Shelby tube was attached to the Porta-Sampler.

5. The Shelby tube was driven into the ground to a depth of 13 inches using the Porta-Sampler. In the event of encountering rocks or other objects that obstructed penetration, the tube was withdrawn, emptied, and used at an adjacent site within a 1-square-foot area.

6. The tube was removed from the soil with the Porta-Sampler. The head was removed and checked to ensure that the tube was filled. If the tube was filled to less than 7 inches, Step 5 was repeated. If the tube was filled over 10 inches, Step 7 was performed. If the tube was filled between 7 and 10 inches, aluminum foil was placed, dull side toward the sample, on top of the sample core, and the remainder of the Shelby tube was filled with clean construction sand. The tube was then marked with the word "Sand" and a note was made on the shipping documents and Site Log. Step 7 was then performed. In the event that the tube could not retain the soil upon extraction, the following procedure was used.

   Another Shelby tube was driven into the ground next to the hole just created. A post-hole driver was used to remove soil immediately adjacent to the inserted Shelby tube. A spatula was used to cap the bottom of the tube and the tube was removed. Steps 7 through 9 were then performed.

7. When the head of the Shelby tube was removed, a 2½-inch-long space was left in the tube. To prevent volatile losses, the shipping plug was inserted into this space.

8. Copper caps were placed on both ends of the Shelby tube and sealed with evidence tape. The seal was covered with clear tape to prevent breakage. The outside of

the tube was cleaned with a wire brush to remove soil clumps. The sample data label was filled out and attached to the Shelby tube and covered with clear tape. Tubes were wrapped in aluminum foil to provide a degree of safety for sampling and laboratory personnel.

9. The tubes were placed in plastic bags. The bags were sealed with evidence tape and placed horizontally in a cooler. Blue Ice was used for cooling to 4°C. A maximum-minimum thermometer or other temperature indicator was placed in each cooler before shipping.

10. The aluminum foil on the head was replaced and the head reused.

11. Steps 1-9 were repeated within a 1-square-foot area immediately adjacent to the previous hole to collect the field duplicate or the contingency sample.

12. The holes were backfilled with either vermiculite or garden soil and any sod removed was replaced.

At the first sampling location in the EDA, six replicate samples were collected within a 2-square-foot area to measure the representativeness of the collection method.

## SAMPLE PREPARATION

During the sample preparation step, the soil from one Shelby tube was split into two replicates. Each replicate consisted of a jar with soil for semivolatile analysis and a vial with soil for volatile analysis, as specified in Chapter 10 of the Quality Assurance Project Plan for Analysis of Love Canal Indicator Chemicals in Soil Pilot Study (QAPP). These replicates were used to measure the interlaboratory and intralaboratory variances.

Coolers of samples were opened immediately upon receipt from the field and the temperature inside of the cooler was taken. If the temperature was higher than 4°C, a note was entered in a log book. The Shelby tubes were placed in a refrigerator at 4°C by sample preparation personnel. The following is a brief description of the soil preparation procedure. This procedure was developed on the basis of analytical results of testing done as part of the soil pilot study on the required mixing times to obtain optimum soil homogeneity and minimize volatile and semivolatile losses. Losses of volatiles and semivolatiles were measured using radioactive counts for 1,2,4-trichlorobenzene and dichlorobenzene under the following conditions: (1) sieving and mixing, (2) mixing in a cold room, and (3) mixing under a hood. The test results indicated that the optimal condition for increasing mixing and reducing losses were to mix for 30 seconds, collect the volatile sample, then mix for another minute and collect the semivolatile sample. All items used were cleaned according to the procedures outlined in the QAPP. The sample preparation procedures are as outlined below:

1. The Shelby tube was removed from the refrigerator and placed under a hood.

2. The copper caps and shipping plug were removed.

3. The soil was removed from the tube using a stainless steel extractor wrapped in aluminum foil, dull side out, and placed into an aluminum pan, which was also kept in a refrigerator until used. If the tube could not be extruded, the contingency tube was used.

4. Soil was mixed for homogeneity for 30 seconds by turning the soil over 50 to 60 times, using a spatula that was also kept in the refrigerator.

5. Soil for the volatile analysis was then selected with care to avoid rocks, glass, and other nonsoil particles.

6. Two 40-ml glass vials were filled with the selected soil with minimal headspace.

7. The vials were capped and sealed with evidence tape, placed in plastic bags, and retained in a separate refrigerator at 4°C until ready for shipment to the laboratories.

8. The remaining soil was mixed for one minute more by turning the soil over 60 to 120 times.

9. Two 120-ml glass jars were filled with the soil for semivolatile analysis.

10. The jars were capped and sealed with evidence tape, placed in plastic bags, and retained in a separate refrigerator with the volatile samples until ready for shipment to the laboratories.

At the beginning of each day, a meeting was held at the preparation laboratory to discuss the day's activities. A log detailing the preparation equipment and containers used during each day was maintained.

## ANALYTICAL RESULTS

Table B-1 presents a summary of the soil pilot study analytical results (see Attachment 1) as percent detects and maximum concentrations for each of the eight LCIC analytes in the EDA as a whole versus the comparison areas taken together. Tables B-2 through B-9 summarize the sampling data (numbers of sites and samples) and analytical results (numbers of nondetects and detects and maximum concentrations) for each of the six EDA sampling quadrants (E1 through E6) and each of the two comparison areas (Cheektowaga and Tonawanda). Figure B-1 is a key map showing the locations of the six EDA sampling sections.

As shown in the tables, tri- and tetrachlorobenzene had the highest significant percent detects in the overall EDA, with 30 to 50 percent detects for each of the two chemicals in sampling sections E1, E2, E4, E5, and E6. Semivolatile analysis of dichlorobenzene resulted in 16 percent total detects in the EDA, with 25 to 40 percent detects in E5 and E6. (Appendix C discusses the discrepancy between the semivolatile and volatile analysis results for dichlorobenzene.) Beta- and gamma-BHC, while not detected in significant percentages over the EDA as a whole, were detected in 50 percent of the E5 samples. Chlorobenzene, chloronaphthalene, and dichlorobenzene (upon volatile analysis) had low percent detects in the EDA as a whole and in any individual sampling section. Only dichlorobenzene (semivolatile analysis) showed any percent detects in the comparison areas, with 14.9 percent in Cheektowaga and 8.5 percent in Tonawanda.

As shown in Tables B-1 through B-9, relatively high maximum concentrations were recorded for tri- and tetrachlorobenzene and beta- and gamma-BHC in the EDA. Concentrations of 71.0 and 181.0 ppb, respectively, resulted for tri- and tetrachlorobenzene in section E5, while 15.4 and 28.3 ppb, respectively, were recorded for E6. Concentrations of 250.0 and 18.9 ppb, respectively, resulted for beta- and gamma-BHC in quadrant E5, while 8.4 and 4.3 ppb, respectively, were recorded for E4. Dichlorobenzene (semivolatile analysis) showed a maximum of 8.6 ppb in E5. Chlorobenzene, chloronaphthalene, and dichlorobenzene (volatile analysis) did not show any significant concentrations in the EDA as a whole or in any individual sampling section. The comparison areas showed no significant concentrations for any of the eight LCIC analytes.

Within the EDA, sampling quadrant E5 showed the highest percent detects and the highest concentrations collectively of the four LCIC analytes for which significant values for these two parameters were recorded, i.e., tri- and tetrachlorobenzene and beta- and gamma-BHC. (Dichlorobenzene-SV

Table B-1
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS
PERCENT DETECTS AND MAXIMUM CONCENTRATIONS FOR
LCICS IN THE EDA AND COMPARISON AREAS

| LCIC Analyzed | Percent Detects (>1.0 ppb) | | Maximum Concentration (ppb) | |
|---|---|---|---|---|
| | EDA | CA | EDA | CA |
| Chlorobenzene | 0 | 0 | n/d[a] | n/d |
| 1,2-Dichlorobenzene (VOA) | 0 | 0 | n/d | n/d |
| 1,2-Dichlorobenzene (SV) | 16.3 | 11.7 | 8.6 | 3.2 |
| 1,2,4-Trichlorobenzene | 31.7 | 1.1 | 71.0 | 1.4 |
| 1,2,3,4-Tetrachlorobenzene | 34.6 | 0 | 181.0 | n/d |
| 2-chloronapthalene | 1.0 | 0 | 1.1 | n/d |
| Beta-BHC | 3.8 | 0 | 250.0 | n/d |
| Gamma-BHC | 2.9 | 0 | 18.9 | n/d |

[a] n/d = nondetect.

Table B-2
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS FOR CHLOROBENZENE

| Sampling Area | No. of Sites | No. of Samples | No. of Nondetects (<1.0 ppb) | No. of Detects (>1.0 ppb) | Maximum Concentration (ppb) |
|---|---|---|---|---|---|
| EDA[a] | | | | | |
| E1 | 4 | 9 | 9 | 0 | n/a |
| E2 | 7 | 15 | 15 | 0 | n/a |
| E3 | 12 | 31 | 31 | 0 | n/a |
| E4 | 9 | 21 | 21 | 0 | n/a |
| E5 | 2 | 4 | 4 | 0 | n/a |
| E6 | 11 | 25 | 25 | 0 | n/a |
| Total | 45 | 105 | 105 | 0 | n/a |
| Comparison Areas | | | | | |
| Cheektowaga | 23 | 47 | 47 | 0 | n/a |
| Tonawanda | 22 | 47 | 47 | 0 | n/a |
| Total | 45 | 94 | 94 | 0 | n/a |

[a] See Figure B-1 for key map of EDA soil pilot study sampling quadrant locations.

Table B-3
SUMMARY OF SOIL PILOT STUDY SAMPLING AND
ANALYTICAL RESULTS FOR 1,2-DICHLOROBENZENE (VOA)

| Sampling Area | No. of Sites | No. of Samples | No. of Nondetects (<1.0 ppb) | No. of Detects (>1.0 ppb) | Maximum Concentration (ppb) |
|---|---|---|---|---|---|
| EDA[a] | | | | | |
| E1 | 4 | 9 | 9 | 0 | n/a |
| E2 | 7 | 15 | 15 | 0 | n/a |
| E3 | 12 | 31 | 31 | 0 | n/a |
| E4 | 9 | 21 | 21 | 0 | n/a |
| E5 | 2 | 4 | 4 | 0 | n/a |
| E6 | 11 | 25 | 25 | 0 | n/a |
| Total | 45 | 105 | 105 | 0 | n/a |
| Comparison Areas | | | | | |
| Cheektowaga | 23 | 47 | 47 | 0 | n/a |
| Tonawanda | 22 | 47 | 47 | 0 | n/a |
| Total | 45 | 94 | 94 | 0 | n/a |

[a]See Figure B-1 for key map of EDA soil pilot study sampling quadrant locations.

Table B-4
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS FOR 1,2-DICHLOROBENZENE (SV)

| Sampling Area | No. of Sites | No. of Samples | No. of Nondetects (<1.0 ppb) | No. of Detects (>1.0 ppb) | Maximum Concentration (ppb) |
|---|---|---|---|---|---|
| EDA[a] | | | | | |
| E1 | 4 | 9 | 9 | 0 | n/a |
| E2 | 7 | 15 | 12 | 3 | 5.1 |
| E3 | 12 | 31 | 28 | 3 | 1.3 |
| E4 | 9 | 22 | 21 | 1 | 1.1 |
| E5 | 2 | 4 | 3 | 1 | 8.6 |
| E6 | 11 | 23 | 14 | 9 | 3.6 |
| Total | 45 | 104 | 87 | 17 | 8.6 |
| Comparison Areas | | | | | |
| Cheektowaga | 23 | 47 | 40 | 7 | 3.2 |
| Tonawanda | 22 | 47 | 43 | 4 | 1.2 |
| Total | 45 | 94 | 83 | 11 | 3.2 |

[a]See Figure B-1 for key map of EDA soil pilot study sampling quadrant locations.

Table B-5
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS FOR 1,2,4-TRICHLOROBENZENE

| Sampling Area | No. of Sites | No. of Samples | No. of Nondetects (<1.0 ppb) | No. of Detects (>1.0 ppb) | Maximum Concentration (ppb) |
|---|---|---|---|---|---|
| EDA[a] | | | | | |
| E1 | 4 | 9 | 6 | 3 | 1.4 |
| E2 | 7 | 15 | 10 | 5 | 3.1 |
| E3 | 12 | 31 | 28 | 3 | 1.3 |
| E4 | 9 | 22 | 14 | 8 | 2.0 |
| E5 | 2 | 4 | 2 | 2 | 71.0 |
| E6 | 11 | 23 | 11 | 12 | 15.4 |
| Total | 45 | 104 | 71 | 33 | 71.0 |
| Comparison Areas | | | | | |
| Cheektowaga | 23 | 47 | 46 | 0 | n/a |
| Tonawanda | 22 | 47 | 47 | 0 | n/a |
| Total | 45 | 94 | 93 | 0 | n/a |

[a]See Figure B-1 for key map of EDA soil pilot study sampling quadrant locations.

Table B-6
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS FOR 1,2,4-TETRACHLOROBENZENE

| Sampling Area | No. of Sites | No. of Samples | No. of Nondetects (<1.0 ppb) | No. of Detects (>1.0 ppb) | Maximum Concentration (ppb) |
|---|---|---|---|---|---|
| EDA[a] | | | | | |
| E1 | 4 | 9 | 4 | 5 | 3.1 |
| E2 | 7 | 15 | 11 | 4 | 2.4 |
| E3 | 12 | 31 | 30 | 1 | 1.0 |
| E4 | 9 | 22 | 10 | 12 | 2.7 |
| E5 | 2 | 4 | 2 | 2 | 181 |
| E6 | 11 | 23 | 11 | 12 | 28.3 |
| Total | 45 | 104 | 68 | 36 | 181 |
| Comparison Areas | | | | | |
| Cheektowaga | 23 | 47 | 47 | 1 | 1.0 |
| Tonawanda | 22 | 47 | 47 | 0 | n/a |
| Total | 45 | 94 | 94 | 1 | 1.0 |

[a] See Figure B-1 for key map of EDA soil pilot study sampling quadrant locations.

Table B-7
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS FOR 2-CHLORONAPHTHALENE

| Sampling Area | No. of Sites | No. of Samples | No. of Nondetects (<1.0 ppb) | No. of Detects (>1.0 ppb) | Maximum Concentration (ppb) |
|---|---|---|---|---|---|
| EDA[a] | | | | | |
| E1 | 4 | 9 | 9 | 0 | n/a |
| E2 | 7 | 15 | 15 | 0 | n/a |
| E3 | 12 | 31 | 31 | 0 | n/a |
| E4 | 9 | 22 | 21 | 1 | 1.1 |
| E5 | 2 | 4 | 4 | 0 | n/a |
| E6 | 11 | 23 | 23 | 0 | n/a |
| Total | 45 | 104 | 103 | 1 | 1.1 |
| Comparison Areas | | | | | |
| Cheektowaga | 23 | 47 | 47 | 1 | 1.4 |
| Tonawanda | 22 | 47 | 47 | 0 | n/a |
| Total | 45 | 94 | 94 | 1 | 1.4 |

[a] See Figure B-1 for key map of EDA soil pilot study sampling quadrant locations.

Table B-8
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS FOR BETA-BHC

| Sampling Area | No. of Sites | No. of Samples | No. of Nondetects (<1.0 ppb) | No. of Detects (>1.0 ppb) | Maximum Concentration (ppb) |
|---|---|---|---|---|---|
| EDA[a] | | | | | |
| E1 | 4 | 9 | 8 | 1 | 4.6 |
| E2 | 7 | 15 | 15 | 0 | n/a |
| E3 | 12 | 31 | 31 | 0 | n/a |
| E4 | 9 | 22 | 21 | 1 | 8.4 |
| E5 | 2 | 4 | 2 | 2 | 250 |
| E6 | 11 | 23 | 23 | 0 | n/a |
| Total | 45 | 104 | 100 | 4 | 250 |
| Comparison Areas | | | | | |
| Cheektowaga | 23 | 47 | 47 | 1 | 13.9 |
| Tonawanda | 22 | 47 | 47 | 0 | n/a |
| Total | 45 | 94 | 94 | 1 | 13.9 |

[a]See Figure B-1 for key map of EDA soil pilot study sampling quadrant locations.

Table B-9
SUMMARY OF SOIL PILOT STUDY SAMPLING AND ANALYTICAL RESULTS FOR GAMMA-BHC

| Sampling Area | No. of Sites | No. of Samples | No. of Nondetects (<1.0 ppb) | No. of Detects (>1.0 ppb) | Maximum Concentration (ppb) |
|---|---|---|---|---|---|
| EDA[a] | | | | | |
| E1 | 4 | 9 | 9 | 0 | n/a |
| E2 | 7 | 15 | 15 | 0 | n/a |
| E3 | 12 | 31 | 31 | 0 | n/a |
| E4 | 9 | 22 | 21 | 1 | 4.3 |
| E5 | 2 | 4 | 2 | 2 | 18.9 |
| E6 | 11 | 23 | 23 | 0 | n/a |
| Total | 45 | 104 | 101 | 3 | 18.9 |
| Comparison Areas | | | | | |
| Cheektowaga | 23 | 47 | 47 | 1 | 8.6 |
| Tonawanda | 22 | 47 | 47 | 0 | n/a |
| Total | 45 | 94 | 94 | 1 | 8.6 |

[a]See Figure B-1 for key map of EDA soil pilot study sampling quadrant locations.

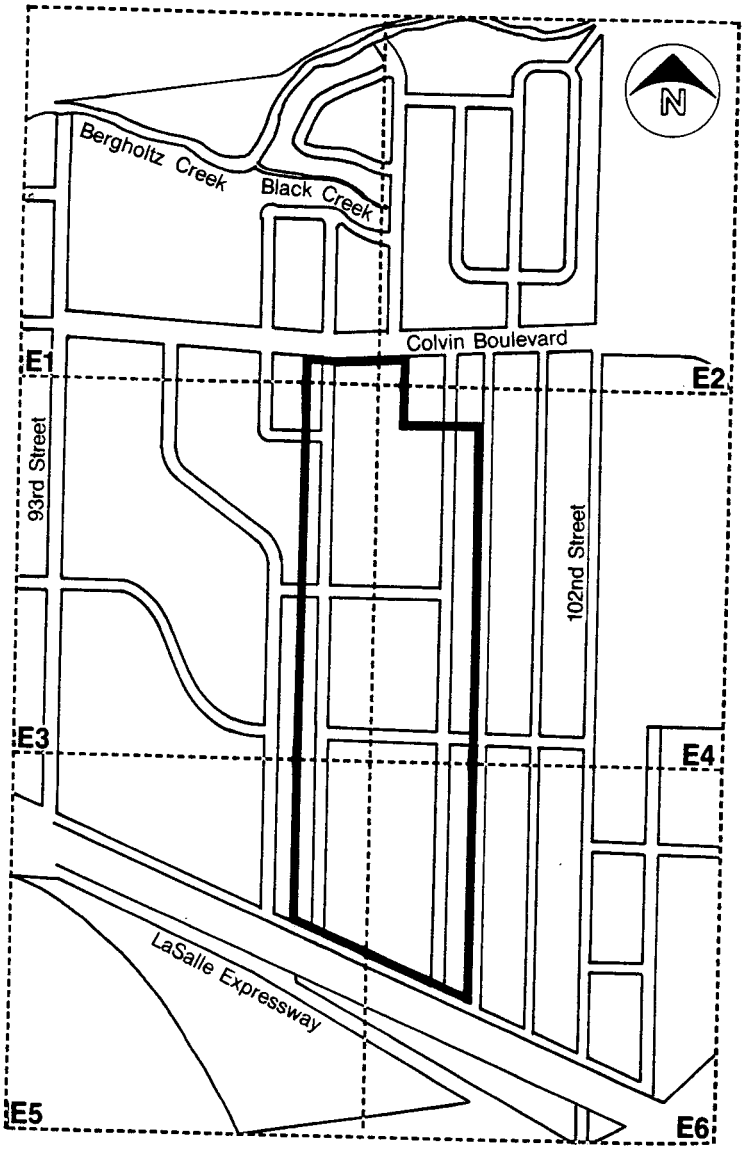



Figure B-1
**EMERGENCY DECLARATION AREA (EDA) STUDY SECTIONS**

values were not considered reliable.) Section E4 had among the highest percent detect for tetrachlorobenzene and second highest for trichlorobenzene and beta- and gamma-BHC; E4 also showed the second highest concentrations for beta- and gamma-BHC. Section E6 showed the highest percent detects (tied with E5) and second highest concentrations for tri- and tetrachlorobenzene. In general, however, concentrations are much higher in E5 than in either E4 or E6 for all four LCIC analytes with significant percent detects, and the percent detects are significantly higher than in E4 for beta- and gamma-BHC.

## SUMMARY AND RECOMMENDATIONS

The soil pilot study demonstrated the successful use of the soil sample collection procedure. The use of a hydraulic Porta-Sampler and Shelby tubes allowed easy collection of relatively undisturbed soil samples.

Soil samples were collected in Shelby tubes at 45 random locations in the EDA and in two comparison areas, Cheektowaga and Tonawanda. In the sample preparation laboratory, the samples were extruded, mixed, and split for shipment to the three analytical laboratories.

The sampling was designed to estimate the magnitude of three sources of variability in the data: spatial, interlaboratory, and analytical. The number of samples chosen was based on a target of having 95 percent power and 95 percent confidence of detecting a 16 percent difference in variability.

The soil collection procedures required collection of soil over a depth of 13 inches. Because the top 13 inches of soil in both the EDA and comparison areas consists mainly of fill and rubble, 40 percent of the Shelby tubes used for the soil pilot were filled only to depths ranging from 6 to 9 inches. Therefore, it is recommended that, in selecting the depth of sample needed, consideration should be given to both the amount of soil needed by the analytical laboratories and the depth to which the LCICs need to be measured. If 13 inches is not necessary, a shorter tube could be used. If 13 inches is required, criteria need to be established for cases where only 6 to 9 inches of soil is collected.

It was observed during sample preparation that the initial mixing for 30 seconds before collection of the volatile sample resulted in less of the bottom portion of the 10-inch length of soil being mixed than occurred for the additional mixing for the semivolatile sample. This observation, combined with the difference in dichlorobenzene concentrations between the volatile and semivolatile analyses, raises the question of whether the mixing protocol is having an impact on the volatile dichlorobenzene concentrations. Studies are currently under way to determine the impact of the partial mixing for volatiles analysis. If the mixing protocol is shown to affect the volatile analysis, the mixing protocol should be modified.

The analytical method was capable of reliably identifying and quantifying LCIC concentrations above 1 ppb. Appendixes C, D, and E provide more in-depth discussion on the performance of the analytical protocol.

Although many of the EDA LCIC concentrations were below 1 ppb, enough data were generated above 1 ppb to allow assessment of the distributional characteristics of the LCICs, especially di-, tri-, and tetra-chlorobenzene. Distributions of LCICs in the comparison area will be much more difficult to determine. Volume II will discuss the distributions in greater detail.

# REFERENCES


1. New York State Department of Health and U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control. Love Canal Emergency Declaration Area Proposed Habitability Criteria. December 1986.

2. CH2M HILL. Quality Assurance Project Plan for Analysis of Love Canal Indicator Chemicals in Soil Pilot Study. Appendix B of Love Canal Emergency Declaration Area Habitability Study. Niagara Falls, New York. May 1986.

Attachment 1

# LOVE CANAL HABITABILITY STUDY SOIL PILOT SUMMARY OF RESULTS

# LEGEND FOR ATTACHMENT 1

ND = Not detected at concentration below 1 ppb

NR = No results were reported because contingency samples were used for reanalysis

NA = The samples were not analyzed because only volatile or semivolatile LCICs, but not both, were required to be reanalyzed

B = A qualifier used when the analyte is found in the blank as well as in a sample.

LOVE CANAL HABITABILITY STUDY SOIL PILOT
SUMMARY OF RESULTS
ALL VALUES REPORTED IN PARTS PER BILLION (PPB)

Geographic Area: Cheektowaga

| Site ID | Sampling ID | Lab ID | Analytical Results | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
| SPCA1S01 | LC2041 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2114 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S02 | LC2021 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2154 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2290 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S03 | LC2181 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2206 | MGM | <1.0 | <1.0 | B 3.2 | B 1.4 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S04 | LC2049 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2064 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S05 | LC2065 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2128 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S06 | LC2068 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2212 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S07 | LC2033 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2130 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2284 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPCA1S08 | LC2207 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2249 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S09 | LC2047 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2152 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2276 | EMS | N.A. | N.A. | <1.0 | <1.0 | 1.0 | 1.4 | 13.9 | 8.6 |
| SPCA1S10 | LC2101 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2184 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S11 | LC2161 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2251 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2292 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S12 | LC2077 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2164 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |

Geographic Area: Cheektowaga

| Site ID | Sampling ID | Lab ID | Analytical Results: Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPCA1S13 | LC2014 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2116 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S14 | LC2013 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2073 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S15 | LC2080 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2239 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S16 | LC2040 | MGM | <1.0 | <1.0 | B 1.7 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2105 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2215 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S17 | LC2066 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2199 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S18 | LC2147 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2191 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S19 | LC2059 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2192 | MGM | <1.0 | <1.0 | B 1.3 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S20 | LC2142 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2170 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S21 | LC2017 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2226 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S22 | LC2173 | CAA | <1.0 | <1.0 | 2.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2180 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S23 | LC2001 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2098 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |

LOVE CANAL HABITABILITY STUDY SOIL PILOT
SUMMARY OF RESULTS
ALL VALUES REPORTED IN PARTS PER BILLION (PPB)

Geographic Area: Tonawanda

| Site ID | Sampling ID | Lab ID | Analytical Results: Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPCA2S01 | LC2185 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2233 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S02 | LC2304 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2313 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S03 | LC2106 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2240 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2378 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPCA2S04 | LC2208 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2228 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S05 | LC2311 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2322 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S06 | LC2030 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2150 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2273 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S07 | LC2048 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2122 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S08 | LC2109 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2139 | MGM | <1.0 | <1.0 | B 1.2 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S09 | LC2018 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2234 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S10 | LC2024 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2042 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S11 | LC2137 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2194 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S12 | LC2103 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2167 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |

Geographic Area: Tonawanda

| Site ID | Sampling ID | Lab ID | Analytical Results | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
| SPCA2S13 | LC2046 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2193 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2286 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S14 | LC2308 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2326 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S15 | LC2007 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2153 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2342 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2355 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPCA2S16 | LC2083 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2120 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2343 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | LC2369 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S17 | LC2061 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2119 | MGM | <1.0 | <1.0 | B 1.2 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S18 | LC2084 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2242 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2267 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S19 | LC2092 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2124 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S20 | LC2309 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2317 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S21 | LC2307 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2321 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S22 | LC2306 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2310 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |

LOVE CANAL HABITABILITY STUDY SOIL PILOT
SUMMARY OF RESULTS
ALL VALUES REPORTED IN PARTS PER BILLION (PPB)

Geographic Area: EDA

| Site ID | Sampling ID | Lab ID | Analytical Results | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
| SPEDAS01 | LC2223 | CAA | <1.0 | <1.0 | <1.0 | B 2.0 | 2.7 | <1.0 | <1.0 | <1.0 |
| | LC2250 | CAA | <1.0 | <1.0 | <1.0 | B 1.7 | 2.4 | <1.0 | <1.0 | <1.0 |
| SPEDAS02 | LC2087 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2222 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2287 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS03 | LC2023 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2188 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2338 | EMS | N.A. | N.A. | <1.0 | <1.0 | 1.1 | <1.0 | B 8.4 | <1.0 |
| SPEDAS04 | LC2039 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2045 | MGM | <1.0 | <1.0 | B 1.3 | B 1.2 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2160 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS05 | LC2294 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | LC2303 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2312 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS06 | LC2107 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2121 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2373 | EMS | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS07 | LC2182 | MGM | <1.0 | <1.0 | B 1.1 | B 1.4 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2232 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS08 | LC2089 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2214 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS09 | LC2044 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2082 | EMS | <1.0 | <1.0 | <1.0 | B 1.7 | B 1.3 | <1.0 | <1.0 | <1.0 |
| SPEDAS10 | LC2126 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2141 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS11 | LC2012 | MGM | <1.0 | <1.0 | <1.0 | B 1.3 | 1.0 | <1.0 | <1.0 | <1.0 |
| | LC2057 | MGM | N.R. | N.R. | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2257 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |

Geographic Area: EDA

| Site ID | Sampling ID | Lab ID | Analytical Results | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
| SPEDAS12 | LC2029 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2079 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2094 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2159 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2195 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2221 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2237 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS13 | LC2027 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2028 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2271 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS14 | LC2075 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2085 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2356 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2357 | EMS | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS15 | LC2056 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2086 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS16 | LC2291 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2293 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2368 | EMS | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS17 | LC2043 | EMS | <1.0 | <1.0 | <1.0 | B 7.6 | 13.1 | <1.0 | <1.0 | <1.0 |
| | LC2169 | CAA | <1.0 | <1.0 | <1.0 | B 10.8 | 15.9 | <1.0 | <1.0 | <1.0 |
| SPEDAS18 | LC2314 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2320 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS19 | LC2144 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2175 | CAA | <1.0 | <1.0 | <1.0 | B 1.1 | 1.6 | <1.0 | <1.0 | <1.0 |
| | LC2341 | EMS | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS20 | LC2305 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2324 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 4.6 | <1.0 |
| SPEDAS21 | LC2026 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2179 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2210 | MGM | <1.0 | <1.0 | B 5.1 | B 3.1 | 1.5 | <1.0 | <1.0 | <1.0 |

Geographic Area: EDA

| Site ID | Sampling ID | Lab ID | Analytical Results | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
| SPEDAS22 | LC2282 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2319 | MGM | <1.0 | <1.0 | <1.0 | B 1.4 | 3.1 | <1.0 | <1.0 | <1.0 |
| | LC2325 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | 2.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS23 | LC2009 | EMS | <1.0 | <1.0 | <1.0 | B 1.5 | B 1.7 | <1.0 | <1.0 | <1.0 |
| | LC2020 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | 1.0 | <1.0 | <1.0 | <1.0 |
| | LC2262 | EMS | <1.0 | <1.0 | <1.0 | 1.1 | 1.2 | <1.0 | <1.0 | <1.0 |
| SPEDAS24 | LC2148 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2229 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS25 | LC2072 | EMS | <1.0 | <1.0 | <1.0 | B 1.2 | B 2.9 | <1.0 | <1.0 | <1.0 |
| | LC2225 | MGM | <1.0 | <1.0 | <1.0 | B 1.2 | 1.8 | <1.0 | <1.0 | <1.0 |
| SPEDAS26 | LC2110 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2134 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2332 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPEDAS27 | LC2051 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2165 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS28 | LC2093 | MGM | <1.0 | <1.0 | B 1.3 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2211 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS29 | LC2002 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | 1.5 | <1.0 | <1.0 | <1.0 |
| | LC2108 | MGM | <1.0 | <1.0 | B 1.2 | B 1.2 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS30 | LC2063 | EMS | <1.0 | <1.0 | <1.0 | B 1.9 | B 2.4 | <1.0 | <1.0 | <1.0 |
| | LC2178 | MGM | <1.0 | <1.0 | <1.0 | 1.1 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS31 | LC2016 | MGM | <1.0 | <1.0 | B 1.2 | B 1.8 | 2.2 | <1.0 | <1.0 | <1.0 |
| | LC2166 | MGM | <1.0 | <1.0 | B 1.0 | B 1.3 | 1.6 | <1.0 | <1.0 | <1.0 |
| SPEDAS32 | LC2315 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2316 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2372 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPEDAS33 | LC2062 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2074 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS34 | LC2025 | EMS | <1.0 | <1.0 | <1.0 | B 9.0 | B 18.3 | <1.0 | <1.0 | <1.0 |
| | LC2151 | MGM | <1.0 | <1.0 | B 1.6 | 15.4 | 28.3 | <1.0 | <1.0 | <1.0 |
| | LC2151R | MGM | <1.0 | <1.0 | B 3.6 | 11.3 | 18.6 | <1.0 | <1.0 | <1.0 |

Geographic Area: EDA

| Site ID | Sampling ID | Lab ID | Analytical Results: Chlorobenzene | 1,2-Dichlorobenzene (VOA) | 1,2-Dichlorobenzene (SV) | 1,2,4-Trichlorobenzene | 1,2,3,4-Tetrachlorobenzene | 2-Chloronaphthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPEDAS35 | LC2129 | MGM | <1.0 | <1.0 | B 1.8 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2162 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS36 | LC2011 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2238 | MGM | <1.0 | <1.0 | <1.0 | B 1.4 | 1.7 | <1.0 | <1.0 | <1.0 |
| | LC2351 | CAA | N.A. | N.A. | <1.0 | 1.2 | 1.8 | <1.0 | <1.0 | <1.0 |
| SPEDAS37 | LC2318 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2323 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2330 | EMS | N.A. | N.A. | <1.0 | <1.0 | B 1.1 | 1.1 | <1.0 | B 4.3 |
| SPEDAS38 | LC2032 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | 1.0 | <1.0 | <1.0 | <1.0 |
| | LC2244 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS39 | LC2258 | MGM | N.R. | N.R. | B 1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2259 | MGM | <1.0 | <1.0 | B 1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2377 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPEDAS40 | LC2171 | MGM | <1.0 | <1.0 | B 1.% | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2248 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS41 | LC2183 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2220 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS42 | LC2131 | MGM | <1.0 | <1.0 | B 1.5 | B 2.1 | 2.1 | <1.0 | <1.0 | <1.0 |
| | LC2198 | CAA | <1.0 | <1.0 | <1.0 | B 1.6 | 2.5 | <1.0 | <1.0 | <1.0 |
| | LC2274 | MGM | <1.0 | <1.0 | B 1.2 | B 2.8 | 4.1 | <1.0 | <1.0 | <1.0 |
| SPEDAS43 | LC2010 | CAA | <1.0 | <1.0 | <1.0 | B 28.4 | 84.2 | <1.0 | 183.0 | 21.2 |
| | LC2209 | MGM | <1.0 | <1.0 | B 3.1 | B 30.0 | 93.8 | <1.0 | 250.0 | 18.2 |
| | LC2209R | MGM | <1.0 | <1.0 | B 8.6 | B 71.0 | 181.0 | <1.0 | 239.0 | 18.9 |
| SPEDAS44 | LC2081 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2100 | MGM | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2302 | CAA | N.A. | N.A. | <1.0 | 12.9 | 22.5 | <1.0 | <1.0 | <1.0 |
| SPEDAS45 | LC2069 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | 1.7 | <1.0 | <1.0 | <1.0 |
| | LC2241 | MGM | <1.0 | <1.0 | B 1.1 | B 1.1 | 2.1 | <1.0 | <1.0 | <1.0 |

GLCOM2/100

# APPENDIX C

## Review and Validation of Laboratory Data for Love Canal Soil Pilot Study

# Appendix C

# REVIEW AND VALIDATION OF LABORATORY DATA FOR SOIL PILOT STUDY

CH2M HILL

February 1987

CONTENTS

TABLES

FIGURES

# LIST OF ABBREVIATIONS

| | |
|---|---|
| EDA | Emergency Declaration Area |
| LCICs | Love Canal Indicator Chemicals |
| QAPP | Quality Assurance Project Plan |
| QA/QC | Quality Assurance/Quality Control |
| DQO | Data Quality Objective |
| VOA | Volatile Organic Analysis |
| SVOA | Semivolatile Organic Analysis |
| CAA | Cambridge Analytical Associates, Inc. |
| EMS | Environmental Monitoring Services, Inc. |
| MGM | CH2M HILL Montgomery, Alabama, Laboratory |
| GC/MS/SIM | Gas Chromatography/Mass Spectrometry/Selected Ion Monitoring |
| EMSL/LV | Environmental Monitoring Systems Laboratory/Las Vegas |
| NEIC | National Enforcement and Investigation Center |
| IS | Internal Standard |
| SS | Surrogate Standard |
| CLP | Contract Laboratory Program |
| MS/MSD | Matrix Spike/Matrix Spike Duplicate |
| RIC | Reconstructed Ion Chromatogram |
| SICP | Selected Ion Current Profile |
| IC | Initial Calibration |
| CC | Continuing Calibration |
| PC | Performance Check |
| RSD | Relative Standard Deviation |
| Std. Dev. | Standard Deviation |
| RPD | Relative Percent Difference |
| % D | Percent Difference |
| RF | Response Factor |
| $\overline{RF}$ | Average Response Factor |
| MDL | Method Detection Limit |
| UCL | Upper Control Limit |
| LCL | Lower Control Limit |
| $R_t$ | Retention Time |

# GLOSSARY

Quality control. A system of activities designed and implemented to provide a quality product.

Quality assurance. A system for integrating the quality planning, quality assessment, and quality improvement efforts of various groups in an organization to enable operations to meet user requirements at an economical level.

Outlier. An extreme value that questionably belongs to the group of values with which it is associated.

Control limits. The limits that have been derived by statistical analysis and are used as criteria for action, or for judging whether a set of data does or does not indicate lack of control.

Accuracy. The difference between an average value and the true value when the latter is known or assumed.

Precision. Relative to the data from a single test procedure, the degree of mutual agreement among individual measurements made under prescribed conditions.

Bias. A systematic error due to the experimental method that causes the measured value to deviate from the true value.

Relative standard deviation. The ration of the standard deviation of a set of numbers to their mean ($\bar{X}$) expressed as a percent.

$$\text{RSD (percent)} = 100 \frac{S}{\bar{X}}$$

Relative percent difference. The ratio of the difference of two results ($D_1 - D_2$) to their mean $\frac{D_1 + D_2}{2}$ expressed as percent.

$$\text{RPD} = 100 \frac{D_1 - D_2}{\frac{D_1 + D_2}{2}}$$

Internal standard. A known amount of a compound is added to a sample extract prior to analysis. The response of the detector to the internal standard is used in calculating the concentration of the analytes of interest. This compensates for any changes in instrument response over time.

Surrogate standard. Compounds that are produced commercially in large amounts and are not found in nature are added to the sample prior to preparation to monitor extraction efficiency.

Laboratory method/holding blank. An aliquot of sand that is stored in the refrigerator along with the field samples. The blank is prepared and analyzed as if it were a sample to show if there is contamination in the instrument or if there are problems with the sample preparation procedure.

Matrix spike. A sample to which a known amount of LCIC compounds is added in the laboratory, then extracted and analyzed. Recoveries are calculated as a percentage of the amount added. This is used to monitor the extraction efficiency of the analytical system and effects caused by the matrix.

Blank. A sample with no analytes of interest (see laboratory method/holding blank).

Chromatogram. The output of a gas chromatograph detector that plots signal versus time. Each peak represents a compound, the area under the peak being proportional to the concentration.

Instrument calibration standards. A mixture of known amounts of all target compounds of interest is analyzed. Response factors are generated for these compounds. Quantifications of these compounds found in the sample are calculated relative to this standard.

Instrument tune. The mass spectrometer is tuned or adjusted to produce a spectrum with well-defined characteristics. This is to ensure generation of spectra with correct mass-to-charge ratios and exact ion intensities,

Gas chromatograph (GC). An analytical instrument that separates organic compounds based on differences in physical and chemical properties such as boiling point, vapor pressure, and polarity.

Mass spectrometer (MS). A detector for GC that bombards a compound with an electron beam and records the result as a spectrum of positive ion fragments.

Retention time (Rt). The time that a compound takes to elute from the GC.

# C.1.0 INTRODUCTION

The Love Canal soil pilot study generated a large body of chemical data. This chemical data base includes the results of analysis of field samples and quality control samples. Data from those samples were critically evaluated and reviewed according to the quality control criteria established for this pilot study (see Section 3.0). The quality and validity of the data set were determined and sources of uncertainty in the chemical measurement process were identified. The significance of these uncertainties for the data set were noted. The data quality objectives set for the soil pilot study have been achieved by all the data reviewed. The identification and quantification of detected LCICs at concentrations greater than 1 ppb are highly reliable. However, the reliability of concentrations at less than 1 ppb is very low because of the interferences present in the samples.

# C.2.0 DESIGN OF ANALYTICAL PILOT STUDY

## C.2.1 INTRODUCTION

The Love Canal Emergency Declaration Area Proposed Habitability Criteria, a report issued by the New York State Department of Health and the U.S. Department of Health and Human Services/Centers for Disease Control (DHHS/CDC) in 1986, recommended that concentrations of Love Canal indicator chemicals (LCICs) in EDA soil be compared to concentrations of LCICs in the soil of selected comparison areas. This comparison would provide data to help determine whether or not the EDA is habitable.

The decision to resample the EDA and perform chemical analyses on the samples using more sensitive techniques was made because the detection limits and possible assignment of values of nondetects are important factors in the habitability decisionmaking process. The reasons for selecting certain halogenated compounds as LCICs are discussed in detail in the habitability criteria report (DOH/CDC, 1986). The chosen soil LCICs include the following chemicals:

- Volatile LCICs
  - Chlorobenzene
  - 1,2-Dichlorobenzene
- Semivolatile LCICs
  - 1,2-Dichlorobenzene
  - 1,2,4,-Trichlorobenzene
  - 2-Chloronaphthalene
  - 1,2,3,4-Tetrachlorobenzene
  - Beta-BHC
  - Gamma-BHC (Lindane)

The relative volatility of 1,2-dichlorobenzene may make acceptable recovery of the compound difficult to achieve using the semivolatile procedures. For this reason, 1,2-dichlorobenzene was analyzed by both volatile and semivolatile protocols.

The soil pilot study was conducted by obtaining soil samples from the EDA and two comparison areas, a neighborhood in Tonawanda, New York, and another in Cheektowaga, New York. The samples were collected and prepared using specially developed procedures. These samples were subjected to an analytical technique with greater sensitivity than the techniques previously used. The results of the analysis were used to determine (1) if low levels of contaminants are present in the EDA and comparison areas, (2) the suitability

of the method for obtaining samples and conducting analyses to detect these low levels of contamination, (3) whether the source of contamination is associated solely with Love Canal, and (4) the variability of the data (see Appendix E).

U.S. EPA Region II has the overall responsibility for the pilot study project management. The EPA's Environmental Monitoring Systems Laboratory at Las Vegas (EMSL/LV) provided independent quality assurance (QA) assistance to EPA Region II during the soil pilot study. EMSL/LV prepared the blind quality control (QC) samples, ran the onsite laboratory, and assessed the final analytical data. Audit of laboratory operations pertaining to chain-of-custody and document control for the soil pilot study was provided by the National Enforcement and Investigation Center (NEIC) Contract Evidence Audit Team (CEAT).

The sampling effort was performed by Environmental Science and Engineering (ESE) under subcontract to CH2M HILL, and sample analysis was conducted by Cambridge Analytical Associates (CAA), Environmental Monitoring Services, Inc. (EMS), and the CH2M HILL Montgomery, Alabama, laboratory (MGM) in parallel.

## C.2.2 ANALYTICAL OBJECTIVES AND USE OF DATA

The overall objective of the analytical phase of the pilot study was to determine what levels of selected volatile and semivolatile LCICs could be detected in soil in the EDA and the comparison areas. The levels of LCICs that could be detected were more than 100 times lower than those detected in previous efforts.

The specific analytical objectives of the pilot study included:

- Evaluate a new analytical procedure for measuring low-level (1 to 10 ug/kg) concentrations of selected volatile and semivolatile LCICs.
- Generate information on the distribution of concentrations of selected volatile and semivolatile LCICs found in the EDA and the comparison areas.
- Test specially developed soil sampling and preparation techniques to determine if these methods affect analytical results.
- Generate information on the sources of intralaboratory and interlaboratory variability in the analytical data so that the analytical protocols can be refined for the full-scale habitability study.

- Develop methods for estimating LCIC detection limits for GC/MS/SIM.

The data resulting from this sampling and analysis activity are being used in the design and preparation of a sample collection and analysis plan for performing a large-scale resampling and reanalysis of the EDA and comparison area soils to determine the habitability of the EDA.

## C.2.3 METHOD DEVELOPMENT AND IMPLEMENTATION

During the early stages of method development, a method was chosen to analyze semivolatile LCICs using fused silica capillary column chromatography with electron capture detection (GC/ECD). The proposed GC/ECD method provided a sensitive screen for GC/MS analysis. Modified GC/MS procedures were to be used for confirmation when possible. Second column confirmation with a different capillary column was used when modified GC/MS techniques could not confirm the target identity or concentration. For analysis of volatile LCICs, purge and trap gas chromatography with electrolytic conductivity detection was proposed. However, during the initial performance evaluation samples analysis, it was found that the GC/ECD semivolatile method blanks analysis results were unacceptable because of apparent contamination from the solvents. It was recommended by EMSL/LV that a GC/MS/SIM technique be used to provide a higher degree of sensitivity and specificity. The MGM laboratory then took the leading role in developing methods for the analysis of LCICs in soil using GC/MS/SIM techniques. It should be pointed out that the isotope dilution GC/MS technique also was considered. Although there are certain advantages to using the isotope dilution GC/MS technique, it was decided that the next best technique, i.e., GC/MS/SIM, should be used because the stable-labeled isotopes required by the former technique for all the compounds of interest were not available.

The LCIC analytical methods used for the Love Canal soil pilot study were extensively evaluated and validated prior to the pilot study. The validation process involved numerous spiking studies in a variety of matrixes by both MGM and CAA laboratories. Also, representatives of all three participating laboratories met in a common laboratory session and applied the method to a set of samples to improve uniformity of interpretation and implementation of the detailed sample preparation techniques. In addition, all three participating laboratories were required to analyze performance evaluation samples prepared by EMSL/LV and were audited by EMSL/LV prior to the soil pilot study. The results from

these extensive experimental studies were carefully evaluated, and revisions to the analytical methods were incorporated as additional experimental data were obtained. The latest revised methods, dated June 23, 1986, were used for the pilot study.

## C.3.0 OVERVIEW OF QUALITY ASSURANCE PROGRAM

Because of the importance of laboratory results in determining practical courses of action that may be followed in the full-scale habitability study, a QA/QC program was implemented for all the participating laboratories. The criteria specified in the QA/QC program were used to monitor laboratory performance during the soil pilot study and to improve the reliability of the chemical data. This section presents an overview of the QA/QC program and a description of the QA/QC requirements that were followed by the participating laboratories. How well the laboratories met these requirements is discussed in sections 4.0 and 5.0.

### C.3.1 SAMPLE HOLDING TIME REQUIREMENTS

Maximum sample holding times prior to analysis were based on the EPA Contract Laboratory Program (CLP) requirements. The samples for volatile LCIC analysis should be analyzed within 10 days of receipt by the laboratory. Samples for semivolatile LCIC analysis should be extracted within 10 days of receipt by the laboratory. Extracts should be analyzed within 40 days of extraction.

### C.3.2 SAMPLE PREPARATION AND ANALYSIS REQUIREMENTS

The sample preparation and analysis procedures used in the soil pilot study are summarized below.

For semivolatiles analysis, a 20-gram portion of soil and 25 ug/kg surrogate standards were mixed with approximately 50 grams of anhydrous sodium sulfate and extracted with 100 ml of 1:1 methylene chloride/acetone three times using an ultrasonic probe. The combined extract was concentrated and the solvent was exchanged into hexane. Alumina and sulfuric acid cleanup techniques were applied to the extracts. The cleaned extract was concentrated again to a volume of approximately 1.0 ml. Immediately prior to GC/MS analysis, internal standards at concentrations of 200 ug/l were added to the cleaned extracts, and the extracts were concentrated down to a volume of 200 ul by a gentle stream of purified nitrogen. A 1- to 2-ul aliquot of the extract was analyzed by capillary column GC/MS operating in the SIM mode. Qualitative identification of the target semivolatile LCICs was based on the criteria described in section C.4.

Quantification of the target LCIC was performed by the internal standard technique using the primary ion and based on dry weight. Each of the LCICs was referenced to the closest internal standard for calculation. A listing of descriptors

and characteristic ions for LCIC surrogate standards and internal standards is given in Table C-1.

For volatiles analysis, inert helium gas was bubbled at 40-ml/min for 12 minutes through a mixture of a 5.0-gram sample, 1.0 ug/kg surrogate standard, and 10 ml of reagent water in a specially designed purging chamber at 40°C. Volatile organics were transferred from the aqueous phase to the vapor phase. The vapor was swept through a sorbent column where the volatiles were trapped. After purging was completed, the sorbent column was heated at 180°C for 4 minutes and backflushed with the inert gas to desorb volatile organics onto a packed GC column. The gas chromatographic oven was temperature-programmed from 100°C to 220°C at a rate of 25°C/minute to separate the target volatile LCICs from other compounds that could interfere with their determination. The volatile LCICs were then detected using an MS operated in the SIM mode. The qualitative identification criteria used in the semivolatile LCIC analysis were also used to verify the volatile LCIC identification. Quantification of the volatile LCICs was performed by the internal standard method and based on dry weight. The SIM areas of the characteristic ions of the target LCIC were used. The response factor (RF) from the daily standard analysis was used to calculate the concentration in the sample. Each of the LCICs was referenced to the closest internal standard for calculation. A listing of descriptors and characteristic ions for LCICs, surrogate standards, and internal standards is given in Table C-2.

### C.3.3 DATA QUALITY OBJECTIVES

The data quality objectives (DQOs) presented in Table C-3 are designed to provide analytical data of known quality to adequately satisfy the soil pilot study objectives and to defend the quality of those data. However, the DQOs are goals that may or may not be achievable using the method selected within the time and resources available. Using the data generated from the pilot study, more definitive DQOs will be developed for the habitability study. The DQOs are assessed on the basis of precision, accuracy, completeness, and method detection limit. These four measures provide very useful indicators of data quality and will be evaluated in Section 4.0. Specific numerical DQOs (Table C-3) for accuracy and precision of sample preparation and analysis procedures were developed for the pilot study through the method development and validation process. The data completeness goal for this project is to obtain valid analytical results for at least 95 percent of the samples collected during the project.

Table C-1
CHARACTERISTIC IONS FOR
SEMIVOLATILE LCICS, SURROGATE, AND INTERNAL STANDARD

| Compound | Primary Ion | Secondary Ions | Reference Internal Standard |
|---|---|---|---|
| 1,2-dichlorobenzene | 146 | 111,148 | 1,4-dichlorobenzene-$d_4$ |
| 1,4-dichlorobenzene-$d_4$ (IS) | 152 | N/A | N/A |
| 1,2,4-trichlorobenzene | 180 | 182,145 | Naphthalene-$d_8$ |
| Naphthalene-$d_8$ (IS) | 136 | N/A | N/A |
| 1,4-dibromobenzene (SS) | 236 | N/A | Naphthalene-$d_8$ |
| 2-chloronaphthalene | 162 | 164,127 | Acenaphthene-$d_{10}$ |
| 1,2,3,4-tetrachlorobenzene | 216 | 214,179 | Acenaphthene-$d_{10}$ |
| Acenaphthene-$d_{10}$ (IS) | 164 | N/A | N/A |
| 1,2,4,5-tetrabromobenzene (SS) | 392 | N/A | Phenanthrene-$d_{10}$ |
| B-BHC | 181 | 183,109 | Phenanthrene-$d_{10}$ |
| G-BHC | 181 | 183,109 | Phenanthrene-$d_{10}$ |
| Phenanthrene-$d_{10}$ (IS) | 188 | N/A | N/A |
| 2,4,6-tribromobiphenyl (SS) | 230 | N/A | Pyrene-$d_{10}$ |
| Pyrene-$d_{10}$ (IS) | 212 | 213 | N/A |

N/A - Not applicable
IS - Internal Standard
SS - Surrogate Standard

# Table C-2
## CHARACTERISTIC IONS FOR VOLATILE LCICS, SURROGATE, AND INTERNAL STANDARDS

| Compound | Primary Ion | Secondary Ions | Reference Internal Standard |
|---|---|---|---|
| Chlorobenzene | 112 | 114,77 | Chlorobenzene-$d_5$ |
| Chlorobenzene-$d_5$ (IS) | 117 | 118 | N/A |
| 1,4-bromofluorobenzene (SS) | 174 | N/A | Chlorobenzene-$d_5$ |
| 1,2-dichlorobenzene | 146 | 148,111 | 1,4-dichlorobenzene-$d_4$ |
| 1,4-dichlorobenzene-$d_4$ (IS) | 152 | N/A | N/A |

N/A - Not Applicable
IS - Internal Standard
SS - Surrogate Standard

# Table C-3
# DATA QUALITY OBJECTIVES

| Parameter | Audit | Compounds | Control Limit (at 95% confidence interval) | Completeness Goal (%) |
|---|---|---|---|---|
| Semivolatiles | Laboratory method/holding blank | All semivolatile LCIC | < 1.0 ug/kg | 95% |
| | Surrogate spike recovery | 1,4-Dibromobenzene | 46 to 88%[a] | 95% |
| | | 2,4,6-Tribromobiphenyl | 57 to 112% | 95% |
| | Matrix spike recovery | 1,2-Dichlorobenzene | 39 to 87% | 95% |
| | | 1,2,4-Trichlorobenzene | 43 to 106% | 95% |
| | | 1,2,3,4-Tetrachlorobenzene | 56 to 113% | 95% |
| | | 2-Chloronaphthalene | 60 to 114% | 95% |
| | | Lindane (gamma-BHC) | 44 to 119% | 95% |
| | | Beta-BHC | 48 to 106% | 95% |
| | Matrix spike duplicate precision | All semivolatile LCIC | ≤ ±30% RPD | 95% |
| | EPA check standard | All semivolatile LCIC | 80 to 120% | 100% |
| | Blind QC sample | All semivolatile LCIC | As specified by EPA | 95% |
| | Holding time | All semivolatile LCIC | Extract within 10 days<br>Analyze within 40 days | 100% |
| | Performance check standard | All semivolatile LCIC | As specified by QAPP | 100% |
| | Initial calibration standard | All semivolatile LCIC | ≤ 30% RSD | 100% |
| | Continuing calibration standard | All semivolatile LCIC | ≤ 25% D | 100% |
| | Internal standard | $d_8$-naphthalene | $R_t$ difference ≤ ±10 seconds<br>Area response: -50% to +100% | 100% |
| Volatiles | Laboratory method/holding blank | Chlorobenzene<br>1,2-Dichlorobenzene | < 1.0 ug/kg | 95% |
| | Surrogate spike recovery | p-Bromofluorobenzene | 74 to 121% | 95% |
| | Matrix spike recovery | Chlorobenzene | 60 to 133% | 95% |
| | | 1,2-Dichlorobenzene | 40 to 150% | 95% |
| | Matrix spike duplicate precision | Chlorobenzene | ≤ ±21% RPD | 95% |
| | | 1,2-Dichlorobenzene | ≤ ±27% RPD | |
| | EPA check standard | Chlorobenzene<br>1,2-Dichlorobenzene | 80 to 120% | 100% |
| | Blind QC sample | Chlorobenzene<br>1,2-Dichlorobenzene | As specified by EPA | 95% |
| | Holding time | All volatile LCIC | Analyze within 10 days | 100% |
| | Performance check standard | All volatile LCIC | As specified by QAPP | 100% |
| | Initial calibration standard | All volatile LCIC | ≤ 30% RSD | 100% |
| | Continuing calibration standard | All volatile LCIC | ≤ ±25% D | 100% |
| | Internal standard | $d_5$-Chlorobenzene | $R_t$ difference ≤ ±10 seconds<br>Area response: -50% to +100% | 100% |

[a] The upper control limit of the blank and the sample surrogate recoveries can be more than 88 percent, but shall be less than 120 percent.

## C.3.4 QUALITY CONTROL SAMPLES AND FREQUENCY REQUIREMENTS

An internal QC program designed to meet the data quality objectives was implemented for all the participating laboratories. The QC checks that were used to monitor interlaboratory and intralaboratory performance to improve the reliability of data were:

- Laboratory method/holding blank analysis
- Surrogate spike analysis
- Matrix spike analysis
- Matrix spike duplicate analysis
- EPA check standard analysis
- Blind QC sample analysis

Laboratory method/holding blank analyses were used to assess possible contamination from the laboratory so that corrective actions could be taken, if necessary. Surrogate spike analyses were used to check the recovery of the analytical procedures. Matrix spike and matrix spike duplicate analyses were used to establish analytical accuracy and precision. EPA check standard analysis was used to check the validity of the initial calibration curve. Blind QC samples, prepared by EMSL/LV by adding a known amount of LCIC to the soil sample, were used to assess the accuracy of the laboratories' analytical method.

These QC checks were interspersed with the field samples and analyzed at the required frequency, as shown in Table C-4. Other QC checks include:

- Initial calibration
- Continuing calibration
- Instrument performance checks
- Internal standard responses and retention times
- A surrogate spike of 1,2,4,5-tetrabromobenzene at a concentration of 1.0 ppb

An aliquot of the performance check standard solution was analyzed at the beginning of each 12-hour period during which the samples were analyzed. The performance check standard was used to demonstrate adequate GC and MS resolution and sensitivity, as well as mass range calibration, before samples were analyzed. The performance check standard solution was also analyzed at the end of each 12-hour period during which semivolatile samples were analyzed. This analysis was used to monitor instrument performance and to validate sample data generated during the 12-hour period. An initial five-point calibration was injected to determine the linearity of

Table C-4
QUALITY CONTROL SAMPLES AND FREQUENCY

| Type of QC Sample | QC Sample Frequency | |
|---|---|---|
| | Semivolatiles | Volatiles |
| Laboratory Method/Holding Blank | Minimum of one in every 10 field samples | Minimum of one in every 10 field samples or one in every 12 hours, whichever is more frequent |
| Matrix Spike/Matrix Spike Duplicate | Minimum of one in every 10 field samples | Minimum of one in every 10 field samples |
| Surrogate Spikes | Added to all blanks and samples including matrix spikes, duplicates, and calibration solutions | Added to all blanks and samples including matrix spikes, duplicates, and calibration solutions |
| EPA Check Standards | Whenever initial calibration is performed | Whenever initial calibration is performed. |
| Blind QC Samples | One per every 20 field samples | One per every 20 field samples |
| Performance Check Standard | At the beginning and the end of each 12-hour analytical run | At the beginning of each 12-hour analytical run |
| Initial Calibration Standard | Initially and whenever % D of continuing calibration is greater than 25% | Initially and whenever % D of continuing calibration is greater than 25% |
| Continuing Calibration Standard | Each 12 hours during sample analysis | Each 12 hours during sample analysis |
| Internal Standard | Every sample including blanks | Every sample including blanks |

Note: % D = percent difference.

response of the target LCIC and to determine the average of RF. A continuing calibration standard containing all target LCICs was analyzed every 12 hours during sample analysis to demonstrate the stability of the initial calibration curve. Multiple internal standards were added to every volatile sample before purging or to every semivolatile sample extract prior to concentration to a final 200 ul. The multiple internal standards were used to control for variability in the purging or concentration, for variability in the injection into the GC/MS, and for variability in the MS response. The internal standards used for semivolatile and volatile analysis are shown in Tables C-1 and C-2, respectively. A low-level, e.g., 1.0 ug/kg, surrogate spike of 1,2,4,5-tetrabromobenzene was added to each semivolatile sample before extraction. This surrogate, with differing levels of other surrogate spikes, was used to better determine errors from the entire analytical process and to estimate the method detection limit (MDL) for each sample.

## C.3.5 SAMPLE RERUN REQUIREMENTS

The participating laboratories were required to meet the QA/QC criteria as specified above. If the required criteria were not met, the laboratories took the necessary corrective actions to locate and eliminate the problem. If the required criteria were not met after necessary corrective actions, the laboratory was required to repurge/reextract and reanalyze certain samples or batches of samples. The sample rerun requirements that the laboratory had to meet are discussed in the QAPP (CH2M HILL, 1986) for analysis of LCICs in the soil pilot study.

## C.3.6 DATA REPORTING REQUIREMENTS

The laboratories were required to provide a variety of data on a timely basis. The reporting requirements for the laboratories fell into two categories based on the format in which the reports were delivered: machine-readable or hardcopy. The machine-readable data consist mainly of the reports and results generated on a daily, semiweekly, or weekly basis that were transferred via telecommunications network to the Horizon Systems Bulletin Board. The majority of the hardcopy data consists of the sample data package that was required within 30 days of the last validated sample received in the laboratory.

The machine-readable data packages consist of IBM PC-compatible data files that were transferred from the laboratories via a telecommunications network to the Horizon Systems Bulletin Board System. This bulletin board has been established solely for the Love Canal Habitability Project.

The final sample data package, which is required within 30 days of the last validated sample received in the laboratory, consists of documents produced throughout the study. The final sample data package is specified in Table C-5.

## C.3.7 DATA ASSESSMENT REQUIREMENTS

Data were assessed by the quality assurance division of the Office of Research and Development at EMSL/LV. A report describing the data quality assessment of the data is presented in Appendix E.

Table C-5
SAMPLE ANALYTICAL DATA PACKAGE

I. Sample Shipment Record Sheet
   1. Chain-of-Custody Form With Signature
   2. Shipping Receipt

II. Case Narrative

III. QC Summary

   1. Volatile Summary Forms
      - o Surrogate Recovery Form (Form IIA)
      - o MS/MSD Recovery Form (Form IIIA)
      - o Method Holding Blank Summary (Form IVA)
      - o Performance Check Solution Summary (Form VA)
      - o Initial Calibration Data (Form VIA)
      - o EPA Check Standard (Form VIC)
      - o Continuing Calibration Check (Form VIIA)

   2. Semivolatile Summary Forms
      - o Surrogate Recovery Form (Form IIB)
      - o MS/MSD Recovery Form (Form IIIB)
      - o Method Holding Blank Summary (Form IVB)
      - o Performance Check Solution Summary (Form VB)
      - o Initial Calibration Data (Form VIB)
      - o EPA Check Standard (Form VID)
      - o Continuing Calibration Check (Form VIIB)

IV. Standard Data Package

   1. Volatile Standards Data
      - o Initial Calibration Data (Form VIA)
      - o EPA Check Standard (Form VIC)
      - o Performance Check Solution Summary (Form VA)
      - o Continuing Calibration Check (Form VIIA)
      - o RIC for IC
      - o Quantitation Report for IC
      - o RIC for EPA Check Standard
      - o Quantitation Report for EPA Check Standard
      - o RIC and SICP for CC/PC
      - o Quantitation Report for CC/PC

   2. Semivolatile Standards Data
      - o Initial Calibration Data (Form VIB)
      - o EPA Check Standard (Form VID)
      - o Performance Check Solution Summary (Form VB)
      - o Continuing Calibration Check (Form VIIB)
      - o RIC for IC
      - o Quantitation Report for IC
      - o RIC for EPA Check Standard
      - o Quantitation Report for EPA Check Standard

Table C-5
(continued)

- RIC and SICP for PC1
- Quantitation Report for PC1
- RIC and SICP for PC2
- Quantitation Report for PC2
- RIC and SICP for CC
- Quantitation Report for CC

V. Sample Data Package

1. Volatile Sample Data
   - LCIC Analysis Data Form (Form I)
   - RIC and SICP for Sample
   - Quantitation Report for Sample
2. Semivolatile Sample Data
   - LCIC Analysis Data Form (Form I)
   - RIC and SICP for Sample
   - Quantitation Report for Sample

VI. Raw QC Data Package

1. Volatile Quality Control Data
   - LCIC Analysis Data Form for Blank (Form I)
   - RIC and SICP for Blank
   - Quantitation Report for Blank
   - LCIC Analysis Data Form for Matrix Spike (Form I)
   - RIC and SICP for Matrix Spike
   - Quantitation Report for Matrix Spike
   - LCIC Analysis Data Form for Matrix Spike Duplicate (Form I)
   - RIC and SICP for Matrix Spike Duplicate
   - Quantitation Report for Matrix Spike Duplicate
   - Internal Standard Response and Rt Data (Form XA)

2. Semivolatile Quality Control Data
   - LCIC Analysis Data Form for Blank (Form I)
   - RIC and SICP for Blank
   - Quantitation Report for Blank
   - LCIC Analysis Data Form for Matrix Spike (Form I)
   - RIC and SICP for Matrix Spike
   - Quantitation Report for Matrix Spike
   - LCIC Analysis Data Form for Matrix Spike Duplicate (Form I)
   - RIC and SICP for Matrix Spike Duplicate
   - Internal Standard Response and Rt Data (Form XB)

Table C-5
(continued)

VII. In-house QC Data Package

1. Volatile In-house QC Data
   - o Sample Log-in Sheets (Form VIII)
   - o Internal Standard Response and Rt Data (Form XC)
   - o Standard Preparation Log (Form XII)
   - o GC/MS Instrument Run Log (Form XIII)
   - o Daily Activities Log (Form XIV)
   - o Daily Activities Log for Volatile Runs (Form XVA)
   - o Copies of SIM Description Parameters

2. Semivolatile In-house QC Data
   - o Sample Log-in Sheets (Form VIII)
   - o Sample Extraction Summary Report (Form IX)
   - o Internal Standard Response and Rt Data (Form XD)
   - o Alumina Activity Verification Summary (Form XI)
     - RIC for Alumina Activity Verification
     - Quantitation Report for Alumina Activity Verification
   - o Standard Preparation Log (Form XII)
   - o GC/MS Instrument Run Log (Form XIII)
   - o Daily Activities Log (Form XIV)
   - o Daily Activities Log for Semivolatile Runs (Form XVB)
   - o Copies of SIM Descriptor Parameters

## C.4.0 QUALITATIVE MEASURES OF DATA QUALITY

The purpose of Sections C.4.0 and C.5.0 is to review and determine the quality of the data generated in the soil pilot study. First, the quality control measures employed by the laboratories were reviewed both qualitatively and quantitatively by statistical methods. Second, the raw data generated for each sample were carefully examined. This section and Section C.5.0 contain the findings of the first part of the review. Appendix E contains the findings of the second part of the review.

### C.4.1 ANALYTICAL DATA BASE

The entire soil pilot study validated data base is available upon request. Table C-6 is a summary of the total number and types of field samples that were received by the participating laboratories for the soil pilot study. All samples were analyzed and reported for LCICs. The laboratory QC samples that were required by the QA program and performed by the analytical laboratories to improve the reliability of the data are summarized in Table C-7.

### C.4.2 ANALYTICAL DATA REPORTING

The analytical sample results generated in the pilot study will be used to choose the most powerful and efficient statistical tests to discern any differences between the EDA and the comparison areas. The participating laboratories were required to report concentrations at less than 1.0 ppb if they met the identification criteria, even though the method detection limit was tentatively set at 1.0 ppb. In addition, the laboratories were required to report and flag samples with a qualifier "k" that met the identification criteria, even if the ion abundance ratios were not within the required limit. The sample analysis results for all soil samples collected at the EDA and comparison areas are given in Appendix B.

It was found that the reliability of identification and quantification at less than 1.0 ppb was very low because of the interferences present in the samples. Therefore, because of the variability of the data at this level, those samples with concentrations of less than 1.0 ppb were not considered valid. Appendix D contains a detailed assessment and explanation of this issue by EMSL/LV. The validated data are given in Attachment 1.

As shown in Table C-6, 10 semivolatile contingency samples, 7 semivolatile contingency samples, and 10 volatile

## Table C-6
## ANALYSES PERFORMED FOR LOVE CANAL SOIL PILOT STUDY

| Samples | Laboratory | | | | | | Total | |
|---|---|---|---|---|---|---|---|---|
| | CAA | | EMS | | MGM | | | |
| | VOA | SVOA | VOA | SVOA | VOA | SVOA | VOA | SVOA |
| Soil Samples | 65 | 57 | 59 | 53 | 51 | 61 | 175 | 171 |
| Field Handling Blanks | 2 | 2 | 2 | 2 | 4 | 4 | 8 | 8 |
| Field Triplicates | 2 | 2 | 3 | 3 | 3 | 3 | 8 | 8 |
| Contingency Storage Blanks | 0 | 0 | 0 | 5 | 8 | 0 | 8 | 5 |
| Contingency Samples | 0 | 10 | 0 | 7 | 10 | 0 | 10 | 17 |
| TOTAL | 69[a] | 71[a] | 64[a] | 70[a] | 76[a] | 68[a] | 209 | 209 |

[a]Volatile and semivolatile samples did not add up because some samples contained both original and contingency sample results.

## Table C-7
## LABORATORY QC SAMPLES FOR ANALYSIS OF SOIL PILOT STUDY SAMPLES

| Samples | CAA | | EMSI | | MGM | | Total | |
|---|---|---|---|---|---|---|---|---|
| | VOA | SVOA | VOA | SVOA | VOA | SVOA | VOA | SVOA |
| Matrix Spike/ Matrix Spike Duplicate | 20 | 18 | 16 | 18 | 22 | 18 | 58 | 54 |
| Method/Holding Blanks | 23 | 16 | 12 | 17 | 28 | 11 | 63 | 44 |
| EPA Check Standard | 1 | 9[a] | 1 | 1 | 1 | 1 | 3 | 11 |
| EPA Blind QC Sample | 6 | 6 | 3 | 3 | 3 | 3 | 12 | 12 |
| TOTAL | 50 | 49 | 32 | 39 | 54 | 33 | 136 | 121 |

[a]Nine EPA check standards were analyzed in order to validate nine initial calibrations performed by the CAA laboratory.

contingency samples were requested by CAA, EMS, and MGM, respectively. The contingency samples were requested by the laboratories for reanalysis because the original samples failed to meet the QC requirements. The results of sample LC2100, collected from site SPEDAS44, were not reported by MGM because sample interferences were so intensive that they masked the internal standard peaks.

The data qualifiers used by the analytical laboratories in Attachment 1 are shown below and must be considered when interpreting the data:

U -- Indicates compound was analyzed for but not detected.

J -- Indicates an estimated value. This qualifier is used when the data indicate the presence of a compound that meets the identification criteria but the concentration is less than 1.0 ppb but greater than zero.

K -- Used when estimating a concentration for a compound where all three characteristic ions are present and maximized within the scan and retention time windows, but the ion abundance ratios are not within guidelines.

B -- Used when the analyte is found in the blank as well as in a sample.

MA -- Used when quantification has been performed by manual integration of peak area or peak height.

R -- Used when sample was reinjected or reextracted.

RE -- Used when two sets of data were submitted. Flag the second result with RE.

Laboratory MGM reported many more 1,2-dichlorobenzene values in the semivolatile fraction than the other two laboratories. The difference is probably due to the higher blank values reported by MGM. The 1,2-dichlorobenzene concentrations reported by MGM should be interpreted as having a significant blank contribution.

There are also substantial differences between the volatile results and the semivolatile results for 1,2-dichlorobenzene. There are two possible explanations. One difference is that more of the volatile sample was taken from the topsoil portion of the Shelby tube than the semivolatile sample. To test this hypothesis, MGM reanalyzed volatile and semivolatile LCICs using semivolatile samples. Six samples: LC2040, LC2206, LC2209, LC2210, LC2151, and LC2182, were reanalyzed; the differences between the volatile and semivolatile results

for 1,2-dichlorobenzene still appeared. Another possible explanation is that the volatile LCICs in the soil samples may not be efficiently purged into the vapor phase at 40°C. This is currently under investigation.

## C.4.3 DATA REVIEW AND VALIDATION

In order to validate the soil pilot study analytical database, the quality control measures employed by each participating laboratory for each sample were reviewed. Two phases of data validation were performed. First, the QC results of the analyses of the soil samples were monitored on a real-time basis via electronic transfer procedure to determine if the analytical process was in control. Second, as part of an in-depth review of individual samples, a retrospective statistical analysis was made of the QC results from the analytical laboratories. The details of the validation process and results are given in this section.

The following parameters are the major sources of uncertainty and indicators of confidence in the GC/MS/SIM analytical process:

- Holding times
- Instrument calibration
- Response factor variability
- Surrogate recoveries
- Matrix spike recoveries
- Matrix spike duplicate recoveries
- Blank contamination
- Internal standard variability
- Compound identification criteria

Each of these nine parameters must be reviewed for the validation of a data set.

### C.4.3.1 HOLDING TIMES

All volatile samples were analyzed within 10 days of receipt by the laboratory, meeting the QAPP requirement. All semivolatile samples were extracted within 10 days of receipt by the laboratory and analyzed within 40 days, also meeting the requirement. It should be pointed out that 10 semivolatile contingency samples, 7 semivolatile contingency samples, and 10 volatile contingency samples were requested for reanalysis by CAA, EMS, and MGM, respectively. The contingency samples were assumed to be within the holding time requirements since they were kept frozen before sending to the laboratories. Table C-8 contains a summary of holding times for all three laboratories. Meeting the holding time criterion generally increases confidence in the reported values.

## Table C-8
## HOLDING TIME SUMMARY

| Fraction | Lab ID | No. of Analysis | Average Days Elapsed Log in/ Analysis | Maximum/ Minimum | Average Days Elapsed Log in/ Extraction | Maximum/ Minimum | Average Days Elapsed Ext/ Analysis | Maximum/ Minimum |
|---|---|---|---|---|---|---|---|---|
| Volatile | CAA | 71 | 4.9 | 10/1 | -- | -- | -- | -- |
| | EMS | 64 | 6.3 | 10/2 | -- | -- | -- | -- |
| | MGM | 76 | 5.9 | 10/0 | -- | -- | -- | -- |
| Semivolatile | CAA | 73 | -- | -- | 3.8 | 10/0 | 12.4 | 27/1 |
| | EMS | 70 | -- | -- | 3.6 | 5/0 | 7.6 | 20/2 |
| | MGM | 61 | -- | -- | 6.6 | 9/4 | 3.5 | 21/1 |

## C.4.3.2 INSTRUMENT CALIBRATION

Each day before sample analysis and standard calibration, the mass spectrometer was tuned and calibrated using perfluorotributylamine (PFTBA or FC-43). Successful tuning and calibration to PFTBA (FC-43) helps ensure that: 1) mass values reported by the instrumentation are accurate, 2) ions of adjacent mass can be separated and identified, and 3) the appearance of the mass spectrum will not be distorted by grossly varying sensitivity from one mass region to another. However, tuning to PFTBA (FC-43) does not ensure that the mass spectrometer is sufficiently sensitive for the detection of trace contaminants in the environment, nor does it ensure optimum peak shape for reasonable quantification. Therefore, other types of calibration, i.e., performance check calibration, initial calibration, and continuing calibration, were required.

An initial five-point calibration composed of LCICs at various concentrations was analyzed to generate a calibration curve. The accuracy of the instrument response for these standards was then checked by an EPA check standard. The response of the instrument was periodically checked by continuing calibration standards to determine if the response, and therefore the bias, was similar to that of the initial calibration. Large deviations from the initial calibration curve could indicate that the instrument response had changed dramatically and that the linear working range of the instrument might no longer be valid. The GC/MS resolution and sensitivity and mass range calibration were also checked periodically by use of a performance check standard.

### C.4.3.2.1 Initial Calibration

All three laboratories met the initial calibration criteria, i.e., relative standard deviation (RSD) of less than 30 percent, reasonably well (see Table C-9). EMS and MGM had performed only one semivolatile five-point initial calibration during the course of the pilot study samples analysis. However, CAA had nine semivolatile initial calibration results because of an injection abnormality caused by using an auto sampler. It was found that the stability of the calibration curve improved significantly when silanized glass wool was placed into the glass insert. This modified injection system was used for all standard and sample analyses performed after August 15, 1986. The calibration standards and samples analyzed before August 15, 1986, were done with strict adherence to the required QA/QC criteria but did not use the modified injection system.

Table C-10 summarizes the volatile initial calibration response factor from the three participating laboratories. The small percent RSD shown in this table demonstrates the good

Table C-9
SUMMARY OF INITIAL CALIBRATION RESULTS

| Fraction | Compound | Lab ID | Avg. RF | % RSD |
|---|---|---|---|---|
| Volatile | chlorobenzene | CAA | 1.19 | 6.1 |
| | | EMS | 0.725 | 5.6 |
| | | MGM | 1.15 | 8.1 |
| | 1,2-dichlorobenzene | CAA | 1.53 | 6.4 |
| | | EMS | 1.95 | 4.6 |
| | | MGM | 1.24 | 7.4 |
| | p-bromofluorobenzene (SS) | CAA | 0.732 | 3.9 |
| | | EMS | 0.455 | 1.3 |
| | | MGM | 0.56 | 7.9 |
| Semivolatile | 1,2-dichlorobenzene | CAA[a] | 1.50[b], 1.53[c] | 7.4[b], 5.4[c] |
| | | EMS | 1.39 | 2.0 |
| | | MGM | 1.63 | 7.9 |
| | 1,2,4-trichlorobenzene | CAA[a] | 0.384[b], 0.366[c] | 8.5[b], 5.5[c] |
| | | EMS | 0.321 | 1.7 |
| | | MGM | 0.379 | 6.1 |
| | 2-chloronaphthalene | CAA[a] | 1.83[b], 1.95[c] | 9.5[b], 8.0[c] |
| | | EMS | 1.17 | 4.3 |
| | | MGM | 1.89 | 5.0 |
| | 1,2,3,4-tetrachlorobenzene | CAA[a] | 1.34[b], 1.21[c] | 9.7[b], 5.2[c] |
| | | EMS | 0.597 | 3.1 |
| | | MGM | 1.02 | 10 |
| | B-BHC | CAA[a] | 0.089[b], 0.111[c] | 17.0[b], 4.1[c] |
| | | EMS | 0.185 | 12 |
| | | MGM | 0.135 | 24 |
| | G-BHC | CAA[a] | 0.138[b], 0.116[c] | 18[b], 6.5[c] |
| | | EMS | 0.188 | 9.4 |
| | | MGM | 0.152 | 25 |
| | 1,4-dibromobenzene (SS) | CAA[a] | 0.406[b], 0.392[c] | 9.4[b], 12[c] |
| | | EMS | 0.23 | 3.5 |
| | | MGM | 0.261 | 5.0 |
| | 2,4,6-tribromobiphenyl (SS) | CAA[a] | 0.313[b], 0.227[c] | 15[b], 3.6[c] |
| | | EMS | 0.333 | 2.9 |
| | | MGM | 0.160 | 19 |
| | 1,2,4,5-tetrabromobenzene (SS) | CAA[a] | 0.400[b], 0.389[c] | 14[b], 9.5[c] |
| | | EMS | 0.168 | 5.4 |
| | | MGM | 0.105 | 27 |

[a] CAA performed nine initial calibrations during the course of pilot study. RF and percent RSD were the mean of these results.

[b] Performed on instrument "G."

[c] Performed on instrument "F."

SS = Surrogate Standard

Table C-10

SUMMARY OF INITIAL CALIBRATION RESPONSE FACTOR FOR THE VOLATILE FRACTION

| Concentration (ug/kg) | Chlorobenzene | | | 1,2-Dichlorobenzne | | | ρ-Bromofluorobenzene | | |
|---|---|---|---|---|---|---|---|---|---|
| | CAA RF | EMS RF | MGM RF | CAA RF | EMS RF | MGM RF | CAA RF | EMS RF | MGM RF |
| 1.0 | 1.298 | 0.79 | 1.155 | 1.694 | 2.062 | 1.084 | 0.767 | 0.449 | 0.555 |
| 5.0 | 1.229 | 0.73 | 1.309 | 1.539 | 1.985 | 1.261 | 0.694 | 0.454 | 0.588 |
| 10.0 | 1.165 | 0.719 | 1.089 | 1.474 | 1.941 | 1.272 | 0.713 | 0.453 | 0.511 |
| 20.0 | 1.138 | 0.678 | 1.111 | 1.454 | 1.811 | 1.329 | 0.750 | 0.465 | 0.526 |
| 40.0 | 1.120 | 0.709 | 1.082 | 1.475 | 1.959 | 1.252 | 0.734 | 0.455 | 0.620 |
| Mean | 1.190 | 0.725 | 1.149 | 1.527 | 1.951 | 1.239 | 0.732 | 0.455 | 0.560 |
| Standard Deviation | 0.073 | 0.041 | 0.093 | 0.098 | 0.089 | 0.092 | 0.029 | 0.006 | 0.04 |
| Relative Standard Deviation | 6.1 | 5.6 | 8.1 | 6.4 | 4.6 | 7.4 | 3.9 | 1.3 | 7.9 |

linearity of the instrument response at this working range and increases the confidence in reported volatile concentrations. EMS shows response factors for chlorobenzene and 1,2-dichlorobenzene that are significantly different from the other two laboratories. EMS used some previously collected EDA soil for its blank matrix while the other two laboratories used sand. The native analytes and matrix effects in the EDA soil may have contributed to the response factor difference.

Tables C-11 and C-12 summarize the semivolatile initial calibration response factors for the three laboratories. Instrument response generally appeared to have good linearity at concentration levels between 0.1 ug/ml and 20.0 ug/ml. However, a few exceptions need to be pointed out. Examination of the RF values of B-BHC, G-BHC, and 1,2,4,5-tetrabromobenzene from MGM indicates a distinct deviation from linearity at the concentration of 0.1 ug/ml and 0.5 ug/ml. This may be caused by the volatility discrimination encountered for internal standard $d_{10}$-phenanthracene in splitless capillary injection. Results reported by MGM at these concentration levels may be biased. The initial calibration performed by CAA on July 29, 1986, shows a higher percent RSD than the other initial calibration analyses. In general, with the few exceptions described here, the small percent RSD of initial calibrations at the analytical laboratories indicates a low probability of large errors in the concentration estimates.

EPA Check Standard

EPA check standard solutions prepared and provided by EMSL/LV were analyzed whenever an initial calibration was performed to assess the validity of the initial calibration curve. A volatile standard solution at a concentration of 5.0 ug/ml and a semivolatile standard solution at a concentration of 2.0 ug/ml were used. The recovery of the target analyte was required to be between 80 and 120 percent of the theoretical concentration.

Table C-13 shows the percent recovery, the standard deviation, the percent relative standard deviation, and the range in the EPA check standard analysis. No statistics were computed for EMS and MGM because only one volatile and one semivolatile measurement were available. For CAA, mean recoveries show very small bias, and the relative standard deviation is in the range of 6.8 to 12.8 percent for semivolatile analytes. Although the check standard measurements do not include the variability associated with sampling, transportation, storage, and preparation of samples, the data, as shown in Table C-13, do indicate that the method has good accuracy and precision.

# Table C-11
## SUMMARY OF INITIAL CALIBRATION RESPONSE FACTOR FOR THE SEMIVOLATILE FRACTION (EMS AND MGM)

| Concentration (µg/ml) | 1,2-dichloro-benzene | | 1,2,4-tri-Chlorobenzene | | 2-chloro-naphthalene | | 1,2,3,4-tetra-Chlorobenzene | | Beta-BHC | | Gamma-BHC | | 1,4-dibromo-benzene | | 2,4,6-tri-bromobiphenyl | | 1,2,4,5-tetra-bromobenzene | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | EMS | MGM | EMS | MGM | EMS | MGM | EMS | MGM | EMS | MGM | EMS | MGM | EMS | MGM | EMS | MGM | EMS | MGM |
| 0.1 | 1.352 | 1.458 | 0.317 | 0.35 | 1.186 | 1.522 | 0.586 | 0.849 | 0.214 | 0.093 | 0.18 | 0.1 | 0.217 | 0.243 | 0.327 | 0.116 | 0.169 | 0.068 |
| 0.5 | 1.376 | 1.567 | 0.316 | 0.364 | 1.171 | 1.737 | 0.621 | 1.013 | 0.194 | 0.115 | 0.202 | 0.127 | 0.227 | 0.255 | 0.319 | 0.147 | 0.179 | 0.087 |
| 2.0 | 1.409 | 1.604 | 0.33 | 0.373 | 1.079 | 1.893 | 0.613 | 1.045 | 0.192 | 0.13 | 0.211 | 0.154 | 0.234 | 0.26 | 0.334 | 0.16 | 0.176 | 0.103 |
| 10.0 | 1.404 | 1.776 | 0.318 | 0.405 | 1.182 | 2.093 | 0.578 | 1.09 | 0.161 | 0.162 | 0.173 | 0.185 | 0.232 | 0.277 | 0.338 | 0.182 | 0.158 | 0.128 |
| 20.0 | 1.421 | 1.735 | 0.323 | 0.398 | 1.212 | 2.2 | 0.589 | 1.122 | 0.162 | 0.171 | 0.172 | 0.19 | 0.238 | 0.267 | 0.344 | 0.191 | 0.16 | 0.137 |
| Mean | 1.392 | 1.628 | 0.321 | 0.378 | 1.166 | 1.889 | 0.597 | 1.024 | 0.185 | 0.135 | 0.188 | 0.151 | 0.23 | 0.26 | 0.333 | 0.159 | 0.168 | 0.105 |
| Standard Deviation | 0.028 | 0.129 | 0.005 | 0.023 | 0.050 | 0.264 | 0.018 | 0.102 | 0.022 | 0.031 | 0.018 | 0.038 | 0.008 | 0.013 | 0.010 | 0.029 | 0.009 | 0.028 |
| % RSD | 2.0 | 7.9 | 1.7 | 6.0 | 4.3 | 14. | 3.1 | 10. | 12. | 23 | 9.4 | 25 | 3.5 | 4.9 | 2.9 | 18. | 5.4 | 27. |

Table C-12

SUMMARY OF INITIAL CALIBRATION RESPONSE FACTOR FOR SEMIVOLATILE FRACTION (CAA)

| Date Analyzed | 1,2-Dichlorobenzene | | | 1,2,4-Trichlorobenzene | | | 2-Chloronaphthalene | | | 1,2,3,4-Tetrachlorobenzene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\overline{RF}$ | Std. Dev. | % RSD | $\overline{RF}$ | Std. Dev. | % RSD | $\overline{RF}$ | Std. Dev. | % RSD | $\overline{RF}$ | Std. Dev. | % RSD |
| 07/24/86[a] | 1.493 | 0.140 | 6.0 | 0.498 | 0.030 | 6.0 | 1.78 | 0.120 | 6.0 | 1.877 | 0.08 | 4.0 |
| 07/25/86[a] | 1.588 | 0.049 | 3.1 | 0.413 | 0.037 | 9.0 | 1.878 | 0.620 | 3.3 | 1.538 | 0.185 | 12 |
| 07/26/86[a] | 1.553 | 0.098 | 6.3 | 0.339 | 0.033 | 9.7 | 1.874 | 0.169 | 9.0 | 1.2 | 0.071 | 5.9 |
| 07/29/86[a] | 1.443 | 0.259 | 18 | 0.326 | 0.065 | 20 | 1.987 | 0.378 | 19 | 1.247 | 0.199 | 16 |
| 07/31/86[a] | 1.386 | 0.115 | 8.3 | 0.353 | 0.014 | 3.9 | 1.805 | 0.155 | 8.6 | 1.261 | 0.096 | 7.6 |
| 08/06/86[a] | 1.477 | 0.029 | 2.0 | 0.407 | 0.008 | 1.9 | 1.818 | 0.122 | 6.7 | 1.263 | 0.052 | 4.1 |
| 08/15/86[a] | 1.537 | 0.119 | 7.8 | 0.349 | 0.031 | 8.8 | 1.665 | 0.233 | 14 | 0.974 | 0.175 | 18 |
| 08/11/86[b] | 1.562 | 0.190 | 1.0 | 0.389 | 0.040 | 1.0 | 1.469 | 0.14 | 9.0 | 1.269 | 0.07 | 5.0 |
| 08/15/86[b] | 1.503 | 0.146 | 9.7 | 0.343 | 0.034 | 9.9 | 1.425 | 0.098 | 6.9 | 1.155 | 0.061 | 5.3 |
| Mean | 1.50 | 0.127 | 6.9 | 0.38 | 0.032 | 7.8 | 1.74 | 0.226 | 9.2 | 1.31 | 0.110 | 8.7 |

[a] Instrument number E.

[b] Instrument number F.

Table C-12
(continued)

| Beta-BHC | | | Gamma-BHC | | | 1,4-Dibromobenzene | | | 2,4,6-Tribromobiphenyl | | | 1,2,4,5-Tetrabromobenzene | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\overline{RF}$ | Std. Dev. | % RSD | $\overline{RF}$ | Std. Dev. | % RSD | $\overline{RF}$ | Std. Dev. | % RSD | $\overline{RF}$ | Std. Dev. | % RSD | $\overline{RF}$ | Std. Dev. | % RSD |
| 0.102 | 0.03 | 2.0 | 0.173 | 0.05 | 2.0 | 0.652 | 0.04 | 5.0 | 0.37 | 0.08 | 2.0 | 0.363 | 0.080 | 2.0 |
| 0.094 | 0.018 | 19 | 0.153 | 0.035 | 23 | 0.48 | 0.058 | 12 | 0.36 | 0.097 | 27 | 0.490 | 0.098 | 20 |
| 0.079 | 0.016 | 20 | 0.142 | 0.034 | 24 | 0.293 | 0.029 | 9.9 | 0.242 | 0.031 | 13 | 0.431 | 0.056 | 13 |
| 0.069 | 0.020 | 29 | 0.112 | 0.031 | 28 | 0.293 | 0.059 | 20 | 0.312 | 0.075 | 24 | 0.362 | 0.087 | 24 |
| 0.067 | 0.017 | 26 | 0.128 | 0.028 | 22 | 0.39 | 0.015 | 3.9 | 0.354 | 0.053 | 15 | 0.396 | 0.051 | 13 |
| 0.105 | 0.012 | 11 | 0.145 | 0.022 | 15 | 0.407 | 0.012 | 2.9 | 0.342 | 0.051 | 15 | 0.409 | 0.049 | 12 |
| 0.108 | 0.016 | 15 | 0.11 | 0.011 | 10 | 0.326 | 0.039 | 12 | 0.209 | 0.023 | 11 | 0.347 | 0.055 | 16 |
| 0.113 | 0.02 | 1.0 | 0.124 | 0.01 | 1.0 | 0.427 | 0.04 | 8.0 | 0.247 | 0.05 | 1.0 | 0.364 | 0.03 | 9.0 |
| 0.109 | 0.008 | 7.1 | 0.108 | 0.013 | 12 | 0.357 | 0.06 | 16 | 0.206 | 0.013 | 6.2 | 0.409 | 0.041 | 10 |
| 0.094 | 0.017 | 14 | 0.133 | 0.026 | 15 | 0.403 | 0.039 | 10 | 0.294 | 0.053 | 13 | 0.397 | 0.061 | 13 |

Table C-13
SUMMARY OF EPA CHECK STANDARD RECOVERY RESULTS

| Fraction | Compound | Lab ID | % Recovery | Standard Deviation | % RSD | Maximum | Minimum |
|---|---|---|---|---|---|---|---|
| Volatile | Chlorobenzene | CAA | 92 | -- | -- | -- | -- |
| | | EMS | 86 | -- | -- | -- | -- |
| | | MGM | 90 | -- | -- | -- | -- |
| | 1,2-dichlorobenzene | CAA | 92 | -- | -- | -- | -- |
| | | EMS | 93 | -- | -- | -- | -- |
| | | MGM | 106 | -- | -- | -- | -- |
| Semivolatile | 1,2-dichlorobenzene | CAA[a] | 100.4 | 9.1 | 9.1 | 115 | 89 |
| | | EMS | 102 | -- | -- | -- | -- |
| | | MGM | 100 | -- | -- | -- | -- |
| | 1,2,4-trichlorobenzene | CAA[a] | 94.8 | 12 | 13 | 112 | 80 |
| | | EMS | 98 | -- | -- | -- | -- |
| | | MGM | 98 | -- | -- | -- | -- |
| | 2-chlorophthalene | CAA[a] | 98.2 | 6.7 | 6.8 | 110 | 90 |
| | | EMS | 98 | -- | -- | -- | -- |
| | | MGM | 102 | -- | -- | -- | -- |
| | 1,2,3,4-tetrachlorobenzene | CAA[a] | 99 | 10 | 10.4 | 120 | 84 |
| | | EMS | 97 | -- | -- | -- | -- |
| | | MGM | 102 | -- | -- | -- | -- |
| | B-BHC | CAA[a] | 101.8 | 13 | 13 | 120 | 84 |
| | | EMS | 89 | -- | -- | -- | -- |
| | | MGM | 106 | -- | -- | -- | -- |
| | G-BHC | CAA[a] | 99 | 9.4 | 9.5 | 112 | 86 |
| | | EMS | 86 | -- | -- | -- | -- |
| | | MGM | 102 | -- | -- | -- | -- |

[a]Percent recovery, standard deviation, and % RSD were calculated using results from nine EPA check standards.

Performance Check Standard

At the beginning and end of each 12-hour analytical run, the semivolatile performance check standard at a concentration of 0.1 ug/ml was analyzed to verify GC/MS sensitivity, resolution, and mass range calibration. For volatile sample analysis, the performance check standard at a concentration of 1.0 ug/kg was analyzed at the beginning of each 12-hour analytical run. LCICs, $d_5$-chlorobenzene, and $d_{10}$-pyrene were required to have a secondary-to-primary ion ratio of within ±20 percent from the theoretical ion ratio. For semivolatile performance check standard analysis, the resolution of chloronaphthalene and BHC isomers had to be demonstrated. The sensitivity of the mass spectrometer had to be verified to have a signal-to-noise ratio of greater than 2.5 for mass 109 of BHC and mass 392 of 1,2,4,5-tetrabromobenzene. Failure to meet these requirements would invalidate all sample data collected after the last acceptable performance check standard and the affected samples would have to be rerun.

The performance check solution was introduced to the GC/MS through the gas chromatograph after FC-43 mass calibration. This results in tuning and calibration under conditions more closely resembling those during an actual sample analysis. The data in Tables C-14, C-15, and C-16 contain the results of the performance check solution calibration for CAA, EMS, and MGM. As shown in these tables, the laboratories met all the required tuning criteria.

Thus it is concluded that the GC/MS had adequate resolution, sensitivity, and mass range calibration. This conclusion, in turn, increases the confidence that the mass spectrometer produced good quality mass spectra and that the target analytes were detected.

Continuing Calibration

Continuing calibration checks at a concentration of 1.0 ug/kg for volatile LCICs and 2.0 ug/ml for semivolatile LCICs were performed every 12 hours during sample analysis. The percent difference for the response factor of any LCIC compound could not be greater than 25 percent from the average response factor of the initial calibration. No samples were analyzed unless these criteria were met. The response of the GC/MS was periodically checked by continuing calibration to determine if the response was similar to that of the initial calibration. Large deviations from the initial calibration curve would indicate that the instrument response had changed dramatically and that the calculated linear working range of the instrument may no longer be valid.

Tables C-17 and C-18 contain summaries of the statistics for continuing calibration of volatiles and semivolatiles,

Table C-14
SUMMARY OF PERFORMANCE CHECK SOLUTION FOR THE VOLATILE FRACTION

| Compound | Required Ratio Limit | Lab ID | Count | Mean | Standard Deviation | % RSD | Range |
|---|---|---|---|---|---|---|---|
| Chlorobenzene (114/112) | 0.26-0.39 | CAA | 14 | 0.34 | 0.00 | 1.45 | 0.02 |
| | | EMS | 11 | 0.36 | 0.01 | 3.46 | 0.04 |
| | | MGM | 21 | 0.29 | 0.02 | 6.59 | 0.07 |
| 1,2-dichlorobenzene (148/146) | 0.52-0.78 | CAA | 14 | 0.63 | 0.01 | 2.19 | 0.04 |
| | | EMS | 11 | 0.69 | 0.06 | 8.98 | 0.22 |
| | | MGM | 21 | 0.64 | 0.04 | 6.31 | 0.17 |
| $D_5$-chlorobenzene (118/117) | 0.052-0.078 | CAA | 14 | 0.07 | 0.00 | 2.88 | 0.01 |
| | | EMS | 11 | 0.07 | 0.01 | 7.91 | 0.02 |
| | | MGM | 21 | 0.06 | 0.01 | 9.19 | 0.02 |

## Table C-15
## SUMMARY OF SEMIVOLATILE PERFORMANCE CHECK SOLUTION RESULTS FOR ION RATIOS

| Compound[a] | Required Ion Ratio Limit | Lab ID | Count | Mean | | Standard Deviation | | % RSD | | Range | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | PC1 | PC2 | PC1 | PC2 | PC1 | PC2 | PC1 | PC2 |
| 1,2-dichlorobenzene (148/146) | 0.52-0.78 | CAA | 31 | 0.64 | 0.64 | 0.02 | 0.01 | 2.59 | 2.29 | 0.07 | 0.07 |
| | | EMS | 19 | 0.66 | 0.66 | 0.02 | 0.03 | 3.79 | 4.84 | 0.08 | 0.11 |
| | | MGM | 11 | 0.63 | 0.63 | 0.01 | 0.01 | 1.72 | 2.18 | 0.03 | 0.05 |
| 1,2,4-trichlorobenzene (182/180) | 0.78-1.17 | CAA | 31 | 0.96 | 0.96 | 0.02 | 0.03 | 1.64 | 2.80 | 0.08 | 0.13 |
| | | EMS | 19 | 0.95 | 0.97 | 0.03 | 0.04 | 3.65 | 4.37 | 0.14 | 0.21 |
| | | MGM | 11 | 0.94 | 0.96 | 0.01 | 0.03 | 1.52 | 2.66 | 0.05 | 0.09 |
| 2-chloronaphthalene (164/162) | 0.26-0.39 | CAA | 31 | 0.32 | 0.32 | 0.01 | 0.01 | 2.76 | 2.31 | 0.03 | 0.03 |
| | | EMS | 19 | 0.33 | 0.34 | 0.01 | 0.02 | 4.30 | 5.23 | 0.05 | 0.07 |
| | | MGM | 11 | 0.32 | 0.32 | 0.01 | 0.02 | 2.80 | 4.94 | 0.03 | 0.05 |
| 1,2,3,4-tetrachlorobenzene (216/214) | 1.04-1.56 | CAA | 31 | 1.29 | 1.29 | 0.02 | 0.02 | 1.64 | 1.67 | 0.10 | 0.08 |
| | | EMS | 19 | 1.30 | 1.30 | 0.05 | 0.06 | 4.11 | 4.30 | 0.21 | 0.21 |
| | | MGM | 11 | 1.28 | 1.29 | 0.03 | 0.02 | 2.20 | 1.83 | 0.08 | 0.08 |
| B-BHC (183/181) | 0.78-1.17 | CAA | 31 | 1.01 | 0.98 | 0.08 | 0.19 | 7.91 | 19.54 | 0.43 | 1.17 |
| | | EMS | 19 | 0.91 | 0.90 | 0.07 | 0.05 | 8.08 | 5.73 | 0.24 | 0.21 |
| | | MGM | 11 | 0.93 | 0.98 | 0.06 | 0.08 | 6.12 | 8.07 | 0.20 | 0.27 |
| G-BHC (183/181) | 0.78-1.17 | CAA | 31 | 1.00 | 1.01 | 0.05 | 0.07 | 5.07 | 6.51 | 0.26 | 0.27 |
| | | EMS | 19 | 0.94 | 0.96 | 0.07 | 0.08 | 6.91 | 7.93 | 0.21 | 0.30 |
| | | MGM | 11 | 0.99 | 0.98 | 0.04 | 0.06 | 3.89 | 6.25 | 0.13 | 0.23 |
| Pyrene-$d_{10}$ (213/212) | 0.14-0.23 | CAA | 31 | 0.16 | 0.16 | 0.01 | 0.01 | 5.70 | 5.06 | 0.04 | 0.04 |
| | | EMS | 19 | 0.18 | 0.18 | 0.02 | 0.01 | 9.66 | 6.10 | 0.05 | 0.04 |
| | | MGM | 11 | 0.17 | 0.17 | 0.01 | 0.00 | 3.80 | 2.16 | 0.02 | 0.01 |

[a] Characteristic ions monitored for the respective compounds.

Table C-16
SUMMARY OF SEMIVOLATILE PERFORMANCE CHECK SOLUTION RESULTS
FOR RESOLUTION AND SENSITIVITY

| Compound | Required QC Limit PC1 | Required QC Limit PC2 | Lab ID | Count | Mean PC1 | Mean PC2 | Std. Dev. PC1 | Std. Dev. PC2 | % RSD PC1 | % RSD PC2 | Max. PC1 | Max. PC2 | Min. PC1 | Min. PC2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BHC's | Baseline Separation | Valley <15% | CAA | 31 | -- | 3.8 | -- | 3.0 | -- | 79 | -- | 13 | -- | 0 |
| | | | EMS | 19 | -- | 0 | -- | 0 | -- | 0 | -- | 0 | -- | 0 |
| | | | MGM | 11 | -- | 3.5 | -- | 6.0 | -- | 173 | -- | 14 | -- | 0 |
| Chloronaphthalenes | Valley <30% | Valley <50% | CAA | 31 | 10.5 | 9.9 | 5.7 | 5.3 | 55 | 54 | 19 | 19 | 2 | 2 |
| | | | EMS | 19 | 5.5 | 5.8 | 2.3 | 2.2 | 42 | 38 | 10.1 | 9.9 | 2.8 | 2.8 |
| | | | MGM | 11 | 4.8 | 5.7 | 1.4 | 2.2 | 28 | 39 | 6.8 | 9.9 | 2.6 | 3.3 |
| B-BHC (109)[a] | S/N >2.5 | S/N >2.5 | CAA | 31 | 11.1 | 9.4 | 9.3 | 5.3 | 84 | 56 | 42 | 24.3 | 3.0 | 2.9 |
| | | | EMS | 19 | 10.7 | 8.4 | 5.6 | 3.6 | 52 | 42 | 23 | 16.8 | 5.0 | 5.0 |
| | | | MGM | 11 | 9.9 | 6.2 | 1.8 | 3.2 | 18 | 51 | 12.2 | 12.7 | 5.8 | 2.7 |
| 1,2,4,5-tetrabromobenzene (392)[a] | S/N >2.5 | S/N >2.5 | CAA | 31 | 75.0 | 77.2 | 17.8 | 17.9 | 24 | 23 | 92 | 98 | 37 | 24.5 |
| | | | EMS | 19 | 14.3 | 13.2 | 12.2 | 9.5 | 85 | 72 | 59.5 | 42.6 | 5.8 | 3.7 |
| | | | MGM | 11 | 12.2 | 13.1 | 1.9 | 1.1 | 16 | 9 | 14.5 | 14.4 | 7.4 | 10.5 |

[a] Characteristic ions monitored for the respective compounds.

## Table C-17
## SUMMARY OF CONTINUING CALIBRATION FOR THE VOLATILE FRACTION

| Compound | Lab ID | Count | Mean RF | Mean % D | Standard Deviation % D | % RSD % D | Maximum % D | Minimum % D |
|---|---|---|---|---|---|---|---|---|
| Chlorobenzene | CAA | 15 | 1.2 | 4.94 | 2.76 | 56 | 9.04 | 0.78 |
| | EMS | 10 | 0.8 | 10.0 | 5.09 | 51 | 18.82 | 1.65 |
| | MGM | 20 | 1.2 | 4.45 | 4.24 | 95 | 16.30 | 0.53 |
| 1,2-dichlorobenzene | CAA | 15 | 1.5 | 4.84 | 3.66 | 76 | 11.43 | 0.34 |
| | EMS | 10 | 2.1 | 8.13 | 5.93 | 73 | 18.77 | 2.11 |
| | MGM | 20 | 1.2 | 9.38 | 5.30 | 56 | 20.65 | 0.40 |
| ρ-bromofluorobenzene | CAA | 15 | 0.7 | 5.86 | 2.72 | 46 | 12.96 | 2.21 |
| | EMS | 10 | 0.4 | 18.46 | 5.40 | 29 | 24.51 | 5.68 |
| | MGM | 20 | 0.5 | 7.78 | 4.99 | 64 | 20.66 | 1.31 |

Table C-18
SUMMARY OF CONTINUING CALIBRATION FOR THE SEMIVOLATILE FRACTION

| Compound | Lab ID | Count | Mean RF | Mean % D | Standard Deviation % D | % RSD % D | Maximum % D | Minimum % D |
|---|---|---|---|---|---|---|---|---|
| 1,2-dichlorobenzene | CAA | 29 | 1.5 | 4.72 | 4.04 | 86 | 17.03 | 0.35 |
| | EMS | 19 | 1.4 | 2.09 | 1.34 | 64 | 5.63 | 0.23 |
| | MGM | 10 | 1.6 | 1.49 | 1.19 | 80 | 4.47 | 0.32 |
| 1,2,4-trichlorobenzene | CAA | 29 | 0.4 | 5.34 | 5.34 | 100 | 18.37 | 0.35 |
| | EMS | 19 | 0.3 | 2.35 | 1.76 | 75 | 6.43 | 0.01 |
| | MGM | 10 | 0.4 | 3.85 | 5.25 | 136 | 17.90 | 0.23 |
| 2-chlorophthalene | CAA | 29 | 1.7 | 5.62 | 4.27 | 76 | 15.35 | 0.81 |
| | EMS | 19 | 1.1 | 7.28 | 3.87 | 53 | 14.32 | 0.69 |
| | MGM | 10 | 1.8 | 7.24 | 2.02 | 28 | 9.49 | 3.79 |
| 1,2,3,4-tetrachlorobenzene | CAA | 29 | 1.1 | 6.79 | 5.40 | 80 | 20.10 | 0.22 |
| | EMS | 19 | 0.6 | 6.98 | 6.01 | 86 | 21.07 | 0.51 |
| | MGM | 10 | 1.0 | 6.94 | 3.57 | 51 | 12.68 | 0.99 |
| B-BHC | CAA | 29 | 0.1 | 6.28 | 6.25 | 100 | 22.16 | 0.63 |
| | EMS | 19 | 0.2 | 14.57 | 7.17 | 49 | 24.71 | 1.85 |
| | MGM | 10 | 0.1 | 11.47 | 7.53 | 66 | 21.34 | 0.88 |
| G-BHC | CAA | 29 | 0.1 | 6.05 | 4.83 | 80 | 20.88 | 0.01 |
| | EMS | 19 | 0.2 | 10.24 | 5.36 | 52 | 21.41 | 2.28 |
| | MGM | 10 | 0.1 | 10.20 | 8.21 | 81 | 21.74 | 1.10 |
| 1,4-dibromobenzene | CAA | 29 | 0.3 | 6.27 | 4.22 | 67 | 17.72 | 0.36 |
| | EMS | 19 | 0.2 | 3.68 | 2.00 | 54 | 7.04 | 0.74 |
| | MGM | 10 | 0.3 | 5.52 | 6.23 | 113 | 21.16 | 0.19 |
| 2,4,6-tribromobiphenyl | CAA | 29 | 0.3 | 6.66 | 6.70 | 101 | 25.10 | 0.30 |
| | EMS | 19 | 0.3 | 11.79 | 7.69 | 65 | 23.63 | 0.09 |
| | MGM | 10 | 0.2 | 10.08 | 7.67 | 76 | 25.99 | 3.33 |
| 1,2,4,5-tetrabromobenzene | CAA | 29 | 0.4 | 5.89 | 3.74 | 64 | 12.90 | 0.02 |
| | EMS | 19 | 0.2 | 13.35 | 6.59 | 49 | 23.97 | 1.17 |
| | MGM | 10 | 0.1 | 20.83 | 11.54 | 55 | 40.51 | 2.08 |

respectively. The mean percent difference was calculated by using the absolute percent difference from the average response factor of the initial calibration. The results show that the instrument has performed satisfactorily for all three laboratories throughout the pilot study. Once again, the response factor of EMS for volatile LCICs differs from those of the other two laboratories, and the soil used by EMS for standard preparation may have been responsible for the difference. The small percent RSD indicates low probability of large errors in the LCIC concentration estimates. This increases the confidence of the reported concentrations.

### C.4.3.3 RESPONSE FACTOR VARIABILITY

The accuracy of quantification is a function of the random error in the analytical method and determinate, or systematic, bias. Random error was assessed by examining the overall variability in the internal standard areas, response factors, and reproducibility of results in the replicates. Systematic bias was assessed qualitatively and quantitatively by reviewing the surrogate and matrix spike results.

The response of each LCIC in the continuing calibration standard affects the final reported concentration. The variability of the response factor is an indication of how well these variables were controlled over the course of the entire dataset analysis. Highly varied responses for each analyte decrease the confidence in reported concentrations.

Continuing calibration checks were performed every 12 hours; the LCIC responses had to be within ±25 percent of the initial calibration response. Table C-19 summarizes the percent difference of continuing calibration checks. Roughly 95 percent of volatile responses were within ±20 percent difference with the exception of p-bromofluorobenzene for EMS. This may be due to the variation in internal standard area or the soil EMS used for the standard preparation. The frequency with which the ±20 percent difference was exceeded was greater for semivolatile LCICs than for volatile LCICs, particularly for BHC, GHC, 2,4,6-tribromobiphenyl and 1,2,4,5-tetrabromobenzene. Although multiple internal standards were used for semivolatile analysis, volatility discrimination may still be encountered in splitless capillary injection. This is particularly true since $d_{10}$-phenanthrene, which is used for quantification of B-BHC, G-BHC and 1,2,4,5-tetrabromobenzene, and $d_{10}$-pyrene, which is used for quantification of 2,4,6-tribromobiphenyl, are the late-eluting internal standards. Other possible factors may relate to the column performance variability for these four compounds at high column temperature.

Response factor variability of continuing calibration standards can be monitored using control charts for response

Table C-19
SUMMARY OF CONTINUING CALIBRATION
PERCENT DIFFERENCE RESULTS

| Compound | Lab ID | Count | Percent Difference Greater Than 10 But Less Than 20 as a % of Total | Percent Difference Greater Than 20 But Less Than 25 as a % of Total |
|---|---|---|---|---|
| Chlorobenzene | CAA | 15 | 0 | 0 |
| | EMS | 10 | 60 | 0 |
| | MGM | 20 | 5 | 0 |
| 1,2-Dichloro-benzene | CAA | 15 | 6.7 | 0 |
| | EMS | 10 | 20 | 0 |
| | MGM | 20 | 25 | 5 |
| P-Bromofluoro-benzene (SS) | CAA | 15 | 0 | 0 |
| | EMS | 10 | 60 | 30 |
| | MGM | 20 | 20 | 5 |
| 1,2-Dichloro-benzene | CAA | 29 | 3.4 | 0 |
| | EMS | 19 | 0 | 0 |
| | MGM | 10 | 0 | 0 |
| 1,2,4-Trichloro-benzene | CAA | 29 | 10 | 0 |
| | EMS | 19 | 0 | 0 |
| | MGM | 10 | 10 | 0 |
| 2-Chloro-naphthalene | CAA | 29 | 10 | 0 |
| | EMS | 19 | 21 | 0 |
| | MGM | 10 | 0 | 0 |
| 1,2,3,4-Tetra-chlorobenzene | CAA | 29 | 10 | 0 |
| | EMS | 19 | 16 | 5.3 |
| | MGM | 10 | 10 | 0 |
| B-BHC | CAA | 29 | 3.1 | 6.9 |
| | EMS | 19 | 58 | 21 |
| | MGM | 10 | 40 | 10 |
| G-BHC | CAA | 29 | 11 | 3.4 |
| | EMS | 19 | 32 | 5.3 |
| | MGM | 10 | 30 | 20 |
| 1,4-Dibromo-benzene (SS) | CAA | 29 | 14 | 0 |
| | EMS | 19 | 0 | 0 |
| | MGM | 10 | 0 | 10 |
| 2,4,6-Tribromo-biphenyl (SS) | CAA | 29 | 18 | 3.4 |
| | EMS | 19 | 37 | 26 |
| | MGM | 10 | 20 | 20 |
| 1,2,4,5-Tetra-bromobenzene (SS) | CAA | 29 | 14 | 0 |
| | EMS | 19 | 52 | 16 |
| | MGM | 10 | 30 | 50 |

SS = Surrogate Standard

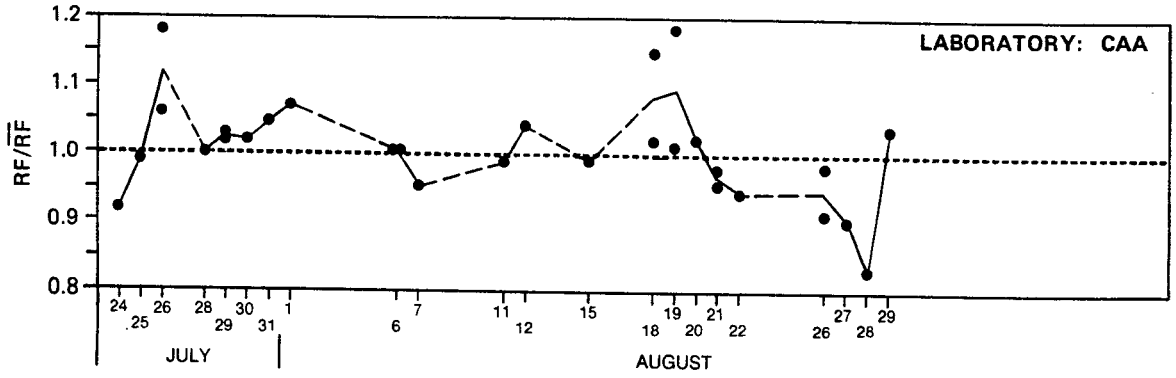
factor (RF). The response factors of each LCIC and surrogate standard were required to fall within ±25 percent of that of the initial calibration average response factor ($\overline{RF}$). If there is no variability, the ratio of RF to $\overline{RF}$ should be equal to one. Therefore, the upper control limit (UCL) and lower control limit (LCL) for the ratio of RF to $\overline{RF}$ should be 1.25 and 0.75, respectively. The control chart can be constructed by drawing the lines of UCL, LCL, and the expected theoretical value of one on a chart. The ratios of $\overline{RF}$ to RF data obtained during the daily continuing calibration analysis can then be plotted as they are obtained. An example of these control charts is given in Figure C-1 for 1,2,4-trichlorobenzene. As shown in Figure C-1, the ratio of RF to $\overline{RF}$ was within the specified limits. No determinate variations were observed in the control chart. The small variability of the ratio of RF to $\overline{RF}$ is an indication of the instrument stability. This increases the confidence of the reported 1,2,4-trichlorobenzene concentration.

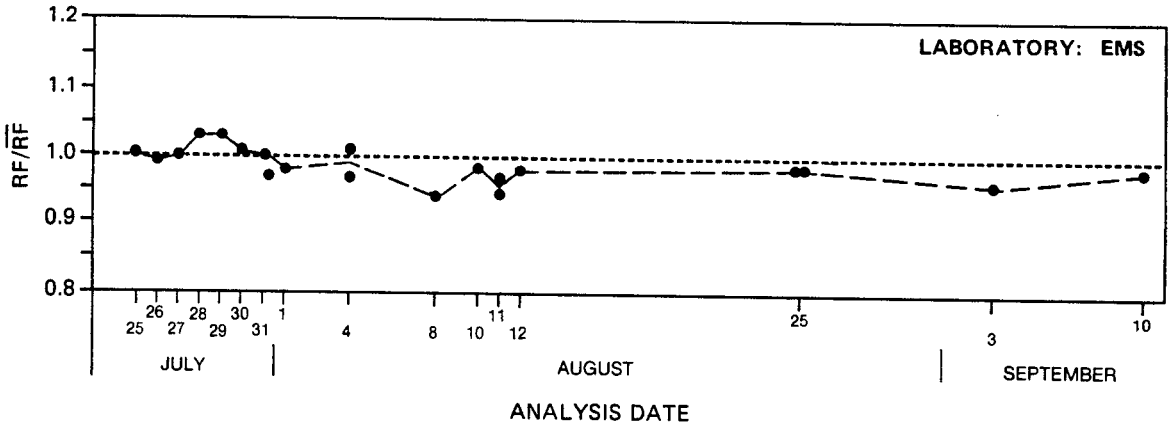
The percent difference criterion of ±25 percent decreases the likelihood of large response factor variability. Although the criterion was met for all three laboratories, performance could still be improved. To increase the accuracy of the quantification, internal standard area variability and column performance criteria may need to be tightened. These are currently under investigation.

C.4.3.4 SURROGATE RECOVERIES ANALYSIS

The recovery of surrogate compounds provides an indication of the efficiency of the analytical process. The surrogate compounds should have extraction and gas chromatographic retention characteristics similar to those of the target analytes. They also should be highly unlikely to be found in any environmental sample. Low recoveries can be caused by matrix effects, poor extraction technique, incorrect response factors, inadequate sensitivity, or improper addition of the surrogate compounds. High surrogate recoveries can occur because of incorrect response factors or improper addition of surrogate compounds. Routinely low recoveries of surrogate compounds decrease the confidence in the reported values; this may indicate a serious bias toward artificially lower reported values.

The compound ρ-bromofluorobenzene was added by the laboratories to each soil sample, including the laboratory method/holding blank, intended for volatiles analysis at a concentration of 2.0 ug/kg. The compounds 1,4-dibromobenzene, 2,4,6-tribromobiphenyl, and 1,2,4,5-tetrabromobenzene were added by the analytical laboratories to each soil sample, including the laboratory method/holding blank, intended for semivolatiles analysis at concentrations of 25 ug/kg, 25 ug/kg, and 1.0 ug/kg, respectively. The compound



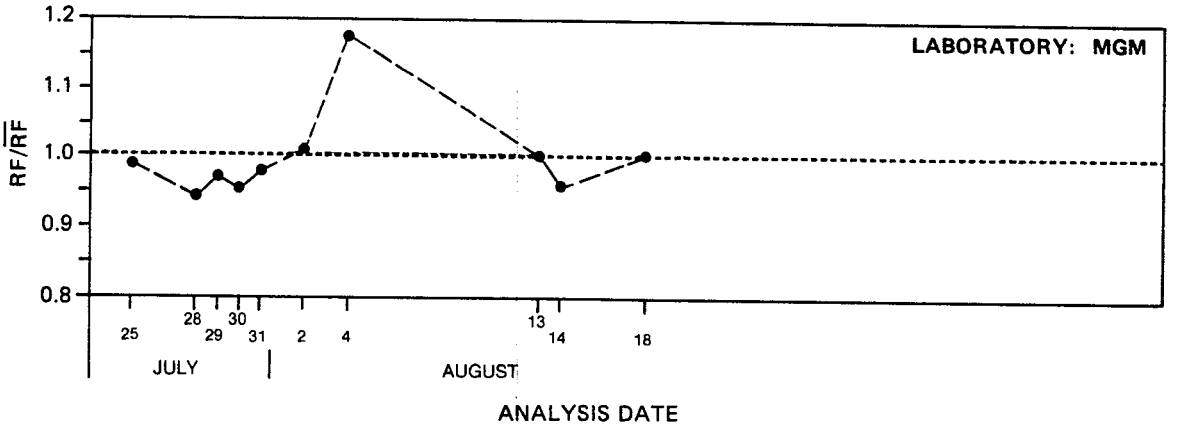




Figure C-1
**CONTROL CHART FOR CONTINUING CALIBRATION RESPONSE FACTOR OF 1,2,4-TRICHLOROBENZENE**

1,2,4,5-tetrabromobenzene was spiked at a concentration of 1.0 ug/kg to estimate the method detection limit for each sample. The surrogate percent recoveries for the four surrogates in both volatile and semivolatile analyses are the concentration of surrogates quantified in the analysis divided by the concentration of surrogates added to the sample, then multiplied by 100 to obtain a percentage of the true values. The surrogate recoveries were required to be within the control limits specified in Table C-3. If the surrogate recoveries were not within the control limits, the laboratory was required to reanalyze the sample after the necessary corrective actions failed. There is no control limit for 1,2,4,5-tetrabromobenzene recovery, since the compound was added at the last phase of the method validation study. The recovery data generated in the pilot study for 1,2,4,5-tetrabromobenzene have been calculated and the control limits that were expressed as 95 percent confidence interval are given in Table C-20, generated from the soil pilot study data.

Table C-20 contains a summary of the statistics and the control limits expressed as 95 percent confidence interval. High measurements are indicative of positive interferences. Low percentages of true values are indicative of losses from a poor extraction technique, reduced equipment efficiency, or inadequate sensitivity. The control limits were set at

ble C-19A
OVERIES OF ρ-BROMOFLUOROBENZENE

atory: CAA

| 7/29 | 7/30 | 7/31 | 8/1 | 8/4 | 8/6 |
|---|---|---|---|---|---|
| 87.5 | 86.4 | 89.0 | 91.9 | 90.9 | 90.6 |
| 91.2 | 89.1 | 91.3 | 93.7 | 92.5 | -- |
| 82.3 | 83.0 | 86.5 | 91.0 | 88.6 | -- |
| 4 | 7 | 5 | 4 | 4 | 1 |

atory: EMS

| 8/1 | 8/2 | 8/3 |
|---|---|---|
| 96.7 | 97.7 | 106 |
| 99.9 | 118 | 109 |
| 93.5 | 87.6 | 102 |
| 8 | 5 | 6 |

atory: MGM

| 7/31 | 8/1 | 8/2 | 8/3 | 8/4 | 8/5 | 8/6 | 8/21 | 8/22 | 8/23 |
|---|---|---|---|---|---|---|---|---|---|
| 97.2 | 95.0 | 96.0 | 108 | 99.3 | 112 | 105 | 105 | 100 | 88.8 |
| 112 | 99.7 | 104 | 112 | 104 | 117 | 111 | 113 | 106 | 93.8 |
| 84.0 | 89.8 | 86.7 | 103 | 90.4 | 105 | 99.6 | 97.4 | 93.1 | 84.1 |
| 11 | 4 | 8 | 2 | 5 | 5 | 2 | 2 | 8 | 8 |

Table C-20
SUMMARY OF SURROGATE ANALYSIS RESULTS

| Surrogate Analyte | Lab ID | Count | Mean % Recovery | St. Dev. % Recovery | % RSD | Maximum % Recovery | Mininum % Recovery | Control Limit (at 95% Confidence Interval) |
|---|---|---|---|---|---|---|---|---|
| ρ-Bromofluorobenze | CAA | 92 | 91.8 | 6.95 | 7.57 | 118 | 52.5 | 78 - 106 |
| | EMS | 74 | 98.8 | 6.77 | 6.85 | 117 | 81.2 | 85 - 112 |
| | MGM | 94 | 97.9 | 8.98 | 9.17 | 119 | 77.4 | 80 - 116 |
| 1,4-Dibromobenzene | CAA | 88 | 68.3 | 14.3 | 20.9 | 98 | 25 | 40 - 97 |
| | EMS | 90 | 56.4 | 7.38 | 13.1 | 76.3 | 38.8 | 42 - 71 |
| | MGM | 81 | 79.4 | 10.4 | 13.1 | 105 | 35.6 | 59 - 100 |
| 2,4,6-Tribromobiphenyl | CAA | 88 | 92.0 | 21.6 | 23.5 | 172 | 200 | 49 - 135 |
| | EMS | 90 | 75.0 | 11.7 | 15.6 | 111 | 57.2 | 52 - 99 |
| | MGM | 81 | 86.6 | 11.7 | 13.5 | 107 | 30.5 | 63 - 110 |
| 1,2,4,5-Tetrabromobenzene | CAA | 88 | 86.4 | 16.7 | 19.3 | 128 | 29.0 | 53 - 120 |
| | EMS | 90 | 76.5 | 25.9 | 33.8 | 165 | 22.7 | 25 - 138 |
| | MGM | 80 | 74.9 | 11.7 | 15.6 | 103 | 27.7 | 52 - 98 |

The recoveries for 1,4-dibromobenzene, 2,4,6-tribromobiphenyl, and 1,2,4,5-tetrabromobenzene were generally good. Eight samples from CAA, one sample from EMS, and one sample from MGM had 1,4-dibromobenzene and 2,4,6-tribromobiphenyl recoveries that were not within specified limits. These outliers may be due to the sample interferences that were observed during sample analysis. The analytical laboratories, in general, have comparable mean surrogate recoveries even for the low-level spiking surrogate compound 1,2,4,5-tetrabromobenzene, which does not have a specified control limit. However, CAA and EMS observed a trend of decreasing recovery with increasing volatility of surrogate compounds. The low recovery of 1,4-dibromobenzene may be due to a volatility discrimination problem observed during the sample extraction procedure. The consistently low recovery of 1,2,4,5-tetrabromobenzene observed for the laboratory EMS may not be attributable to poor extraction efficiency but rather to nonlinearity of response factors in the range of the sample spike concentration. The variability observed during the sample extraction has yet to be explained and corrected. The corrective actions for elimination of the variability observed during the sample extraction will be discussed in section C.8.0.

The control limits reported in Table C-20 are generally comparable to the specified control limits provided initially to the laboratories for use in meeting the QC requirements (Table C-3). Also, the surrogate recovery windows specified for this study are somewhat tighter than those for the CLP soil analysis. The use of four surrogate compounds and the good recovery for all four, with only the minor exceptions described, greatly increase the confidence in both the methods employed and the reported concentrations.

### C.4.3.5 MS/MSD RECOVERIES ANALYSIS

The analysis of matrix spikes provides additional information on the effectiveness of the analytical techniques employed. The matrix spike recoveries provide information similar to that derived from surrogate compound recovery. The analysis of matrix spike/matrix spike duplicates is used to measure precision. The precision is reported by the relative percent difference (RPD).

One matrix spike and one matrix spike duplicate were analyzed at a frequency of every ten or fewer field samples. The percent recovery and RPD for each individual LCIC spiking compound were calculated. The percent recovery and RPD were evaluated to determine whether they were within the control limits specified in Table C-3. If the percent recovery and/or RPD of the matrix spike/matrix spike duplicate

were not within the specified limits, the samples were not required to be reanalyzed, since the control limits were used only for advisory purposes.

The matrix spike recoveries and matrix spike/matrix spike duplicate precision are shown in Tables C-21 and C-22, respectively. Matrix spike recoveries were within specified limits for the 58 volatile matrix spikes analyzed. The excellent recoveries for the matrix spikes increase the confidence in the reported concentrations of volatiles. The control limits reported in Table C-21 for volatiles analysis are much tighter than those specified in Table C-3. An exception to the above are the matrix recoveries for 1,2-dichlorobenzene from MGM. The reported values appear to be biased toward higher recoveries that are indicative of positive interferences.

The interferences may be from sample matrix effects, laboratory blank contribution, or incorrect instrument response. The semivolatile spike recoveries were, in general, acceptable and within control limits. Seven, 8, and 3 out of 108 spike recoveries for CAA, EMS, and MGM, respectively, were outside of the control limits. As shown in Table C-21, most of the outliers were B-BHC, or G-BHC recoveries that were too high; two 1,2-dichlorobenzene recoveries from CAA were slightly too low. The recoveries of B-BHC or G-BHC were biased toward higher values, which may be due to the presence of hydrocarbon interferences. The quantification ion used for BHCs will be changed to prevent hydrocarbon interferences. The low recovery of 1,2-dichlorobenzene may be caused by the volatility discrimination problem, which must be corrected and validated before the full habitability study begins. Possible areas that can introduce variability and bias are discussed in section C.8.0 and possible corrective actions are recommended. The good recovery of all LCIC compounds, with only the above minor exceptions, greatly increases the confidence in both the methods employed and in the reported concentrations.

Figure C-3 is an example of the MS/MSD recoveries control charts for 1,2,4-trichlorobenzene. The control charts were obtained by plotting the MS/MSD percent recovery data as these were obtained during the course of the soil pilot study. The charts are used to document laboratory performance and to motivate better performance. As shown in Figure C-3, the recoveries of 1,2,4-trichlorobenzene were within the established UCL and LCL. Except for a few, all recovery values from CAA and EMS are lower than the mean value. This is probably because of an inherent negative determinative error in the extraction procedure used. Possible areas that can introduce the determinative error will be discussed in Section C.8.0. In general, the recoveries are all "in control," i.e., within the established control

# Table C-21
## SUMMARY OF MATRIX SPIKE RECOVERY RESULTS

| Compound | Lab ID | Count | Mean % Recovery | St. Dev. % Recovery | % RSD | Maximum % Recovery | Mininum % Recovery | Control Limit (at 95% Confidence Interval) |
|---|---|---|---|---|---|---|---|---|
| Chlorobenzene | CAA | 20 | 98.6 | 5.4 | 5.5 | 108 | 88 | 87.8 - 109 |
| | EMS | 16 | 86.1 | 8.1 | 9.4 | 104 | 74 | 69.9 - 102 |
| | MGM | 22 | 99.6 | 6.5 | 6.5 | 110 | 89 | 86.6 - 113 |
| 1,2-Dichlorobenzene (VOA) | CAA | 20 | 101 | 10.3 | 10.2 | 128 | 87 | 80.4 - 122 |
| | EMS | 16 | 86.0 | 10.3 | 12.0 | 108 | 72 | 65.7 - 107 |
| | MGM | 22 | 123 | 10.7 | 8.7 | 142 | 108 | 102 - 144 |
| 1,2-Dichlorobenzene (SVOA) | CAA | 18 | 53.1 | 11.9 | 22.4 | 72 | 35 | 29.3 - 76.9 |
| | EMS | 18 | 60.1 | 7.6 | 12.6 | 71.9 | 45 | 44.9 - 75.3 |
| | MGM | 18 | 61.9 | 8.2 | 13.2 | 75 | 48 | 45.5 - 78.3 |
| 1,2,4-Trichlorobenzene | CAA | 18 | 65.1 | 12.2 | 18.7 | 98 | 47 | 40.7 - 89.5 |
| | EMS | 18 | 71.3 | 11.1 | 15.6 | 92 | 55 | 49.1 - 93.5 |
| | MGM | 18 | 76.1 | 8.7 | 11.4 | 95 | 63 | 58.7 - 93.5 |
| 2-Chloronaphthalene | CAA | 18 | 74.3 | 8.7 | 11.7 | 95 | 62 | 56.9 - 91.7 |
| | EMS | 18 | 80.2 | 9.9 | 12.3 | 98 | 62 | 60.4 - 100 |
| | MGM | 18 | 88.2 | 5.3 | 6.0 | 102 | 80 | 77.6 - 98.8 |
| 1,2,3,4-Tetrachlorobenzene | CAA | 18 | 71.9 | 10.3 | 14.3 | 97 | 59 | 51.3 - 92.5 |
| | EMS | 18 | 77.7 | 12.4 | 15.9 | 103 | 58 | 52.9 - 102 |
| | MGM | 18 | 86.2 | 10.3 | 11.9 | 113 | 72 | 65.6 - 107 |
| B-BHC | CAA | 18 | 98.4 | 15.8 | 16.1 | 132 | 76 | 66.8 - 130 |
| | EMS | 18 | 91.5 | 13.7 | 14.9 | 121 | 67.6 | 64.1 - 119 |
| | MGM | 18 | 87.1 | 9.1 | 10.4 | 103 | 64 | 68.9 - 105 |
| G-BHC | CAA | 18 | 90.7 | 12.2 | 13.4 | 109 | 66 | 66.3 - 115 |
| | EMS | 18 | 92.8 | 26.3 | 28.3 | 158 | 62.5 | 40.2 - 145 |
| | MGM | 18 | 87.8 | 11.6 | 13.2 | 110 | 71 | 64.6 - 111 |

Table C-22
SUMMARY OF MATRIX SPIKE/MATRIX SPIKE DUPLICATE
PRECISION RESULTS

| Compound | Lab ID | Count | Mean % RPD | Std. Dev. % RPD | Max. % RPD | Min. % RPD |
|---|---|---|---|---|---|---|
| Chlorobenzene | CAA | 10 | 5.4 | 4.2 | 11 | 1 |
| | EMS | 8 | 4.8 | 3.9 | 11 | 0 |
| | MGM | 11 | 6.2 | 5.3 | 15 | 0 |
| 1,2-Dichlorobenzene (VOA) | CAA | 10 | 5.5 | 3.7 | 14 | 1.6 |
| | EMS | 8 | 7.8 | 4.1 | 12 | 1.2 |
| | MGM | 11 | 9.8 | 7.3 | 22 | 0 |
| 1,2-Dichlorobenzene (SVOA) | CAA | 9 | 23.6 | 14.8 | 44 | 3.0 |
| | EMS | 9 | 11.6 | 10.2 | 26 | 0.2 |
| | MGM | 9 | 14.6 | 11.2 | 36 | 1.5 |
| 1,2,4-Trichlorobenzene | CAA | 9 | 15.4 | 12.3 | 43 | 1.3 |
| | EMS | 9 | 9.2 | 7.5 | 27 | 1.9 |
| | MGM | 9 | 11.5 | 8.4 | 24 | 1.3 |
| 2-Chloronaphthalene | CAA | 9 | 7.7 | 5.7 | 17 | 0 |
| | EMS | 9 | 6.5 | 4.0 | 12 | 0.4 |
| | MGM | 9 | 3.9 | 2.9 | 7.9 | 0 |
| 1,2,3,4-Tetrachlorobenzene | CAA | 9 | 11.6 | 6.2 | 20 | 0 |
| | EMS | 9 | 5.1 | 3.4 | 9.9 | 0.4 |
| | MGM | 9 | 8.9 | 7.9 | 28 | 0 |
| B-BHC | CAA | 9 | 13.0 | 6.6 | 23 | 2.9 |
| | EMS | 9 | 7.2 | 8.2 | 27 | 0.3 |
| | MGM | 9 | 7.3 | 7.1 | 21 | 1.1 |
| G-BHC | CAA | 9 | 13.3 | 4.1 | 19 | 4.8 |
| | EMS | 9 | 8.5 | 10.2 | 34 | 0.8 |
| | MGM | 9 | 3.9 | 3.6 | 12 | 0 |

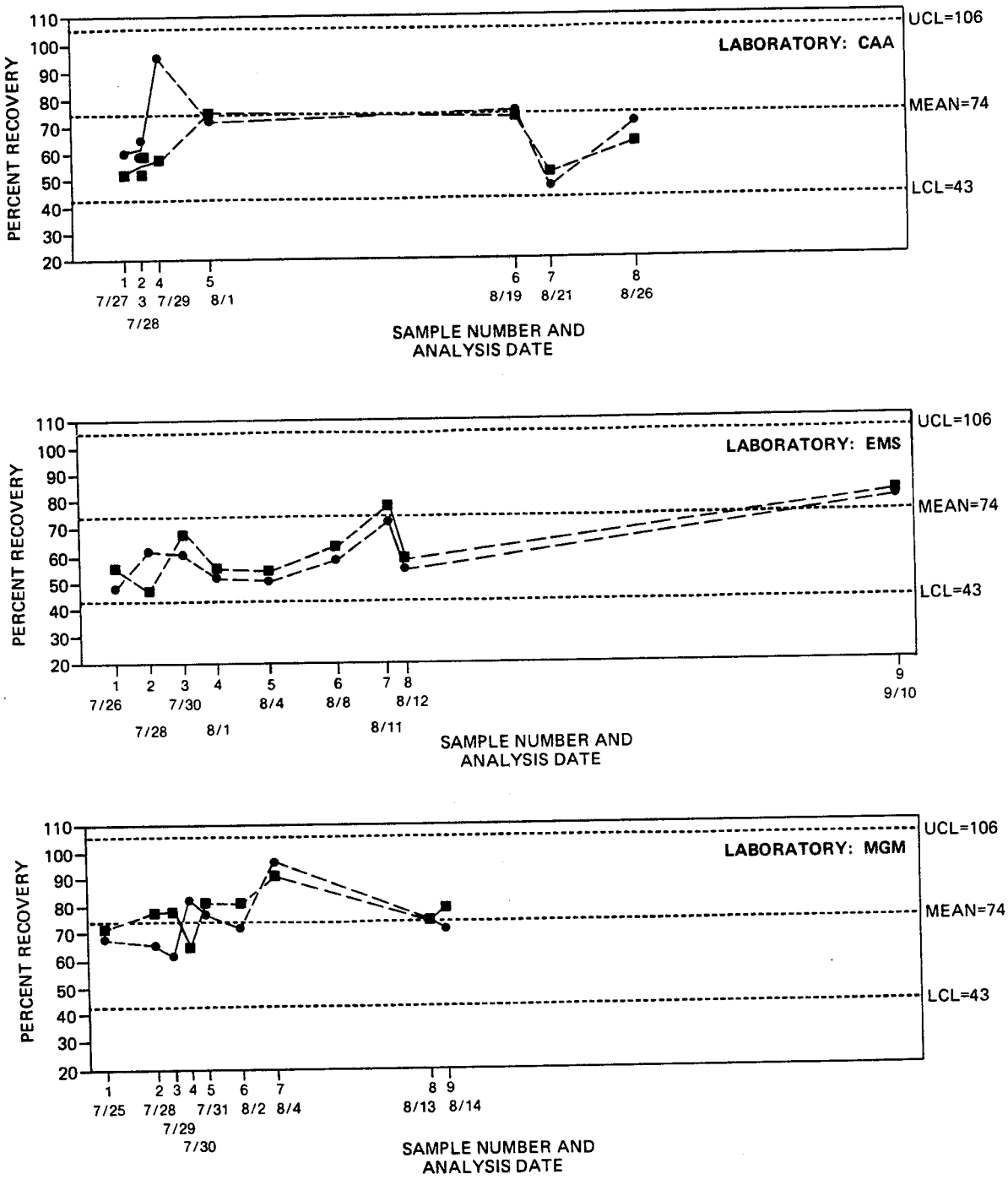



Figure C-3
**CONTROL CHART FOR MS/MSD RECOVERIES OF 1,2,4-TRICHLOROBENZENE**

limits. This increases the confidence in both the method employed and in the reported concentrations for 1,2,4-trichlorobenzene.

Analysis of a duplicate matrix spike provides an indication of the reproducibility, or the precision, of the analytical technique. The precision is measured by the % RPD of the matrix spike/matrix spike duplicate analysis. The percent RPD is the difference of the two results divided by the mean of the two results, then multiplied by 100 to obtain a percentage. Table C-22 shows the relative percent difference for matrix spike/matrix spike duplicate analysis. The volatiles matrix spike duplicate analyses demonstrated the reproducibility of quantification. The semivolatiles matrix spike duplicate analyses have wider RPD than those of volatiles analyses. The percent RPD was in general within the specified limit of ±30 percent. The semivolatiles matrix spike duplicate analyses in general demonstrated acceptable precision.

The control chart statistic for controlling precision can be estimated from the percent relative standard deviation data of matrix spike/matrix spike duplicate analyses. The maximum control limit for matrix spike/matrix spike duplicate analyses is shown in Table C-3. Although the relative percent different (RPD) results were reported by the laboratories, the % RSD is more appropriate to be used to estimate the precision. The % RSD (precision) control chart for matrix spike/matrix spike duplicate analyses of 1,2,4-trichlorobenzene are given in Figure C-4. As shown in Figure C-4, the precision results for 1,2,4-trichlorobenzene were within the established control limit except for two results from CAA. In general, Figure C-4 demonstrates good precision since the results fall approximately along a horizontal line. This confirms what was described above.

C.4.3.6 BLANK CONTAMINATION

The analysis of method/holding blanks provides information on background levels of analytes or low-level contamination of the samples during analysis. The presence of compounds in blanks can increase uncertainty with regard to the reported concentrations. However, failure to document the background or contamination levels of analytes decreases the confidence in reported values, particularly low-concentration values.

A laboratory method/holding blank was analyzed with every 10 or fewer field samples for semivolatiles analysis. For volatiles analysis, the blank was analyzed once every 10 field samples or every 12 hours of analysis, whichever was more frequent. A laboratory method/holding blank is a sand blank that is placed in the refrigerator at the same time a batch

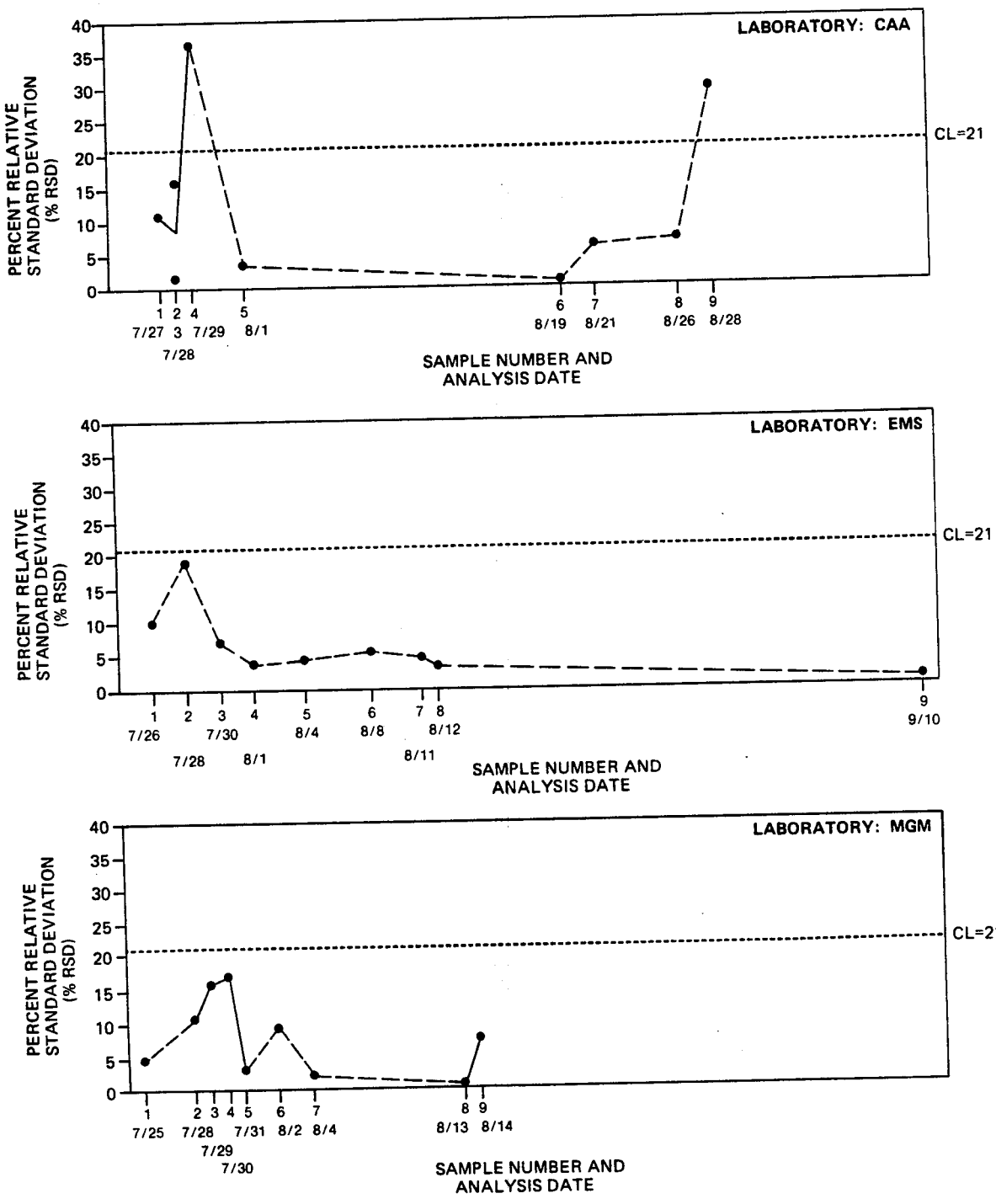



Figure C—4
**CONTROL CHART FOR MS/MSD PRECISION OF 1,2,4-TRICHLOROBENZENE**

of field samples is received and stored in the refrigerator. The blank is treated and analyzed using the same procedures as the field samples. The laboratory method/holding blank was required to contain no more than 1.0 ug/kg of LCIC (Table C-3).

The results of laboratory method/holding blank analysis are presented in Table C-23. As shown in Table C-23, the laboratory method/holding blank results from all three laboratories met the specified control limits. Low levels of chlorobenzene and 1,2-dichlorobenzene were found in the volatiles blanks. EMS reported chlorobenzene and 1,2-dichlorobenzene in every volatiles blank analyzed, because of its use of a composite Love Canal EDA soil for its blanks. The frequency with which method/holding blanks were analyzed and the levels that were detected indicated that no major contamination or carryover problems occurred during the course of volatiles analyses. For semivolatiles blank analysis, MGM reported higher levels of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene than the other two laboratories. For 1,2-dichlorobenzene, MGM had a positive bias of about 0.5 ppb compared to CAA and a positive bias of about 0.6 ppb compared to EMS. For 1,2,4-trichlorobenzene, the positive bias was about 0.2 ppb between MGM and CAA and about 0.1 ppb between MGM and EMS. EMS detected 2-chloronaphthalene and 1,2,3,4-tetrachlorobenzene more frequently than the other two laboratories.

The blank contaminations may be due to the fact that the solvents and/or reagents used by the participating laboratories are different in purity. It may be necessary to use the same clean solvents and reagents for all laboratories in the future study if the concentration at below one ppb is important to the future EDA habitability study. Although the presence of these compounds in the blanks introduces uncertainty in the sample results, especially those around 1.0 ppb, the amount of blank contribution to the sample at concentration higher than 1.0 ppb is probably negligible.

Field handling blanks were also analyzed by the analytical laboratories. The field handling blanks provide a measure of cross-contamination sources, decontamination efficiency, and other potential errors that could be introduced from various sources other than the sample. The field handling blank undergoes all the steps of sample collection, extrusion, mixing, shipping, and analysis that a normal sample does. Table C-24 contains the results from eight field handling blanks that were analyzed by the laboratories. A summary of the statistics of the field handling blank results is shown in Table C-25. The results confirmed that MGM had a positive bias for 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. The bias may be caused by laboratory reagent contamination and by the fact that MGM exhibits better recovery of these two compounds than the other two laboratories. The

# Table C-23
## SUMMARY OF LABORATORY METHOD/HOLDING BLANK RESULTS

| | Number of Blanks Analyzed | CAA | | | | | Number of Blanks Analyzed | EMS | | | | | Number of Blanks Analyzed | MGM | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Count[a] | Mean | Standard Deviation | Maximum | Minimum | | Count[a] | Mean | Standard Deviation | Maximum | Minimum | | Count[a] | Mean | Deviation | Maximum | Minimum |
| Chlorobenzene | 23 | 9 | 0.06 | 0.03 | 0.12 | 0.028 | 12 | 12 | 0.12 | 0.08 | 0.26 | 0.039 | 28 | 2 | 0.03 | 0.01 | 0.037 | 0.020 |
| 1,2-dichlorobenzene (VOA) | 23 | 1 | 0.03 | -- | -- | -- | 12 | 12 | 0.12 | 0.10 | 0.37 | 0.003 | 28 | 2 | 0.01 | 0.0 | 0.016 | 0.013 |
| 1,2-dichlorobenzene (SVOA) | 16 | 6 | 0.23 | 0.24 | 0.72 | 0.10 | 17 | 6 | 0.12 | 0.04 | 0.17 | 0.07 | 11 | 11 | 0.69 | 0.08 | 0.86 | 0.57 |
| 1,2,4-trichlorobenzene | 16 | 10 | 0.09 | 0.04 | 0.17 | 0.04 | 17 | 15 | 0.21 | 0.07 | 0.34 | 0.08 | 11 | 11 | 0.31 | 0.05 | 0.46 | 0.27 |
| 2-chloronaphthalene | 16 | 2 | 0.06 | 0.01 | 0.06 | 0.05 | 17 | 7 | 0.20 | 0.19 | 0.53 | 0.03 | 11 | 1 | 0.055 | -- | -- | -- |
| 1,2,3,4-tetrachlorobenzene | 16 | -- | -- | -- | -- | -- | 17 | 9 | 0.17 | 0.08 | 0.28 | 0.06 | 11 | -- | -- | -- | -- | -- |
| B-BHC | 16 | -- | -- | -- | -- | -- | 17 | 1 | 0.36 | -- | -- | -- | 11 | -- | -- | -- | -- | -- |
| G-BHC | 16 | -- | -- | -- | -- | -- | 17 | 14 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |

[a]The number in this column represents the total number of blanks that have quantifiable results.

Table C-24
SUMMARY OF FIELD HANDLING BLANK RESULTS

| Site ID | Sample ID | Lab ID | Chloro-benzene | 1,2-Dichloro-benzene | 1,2-Dichloro-benzene | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetra-Chlorobenzene | 2-Chloro-naphthalene | B-BHC | G-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPCA1S14 | LC2071 | EMS | 0.33 | <1.0 | <1.0 | 0.15 | 0.11 | 0.23 | <1.0 | <1.0 |
| SPCA1S17 | LC2266 | MGM | 0.34 | <1.0 | 0.7 | 0.4 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S02 | LC2298 | CAA | 0.98 | <1.0 | 0.18 | <1.0 | <1.0 | 0.07 | <1.0 | <1.0 |
| SPCA2S06 | LC2277 | EMS | <1.0 | <1.0 | 0.36 | 0.28 | 0.11 | 0.25 | <1.0 | <1.0 |
| SPEDAS02 | LC2268 | MGM | <1.0 | <1.0 | 0.7 | 0.3 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS04 | LC2039 | MGM | 0.28 | <1.0 | 1.1 | 0.5 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS27 | LC2296 | MGM | 0.1 | <1.0 | 0.8 | 0.3 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS44 | LC2278 | CAA | 0.12 | <1.0 | <1.0 | 0.14 | <1.0 | 0.10 | <1.0 | <1.0 |

Note: All concentrations were reported as ug/kg and on a dry weight basis.

Table C-25
SUMMARY STATISTICS OF FIELD HANDLING BLANK RESULTS

| Compound | Lab ID | Mean | Standard Deviation | % RSD | Maximum | Minimum |
|---|---|---|---|---|---|---|
| Chlorobenzene | CAA | 0.55 | 0.61 | 111 | 0.98 | 0.12 |
| | EMS | 0.33 | -- | -- | 0.33 | -- |
| | MGM | 0.24 | 0.12 | 50 | 0.34 | 0.10 |
| 1,2-dichlorobenzene (VOA) | CAA | <1.0 | | | | |
| | EMS | <1.0 | | | | |
| | MGM | <1.0 | | | | |
| 1,2-dichlorobenzene (SVOA) | CAA | 0.18 | -- | -- | 0.18 | -- |
| | EMS | 0.36 | -- | -- | 0.36 | -- |
| | MGM | 0.83 | 0.19 | 23 | 1.1 | 0.70 |
| 1,2,4-trichlorobenzene | CAA | 0.14 | -- | -- | 0.14 | -- |
| | EMS | 0.22 | 0.09 | 41 | 0.28 | 0.15 |
| | MGM | 0.38 | 0.10 | 26 | 0.5 | 0.3 |
| 1,2,3,4-tetrachlorobenzene | CAA | <1.0 | | | | |
| | EMS | 0.11 | 0 | 0 | 0.11 | -- |
| | MGM | <1.0 | | | | |
| 2-chloronaphthalene | CAA | 0.085 | 0.2 | 25 | 0.10 | 0.07 |
| | EMS | 0.24 | 0.01 | 6 | 0.25 | 0.23 |
| | MGM | <1.0 | | | | |
| B-BHC | CAA | <1.0 | | | | |
| | EMS | <1.0 | | | | |
| | MGM | <1.0 | | | | |
| G-BHC | CAA | <1.0 | | | | |
| | EMS | <1.0 | | | | |
| | MGM | <1.0 | | | | |

1,2-dichlorobenzene and 1,2,4-trichlorobenzene results reported by MGM for field samples were interpreted as having a blank contribution at the levels shown in Table C-25.

C.4.3.7 INTERNAL STANDARD VARIABILITY

The response of the GC/MS to the internal standard determines the final reported concentration. The internal standard will compensate for changes in instrument response, injection volume, final extract volume, or any other variable that can affect response of analytes. The variability of the internal standard response is an indication of how well these variables were controlled over the course of the entire dataset analysis. Widely varied internal standard responses increase the uncertainty in reported concentrations.

The internal standard response for $d_8$-naphthalene and $d_5$-chlorobenzene was required to change by not more than a factor of two (-50 percent to +100 percent) from the latest daily calibration standard. Area responses for internal standards other than $d_8$-naphthalene and $d_5$-chlorobenzene were not required to meet this limit.

The internal standard response was evaluated for all standards, blanks, and samples. Table C-26 contains an internal standard area variation statistical summary. All responses for $d_5$-chlorobenzene and $d_8$-naphthalene were within a factor of two from the latest daily calibration standard. For other internal standards, with the exception of $d_4$-1,4-dichlorobenzene for MGM, the responses were more variable than those of $d_5$-chlorobenzene and $d_8$-naphthalene. This was not unexpected, because a highly sensitive analytical methodology was employed for soil sample analysis and no control limits were specified. However, it will likely be necessary to set up control limits for all the internal standard responses for the full habitability study. The need for these control limits is currently being investigated. The variability of $d_4$-1,4-dichlorobenzene at MGM is more likely due to the presence of interferences from samples and/or reagents than to an instrument problem. The quantification of 1,2-dichlorobenzene should not be affected since the reported concentrations were all less than 1.0 ug/kg. The fact that internal standard responses observed over the course of the study did not vary greatly, with the minor exception mentioned above, increases the confidence in the reported values.

Area response variability for internal standards can be monitored using control charts. The area response for internal standards was required to be within a factor of two from the last daily calibration standard. Therefore, the UCL and LCL should be +100 percent and -50 percent, respectively. The control charts for monitoring area response variability were

Table C-26
SUMMARY OF INTERNAL STANDARD AREA VARIATION RESULTS

| Fraction | Internal Standard | Lab ID | Count | Mean % Variation | Standard Deviation % Variation | Range % Variation |
|---|---|---|---|---|---|---|
| Volatile | $d_5$-chlorobenzene | CAA | 114 | -15.1 | 25.5 | 133 |
| | | EMS | 92 | -9.8 | -18.6 | 100 |
| | | MGM | 126 | -2.5 | 5.6 | 31 |
| | $d_4$-1,4-dichlorobenzene | CAA | 114 | -28.3 | 28.5 | 133 |
| | | EMS | 92 | -10.6 | 19.3 | 101 |
| | | MGM | 126 | -13.0 | 17.4 | 94.4 |
| Semi-volatile | $d_8$-naphthalene | CAA | 107 | 24.6 | 15.4 | 125 |
| | | EMS | 107 | 3.9 | 17.3 | 89.1 |
| | | MGM | 47 | 2.5 | 27.5 | 146 |
| | $d_4$-1,4-dichlorobenzene | CAA | 107 | -27.5 | 17.3 | 127 |
| | | EMS | 107 | 0.9 | 19.2 | 105 |
| | | MGM | 47 | -5.1 | 22.8 | 133 |
| | $d_{10}$-phenanthrene | CAA | 107 | -6.8 | 19.4 | 139 |
| | | EMS | 107 | 45.6 | 36.2 | 167 |
| | | MGM | 47 | 33.8 | 42.1 | 210 |
| | $d_{10}$-acenaphthrene | CAA | 107 | -15.2 | 16.1 | 94.3 |
| | | EMS | 107 | 13.3 | 22.3 | 167 |
| | | MGM | 47 | 9.3 | 31.6 | 158 |
| | $d_{10}$-pyrene | CAA | 107 | -1.8 | 24.2 | 142 |
| | | EMS | 107 | 55.4 | 43.0 | 250 |
| | | MGM | 47 | 50.5 | 56.2 | 264 |

obtained by plotting the mean and percent deviation from the analysis data as they were obtained during the course of the soil pilot study. Figure C-5 is an example of the internal standard area percent deviation control chart for $d_8$-naphthalene. Table C-26A summarizes the statistics. As shown in Figure C-5, the percent deviation of $d_8$-naphthalene was within the established UCL and LCL. No trends and cycles resulting from assignable causes were observed in the control charts for EMS and MGM. For CAA, all percent deviation values are toward the negative side, probably because instrument sensitivity was less during the sample analysis. The control charts demonstrate that internal standard responses observed over the course of the study for $d_8$-naphthalene did not vary greatly for any of the participating laboratories. This increases the confidence in the reported values.

C.4.3.8 COMPOUND IDENTIFICATION CRITERIA

The stringency of a laboratory's mass spectral matching criteria affects the uncertainty associated with a reported result. Criteria with minimum standards that are too lax will result in false positives, which will bias the results toward increased detection. Similarly, criteria that are overly stringent, with a goal of unequivocal identification of compounds, may result in false negatives. The censoring of the data in this manner biases the reported values of low-level compounds.

The compound identification criteria that were employed during the pilot study are as follows:

- The primary ion and two secondary ions for each LCIC must maximize within one scan of each other.
- The relative intensities of the ion currents of the primary ion and its associated cluster ion must agree within ±20 percent of that obtained from the daily standard.
- The retention time must be within ±10 seconds of that obtained from the daily standard.
- The sample component relative retention time (RRT) must be within ±0.007 RRT units of the standard component in the daily standard.

The identification criteria were followed by all three laboratories during the course of study. The laboratories reported the compound concentration with detectable levels that met all of the identification criteria. However, samples with concentrations of less than 1 ppb were considered unreliable because of the variability of the data at this level. The reliability of concentration at less than 1 ppb

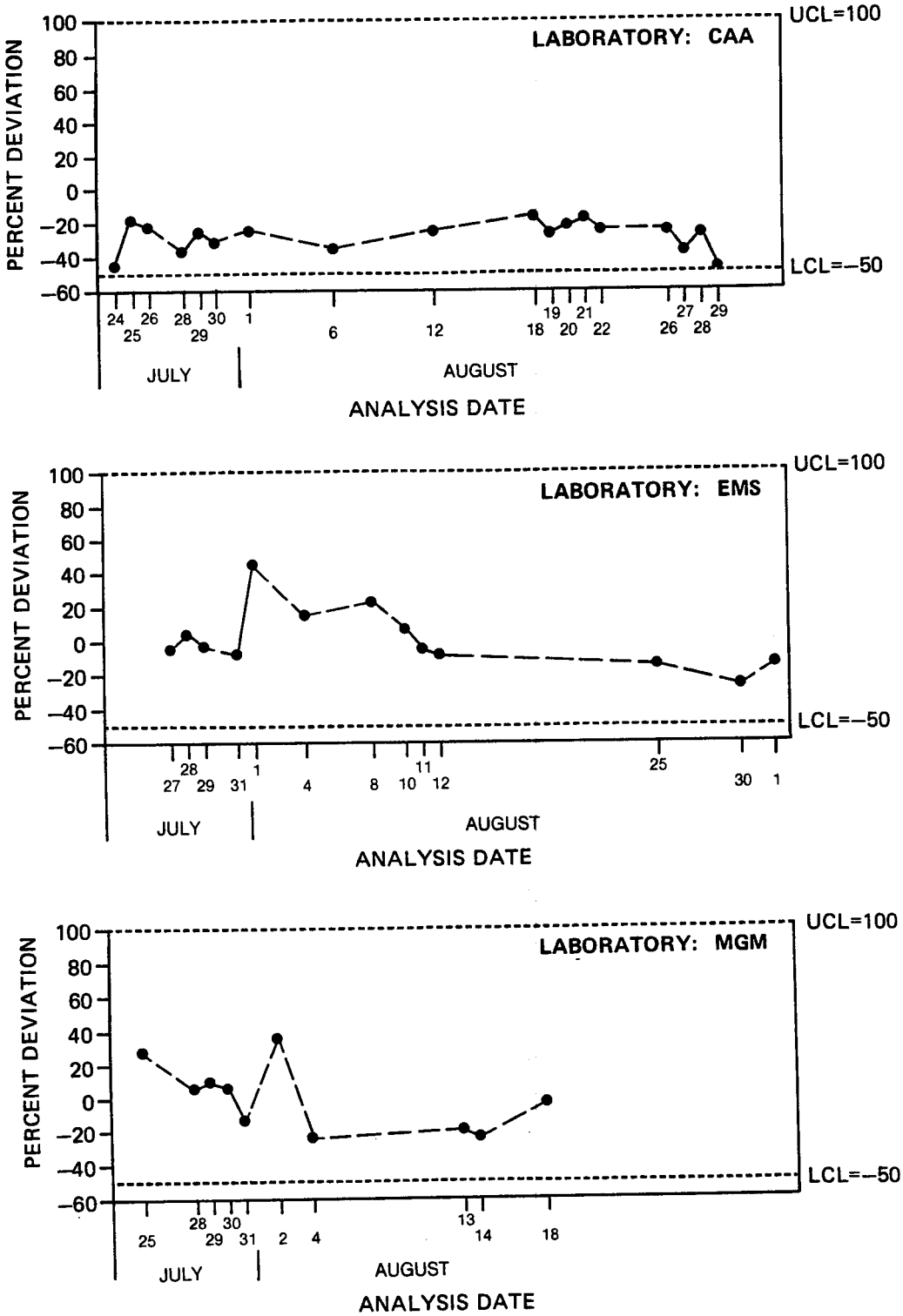



Figure C-5
**CONTROL CHART FOR INTERNAL STANDARD AREA — PERCENT DEVIATION OF $D_8$-NAPHTHALENE**

Table C-26A
SUMMARY OF INTERNAL STANDARD AREA DEVIATION OF $D_8$-NAPHTHALENE

Laboratory: CAA

| Analysis Date | 7/24 | 7/25 | 7/26 | 7/28 | 7/29 | 7/30 | 8/1 | 8/6 | 8/12 | 8/18 | 8/19 | 8/20 | 8/21 | 8/22 | 8/26 | 8/27 | 8/28 | 8/29 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | -45.8 | -18.5 | -21.4 | -37.5 | -26.7 | -31.1 | -25.9 | -37.8 | -24.8 | -17.3 | -25.8 | -21.4 | -18.9 | -22.9 | -22.5 | -37.1 | -27.9 | -46.7 |
| Maximum | -- | 15.4 | -12.2 | -26.1 | -20.9 | -28.0 | -18.4 | -29.4 | -15.4 | +1.43 | -13.7 | -6.65 | -5.57 | -- | -10.5 | -29.7 | -- | -- |
| Minimum | -- | -24.3 | -25.4 | -47.7 | -29.8 | -36.5 | -32.8 | -43.4 | -33.0 | -30.4 | -38.1 | -44.1 | -38.3 | -- | -31.1 | -42.1 | -- | -- |
| Count | 1 | 3 | 6 | 5 | 3 | 4 | 7 | 3 | 4 | 8 | 8 | 4 | 7 | 1 | 4 | 4 | 1 | 1 |

Laboratory: EMS

| Analysis Date | 7/27 | 7/28 | 7/29 | 7/31 | 8/1 | 8/4 | 8/8 | 8/10 | 8/11 | 8/12 | 8/25 | 8/30 | 9/1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | -4.07 | +4.28 | -1.53 | -9.45 | +48.5 | +15.6 | +21.6 | +6.47 | -3.63 | -8.66 | -10.9 | -25.9 | -11.8 |
| Maximum | +21.5 | +16.5 | +6.58 | -- | +59.0 | +39.9 | -- | +18.7 | +4.51 | -- | -1.30 | -21.7 | -10.3 |
| Minimum | -17.6 | -15.0 | -11.3 | -- | +38.0 | -1.35 | -- | -5.23 | -26.1 | -- | -21.6 | -30.1 | -13.3 |
| Count | 6 | 6 | 4 | 1 | 5 | 12 | 1 | 10 | 7 | 1 | 7 | 2 | 2 |

Laboratory: MGM

| Analysis Date | 7/25 | 7/28 | 7/29 | 7/30 | 7/31 | 8/2 | 8/4 | 8/13 | 8/14 | 8/18 |
|---|---|---|---|---|---|---|---|---|---|---|
| Mean | +29.4 | +6.43 | +9.32 | +8.51 | -12.9 | +38.1 | -23.9 | -19.5 | -21.6 | -3.61 |
| Maximum | +63.3 | +16.5 | +32.9 | +57.9 | +0.63 | +100 | -14.6 | +1.57 | +10.9 | +47.2 |
| Minimum | +18.4 | -4.21 | -32.0 | -25.2 | -32.9 | -5.97 | -32.4 | -29.7 | -8.97 | -34.2 |
| Count | 7 | 8 | 10 | 5 | 10 | 8 | 9 | 7 | 3 | 4 |

is very low because of interferences in the sample that affect identification and quantification. The data may be useful in statistical analyses because of the random nature of the variability, but the individual values have very low reliability. A more detailed assessment and explanation of this is given in Appendix D.

### C.4.4 SUMMARY

In summary, the results of the quality control samples are within the specified control limits with a few exceptions described above. These exceptions are probably minor when compared to the other sources of variability, e.g., sample collection, extrusion, mixing, shipping, and storage. The participating laboratories thoroughly followed the analytical statement of work as specified in the QAPP for soil pilot study (CH2M HILL, 1986).

## C.5.0 QUANTITATIVE MEASURES OF DATA QUALITY

The quality of environmental data can be measured by: precision, accuracy, completeness, and the method detection limit. These measures, which have been established on the basis of widely accepted statistical principles, provide very useful indicators of data quality. Section C.4.0 compiled all method performance data to evaluate whether the required quality control limits have been met. In this section, the quality of these data will be evaluated quantitatively to see if the data quality objectives (DQO) specified in the QAPP have been achieved. This will provide a basis to identify if further QA program and QC procedures are necessary to improve the success of the full habitability study.

### C.5.1 ESTIMATE OF DATA PRECISION

Precision is a measure of agreement among individual measurements of the same property, under prescribed similar conditions. Precision is determined by measuring the agreement among a number of individual measurements (replicates) of the same sample or concentration. This agreement is expressed as relative standard deviation (RSD) or relative range (RR) in case of duplicates. The percent relative standard deviation is the standard deviation divided by the mean and multiplied by 100 to obtain a percentage.

Precision estimates can be obtained from analyses of field duplicates, field triplicates, surrogates, matrix spike/matrix spike duplicates (MS/MD), and EPA blind QC samples. The field duplicate and triplicate samples were randomly split and delivered blind to the laboratories with different sample numbers. The purpose of the field duplicate and triplicate samples was to establish interlaboratory and intralaboratory precision.

Table C-27 shows the relative standard deviations for surrogate and matrix spike analyses. These analyses represent intralaboratory precision; they may include variation because of sample heterogeneity but do not include interlaboratory variation. Also, these data have been obtained over a period of weeks, and the values may include week-to-week variations that may significantly exceed variations within a given analysis day. Table C-28 contains the field triplicate results and Table C-29 summarizes the relative standard deviations for field triplicate analysis. No values from Table C-28 were excluded, but triplicate data sets with more than one missing value (because of nondetection) were excluded. The relative standard deviations, as shown in Table C-29, were calculated using all data from the three

## Table C-27
## RELATIVE STANDARD DEVIATIONS (RSD) FOR SURROGATE AND MATRIX SPIKE ANALYSES

| Sample Type | Compound | Number of Data by Laboratory | | | % RSD by Laboratory | | | |
|---|---|---|---|---|---|---|---|---|
| | | CAA | EMS | MGM | CAA | EMS | MGM | ALL |
| Surrogate | P-bromofluorobenzene | 92 | 74 | 94 | 7.57 | 6.85 | 9.17 | 11.0 |
| | 1,4-dibromobenzene | 88 | 90 | 81 | 20.9 | 13.1 | 13.1 | 31.7 |
| | 2,4,6-tribromobiphenyl | 88 | 90 | 81 | 23.5 | 15.6 | 13.5 | 11.4 |
| | 1,2,4,5-tetrabromobenzene | 88 | 90 | 81 | 19.3 | 33.8 | 15.6 | 32.5 |
| Matrix Spike | chlorobenzene | 20 | 16 | 22 | 5.5 | 9.4 | 6.5 | 10.1 |
| | 1,2-dichlorobenzene (VOA) | 20 | 16 | 22 | 10.2 | 12.0 | 8.7 | 31.8 |
| | 1,2-dichlorobenzene (SVOA) | 18 | 18 | 18 | 22.4 | 12.6 | 13.2 | 20.7 |
| | 1,2,4-trichlorobenzene | 18 | 18 | 18 | 18.7 | 15.6 | 11.4 | 20.3 |
| | 2-chloronaphthalene | 18 | 18 | 18 | 11.7 | 12.3 | 6.0 | 16.6 |
| | 1,2,3,4-tetrachlorobenzene | 18 | 18 | 18 | 14.3 | 15.9 | 11.9 | 20.5 |
| | B-BHC | 18 | 18 | 18 | 16.1 | 14.9 | 10.4 | 31.9 |
| | G-BHC | 18 | 18 | 18 | 13.4 | 28.3 | 13.2 | 22.0 |

Note: See Tables C-20 and C-21.

## Table C-28
## SUMMARY OF FIELD TRIPLICATE RESULTS

| Site I.D. | Sample I.D. | Lab I.D. | Chlorobenzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SVOA) | 1,2,4-Trichloro-benzene | 1,2,3,4,-Tetra-chlorobenzene | 2-Chloro-napththalene | B-BHC | G-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPCA1S11 | LC2161 | MGM | <1.0 | <1.0 | 0.8 | 0.6 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2251 | MGM | <1.0 | <1.0 | 1.0 | 0.6 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2292 | CAA | <1.0 | <1.0 | <1.0 | 0.34 | 0.11 | <1.0 | <1.0 | <1.0 |
| SPCA1S16 | LC2215 | MGM | <1.0 | <1.0 | 0.9 | 0.4 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2040 | MGM | 0.10 | <1.0 | 1.7 | 0.8 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2105 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 0.20 | <1.0 | <1.0 |
| SPCA2S06 | LC2030 | EMS | 0.054 | <1.0 | <1.0 | 0.31 | <1.0 | 0.089 | <1.0 | <1.0 |
| | LC2150 | MGM | <1.0 | <1.0 | 0.9 | 0.40 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2273 | MGM | <1.0 | <1.0 | 0.8 | 0.50 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S18 | LC2084 | CAA | 0.12 | 0.25 | <1.0 | 0.15 | 0.90 | 0.10 | <1.0 | <1.0 |
| | LC2242 | CAA | <1.0 | <1.0 | <1.0 | 0.17 | <1.0 | 0.13 | <1.0 | <1.0 |
| | LC2267 | MGM | <1.0 | <1.0 | 1.1 | 0.60 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS21 | LC2026 | EMS | 0.195 | <1.0 | <1.0 | 0.4 | 0.35 | 0.114 | <1.0 | <1.0 |
| | LC2210 | MGM | <1.0 | <1.0 | 5.1 | 3.1 | 1.5 | 0.90 | <1.0 | <1.0 |
| | LC2179 | EMS | 0.136 | <1.0 | <1.0 | 0.467 | 0.504 | 0.308 | <1.0 | <1.0 |
| SPEDAS22 | LC2319 | MGM | <1.0 | <1.0 | 0.9 | 1.4 | 3.1 | <1.0 | <1.0 | <1.0 |
| | LC2325 | CAA | 0.07 | <1.0 | 0.45 | 0.84 | 2.0 | 0.18 | <1.0 | <1.0 |
| | LC2282 | CAA | <1.0 | <1.0 | 0.14 | 0.23 | 0.35 | 0.08 | <1.0 | <1.0 |
| SPEDAS23 | LC2020 | EMS | <1.0 | 0.185 | <1.0 | 0.923 | 1.011 | <1.0 | <1.0 | <1.0 |
| | LC2009 | EMS | 0.047 | <1.0 | 0.403 | 1.536 | 1.666 | <1.0 | <1.0 | <1.0 |
| | LC2262 | EMS | <1.0 | 0.046 | <1.0 | 1.140 | 1.202 | 0.087 | <1.0 | <1.0 |
| SPEDAS42 | LC2131 | MGM | <1.0 | <1.0 | 1.5 | 2.1 | 2.1 | <1.0 | <1.0 | <1.0 |
| | LC2198 | CAA | 0.05 | <1.0 | 0.34 | 1.6 | 2.5 | 0.09 | <1.0 | <1.0 |
| | LC2274 | MGM | <1.0 | <1.0 | 1.2 | 2.8 | 4.1 | <1.0 | <1.0 | <1.0 |

Note: All concentrations were reported as ug/kg and on a dry weight basis.

Table C-29
SUMMARY STATISTICS OF FIELD TRIPLICATE ANALYSIS

| Compound | Number of Data | Mean % RSD | Std. Dev. % RSD | Max. % RSD | Min. % RSD |
|---|---|---|---|---|---|
| Chlorobenzene | 1 | 23.5 | -- | -- | -- |
| 1,2-dichlorobenzene (VOA) | 1 | 83.3 | -- | -- | -- |
| 1,2-dichlorobenzene (SVOA) | 5 | 40.6 | 28.7 | 76.0 | 8.23 |
| 1,2,4-trichlorobenzene | 8 | 53.0 | 33.8 | 117 | 25.0 |
| 1,2,3,4-tetrachlorobenzene | 4 | 54.5 | 27.0 | 79.5 | 26.4 |
| 2-chloronaphthalene | 3 | 54.6 | 38.3 | 93.2 | 16.7 |

Note: See Table C-28.

laboratories and thus may include interlaboratory variation. The data also include the variability associated with sampling, transportation, storage, and preservation of soil samples.

As shown in Table C-27, the precision of both volatile and semi-volatile methods is generally within 20 percent. This represents acceptable intralaboratory precision and acceptable reproducibility of quantification. The measurement precision of LCICs in any soil sample, at the 95 percent probability interval, may be estimated using the formula: concentration ±1.96 x (standard deviation). The percent standard deviations in Table C-29 are more variable than those in Table C-27. This is not unexpected, since the data in Table C-29 include the variations from the entire measurement process, e.g., sampling, transportation, preparation, calibration, analysis, and interlaboratory variability. In addition, the increased method variability at the low concentration level found in the field triplicate samples and possible blank contributions may increase the relative standard deviation.

One EPA blind QC sample was included with each 20 field samples. The blind QC samples were prepared by EMSL-LV using a sand matrix and sealed in a special vial containing a known concentration of LCICs. The three blind QC samples used during the course of the study were in three concentration levels and labeled as SVSM#2, SVSM#3, and SVSM#4. The true concentrations were not revealed to the analytical laboratories. Table C-30 summarizes the percent accuracy of the blind QC sample analyses from the analytical laboratories. The percent accuracy of a blind QC sample analysis is the analytical result divided by the true value and multiplied by 100 to obtain a percentage. The relative standard deviations for percent accuracy of the blind QC samples are shown in Table C-31. Although the blind QC samples are prepared homogeneously using sand and do not include the variability associated with sampling, they may be used to provide a rough estimate of interlaboratory data precision. The standard deviations presented in Table C-31 can be used to calculate the precision estimates for the field data, at the 95 percent probability interval, by means of the following formula: concentration ±1.96 x (standard deviation).

It has been suggested that percent RSD of less than 40 is acceptable for precision between laboratories for a trace method (EPA, 1979). The data as shown in Table C-31 are within this criterion. This increases the confidence of the sample results reported by the analytical laboratories.

Seven samples were collected from sample site SPEDAS12 and were sent to CAA for analysis of LCICs. Table C-32 reports the results. Estimates of precision could be made for

# Table C-30
## SUMMARY OF EPA BLIND QC SAMPLE RESULTS

| Sample ID | Compound | True Concentration (ug/kg) | MGM | | EMS | | CAA | |
|---|---|---|---|---|---|---|---|---|
| | | | Concentration Found (ug/kg) | % Recovery | Concentration Found (ug/kg) | % Recovery | Concentration Found (ug/kg) | % Recovery |
| SVSM #2 | Chlorobenzene | 20 | 16 | 80 | 11.1, 12.6 | 56, 63 | 19.6, 19.9 | 98, 99 |
| | 1,2-dichlorobenzene (VOA) | 15 | 19 | 127 | 10.1, 11.4 | 67, 76 | 17.0, 17.2 | 113, 115 |
| | 1,2-dichlorobenzene (SVOA) | 10 | 7.7 | 77 | 5.9 | 59 | 6.7, 6.2 | 67, 62 |
| | 1,2,4-trichlorobenzene | 25 | 17 | 68 | 16.4 | 66 | 20, 19 | 80, 76 |
| | 1,2,3,4-tetrachlorobenzene | 22.5 | 17 | 75 | 20.0 | 89 | 14, 13 | 62, 58 |
| | 2-chloronaphthalene | 35 | 26 | 74 | 33.0 | 94 | 24, 25 | 69, 71 |
| | B-BHC | 22.5 | 22 | 98 | 17.2 | 76 | 18, 20 | 80, 89 |
| | G-BHC | 20 | 17 | 85 | 13.2 | 66 | 15, 16 | 75, 80 |
| SVSM #3 | Chlorobenzene | 10 | 9.9 | 99 | 9.95 | 99 | 9.77, 9.68 | 98, 97 |
| | 1,2-dichlorobenzene (VOA) | 10 | 15.4 | 154 | 9.63 | 96 | 10.9, 10.5 | 109, 105 |
| | 1,2-dichlorobenzene (SVOA) | 15 | 10 | 67 | 8.4 | 56 | 14, 12 | 93, 80 |
| | 1,2,4-trichlorobenzene | 37.5 | 27 | 72 | 22.9 | 61 | 36, 30 | 96, 80 |
| | 1,2,3,4-tetrachlorobenzene | 33.8 | 26 | 77 | 27.2 | 80 | 28, 13 | 83, 38 |
| | 2-chloronaphthalene | 52.5 | 41 | 78 | 47.8 | 91 | 49, 23 | 93, 44 |
| | B-BHC | 33.8 | 30 | 89 | 27.8 | 82 | 38, 33 | 112, 98 |
| | G-BHC | 30 | 22 | 73 | 15.3 | 51 | 32, 26 | 107, 87 |
| SVSM #4 | Chlorobenzene | 4.8 | 4.5 | 94 | 3.7 | 77 | 4.6, 4.3 | 96, 90 |
| | 1,2-dichlorobenzene (VOA) | 6.0 | 6.7 | 112 | 5.0 | 83 | 5.8, 5.5 | 97, 92 |
| | 1,2-dichlorobenzene (SVOA) | 4.8 | 4.0 | 83 | 3.1 | 65 | 3.2, 3.7 | 67, 77 |
| | 1,2,4-trichlorobenzene | 6.0 | 5.1 | 85 | 3.9 | 65 | 4.3, 4.7 | 72, 78 |
| | 1,2,3,4-tetrachlorobenzene | 3.6 | 3.6 | 100 | 2.0 | 56 | 2.7, 3.0 | 75, 83 |
| | 2-chloronaphthalene | 4.8 | 6.3 | 131 | 4.2 | 87 | 5.0, 5.0 | 104, 104 |
| | B-BHC | 3.6 | 4.4 | 122 (229)[a] | 3.8 | 105 (154)[a] | 5.4, 5.1 | 150, 142 (279, 260)[a] |
| | G-BHC | 4.8 | 11 | | 7.4 | | 13.4, 12.5 | |

[a] Recoveries were biased high due to addition error of G-BHC to the blind QC samples.

Table C-31
SUMMARY STATISTICS OF EPA BLIND QC SAMPLES
PERCENT RECOVERY

| Compound | | SVSM #2 | SVSM #3 | SVSM #4 |
|---|---|---|---|---|
| Chlorobenzene | Count | 5 | 4 | 4 |
| | Mean | 79.2 | 98.3 | 89.3 |
| | Std. Dev. | 19.7 | 0.96 | 8.5 |
| | % RSD | 24.8 | 0.97 | 9.56 |
| 1,2-dichlorobenzene (VOA) | Count | 5 | 4 | 4 |
| | Mean | 99.6 | 116 | 96.0 |
| | Std. Dev. | 26.4 | 25.9 | 12.1 |
| | % RSD | 26.5 | 22.3 | 12.6 |
| 1,2-dichlorobenzene (SVOA) | Count | 4 | 4 | 4 |
| | Mean | 66.3 | 74.0 | 73.0 |
| | Std. Dev. | 7.9 | 16.0 | 8.5 |
| | % RSD | 11.9 | 21.6 | 11.6 |
| 1,2,4-trichlorobenzene | Count | 4 | 4 | 4 |
| | Mean | 72.5 | 77.3 | 75.0 |
| | Std. Dev. | 6.6 | 14.7 | 8.5 |
| | % RSD | 9.1 | 19.1 | 11.4 |
| 1,2,3,4-tetrachlorobenzene | Count | 4 | 4 | 4 |
| | Mean | 71.0 | 69.5 | 78.5 |
| | Std. Dev. | 14.0 | 21.1 | 18.3 |
| | % RSD | 19.8 | 30.4 | 23.3 |
| 2-chloronaphthalene | Count | 4 | 4 | 4 |
| | Mean | 77.0 | 76.5 | 106 |
| | Std. Dev. | 11.5 | 22.7 | 18.2 |
| | % RSD | 15.0 | 29.6 | 17.1 |
| B-BHC | Count | 4 | 4 | 4 |
| | Mean | 85.8 | 95.3 | 130 |
| | Std. Dev. | 9.8 | 13.0 | 20.3 |
| | % RSD | 11.4 | 13.6 | 15.6 |
| G-BHC | Count | 4 | 4 | --[a] |
| | Mean | 76.5 | 79.5 | --[a] |
| | Std. Dev. | 8.1 | 23.6 | --[a] |
| | % RSD | 10.6 | 29.7 | --[a] |

Note: See Table C-30.

[a]No data were available due to incorrect addition of the concentration of G-BHC.

# Table C-32
## SUMMARY OF FIELD HEPTAPLICATE RESULTS

| Site ID | Sample ID | Chlorobenzene (ppb) | 1,2-dichloro-benzene (ppb) | 1,2-dichloro-benzene (ppb) | 1,2,4-trichloro-benzene (ppb) | 1,2,3,4-tetrachloro-benzene (ppb) | 2-chloro-naphthalene (ppb) | B-BHC (ppb) | G-BHC (ppb) |
|---|---|---|---|---|---|---|---|---|---|
| SPEDAS12 | LC2094 | <1.0 | <1.0 | <1.0 | 0.36 B | 0.35 | <1.0 | <1.0 | <1.0 |
| | LC2195 | 0.04 | <1.0 | <1.0 | 0.33 B | 0.33 | <1.0 | <1.0 | <1.0 |
| | LC2221 | 0.06 | <1.0 | <1.0 | 0.21 B | 0.17 | <1.0 | <1.0 | <1.0 |
| | LC2079 | <1.0 | <1.0 | <1.0 | 0.38 B | 0.30 | <1.0 | <1.0 | <1.0 |
| | LC2029 | <1.0 | <1.0 | <1.0 | 0.23 B | 0.20 | <1.0 | <1.0 | <1.0 |
| | LC2237 | 0.07 | <1.0 | <1.0 | 0.38 B | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2159 | 0.03 | <1.0 | <1.0 | 0.45 B | 0.36 | <1.0 | <1.0 | <1.0 |
| | Count | 4 | -- | -- | 7 | 6 | -- | -- | -- |
| | Mean | 0.05 | -- | -- | 0.33 | 0.29 | -- | -- | -- |
| | Std. Dev. | 0.02 | -- | -- | 0.09 | 0.08 | -- | -- | -- |
| | % RSD | 40 | -- | -- | 27 | 28 | -- | -- | -- |
| | Max. | 0.07 | -- | -- | 0.45 | 0.36 | -- | -- | -- |
| | Min. | 0.03 | -- | -- | 0.21 | 0.17 | -- | -- | -- |

chlorobenzene, 1,2,4-trichlorobenzene, and 1,2,3,4-tetrachlorobenzene because a sufficient number of results were obtained to yield meaningful comparisons. No estimates of precision could be made for the other five compounds because none were detected. Although the relative standard deviations of these analyses are comparable to the results that were discussed above, a more variable result should not be unexpected because of method variability at this concentration level. The precision estimate for the field data can be calculated at the 95 percent confidence interval by using the formula: Field results (ppb) ± 1.96 x [standard deviation from Table C-32 (ppb)].

## C.5.2 ESTIMATE OF DATA ACCURACY

Accuracy is a measure of the closeness of an individual measurement or the average of a number of measurements to the true value. It is determined by analyzing a reference material of known pollutant concentration or by reanalyzing a sample to which a material of known concentration or amount of pollutant has been added. Accuracy is usually expressed either as a percent recovery or as a percent bias. Percent recovery is the mean analytical value expressed as a percentage of the true value, and the percent bias is the difference between the true value and the mean analytical value expressed as a percentage of the true value. Determination of accuracy always includes the effects of variability (precision), so accuracy is reported as a 95 percent probability interval, which is the mean bias or percent recovery ±1.96 (standard deviation) (Mitchell, 1985).

Accuracy can be estimated from matrix spike analyses, surrogate analyses, and EPA blind QC sample analyses. These are summarized in Tables C-33 and C-34. The percent bias shown in these tables was used to estimate the accuracy of the analyses. However, it is not certain which of the statistics in Tables C-33 and C-34 are good estimates of the true accuracy and bias of the method. The surrogate and matrix spike analyses might not allow the analyte to be fully incorporated in the sample for sufficient time to properly simulate environmental LCICs. The accuracy and bias for the EPA blind QC samples are based on nominal concentrations that are believed to be correct but have not been rigorously verified.

As shown in Table C-33, the percent bias for volatile method surrogate and matrix spike analyses is all less than ±10 percent; however, the data in Table C-34 for EPA blind QC samples are more variable. The percent bias data from the semivolatile method have a significant bias compared to the volatile method because the extraction procedure is not 100 percent efficient, and the method does not provide a procedure to

# Table C-33
# METHOD BIAS SUMMARY FOR SURROGATE AND MATRIX SPIKE ANALYSES

| Sample Type | Compound | Number of Data | Mean Percent Recovery | Mean Percent Bias |
|---|---|---|---|---|
| Surrogate | P-bromofluorobenzene | 332 | 95.1 | 4.9 |
| | 1,4-dibromobenzene | 311 | 67.7 | 4.8 |
| | 2,4,6-tribromobipheny1 | 311 | 84.5 | 33.7 |
| | 1,2,4,5-tetrabromobenzene | 311 | 79.4 | 18.5 |
| Matrix Spike | chlorobenzene | 58 | 97.4 | 2.6 |
| | 1,2-dichlorobenzene (VOA) | 58 | 104.6 | 4.6 |
| | 1,2-dichlorobenzene (SVOA) | 54 | 55.0 | 45.0 |
| | 1,2,4-trichlorobenzene | 54 | 67.2 | 32.8 |
| | 2-chloronaphthalene | 54 | 78.3 | 21.7 |
| | 1,2,3,4-tetrachlorobenzene | 54 | 75.1 | 24.9 |
| | B-BHC | 54 | 83.0 | 17.0 |
| | G-BHC | 54 | 85.8 | 14.2 |

Note: See Tables C-20 and C-21.

# Table C-34
## METHOD BIAS SUMMARY FOR EPA BLIND QC SAMPLES

| Compound | SVSM #2 | | SVSM #3 | | SVSM #4 | |
|---|---|---|---|---|---|---|
| | Mean Percent Recovery | Mean Percent Bias | Mean Percent Recovery | Mean Percent Bias | Mean Percent Recovery | Mean Percent Bias |
| Chlorobenzene | 77.2 | -22.8 | 98.3 | -1.7 | 89.3 | -10.7 |
| 1,2-dichlorobenzene (VOA) | 99.6 | -0.4 | 116 | +16 | 96.0 | -4.0 |
| 1,2-dichlorobenzene (SVOA) | 66.3 | -33.7 | 74.0 | -26.0 | 73.0 | -27.0 |
| 1,2,4-trichlorobenzene | 72.5 | -27.5 | 77.3 | -22.7 | 75.0 | -25.0 |
| 1,2,3,4-tetrachlorobenzene | 71.0 | -29.0 | 69.5 | -30.5 | 78.5 | -21.5 |
| 2-chloronaphthalene | 77.0 | -23.0 | 76.5 | -23.5 | 106 | +6 |
| B-BHC | 85.8 | -14.2 | 95.3 | -4.7 | 130 | +30 |
| G-BHC | 76.5 | -23.5 | 79.5 | -20.5 | -- | -- |

Note: See Table C-31.

correct for these losses. It has been suggested that procedures that involve an extensive cleanup and a great amount of experimental manipulation should be considered adequately quantitative when values ±30 percent or better are obtained on recovery samples fortified at the ppb level (EPA, 1979). Recoveries of semivolatile LCICs generally fall in the 55 to 130 percentage range (Tables C-33 and C-34). Therefore, it is recommended that the semivolatile extraction procedures may need minor modifications. Further training of the participating laboratories on sample extraction procedures will be needed before the full-scale habitability study begins.

### C.5.3 DATA COMPLETENESS

Completeness is a measure of the amount of valid data obtained from the analytical measurement system. It is defined as the total number of samples taken for which acceptable analytical data are generated, divided by the total number of samples collected, and multiplied by 100. Completeness is not intended to be a measure of representativeness, that is, how closely the measured results reflect the actual concentration or distribution of the pollutant in the media sampled. The completeness goal for this pilot study was to obtain valid analytical results for at least 95 percent of the samples collected during the project.

Table C-35 summarizes validation results of all QC data expressed as percent completeness. As shown in Table C-35, the 95 percent completeness goal was achieved with the exception of the matrix spike recovery results from CAA and EMS. The percent completeness of the matrix spike recovery results of both laboratories was slightly lower than 95 percent. This is considered acceptable because the laboratory was not required to reanalyze the sample if the matrix spike recovery was outside the specified control limits. The control limits were used for advisory purposes only.

In essence, the data quality objectives and their goals have been achieved. However, the goals may need to be reevaluated in relation to the time, resources, and methodology available for the full-scale habitability study.

# Table C-35
## DATA COMPLETENESS SUMMARY

| QA Audit | Compounds | Required Control Limits | Completeness Goal (%) | Completeness Achieved CAA (%) | EMS (%) | MGM (%) |
|---|---|---|---|---|---|---|
| Laboratory method/holding blank | All LCIC | <1.0 ug/kg | 95 | 100 | 100 | 100 |
| Surrogate Spike Recovery | p-Bromofluorobenzene (VOA) | As specified in Table C-3 | 95 | 98.4 | 100 | 100 |
| | 1,4-Dibromobenzene (SVOA) | | 95 | 95.2 | 98.7 | 98.4 |
| | 2,4,6-Tribromobiphenyl (SVOA) | | 95 | | | |
| Matrix Spike Recovery | All volatile LCIC | As specified in Table C-3 | 95 | 100 | 100 | 100 |
| | All semi-volatile LCIC | | 95 | 93.5 | 92.6 | 97.2 |
| Matrix Spike Duplicate | All volatile LCIC | As specified in Table C-3 | 95 | 100 | 100 | 100 |
| | All semi-volatile LCIC | $\leq$ ±30% RPD | 95 | 98.2 | 98.1 | 98.1 |
| Performance Check Standard | All LCIC plus $d_5$-chlorobenzene, $d_{10}$-pyrene, and 1,2,4,5-tetrabromobenzene | As specified in the QAPP | 100 | 100 | 100 | 100 |
| Initial Calibration Standard | All LCIC | $\leq$30% RSD | 100 | 100 | 100 | 100 |
| Continuing Calibration Standard | All LCIC | $\leq$±25% D | 100 | 100 | 100 | 100 |
| EPA Check Standard | All LCIC | 80 to 120% | 100 | 100 | 100 | 100 |
| Internal Standard | $d_5$-Chlorobenzene and | Rt difference $\leq$±10 seconds | 95 | 100 | 100 | 100 |
| | $d_8$-naphthalene | Area response: -50% to +100% | 95 | 100 | 100 | 100 |
| Holding Time | All LCIC | As specified in the QAPP | 100 | 100 | 100 | 100 |

## C.6.0 ANALYTICAL METHOD EVALUATION

The analytical methods were used in the analysis of over two hundred soil pilot study samples. All three participating laboratories were successful in applying the methods to the analysis of the soil samples and meeting the data quality objectives stated in the quality assurance project plan.

Although the performance of the method was acceptable during the pilot study, all participating laboratories encountered problems that need further evaluation. The following discussion outlines some of the problems that were encountered for the volatile and semivolatile analyses and the proposed corrective actions.

### C.6.1 SEMIVOLATILE ANALYSIS

The analytical method specifies a clean-up step that uses concentrated sulfuric acid to further remove polar impurities from the sample extract. Just prior to starting the pilot study, experiments confirmed that small quantities of the concentrated sulfuric acid were occasionally carried over to the final extract used in the analysis. Experiments proved that the sulfuric acid was causing fairly rapid hydrogen/dueterium exchange for the dueterated internal standards. The exchange was demonstrated to cause a severe false high bias due to the reduction of the internal standards concentrations in the extracts. All laboratories were informed of this potential problem before the start of the pilot study analyses. All laboratories directed special attention to this problem, and did not encounter difficulties related to deuterium exchange during the pilot study analyses. Further validation experiments have been performed involving washing the final extract with a sodium bicarbonate solution to ensure effective removal of sulfuric acid. Results of these experiments indicate the wash step is an effective means of preventing this problem. Future revisions of the methods will incorporate this procedure.

All three participating laboratories experienced problems of hydrocarbon interference with the ions used to monitor the BHC isomers. The interferences caused problems with qualitative identification in sample analyses and also affected meeting the signal/noise criteria of the check solution at the end of batch analysis. The interference is primarily because of hydrocarbon contamination in samples that demonstrate a relatively high hydrocarbon background that overlaps the elution of the BHC compounds. Further validation experiments have been performed using a different selection of characteristic masses that reduce the interference considerably. The data are currently being evaluated by MGM for

possible incorporation of the new ions into the next revision of the method. The BHC compounds elute at the same time as the hydrocarbon interference.

CAA and EMS observed a trend of decreasing recovery with increasing volatility of surrogate compounds during semivolatile analysis. CAA and EMS reported lower recoveries of 1,4-dibromobenzene and 1,2-dichlorobenzene than those of MGM. The low recoveries of 1,4-dibromobenzene and 1,2-dichlorobenzene may be due to a volatility discrimination problem observed during the sample preparation procedure. Before the full-scale habitability study begins, CAA, EMS, and other participating laboratories need training by MGM on sample extraction procedure to eliminate the volatility discrimination problem.

## C.6.2 VOLATILE ANALYSIS

The method used for volatile analysis in the pilot study is very similar to other well-established methods for determination of volatiles in soil. The main difference lies in the use of selected ion monitoring to detect the compounds at lower concentrations. All laboratories encountered problems with the chromatographic resolution of the dichlorobenzene isomers using the packed column. The chromatographic performance of the dichlorobenzenes on the Carbopak/SP-1000 is marginal, giving very broad peaks with very poor resolution. Since the targeted dichlorobenzene isomer is also determined and chromatographically resolved in the semivolatile fraction, the utility of its determination in the volatile fraction is questionable and needs further evaluation. It is suggested that volatile analysis be dropped from the study because of the high percentage of nondetects for volatile LCICs and the poor chromatographic performances of 1,2-dichlorobenzene.

## C.7.0 SUMMARY AND CONCLUSIONS

To improve the effectiveness of the soil pilot study, an extensive analytical monitoring program was implemented. Key elements of the program included analytical method development and validation, QA/QC program design, data validation, and assessment procedures development. This section contains a summary and discussion of the results obtained from this analytical monitoring program.

There are numerous potential sources of error in the analytical process. The quality control procedures that were developed for the soil pilot study have provided mechanisms to monitor these errors. One indication of the effectiveness of the QA program was the degree to which all three participating laboratories met the percent data completeness criterion. The data from the QC sample analyses met the 95 percent data completeness goal, with the exception of the matrix spike recovery results from CAA and EMS. The completeness of the matrix spike recovery results from these two laboratories was slightly lower than 95 percent. Another indication of the effectiveness of the QA program was the fact that no samples were invalidated retrospectively by EMSL-LV during its review of the data. To a great extent, the high percentages of data completeness and validated samples were due to the degree to which all three of the analytical laboratories adhered to the required quality control procedures. Other factors contributing to these high percentages were the EMSL-LV's and CH2M HILL's management of the monitoring efforts, timely identification of potential problems through electronic data transfer and onsite visits, and initiation of corrective actions before these problems became critical. In summary, the data quality objectives specified in the QAPP have been achieved, and the results satisfy the soil pilot study objectives.

During data review, we found that the reliability of the positive chemical identifications was very high. Only one sample, i.e., LC2103, had 1,2-dichlorobenzene identified incorrectly in the semivolatiles analysis. A major reason for this high reliability is the use of well-defined and stringent compound identification criteria. All the participating laboratories rely upon criteria designed to ensure unambiguous, unequivocal identification of a compound. One exception to this is that compounds with results reported at less than 1 ppb have low reliability in identification and quantification because of the interferences present in the sample.

Quantification of volatile LCICs is reliable because the surrogate standard recoveries and matrix spike recoveries

have no significant bias. Concentrations reported for semivolatile LCICs have a low bias because the extraction procedure is not 100 percent efficient and the method does not provide a procedure to correct for these losses. This is demonstrated by consistently low surrogate standard recoveries and low matrix spike recoveries. The low recoveries of 1,2-dichlorobenzene and 1,4-dibromobenzene are particularly significant because they imply that volatility discrimination occurs during extraction procedures. Concentrations for other semivolatile LCICs are considered adequately quantitative because their matrix spike recoveries and surrogate standard recoveries are within ±30 percent of accuracy. MGM shows a positive bias of about 0.5 to 0.6 ppb of 1,2-dichlorobenzene and about 0.1 to 0.2 ppb for 1,2,4-trichlorobenzene compared to the other two laboratories. The biases from the blank contribution introduce uncertainty in the sample results of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, especially those around 1 ppb. Therefore, the 1,2-dichlorobenzene and 1,2,4-trichlorobenzene concentrations reported by MGM are biased toward higher than true values because of laboratory blank contamination of samples. Although this blank contamination was within the limits set by the QAPP, subsequent analysis of the data for the statistical design of the habitability study has shown blank contamination at these levels to be unacceptable. The QAPP will be revised to correct for this problem.

The method detection limit was tentatively targeted for 1 ppb at the beginning of the study. The laboratories, however, were required to report concentrations at less than 1 ppb if they met the identification criteria. During the last stage of method development, it was decided that a detection limit surrogate, 1,2,4,5-tetrabromobenzene, would be added to each sample at the 1 ppb level. The intention was that the ability to detect the surrogate would be related to the detection limit of the method for that particular sample. The results of this study show a high percentage of LCIC compounds found at concentrations of less than 1 ppb. The reliability of concentrations of less than 1 ppb is low. Interferences present in the sample preclude reliable identification and quantification. This is further demonstrated by the large variability of detection limits for the surrogate analysis. This unreliability led to using 1 ppb as the detection limit for the pilot study results.

In summary, the quality of the analytical results is within acceptable accuracy and precision with a few minor exceptions. The participating laboratories thoroughly followed the analytical statement of work specified in the QAPP for the soil pilot study. The analytical method was successfully applied to the analysis of the soil samples and met the data quality objectives.

## C.8.0 RECOMMENDATIONS

The following are recommendations for further improving the methodology and overall data quality for the future EDA habitability study.

1. Variability and bias in the semivolatile sample extraction procedures should be investigated. Based on the results from surrogate analyses, matrix spike/matrix spike duplicate analyses, and EPA blind QC samples analyses, we found that semivolatile sample extraction procedures can introduce variability and bias to the 1,2-dichlorobenzene concentration. Examples of possible areas that can introduce variability and bias are:

   - The sonicators used by the participating laboratories are different and may result in inefficient extraction, with corresponding introduction of variability and bias in results.

   - The micro Snyders columns used by the participating laboratories vary in design and may result in a loss of analyte during concentration and solvent exchange, with corresponding introduction of variability and bias in results.

   - Reagents used by the participating laboratories vary in purity and may result in contamination of the sample, with corresponding introduction of variability and bias in results.

   - Bias and variability may be introduced to the sample results if the specified sample extraction procedures are not followed.

   It is, therefore, recommended that CAA, EMS, and other participating laboratories need training by MGM on sample extraction procedures before the full-scale habitability study. The bias and variability in the sample extraction procedures should be checked by performance evaluation sample analysis prepared by EMSL/LV.

2. MGM reported higher levels of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene than the other two laboratories in the semivolatile method/holding blank analysis. The blank contamination may be due to variations in purity of the solvents and/or reagents used by the participating laboratories because of different chemical suppliers. It is recommended that clean solvents and reagents from one chemical supplier with the same lot number be used for the full-scale habitability study. The allowable

concentration limits set for the method/holding blank analysis also should be revised in the QAPP for the full-scale habitability study.

3. Variability in the instrument measurement step is controlled through the periodic use of continuing calibration standards and the use of internal standards. It was found that the response factors of ρ-bromofluorobenzene, B-BHC, G-BHC, 2,4,6-tribromobiphenyl and 1,2,4,5-tetrabromobenzene were frequently over 20 percent different from the $\bar{RF}$s of the initial calibration curves. It is suggested that internal standard area variation acceptance windows be defined not only for $d_5$-chlorobenzene and $d_8$-naphthalene but also for the other internal standards. It may also be desirable to narrowly define continuing calibration standard percent difference acceptance windows (currently within ±25 percent from the $\bar{RF}$ of the initial calibration curve) to somewhere on the order of 10 percent to 20 percent.

4. A high percentage of soil samples showed LCICs at concentrations of less than 1 ppb. The reliability of measurements of concentrations at less than 1 ppb is low because the interferences present in the sample preclude the reliable identification and quantification of the LCICs. Compound identification criteria may need to be modified in order to maintain comparable results between the participating laboratories. For example, if there are peaks that will affect the maximization or quantification of peaks of interest, it may be necessary to narrow the relative retention time window to eliminate the interfering peaks. More research is being conducted to define further the identification criteria. In addition, the analytical laboratories will be trained in consistent and uniform application of the criteria.

5. Although the performance of the method was acceptable during the pilot study, some problems that were encountered during the pilot study need further evaluation. For example:

   - Rapid hydrogen/deuterium exchange for the deuterated internal standards because of carryover of sulfuric acid to the final extract
   - Hydrocarbon interference with the ions used to monitor the BHC isomers
   - Poor chromatographic performance of 1,2-dichlorobenzene in the volatile analysis

It is recommended that these problems and the others as described in (1) above need further evaluation prior to the full-scale habitability study.

6. The data quality objectives have been achieved for the soil pilot study. To a great extent, this was due to the adherence of the analytical laboratories to the required quality control procedures. However, it may be necessary to reevaluate those quality control procedures and data quality objectives to determine if they are achievable for the future full-scale study. This should be discussed in detail in the QAPP that will be prepared for the full-scale habitability study.

7. There are substantial differences between the nonquantifiable percentages from volatile analysis versus semivolatile analysis for 1,2-dichlorobenzene. One possible explanation is that the volatile sample was taken from the topsoil portion of the Shelby tube while the semivolatile sample was obtained from more of the clay subsoil. It is necessary to evaluate this soil mixing procedure to eliminate the variability and bias.

8. Except for a few hot spots, the full-scale habitability study should focus on the analysis of low levels of LCICs at around 1 ppb to 10 ppb level. To achieve this concentration level, it is necessary to modify some quality control procedures in the analytical protocol. For example, instrument calibration procedures, sample preparation procedures and compound identification criteria may need to be modified and validated to limit the sources of variability and bias and to increase the confidence of the reported concentrations at these low levels.

## REFERENCES


1. Love Canal Emergency Declaration Area Proposed Habitability Criteria, New York State Department of Health and Department of Health and Human Services/Centers for Disease Control, December 1986.

2. Love Canal Pilot Soil Sampling Study Quality Assurance Project Plan, CH2M HILL, July 11, 1986.

3. Manual for Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples, EPA600-1-79-008, January 1979.

4. W. Mitchell, R. Rhodes, and F. McElroy, "Determination of Measurement Data Quality and Establishment of Achievable Goals for Environmental Measurements," Quality Assurance for Environmental Measurements, ASTM STP 867, J.K. Taylor and T.W. Stanley, Eds., ASTM, 1985.

Attachment 1
UNVALIDATED SAMPLE ANALYSIS RESULTS

## LEGEND FOR ATTACHMENT 1

| | | |
|---|---|---|
| ND | = | Not detected at concentration below 1 ppb |
| NR | = | No results were reported because contingency samples were used for reanalysis |
| NA | = | The samples were not analyzed because only volatile or semivolatile LCICs, but not both, were required to be reanalyzed |
| B | = | A qualifier used when the analyte is found in the blank as well as in a sample. |

# LOVE CANAL HABITABILITY STUDY SOIL PILOT
## SUMMARY OF RESULTS
## ALL VALUES REPORTED IN PARTS PER BILLION (PPB)

Geographic Area: Cheektowaga

| Site ID | Sampling ID | Lab ID | Analytical Results: Chlorobenzene | 1,2-Dichlorobenzene (VOA) | 1,2-Dichlorobenzene (SV) | 1,2,4-Trichlorobenzene | 1,2,3,4-Tetrachlorobenzene | 2-Chloronaphthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPCA1S01 | LC2041 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2114 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S02 | LC2021 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2154 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2290 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S03 | LC2181 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2206 | MGM | <1.0 | <1.0 | B 3.2 | B 1.4 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S04 | LC2049 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2064 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S05 | LC2065 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2128 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S06 | LC2068 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2212 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S07 | LC2033 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2130 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2284 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPCA1S08 | LC2207 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2249 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S09 | LC2047 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2152 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2276 | EMS | N.A. | N.A. | <1.0 | <1.0 | 1.0 | 1.4 | 13.9 | 8.6 |
| SPCA1S10 | LC2101 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2184 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S11 | LC2161 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2251 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2292 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S12 | LC2077 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2164 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |

Geographic Area: Cheektowaga

| Site ID | Sampling ID | Lab ID | Analytical Results: Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPCA1S13 | LC2014 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2116 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S14 | LC2013 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2073 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S15 | LC2080 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2239 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S16 | LC2040 | MGM | <1.0 | <1.0 | B 1.7 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2105 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2215 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S17 | LC2066 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2199 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S18 | LC2147 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2191 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S19 | LC2059 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2192 | MGM | <1.0 | <1.0 | B 1.3 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S20 | LC2142 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2170 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S21 | LC2017 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2226 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S22 | LC2173 | CAA | <1.0 | <1.0 | 2.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2180 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA1S23 | LC2001 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2098 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |

# LOVE CANAL HABITABILITY STUDY SOIL PILOT
## SUMMARY OF RESULTS
## ALL VALUES REPORTED IN PARTS PER BILLION (PPB)

Geographic Area: Tonawanda

| Site ID | Sampling ID | Lab ID | Analytical Results | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Chloro-benzene | 1,2-Dichloro-benzene (VOA) | 1,2-Dichloro-benzene (SV) | 1,2,4-Trichloro-benzene | 1,2,3,4-Tetrachlo-benzene | 2-Chloronap-hthalene | Beta-BHC | Gamma-BHC |
| SPCA2S01 | LC2185 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2233 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S02 | LC2304 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2313 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S03 | LC2106 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2240 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2378 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPCA2S04 | LC2208 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2228 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S05 | LC2311 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2322 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S06 | LC2030 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2150 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2273 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S07 | LC2048 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2122 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S08 | LC2109 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2139 | MGM | <1.0 | <1.0 | B 1.2 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S09 | LC2018 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2234 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S10 | LC2024 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2042 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S11 | LC2137 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2194 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S12 | LC2103 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2167 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |

Geographic Area: Tonawanda

| Site ID | Sampling ID | Lab ID | Analytical Results: Chlorobenzene | 1,2-Dichlorobenzene (VOA) | 1,2-Dichlorobenzene (SV) | 1,2,4-Trichlorobenzene | 1,2,3,4-Tetrachlorobenzene | 2-Chloronaphthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPCA2S13 | LC2046 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2193 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2286 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S14 | LC2308 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2326 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S15 | LC2007 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2153 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2342 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2355 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPCA2S16 | LC2083 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2120 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2343 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | LC2369 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S17 | LC2061 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2119 | MGM | <1.0 | <1.0 | B 1.2 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S18 | LC2084 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2242 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2267 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S19 | LC2092 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2124 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S20 | LC2309 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2317 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S21 | LC2307 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2321 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPCA2S22 | LC2306 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2310 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |

# LOVE CANAL HABITABILITY STUDY SOIL PILOT
## SUMMARY OF RESULTS
## ALL VALUES REPORTED IN PARTS PER BILLION (PPB)

Geographic Area: EDA

| Site ID | Sampling ID | Lab ID | Analytical Results: Chlorobenzene | 1,2-Dichlorobenzene (VOA) | 1,2-Dichlorobenzene (SV) | 1,2,4-Trichlorobenzene | 1,2,3,4-Tetrachlorobenzene | 2-Chloronaphthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPEDAS01 | LC2223 | CAA | <1.0 | <1.0 | <1.0 | B 2.0 | 2.7 | <1.0 | <1.0 | <1.0 |
| | LC2250 | CAA | <1.0 | <1.0 | <1.0 | B 1.7 | 2.4 | <1.0 | <1.0 | <1.0 |
| SPEDAS02 | LC2087 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2222 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2287 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS03 | LC2023 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2188 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2338 | EMS | N.A. | N.A. | <1.0 | <1.0 | 1.1 | <1.0 | B 8.4 | <1.0 |
| SPEDAS04 | LC2039 | MGM | <1.0 | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2045 | MGM | <1.0 | <1.0 | B 1.3 | B 1.2 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2160 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS05 | LC2294 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| | LC2303 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2312 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS06 | LC2107 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2121 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2373 | EMS | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS07 | LC2182 | MGM | <1.0 | <1.0 | B 1.1 | B 1.4 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2232 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS08 | LC2089 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2214 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS09 | LC2044 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2082 | EMS | <1.0 | <1.0 | <1.0 | B 1.7 | B 1.3 | <1.0 | <1.0 | <1.0 |
| SPEDAS10 | LC2126 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2141 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS11 | LC2012 | MGM | <1.0 | <1.0 | <1.0 | B 1.3 | 1.0 | <1.0 | <1.0 | <1.0 |
| | LC2057 | MGM | N.R. | N.R. | <1.0 | B 1.1 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2257 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |

Geographic Area: EDA

| Site ID | Sampling ID | Lab ID | Analytical Results: Chlorobenzene | 1,2-Dichlorobenzene (VOA) | 1,2-Dichlorobenzene (SV) | 1,2,4-Trichlorobenzene | 1,2,3,4-Tetrachlorobenzene | 2-Chloronaphthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPEDAS12 | LC2029 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2079 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2094 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2159 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2195 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2221 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2237 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS13 | LC2027 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2028 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2271 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS14 | LC2075 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2085 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2356 | CAA | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2357 | EMS | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS15 | LC2056 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2086 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS16 | LC2291 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2293 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2368 | EMS | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS17 | LC2043 | EMS | <1.0 | <1.0 | <1.0 | B 7.6 | 13.1 | <1.0 | <1.0 | <1.0 |
| | LC2169 | CAA | <1.0 | <1.0 | <1.0 | B 10.8 | 15.9 | <1.0 | <1.0 | <1.0 |
| SPEDAS18 | LC2314 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2320 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS19 | LC2144 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2175 | CAA | <1.0 | <1.0 | <1.0 | B 1.1 | 1.6 | <1.0 | <1.0 | <1.0 |
| | LC2341 | EMS | N.A. | N.A. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS20 | LC2305 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2324 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | 4.6 | <1.0 |
| SPEDAS21 | LC2026 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2179 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2210 | MGM | <1.0 | <1.0 | B 5.1 | B 3.1 | 1.5 | <1.0 | <1.0 | <1.0 |

Geographic Area: EDA

| Site ID | Sampling ID | Lab ID | Analytical Results: Chlorobenzene | 1,2-Dichlorobenzene (VOA) | 1,2-Dichlorobenzene (SV) | 1,2,4-Trichlorobenzene | 1,2,3,4-Tetrachlorobenzene | 2-Chloronaphthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPEDAS22 | LC2282 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2319 | MGM | <1.0 | <1.0 | <1.0 | B 1.4 | 3.1 | <1.0 | <1.0 | <1.0 |
| | LC2325 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | 2.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS23 | LC2009 | EMS | <1.0 | <1.0 | <1.0 | B 1.5 | B 1.7 | <1.0 | <1.0 | <1.0 |
| | LC2020 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | 1.0 | <1.0 | <1.0 | <1.0 |
| | LC2262 | EMS | <1.0 | <1.0 | <1.0 | 1.1 | 1.2 | <1.0 | <1.0 | <1.0 |
| SPEDAS24 | LC2148 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2229 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS25 | LC2072 | EMS | <1.0 | <1.0 | <1.0 | B 1.2 | B 2.9 | <1.0 | <1.0 | <1.0 |
| | LC2225 | MGM | <1.0 | <1.0 | <1.0 | B 1.2 | 1.8 | <1.0 | <1.0 | <1.0 |
| SPEDAS26 | LC2110 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2134 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2332 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPEDAS27 | LC2051 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2165 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS28 | LC2093 | MGM | <1.0 | <1.0 | B 1.3 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2211 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS29 | LC2002 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | 1.5 | <1.0 | <1.0 | <1.0 |
| | LC2108 | MGM | <1.0 | <1.0 | B 1.2 | B 1.2 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS30 | LC2063 | EMS | <1.0 | <1.0 | <1.0 | B 1.9 | B 2.4 | <1.0 | <1.0 | <1.0 |
| | LC2178 | MGM | <1.0 | <1.0 | <1.0 | 1.1 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS31 | LC2016 | MGM | <1.0 | <1.0 | B 1.2 | B 1.8 | 2.2 | <1.0 | <1.0 | <1.0 |
| | LC2166 | MGM | <1.0 | <1.0 | B 1.0 | B 1.3 | 1.6 | <1.0 | <1.0 | <1.0 |
| SPEDAS32 | LC2315 | MGM | N.R. | N.R. | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2316 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2372 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPEDAS33 | LC2062 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2074 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS34 | LC2025 | EMS | <1.0 | <1.0 | <1.0 | B 9.0 | B 18.3 | <1.0 | <1.0 | <1.0 |
| | LC2151 | MGM | <1.0 | <1.0 | B 1.6 | 15.4 | 28.3 | <1.0 | <1.0 | <1.0 |
| | LC2151R | MGM | <1.0 | <1.0 | B 3.6 | 11.3 | 18.6 | <1.0 | <1.0 | <1.0 |

Geographic Area: EDA

| Site ID | Sampling ID | Lab ID | Analytical Results: Chlorobenzene | 1,2-Dichlorobenzene (VOA) | 1,2-Dichlorobenzene (SV) | 1,2,4-Trichlorobenzene | 1,2,3,4-Tetrachlobenzene | 2-Chloronaphthalene | Beta-BHC | Gamma-BHC |
|---|---|---|---|---|---|---|---|---|---|---|
| SPEDAS35 | LC2129 | MGM | <1.0 | <1.0 | B 1.8 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2162 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS36 | LC2011 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2238 | MGM | <1.0 | <1.0 | <1.0 | B 1.4 | 1.7 | <1.0 | <1.0 | <1.0 |
| | LC2351 | CAA | N.A. | N.A. | <1.0 | 1.2 | 1.8 | <1.0 | <1.0 | <1.0 |
| SPEDAS37 | LC2318 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2323 | EMS | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2330 | EMS | N.A. | N.A. | <1.0 | <1.0 | B 1.1 | 1.1 | <1.0 | B 4.3 |
| SPEDAS38 | LC2032 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | 1.0 | <1.0 | <1.0 | <1.0 |
| | LC2244 | MGM | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS39 | LC2258 | MGM | N.R. | N.R. | B 1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2259 | MGM | <1.0 | <1.0 | B 1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2377 | MGM | <1.0 | <1.0 | N.A. | N.A. | N.A. | N.A. | N.A. | N.A. |
| SPEDAS40 | LC2171 | MGM | <1.0 | <1.0 | B 1.% | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2248 | CAA | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS41 | LC2183 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| | LC2220 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| SPEDAS42 | LC2131 | MGM | <1.0 | <1.0 | B 1.5 | B 2.1 | 2.1 | <1.0 | <1.0 | <1.0 |
| | LC2198 | CAA | <1.0 | <1.0 | <1.0 | B 1.6 | 2.5 | <1.0 | <1.0 | <1.0 |
| | LC2274 | MGM | <1.0 | <1.0 | B 1.2 | B 2.8 | 4.1 | <1.0 | <1.0 | <1.0 |
| SPEDAS43 | LC2010 | CAA | <1.0 | <1.0 | <1.0 | B 28.4 | 84.2 | <1.0 | 183.0 | 21.2 |
| | LC2209 | MGM | <1.0 | <1.0 | B 3.1 | B 30.0 | 93.8 | <1.0 | 250.0 | 18.2 |
| | LC2209R | MGM | <1.0 | <1.0 | B 8.6 | B 71.0 | 181.0 | <1.0 | 239.0 | 18.9 |
| SPEDAS44 | LC2081 | CAA | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2100 | MGM | <1.0 | <1.0 | N.R. | N.R. | N.R. | N.R. | N.R. | N.R. |
| | LC2302 | CAA | N.A. | N.A. | <1.0 | 12.9 | 22.5 | <1.0 | <1.0 | <1.0 |
| SPEDAS45 | LC2069 | EMS | <1.0 | <1.0 | <1.0 | <1.0 | 1.7 | <1.0 | <1.0 | <1.0 |
| | LC2241 | MGM | <1.0 | <1.0 | B 1.1 | B 1.1 | 2.1 | <1.0 | <1.0 | <1.0 |

# APPENDIX D
## Love Canal Habitability Soil Pilot Study Quality Assurance Review

APPENDIX D

# LOVE CANAL HABITABILITY SOIL PILOT STUDY
# QUALITY ASSURANCE REVIEW

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Contract No. 68-03-3249

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# LOVE CANAL HABITABILITY SOIL PILOT STUDY QUALITY ASSURANCE REVIEW

The EMSL-LV was requested by EPA Region II to provide Quality Assurance (QA) support for the Love Canal Habitability Soil Pilot Study. This support included review of the method and Quality Assurance Project Plan (QAPP), on-site evaluations of the laboratories, preparation and data review of Performance Evaluation (PE) samples, review of the final data packages, review of the final report, and participation in various meetings to provide "real time" QA feedback. This report consists of a summary of the EMSL-LV involvement in the project.

## INTRODUCTION

### Method Review

The analytical method at the time EMSL-LV support was requested consisted of an extraction procedure which was followed by an alumina cleanup and analysis by gas chromatography using an electron capture detector (GC-ECD). The available method validation data indicated there was a major problem with method specificity at low concentrations; this was confirmed by analysis of PE samples. A new analytical method was

designed and validated that used a gas chromatograph/mass spectrometer (GC/MS) in the selected ion monitoring (SIM) mode to achieve the desired compound specificity and to meet the project detection limit requirements. The method validation included fine-tuning and ruggedness testing of the extraction and cleanup steps as well as the instrumental analysis. The EMSL-LV reviewed the method validation results and the results of a multilaboratory internal PE sample before an EPA PE sample was provided to the laboratories.

PE Samples

A total of five batches of PE materials were provided by the EMSL-LV. The first was provided to evaluate the GC-ECD method which was shown to be unsuitable for the goals of the project. A second set of PE samples was provided to the laboratories before analysis of Love Canal samples was started. Successful analysis of these samples was a prerequisite for participation in the Love Canal pilot study. The other three batches of PE samples were analyzed during the pilot study at approximately 20 sample intervals. The results of these PE sample analyses were telephoned to the EMSL-LV as soon as they were available from the laboratories. This would have allowed immediate corrective action if a problem had been discovered.

## On-Site Evaluations

On-site evaluations were performed a minimum of three times at each laboratory. The first was performed before analysis of the PE samples to determine if the laboratory appeared capable of performing the required analyses and to determine what, if any, additional QA procedures needed to be incorporated to meet project criteria. The second was performed after analysis of the first GC/MS SIM PE sample; the purpose of this evaluation was to observe the progress the laboratory had made in correcting any deficiencies found in the first evaluation and to discuss any problems found in the PE sample results or data package. The third on-site evaluation occurred 1 to 2 weeks after sample analysis started. The purpose was to observe actual sample analysis in progress and determine if the analytical protocol was being followed. The sample preparation operation was also observed at this time. Observation of the sample preparation and analysis is essential to a complete evaluation of the laboratory capability.

An on-site evaluation was also made of the sample collection process during the first days of sample collection to determine if the sampling protocol was being followed.

## QAPP Review

The EMSL-LV reviewed several iterations of the QAPP during the developmental phase of the project. The QAPP was reviewed for such things as technical acceptability, completeness, clarity, internal consistency, and compliance with project goals. The QA specified was reviewed and compared to the project goals to determine if the specified procedures would produce data of the desired quality. The details of the QA requirements specified in the QAPP are discussed in Appendix D.

## Data Review

The Data review consisted of two main portions the first portion was a review of electronically transmitted QA data which was performed as soon as possible after the samples were analyzed in order to eliminate the possibility that a large number of samples would be analyzed by a laboratory that was out of control. The second portion was a review of the paper data package provided by each laboratory: this included all forms, quantitation reports, chromatograms, copies of standard and instrument logbooks, and any other pertinent information. This data package was examined to determine not only that the explicit QA requirements had been met but also that the implicit requirements of good laboratory practice and data integrity had been met. The paper data was reconciled with the electronic data, and a detailed electronic comparison of the data with the QA criteria was made with the appropriate data qualifiers then appended to the results in the database.

## Statistics and Chemometrics

The EMSL-LV provided review input during the planning phases on methods to evaluate detection limits, surrogate spike results, internal standard performance, laboratory comparability, statistical methods and other topics. The reports on detection limits, and method performance were also reviewed. The reports on chemometrics and the statistical requirements for the main study will be reviewed when it is available.

# THE EMSL-LV PARTICIPATION IN MEETINGS

The EMSL-LV and contractor personnel participated in a variety of meetings during the entire course of the study in order to provide immediate feedback on the effect various considered alternatives might have on data quality. The topics of the meetings included the chemistry of the method, electronic data handling, content of the QAPP, detection limits, statistics, and interpretation of data quality.

# DETAILED COMMENTS

## Method Review

The EMSL-LV review of the analytical method began in October 1985 with the then proposed GC-ECD analytical method. The available method validation data was reviewed and the data from soil samples similar to

the expected Love Canal soil indicated there was a problem with identification and quantitation of the Love Canal Indicator Chemicals (LCIC) present in the samples at low concentrations. The extraction and cleanup steps were also reviewed at this time and suggestions were made to improve the technical quality of the method in addition to discussions of QA and clarity issues.

A set of PE samples was prepared and sent to the laboratories by the EMSL-LV. The results of the PE samples confirmed that the GC-ECD method was not satisfactory for the analysis of LCIC at low concentrations. A meeting was held in Reston, Virginia, in January, 1986; at this meeting it was decided to replace the GC-ECD method with a GC/MS SIM method of analysis (the extraction and cleanup steps would stay the same with minor changes). The EMSL-LV reviewed the method development data as it became available to assure that the method would meet the goals of the project. The extraction and cleanup steps were also optimized at this time, and their ruggedness was being determined. Changes were made in such parameters as soil sample size, concentration methods, and clean-up column elution solvents.

After a method that appeared satisfactory was developed, the laboratories analyzed a spiked sample generated by one of the laboratories. The results of these analyses were reviewed, and as the method appeared to provide satisfactory results, a PE sample set from the EMSL-LV was sent to each laboratory in order to evaluate their

analytical performance as well as their ability to assemble a satisfactory data package.

The results of the PE sample analyses as well as the results of other QA operations that were occurring simultaneously indicated that the method could reasonably be expected to provide data that would meet the goals of the project. The laboratory performance on the PE samples is presented in Table I.

PE Samples

A total of five sets of PE samples were prepared by the EMSL-LV for the Love Canal Soil Pilot Study. The first set was analyzed using the GC-ECD procedure, and the results of these analyses were responsible for the change to the GC/MS SIM method. The second set was provided before the collection and analysis of samples began in order to confirm the performance of the GC/MS SIM method. The remaining three sets were analyzed during the pilot study at approximately twenty sample intervals in order to help establish that the laboratories were continuing to analyze samples in a satisfactory manner.

The following tables present the results of the PE sample analyses:

TABLE I

INITIAL GC/MS SIM PERFORMANCE EVALUATION SAMPLE

| Lab Sample ID | Compound | Theoretical Concentration ug/kg | MGM % rec | | EMSI % rec | | CAA % rec | |
|---|---|---|---|---|---|---|---|---|
| KPS | Volatiles | | | | | | | |
| | Chlorobenzene | 14.4 | -- | 83 | 21 | 77 | 131 | 131 |
| | 1,2-Dichlorobenzene | 9.6 | -- | 102 | 27 | 61 | 147 | 152 |
| | Semivolatiles | | | | | | | |
| | 1,2-Dichlorobenzene | 7.2 | 78 | 76 | 51 | 63 | 69 | 60 |
| | 1,2,4-Trichlorobenzene | 9 | 79 | 77 | 55 | 62 | 70 | 66 |
| | 1,2,3,4-Tetrachlorobenzene | 5.4 | 83 | 83 | 59 | 68 | 72 | 65 |
| | 2-Chloronaphthalene | 7.2 | 118 | 122 | 82 | 102 | 102 | 110 |
| | B-BHC | 5.4 | 113 | 87 | 111 | 104 | 78 | 59 |
| | G-BHC (1) | 7.2 | 196 | 196 | 247 | 247 | 180 | 167 |
| KLS | Volatiles | | | | | | | |
| | Chlorobenzene | 7.2 | 100 | 99 | 99 | 76 | 150 | 144 |
| | 1,2-Dichlorobenzene | 4.8 | 115 | 115 | 58 | 58 | 154 | 160 |
| | Semivolatiles | | | | | | | |
| | 1,2-Dichlorobenzene | 4.8 | 79 | 73 | 58 | 50 | 73 | 69 |
| | 1,2,4-Trichlorobenzene | 6 | 67 | 78 | 60 | 55 | 75 | 65 |
| | 1,2,3,4-Tetrachlorobenzene | 3.6 | 83 | 83 | 61 | 64 | 125 | 67 |
| | 2-Chloronaphthalene | 4.8 | 119 | 117 | 92 | 98 | 190 | 117 |
| | B-BHC | 3.6 | 110 | 114 | 97 | 106 | 110 | 86 |
| | G-BHC | 4.8 | 183 | 185 | 242 | 240 | 177 | 173 |
| UKPS | Volatiles | | | | | | | |
| | Chlorobenzene | 7.2 | 90 | 83 | 62 | 51 | 119 | 135 |
| | 1,2-Dichlorobenzene | 4.8 | 108 | 104 | 42 | 31 | 146 | 150 |
| | Semivolatiles | | | | | | | |
| | 1,2-Dichlorobenzene | 4.5 | 73 | 78 | 58 | 62 | 67 | 60 |
| | 1,2,4-Trichlorobenzene | 3.6 | 83 | 83 | 61 | 61 | 67 | 69 |
| | 1,2,3,4-Tetrachlorobenzene | 3.2 | 172 | 81 | 53 | 56 | 66 | 63 |
| | 2-Chloronaphthalene | 5.4 | 185 | 85 | 63 | 69 | 76 | 72 |
| | B-BHC | 3.2 | 113 | 97 | 75 | 91 | 81 | 47 |
| | G-BHC | 4.5 | 69 | 67 | 89 | 124 | 100 | 64 |

INITIAL GC/MS SIM PERFORMANCE EVALUATION SAMPLE (Continued)

| Lab Sample ID | Compound | Theoretical Concentration ug/kg | MGM % rec | | EMSI % rec | | CAA % rec | |
|---|---|---|---|---|---|---|---|---|
| | Volatiles | | | | | | | |
| UKLS | Chlorobenzene | 2.4 | 100 | 100 | 83 | 83 | 154 | 154 |
| | 1,2-Dichlorobenzene | 3 | 113 | 110 | 40 | 50 | 183 | 180 |
| | Semivolatiles | | | | | | | |
| | 1,2-Dichlorobenzene | 3 | 87 | 80 | 70 | 67 | 67 | 70 |
| | 1,2,4-Trichlorobenzene | 2.4 | 108 | 96 | 67 | 67 | 71 | 67 |
| | 1,2,3,4-Tetrachlorobenzene | 2.1 | 171 | 81 | 57 | 57 | 67 | 62 |
| | 2-Chloronaphthalene | 3.6 | 161 | 81 | 72 | 69 | 81 | 83 |
| | B-BHC | 2.1 | 176 | 138 | 81 | 86 | 119 | 76 |
| | G-BHC | 3 | 80 | 67 | 117 | 127 | 80 | 67 |

Note 1: The theoretical concentration is for reference only. In some of the samples the theoretical concentration is in error, e.g., G-BHC in sample KLS.

Note 2: Laboratory CAA has high recoveries on the volatile analyses; this was traced to a systematic measuring problem which was corrected before sample analysis started.

Note 3: The occasional high values for 1,2,3,4-tetrachlorobenzene and 2-chloronaphthalene were caused by sulfuric acid carryover into the extract which caused deuterium exchange in the acenaphthene-d10 internal standard. This problem was detected before sample analysis was started and the internal standard areas were closely monitored during the study to prevent this problem from affecting sample results.

TABLE II

PE SAMPLE RESULTS (analyzed during sample analysis)

| Lab Sample ID | Compound | Theoretical Concentration ug/kg | MGM % rec | EMSI % rec | CAA % rec | |
|---|---|---|---|---|---|---|
| | Volatiles | | | | | |
| SVSM # 2 | Chlorobenzene | 20 | 80 | 56,63 | 98 | 99 |
| | 1,2-Dichlorobenzene | 15 | 127 | 67,76 | 113 | 115 |
| | Semivolatiles | | | | | |
| | 1,2-Dichlorobenzene | 10 | 77 | 59 | 67 | 62 |
| | 1,2,4-Trichlorobenzene | 25 | 68 | 66 | 80 | 76 |
| | 1,2,3,4-Tetrachlorobenzene | 22.5 | 75 | 89 | 62 | 58 |
| | 2-Chloronaphthalene | 35 | 74 | 94 | 69 | 71 |
| | B-BHC | 22.5 | 98 | 76 | 80 | 89 |
| | G-BHC | 20 | 85 | 66 | 76 | 80 |
| | Volatiles | | | | | |
| SVSM # 3 | Chlorobenzene | 10 | 99 | 99 | 98 | 97 |
| | 1,2-Dichlorobenzene | 10 | 154 | 96 | 109 | 105 |
| | Semivolatiles | | | | | |
| | 1,2-Dichlorobenzene | 15 | 67 | 56 | 93 | 80 |
| | 1,2,4-Trichlorobenzene | 37.5 | 72 | 61 | 96 | 80 |
| | 1,2,3,4-Tetrachlorobenzene | 33.8 | 77 | 80 | 83 | 38 (1) |
| | 2-Chloronaphthalene | 52.8 | 78 | 91 | 93 | 44 (1) |
| | B-BHC | 33.8 | 89 | 82 | 112 | 98 |
| | G-BHC | 30 | 73 | 51 | 107 | 87 |
| | Volatiles | | | | | |
| SVSM # 4 | Chlorobenzene | 4.8 | 94 | 99 | 98 | 97 |
| | 1,2-Dichlorobenzene | 6.0 | 112 | 96 | 109 | 105 |
| | Semivolatiles | | | | | |
| | 1,2-Dichlorobenzene | 4.8 | 83 | 65 | 67 | 77 |
| | 1,2,4-Trichlorobenzene | 6.0 | 85 | 65 | 72 | 78 |
| | 1,2,3,4-Tetrachlorobenzene | 3.6 | 100 | 56 | 75 | 83 |
| | 2-Chloronaphthalene | 4.8 | 131 | 87 | 104 | 104 (1) |
| | B-BHC | 3.6 | 122 | 105 | 150 | 141 |
| | G-BHC | 4.8 | 229(2) | 154(2) | 279(2) | 260 (2) |

Laboratory CAA performed analyses in duplicate. Laboratory EMSI performed duplicate analyses on the volatiles on sample SVSM #2.

(1) The internal standard for these compounds had an interference.
(2) The theoretical amount was miscalculated on this sample.

The initial PE sample set consisted of four samples, two whose theoretical concentration was known to the laboratories and two whose concentration was unknown to the laboratories. Two different methods of spiking PE samples were also tested. Samples KPS and UKPS had the LCIC spiked onto the sand before the PE samples were sent out from the EMSL-LV, while samples KLS and UKLS were shipped to the laboratories as blank sand with an ampule of solution to be added to the soil just before analysis. As can be seen from the tables there was no major difference between the two methods of PE sample preparation. The samples KPS and KLS had the theoretical concentrations known to the laboratories; samples UKPS and UKLS had concentrations which were unknown to the laboratories at the time of analysis.

The three sets of PE samples (also referred to as blind QC samples) were spiked with LCIC at the EMSL-LV and distributed to the laboratories to analyze at the appropriate time (every twenty samples) in their analytical sequence.

The results of the initial set of PE samples were analyzed and the problems noted at the bottom of Table I were identified and resolved. The PE data was determined to be of sufficient quality that the Pilot Study could progress with the assumption that the analytical method and the laboratories could provide data of the required quality.

On-Site Evaluations

On-site evaluations were performed at each of the three laboratories, three different times during the course of the Pilot Study. The first visit was to evaluate the laboratories to determine if their physical plant, instrumentation, and personnel capabilities were adequate for the project. The QA procedures that the laboratories were currently using on existing programs were also evaluated to determine what changes in recordkeeping and laboratory practices would be needed to produce data of the desired technical and administrative quality. The on-site evaluations showed that the laboratories selected should be capable of performing analyses of the desired quality; however, each laboratory had a variety of operational changes and documentation procedures to implement before sample analysis could be started.

The second series of on-site evaluations was performed after the analysis of the initial PE sample but before sample analysis was started. The objective of this set of on-site evaluations was to determine if all of the changes recommended during the first evaluation

had been implemented and to help resolve any problems indicated by the results of the PE samples. The laboratories had complied with most of the recommendations from the first on-site evaluation and were making progress on the remainder. Any problems noted in the PE results or in the data package were discussed with the laboratories; they were either resolved, or experimental work was initiated to solve the problem. The problems noted in Table I were resolved in this manner.

The third series of on-site evaluations was performed 1 to 2 weeks after sample analysis had started. The object of this set of on-site evaluations was to observe the actual analysis of samples in progress in order to determine that the methods were being followed precisely and to look for any problems that might affect the quality of the data that might not have been apparent until actual samples were analyzed. A variety of minor problems were discovered during the evaluations, and some examples of problems and resolutions follow. Laboratory EMSI was using a drying column of different dimensions than required; they switched to the proper column. Laboratory MGM was having a contamination problem in the semivolatile analysis; the evaluation team stayed on-site providing assistance until the contamination disappeared. All three laboratories were having problems with the very fine clay particles in the extraction process; a decision was made to recommend centrifuging the extract before concentration. The method required the use of powdered sodium sulfate for drying the samples as specified in the CLP procedures, but all three laboratories were using

granular sodium sulfate; it was decided to allow the continued use of granular sodium sulfate because of the length of time required to obtain powdered sodium sulfate and because the method validation work and the PE samples had been analyzed using granular sodium sulfate.

The sample preparation was also observed during the on-site evaluation at laboratory CAA. This was a separate area of the laboratory where the samples were extruded from the Shelby tubes and split into subsamples for the laboratories. Two minor, potential problems were observed and corrected, one of these was a potential source of cross contamination and the other was to improve the seal on the sample bottles. Another problem was noted and left unresolved for the pilot study because no quick solution was apparent. The samples observed consisted of a layer of topsoil and a layer of clay. The method required a 30-second mixing time before the volatiles samples were removed and then further mixing before the aliquots were taken for semivolatile samples. It was observed that the volatile samples were taken primarily from the topsoil portion of the sample since that was the portion most easily mixed and reduced to appropriate size to fit into the volatile vials. If there is a difference in the LCIC content of the topsoil and clay, this could bias the results.

An on-site field evaluation was also conducted at the beginning of sample collection. In addition to auditing the sampling effort at the Love Canal site, the sample preparation procedures were observed in

Boston at Cambridge Analytical Associates, and the documentation methods were inspected at Horizon Systems Corporation in Reston, Virginia. The audit was conducted to ensure that the protocols required by the project plan and the QA plan were in place and functioning well.

Specifically, the audit:

- verified that the sampling methodology and QA measures were being performed in accordance with the program requirements,

- verified that project documentation was in order (i.e., records, chain-of-custody forms, analytical tags, logbooks, worksheets),

- verified the identity and qualifications of key project personnel, and,

- identified areas that needed corrective action.

Sampling methods and sample-handling procedures were observed first-hand. This sampling method audit encompassed checking equipment, sampling methods, sampling locations, site documentation, decontamination, container preparation (i.e., labeling, storing, preserving, and documentation), field logbooks and notes. The sample handling procedures observed included mixing, compositing, splitting,

packaging, and shipping. In addition it was verified that all documentation was in order and that it was sufficient to establish the disposition of any collected sample by inventorying the sample records and archived samples. The flow of specific samples was traced through the system. Records reviewed included chain-of-custody forms, sample tags, custody seals, shipment forms, logbooks, and archived samples.

In general, the on-site evaluations showed that the project plan and QA plan were being followed and that the data produced should be adequate quality for the purposes of the pilot study.

QAPP Review

The EMSL-LV reviewed and commented on several iterations of the Quality Assurance Project Plan. The primary object of the reviews was to determine that a clear, concise, achievable set of data quality objectives were stated and to determine that the project plan and analytical methodology would provide data that would meet the data quality objectives. The requirement was that the data quality must be equivalent to or better than CLP data quality.

The following sections of the QAPP were reviewed: Data Quality Objectives, analytical methodology, laboratory SOP's, data reporting forms, personnel qualifications, quality control procedures, data reduction, and reporting procedures, and sampling plans.

The final iteration of the QAPP was deemed to be of adequate quality for the purposes of the pilot study.

Data Review

The EMSL-LV review of the Love Canal Pilot Study data consisted of three major portions, review of electronically transmitted QA data as the analyses were proceeding, an electronic audit of those QA criteria amenable to computer checking, and a review of the paper data packages to check for any flaws in the data quality and to verify those items found in the electronic audit. The review process and results of each of these steps is detailed below.

The QAPP for electronic data transmission and review called for the laboratories to upload QA data daily to the Horizon Systems bulletin board where it would be processed and made available for review within 2 to 3 days of sample analysis. A variety of problems prevented this system from working as well as planned. These included excessive workloads in the laboratories and software problems. The system was working by about one-third of the way through the analyses and thereafter provided QA data within 1 to 2 weeks of sample analysis. The primary reason for the on-line data review was to allow reapportioning of samples among the laboratories if one laboratory started having QA problems. The laboratories all remained generally in control so that sample reapportioning was not necessary. A number of sample reanalyses

and use of contingency samples was necessary due to failure to meet QA criteria however this was on an individual sample basis rather than a laboratory being out of control on a large block of analyses. The electronic data transmission and on-line review approach has been developed to the point that it would be a valuable QA tool for a larger scale study involving a greater number of participating facilities.

The types of QA data reviewed on an on-line basis were surrogate recoveries, matrix spike recoveries, internal standard areas and retention times, initial and continuing calibration response factors, and extraction and analysis times. If these criteria are within the QAPP specified control limits, it is a good indication that the analytical system of the laboratory is operating within control limits.

An electronic data audit was performed on the sample data contained in the Love Canal data base to evaluate the quality of the data based on those criteria which are amenable to computer review. This included comparing the sample data with the control limits established in the QAPP for the following items: surrogate recoveries, matrix spike recoveries, internal standard areas, holding times, internal standard retention times, initial calibration response factors, and continuing calibration response factors. The analyte concentrations were also calculated from the electronically transmitted data and were compared with the paper copies of the data supplied by the laboratories. The electronic audit not only provided a means of rapidly determining which

samples did not meet QA criteria but also provided an excellent means of checking for errors in the data base since missing values or large data entry errors will result in a sample not meeting criteria the data for this sample may then be examined to determine if it is a sample or data base problem.

The manual data review different somewhat from the standard CLP data evaluation because the electronic audit checked many of the items that are normally evaluated in a data audit. This allowed a more in-depth evaluation than the normal CLP audit with emphasis on meeting QAPP and method requirements and good laboratory and documentation practices. The normal QA criteria evaluation needed only spot checking to determine that the electronic audit was correct.

Many of the problems noted on the manual review had no effect on the analytical data quality (i.e., the number reported), but indicated the need for more precise specification of these items in the QAPP of a main study. Some examples of this type of problem are: "Lab Sample ID" is reported on several different forms and within a laboratory would be reported differently on different forms. This was a common problem which makes tracking of sample data from form to form difficult. Similarly, the laboratories did not provide an adequate cross-reference between laboratory sample numbers and LC numbers, this reference was obtainable from the data package from each laboratory but in some cases with extreme difficulty. Also the standards log from laboratory EMSI

did not contain adequate information to establish traceability or to recalculate the concentrations used. This indicates a more explicit criteria is required for standard documentation. Finally, the computer software used for calculations occasionally would shift numbers two decimal places to the left when printing them although it used them properly in the calculations. This problem needs to be located since it requires manual checking of each entry.

Each laboratory had a variety of problems that could have had an impact on the data even though the QA criteria was met. These problems will be discussed on a laboratory by laboratory basis.

MGM

A significant level of blank contamination was present for 1,2-dichlorobenzene and trichlorobenzene in the semivolatile analysis. The levels found were within criteria but had a definite effect on the low level samples as their percentage of detects for these compounds is much higher than the other laboratories.

The high standard of the semivolatile initial calibration saturated the detector so the operator reduced the electron multiplier voltage for this standard without reanalzying the other standards. This should have little effect on the data because the daily standard is used for quantitation, however it could bias the initial calibration and effect the acceptable QA range of the daily continuing calibration standard.

The semivolatile initial calibration data had two different gas chromatograph temperature programs on the data system printouts, one reported by the instrument and the other entered by the operator. This had no effect on the analytical data as the instrument reported value was the correct temperature program; however, it is an inconsistency that must be avoided to insure data defendability.

The instrument data system was set up so that a peak had to be present at all three masses for the data system to recognize a peak and quantitate it. This caused no problem on samples which had a significant amount of analyte present, however it resulted in censoring of low level peaks which might not have met all of the identification criteria but might still have been useful to the statisticians. It also made evaluation of the low level data very difficult because the missing data could not be checked to determine if it met criteria.

CAA

Two instruments were used for analyzing semivolatile extracts, and in several instances it was difficult to determine which instrument was used and in one case (data package page 30010) the wrong instrument was apparently reported. A detailed examination of the records indicated that this was only a reporting error and that the sample had been analyzed properly.

Daily semivolatile initial calibrations were required at the beginning of the analysis period because the laboratory had difficulty in meeting continuing calibration criteria. This allowed analysis to continue since the QA criteria were met, however it was indicative of an instrumental problem which was eventually diagnosed and corrected. The QA data during this period did not indicate there were any problems with the analytical results.

The laboratory exercised some censoring of low level data which did not meet all of the identification criteria. This had some effect on the interlaboratory comparability of this data as it gave a different definition to "nondetects." This also made evaluating the low level data nearly impossible because the criteria could not be checked without the missing data.

An interference was present at the tertiary ion of 1,2-dichlorobenzene in the semivolatile blanks, prevented the peak from meeting identification criteria and prevented 1,2-dichlorobenzene from being reported in the blank. This also occurred at EMSI and relates to a blank definition problem which will be discussed later.

EMSI

The standards log for standard 507178606 shows that 27.15 mg of 1,2,4,5-tetrabromobenzene surrogate was weighed out and the amount

rounded to 25 mg for calculations. This incorporates a known 10% bias in the surrogate concentration and if the same solution is not used for spiking samples this could result in biased surrogate recoveries.

The standards log does not provide information adequate to trace standards to the original material used or to EPA standards nor does it provide adequate information to recalculate the concentrations used in the standards. The laboratory obtained adequate results on the performance evaluation samples; so the standards were presumably correct.

Many low level responses on the chromatograms have different areas than those reported on the quantitation reports. This is a normal behavior of the data system and should not be considered an error; the data reviewer must be aware that this occurs and interpret low level results accordingly.

The laboratory had interferences with the BHC ions which caused problems with the identification and quantitation, especially during the last few days of analysis when the interference was also occurring in the blank. Positive BHC results from this laboratory should be regarded as suspect unless confirmed by independent means.

## CHEMOMETRICS AND STATISTICS

The method detection limit procedures proposed by the project statisticians were reviewed for technical validity and applicability. The EMSL-LV supported the consensus decision to use Hubaux-Vos models to estimate the detection limit because better methods were then unavailable. It was suggested that the tertiary ion of each LCIC be used in the model, as detection of this ion will very likely ensure sufficient sensitivity to the more abundant ions. The detection limit study gave limits comparable to the concentrations the chemists considered valid, even though some of the assumptions made for the detection limits are not necessarily chemically correct, e.g., GC/MS response at low concentrations tends to be nonlinear, but is assumed linear.

The chemometrics appendix was unavailable for review at the time of this report. It is expected to evaluate the effectiveness of surrogates and internal standards and to examine various aspects of interlaboratory and intralaboratory variation.

The statistical analysis report of the number and distribution of samples needed to determine habitability was unavailable for review at the time of this report. The plans for this analysis have been reviewed and two major concerns have been expressed by the reviewers. First, the possibility of spatial correlation over each site was ignored, and

samples taken from each site are treated as a random sample from a standard distribution. The other major concern is that LCIC will probably be positively identified in very few samples and thus the statistical test could be interpreted as comparing the extreme values (outliers?) of one data set to the extreme values of other data sets. It is not known if this is a valid way to determine habitability.

## SUMMARY AND RECOMMENDATIONS

A number of problems were apparent in the pilot study that need to be addressed for the main study; most of these deal with how low concentrations are interpreted, how interferences are dealt with, and improvements in documentation. A discussion of these items follows.

The definition of an acceptable blank must be modified to include interferences at the retention time and ions monitored for each LCIC. The QAPP for the pilot study defined an acceptable blank as having less than one ppb of LCIC present, this overlooked the possibility of the presence of interferences and the effect blank contamination would have on low level concentrations. Both of these occurred in the pilot study. Laboratory MGM had a consistent blank level of about 0.6 ppb of 1,2-dichlorobenzene in the semivolatile analysis. This caused MGM to report positive values between 1 and 2 ppb for nearly all of the

samples. The other two laboratories had about the same amount of 1,2-dichlorobenzene present; however, an interference at the tertiary ion prevent identification of the compound. This had no effect on data over 5 ppb; however, it needs to be considered when interpreting data for lower concentrations. The level of blank contamination will have a definite effect on the detection limits achievable for the main study; for a minimal effect on quantitation the blank level of an LCIC should be no more than 20 percent of the amount found in a field sample. The effect on non-LCIC interference is much more complex and may have a much greater effect, e.g., an interference at one ion could easily increase the amount of LCIC needed to meet detection criteria by a factor of 10 to 100. Recommended actions for the main study are (1) to redefine the acceptable level of blank contamination, (2) determine the effect of blank contamination on quantitation limits, (3) minimize the level of blank contamination, and (4) attempt to standardize it among the laboratories. This should not require a large analytical effort but may require significant planning effort and QAPP changes.

The decision about what low level data to report was made differently in each laboratory, this primarily involved concentrations less than one ppb. This reduced the comparability of the low level data between laboratories and made evaluation of this data extremely difficult since the numerical data was censored in different ways by two of the laboratories. Recommended action for the main study is to give much more explicit instruction in the QAPP for interpreting low level

data and to have an arbitrary level below which the laboratories are not required to attempt to report data. These instructions must consider differences in GC/MS software systems and specify integration and rejection parameters to the extent possible. This should require minimal effort to implement and could result in more efficient laboratory operation.

It was noted that in many instances the computer-generated quantitation report produced different area counts for LCIC peaks at low levels than those obtainable from the ion chromatograms. This is only a problem at low concentrations and is a normal occurrence in GC/MS data systems. It does, however, present major problems in trying to determine which value is the most correct. A recommended action to limit this would be to have an arbitrary limit below which the laboratories will not be required to report data. This would reduce the data interpretation time required in the laboratories and by the data reviewers and will limit the amount of unreliable data reported.

In the pilot study, there were many instances where a sample would have a positive response and the blind duplicate, either within or between laboratories, would be reported as a nondetect. Some of these would be due to nonuniformity of the samples; however, it was obvious in examining the low level data that in many cases the peak was present in both samples but due to interferences or random variations the response did not meet identification criteria for one of the samples. This

requires a decision to be made on the value of low level data and how to interpret data when it is known that a duplicate sample may give a different result.

Interferences were noted with the BHC quantitation masses used. The use of alternative masses needs to be explored and tested in the laboratory to determine the most appropriate masses to use for quantitation of these compounds. This could require the analysis of up to twenty samples to optimize and validate the instrumental conditions.

In several instances the ion ratio criteria for compound identification was not met when using peak areas for quantitation because of interfering peaks; however, when peak heights were used the ion ratios were within criteria. Quantitation using peak areas is generally considered more accurate than peak height quantitation therefore the main study should continue to use area quantitation except in those instances when peak shape is distorted by interferences. Requiring ion ratios to be checked using peak height when the area ratios are out of criteria will require some extra effort by the laboratories, the extent of which will depend on the frequency of occurrence of the situation. The maximum per sample time increase should not exceed ten minutes in the worst case.

In conjunction with the previous item the mass chromatograms which are a required part of the data package must be displayed over an appropriate time interval so that the peaks of interest may be examined for peak height and shape. This may require closer attention to detail by the laboratories but should not have a significant time impact.

The use of the low level surrogate needs to be evaluated and possibly some changes made in its application since the response to this compound varied greatly between laboratories. A different quantitation mass may need to be selected or perhaps a different compound should be selected for this purpose. This experimentation could be done simultaneously with other method validation work and need not adversely effect the number of validation samples needed.

The following are suggested method and procedural improvements whose impact on the main study has yet to be evaluated.

A wash step should be added after the sulfuric acid cleanup step.

An area criteria is needed for all internal standards.

Powder sodium sulfate should be added to the sample during extraction instead of granular.

A response factor criteria is needed to eliminate possible calibration errors.

A mass intensity calibration criteria is needed.

A procedure for resubmitting problem data is needed.

An improved sample mixing procedure is needed in the extrusion facility.

The delivery schedule for QA and final data needs to be evaluated.

## CONCLUSIONS

The three main purposes of the pilot study were, (1) to develop an analytical method for the Love Canal Indicator Chemicals, (2) develop quality assurance and documentation control procedures that would provide credibility to the data, and (3) to provide data for a statistical determination of the number and distribution of samples needed for a main study to determine habitability.

The analytical method appears to function satisfactorily for concentrations above one ppb for all LCIC except the BHCs which had interference problems which would give a highly variable detection limit. The individual values for all LCIC below one ppb are highly

suspect and conclusions should not be drawn from the individual results. While the pilot study data is of reasonable quality the resolution of the problems and suggestions outlined above would significantly improve the data quality.

In general the quality assurance and documentation appear adequate to determine the quality of the data with a few exceptions as noted in this report. Implementation of the recommended changes and additions would provide additional documentation of data quality and improve its overall quality.

The final reports of the Chemometrics and Statistics sections of the study have not yet been completed so a complete evaluation cannot be made at this time. The statistical method detection limit procedure developed appears to provide limits consistent with the limits below which the chemists lack confidence in the data. The planning phases of the statistical analysis have been observed and that approach seems reasonable; however, until a report is available giving the assumptions made and the results obtained no statement of the quality of the analysis can be made.

Tables III and IV listing those samples with quality assurance defects and the impact the defect has on the data follows.

TABLE III

LOVE CANAL HABITABILITY SOIL PILOT STUDY

INDIVIDUAL SAMPLES WITH DATA QUALITY DEFECTS

QA criteria - Internal standard retention time out of criteria*

Data impact - Minimal impact since the data system found the peak

| Sample Identification | Site Identification | Fraction | Compound Affected |
|---|---|---|---|
| LC2011 | SPEDAS36 | VOA | d4-1,4-dichlorobenzene |
| LC2046 | SPCA2S13 | VOA | d4-1,4-dichlorobenzene |
| LC2087 | SPEDAS02 | VOA | d4-1,4-dichlorobenzene |
| LC2103 | SPCA2S12 | VOA | d4-1,4-dichlorobenzene |
| LC2134 | SPEDAS26 | VOA | d4-1,4-dichlorobenzene |
| LC2198 | SPEDAS42 | VOA | d4-1,4-dichlorobenzene |
| LC2237 | SPEDAS12 | VOA | d4-1,4-dichlorobenzene |
| LC2311 | SPCA2S05 | VOA | d4-1,4-dichlorobenzene |
| LC2314 | SPEDAS18 | VOA | d4-1,4-dichlorobenzene |
| LC2325 | SPEDAS22 | VOA | d4-1,4-dichlorobenzene |
| LC2017 | SPCA1S21 | VOA | d4-1,4-dichlorobenzene |
| LC2043 | SPEDAS17 | VOA | d4-1,4-dichlorobenzene |
| LC2047 | SPCA1S09 | VOA | d4-1,4-dichlorobenzene |
| LC2049 | SPCA1S04 | VOA | d4-1,4-dichlorobenzene |
| LC2075 | SPEDAS14 | VOA | d4-1,4-dichlorobenzene |
| LC2144 | SPEDAS19 | VOA | d4-1,4-dichlorobenzene |
| LC2152 | SPCA1S09 | VOA | d4-1,4-dichlorobenzene |
| LC2154 | SPCA1S02 | VOA | d4-1,4-dichlorobenzene |
| LC2160 | SPEDAS04 | VOA | d4-1,4-dichlorobenzene |
| LC2179 | SPEDAS21 | VOA | d4-1,4-dichlorobenzene |
| LC2207 | SPCA1S08 | VOA | d4-1,4-dichlorobenzene |
| LC2012 | SPEDAS11 | SVOA | d10-acenaphthene |
| LC2012 | SPEDAS11 | SVOA | d10-phenanthrene |
| LC2012 | SPEDAS11 | SVOA | d10-pyrene |
| LC2014 | SPCA1S13 | SVOA | d10-pyrene |
| LC2033 | SPCA1S07 | SVOA | d10-pyrene |
| LC2057 | SPEDAS11 | SVOA | d10-pyrene |
| LC2151 | SPEDAS34 | SVOA | d10-pyrene |
| LC2161 | SPCA1S11 | SVOA | d10-pyrene |
| LC2180 | SPCA1S22 | SVOA | d10-pyrene |
| LC2215 | SPCA1S16 | SVOA | d10-pyrene |
| LC2251 | SPCA1S11 | SVOA | d10-pyrene |
| LC2273 | SPCA2S06 | SVOA | d10-pyrene |

* The purpose of this criteria is to insure that the GC/MS data system would find the LCIC peaks if present. None of the values were far enough out of criteria to make this a problem.

TABLE IV
LOVE CANAL HABITABILITY SOIL PILOT STUDY
INDIVIDUAL SAMPLES WITH DATA QUALITY DEFECTS (Continued)

QA Criteria - Surrogate percent recovery out of criteria.*
Data Impact - Quantitation is semiquantitative.

| Sample Identification | Site Identification | Fraction | Compound Affected |
|---|---|---|---|
| LC2046 | SPCA2S13 | SVOA | 1,4-dibromobenzene |
| LC2066 | SPCA1S17 | SVOA | 1,4-dibromobenzene |
| LC2084 | SPCA2S18 | SVOA | tribromobiphenyl |
| LC2092 | SPCA2S19 | SVOA | 1,4-dibromobenzene |
| LC2120 | SPCA2S16 | SVOA | tribromobiphenyl |
| LC2120 | SPCA2S16 | SVOA | 1,4-dibromobenzene |
| LC2184 | SPCA1S10 | VOA | bromofluorobenzene |
| LC2191 | SPCA1S18 | SVOA | tribromobiphenyl |
| LC2233 | SPCA2S01 | SVOA | 1,4-dibromobenzene |
| LC2286 | SPCA2S13 | SVOA | tribromobiphenyl |
| LC2287 | SPEDAS02 | SVOA | tribromobiphenyl |
| LC2287 | SPEDAS02 | SVOA | 1,4-dibromobenzene |
| LC2302 | SPEDAS44 | SVOA | tribromobiphenyl |
| LC2369 | SPCA2S16 | SVOA | tribromobiphenyl |
| LC2206 | SPCA1S03 | SVOA | tribromobiphenyl |
| LC2206 | SPCA1S03 | SVOA | 1,4-dibromobenzene |
| LC2304 | SPCA2S02 | SVOA | 1,4-dibromobenzene |
| LC2307 | SPCA2S21 | SVOA | 1,4-dibromobenzene |
| LC2313 | SPCA2S02 | SVOA | 1,4-dibromobenzene |

* The purpose of this criteria is to monitor the extraction and concentration steps of the analysis. Values out of criteria indicate a possible problem in these steps that could effect the quantitation.

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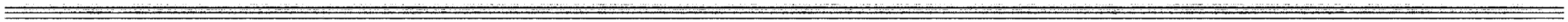
# APPENDIX E

## Estimating Method Detection Limits for the Love Canal Habitability Study



# Appendix E

# ESTIMATING METHOD DETECTION LIMITS FOR THE LOVE CANAL HABITABILITY STUDY

CH2M HILL

February 1987

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TABLES

FIGURES

## SUMMARY

Environmental studies, such as the Love Canal Habitability Study, require a careful definition and evaluation of the detection limit associated with the chemical analysis. This is especially necessary when a large number of analyses are expected to produce nondetectable results. There are two desirable attributes of a detection limit. First, a detection limit should provide an estimate of analyte concentration such that if a sample contained a greater concentration, it would be highly likely to be detected. Secondly, a detection limit should reflect the efficacy of the analytical process; the value estimated should be one that would be likely to be detected in environmental samples. These two properties are not the same for a complex analytical process like the GC/MS, and cannot be generated from one estimator.

The complexity of the GC/MS stems from a multipart process that consists of both identifications and quantification. At low concentrations of analytes, identification or quantification or both can fail, preventing a compound from being detected. These processes appear to be independent and are not as yet well understood.

During the pilot study a preliminary estimator of the method detection limit for the quantitative aspects of the analytic process was developed. This estimator provides a value for analyte concentration which, if present in a sample, should be detected with high probability. It does not, however, provide any guidance as to whether a particular sample's concentration is at a detectable level.

The method detection limit for each laboratory is proposed to be developed as part of the laboratory's calibration process. The estimation will require that a series of dilutions from a standard concentration of LCICs be spiked into previously analyzed (clean) Love Canal soil. These spiked soils will then be analyzed and the raw GC/MS instrumentation results recorded. A statistical regression of the instrument results on the spike concentrations will provide the data needed to estimate the method detection limit.

## E.1.0 INTRODUCTION

Critiques of the 1980 EPA study of contamination at Love Canal pointed out that for data sets with many nondetectable values a consistent estimate of the detection limit of the analysis is required. The 1980 study did not estimate detection limits, in part because of the high levels of contamination expected. However, the unexpected results of mostly nondetectable concentrations of contaminants actually found and an undefined detection limit meant that the data could not be used to determine public health implications.

It is clear that a well-defined procedure for estimating the detection limit is required for the habitability study. Unfortunately, the phrase "detection limit" has several different meanings when used by different authors in differing contexts. Several of the alternate definitions and methods of estimating detection limits are surveyed in this section. The definition proposed to be used in the habitability study is:

> The method detection limit (MDL) is the (true) concentration of a compound in an environmental sample at which 95 percent of estimated concentrations will exceed 95 percent of estimated concentrations produced by analysis of blanks.

The MDL will be estimated for each laboratory as part of that laboratory's calibration for the analytical protocol. The analytical process used to estimate the MDL will be the process used to analyze unknown samples but without the imposition of strict identification criteria. This modified analysis will be used on a series of experimental samples that are "blank" Love Canal EDA soils spiked with known concentrations of the LCICs. The MDL will then be estimated from the regression of the relative response of the laboratory's GC/MS on the known concentrations.

This procedure was followed as part of the pilot study. An analysis of the results of the process is presented in Section E.5.

## E.2.0 USES OF DETECTION LIMITS

### E.2.1 SINGLE VERSUS MULTIPLE SAMPLE STUDIES

A detection limit must be defined within the context of its intended use. There are two different uses for which detection limits are commonly discussed. The first is in the context of a single analysis where a definitive estimate of the concentration of an analyte in a single sample is requested. The second is in the context of a multiple analysis environmental study where estimates of analyte concentrations in many samples are requested.

When an analysis from a single sample study is performed, it may happen that the analyte concentration is below the level at which it can be reliably identified or consistently quantified. In this case, rather than supplying an uncertain estimate, the analyst will label the analyte as nondetectable and provide an estimate of the minimum concentration that would have been reported had it been present, a detection limit. This procedure provides assurance that concentrations that are reported have a high level of confidence.

Although samples from an environmental study may appear to the analyst to be a sequence of individual samples, the detection limit goals are quite different. In an environmental study, individual concentrations can be estimated with lower confidence so as to give increased confidence in the overall estimate of an environmental mean. This has two consequences for the procedures that the analyst follows in estimating the concentration of an analyte.

First, concentrations should be estimated whenever possible, even if these estimates are highly uncertain. Second, a detection limit must be estimated that applies to the entire sequence of environmental samples rather than to an individual sample. A definition of this detection limit will be developed later in this appendix. Here the desirable properties of such a detection limit will be explored.

Problems can arise in environmental studies if a detection limit developed for individual samples is used to censor the data in an environmental study. For example, reliable concentration data can be obtained from many samples even if individual concentrations are uncertain. This process is illustrated by Figure E.2.1.

This figure illustrates a hypothetical chromatogram with an elution peak at time t*. This peak represents a small signal added to analytic noise. If this were the only sample, an analyst would not be confident that the analyte was

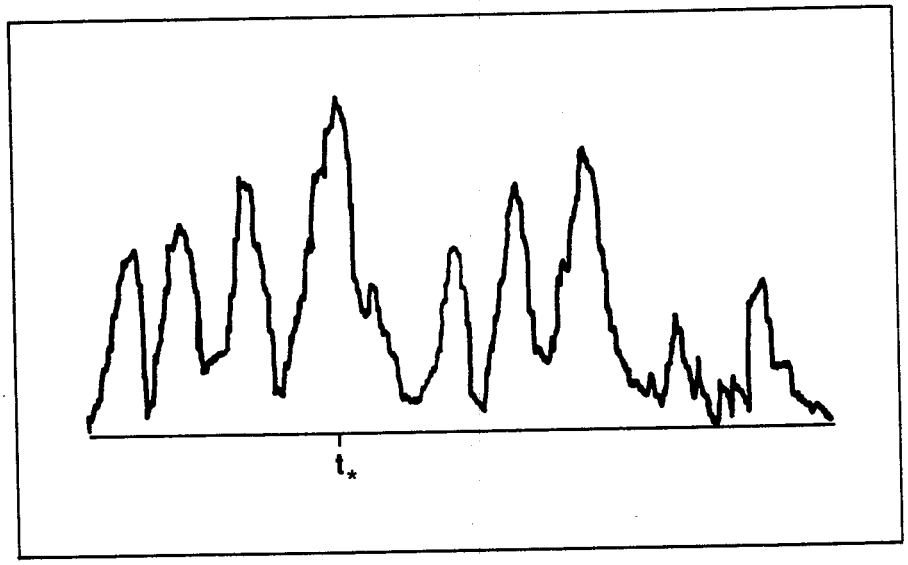



Figure E.2.1
**HYPOTHETICAL CHROMATOGRAM WITH ANALYTE AT $t_*$**

present because the signal appears swamped in the noise. However, if the analysis were replicated 90 times (or if 90 samples with similar concentrations were analyzed) then the signal could be differentiated from the noise with much greater confidence, because the standard error of the mean noise level decreases with increasing sample size.

Note, however, that if each of the 90 replicates had been censored as "nondetect" no such inference could be made. The analyst would be no more certain of the presence of low-level concentrations of analyte after 90 analyses than after one.

A second problem that can arise from censored or censor data is uncertainty of an environmental mean. Suppose that 100 environmental samples are taken and analyzed for a single analyte. Further suppose 80 of these have estimated concentrations below the individual sample detection limit of 5, while 20 have reported concentrations with an average of 9 ppb. In this sample the mean value of the environmental samples (which estimates the mean of the region sampled) is not estimable. What can be inferred is that the population mean is no less than 1.8 and possibly as much as 5.8. If 1,000 samples were taken with 800 reported nondetects and 200 values with a mean of 9 (so that the proportions were the same), then no further narrowing of the range of uncertainty would occur.

Thus, censoring estimated concentration values below the individual sample detection limit removes a major advantage of increasing the number of environmental samples, i.e., the reduction of uncertainty in the estimate of the mean as the standard error decreases.

The argument for not censoring concentration estimates that are less than the individual sample detection limit is not an argument for eliminating this detection limit. The individual sample detection limit provides useful information even if it is not used for censoring.

First, the detection limit provides a measure of instrument and laboratory sensitivity. A lower detection limit indicates a more sensitive procedure.

Second, the detection limit provides a dividing point in an environmental data set between the values that can be examined individually (perhaps indicating a "hot spot" or areas of concern) and values to which no individual significance can be ascribed. These latter values definitely need to be included in an environmental data set as previously illustrated, yet should not be given much credence individually. This was one philosophy followed in developing the scientific data from the pilot study.

Finally, it is important to recall that a detection limit describes only a concentration level for reliable detection, not reliable quantification. In other words, a detection limit of say 5 ppb, only tells you that 95 percent of measurements made on samples with a 5 ppb analyte concentration are greater than 95 percent of measurements made on samples with no analyte.

To further illustrate this, suppose a bias of 2 ppb exists when the detection limit is found to be 5 ppb. Then all measurements are increased by 2 ppb. However all that can be said still is that 95 percent of measurements made on samples with a true concentration of 5 ppb (even though the instrument reads 7 ppb) are greater than 95 percent of measurements made on blanks. What this means is that a detection limit is the smallest concentration that can be reliably distinguished from zero, but it is not an upper bound on a measurement reported as nondetect.

## E.2.2 DEFINING DETECTION LIMITS

Statistically valid estimates of detection limits require precise definitions of detection limits. The definitions given here are extensions of the standard definitions found, for example, in Currie (1968), Colle et al. (1980), and Glaser et al. (1983).

The capability of the instrumentation at low concentrations is limited by random instrument fluctuations and interference from reagents used in sample analysis. These noise levels vary with retention time because reagents elute at characteristic retention times and because instrument noise is not stationary. As is customary, the 95th percentile of procedural blank measurements at the retention time of the target analyte is here used to describe the level of noise that interferes with analyte measurement. (Procedural blanks contain only the reagents used in sample analysis.) When the 95th percentile of blank measurements at the retention time of the target analyte is measured in area units, it is called a criterion area and denoted by CA. (See Currie, 1968.) CAs are not comparable across different laboratories or across different instruments at the same laboratory because area units are not comparable. The CA might be used internally by a laboratory to monitor instrument capabilities, however. The 95th percentile of noise in concentration units, called the criterion limit and denoted by CL, is proposed to compare instruments.

Note that neither the CA nor the CL is a detection limit; CA and CL describe noise, not what can be distinguished from noise reliably. On the other hand, Currie notes that CL has the following use. Suppose a procedural blank area at the

retention time of the analyte is converted into an estimated concentration using the relative response factor of the analyte and then mistakenly reported as the estimated concentration of the analyte. With probability .95, a concentration produced in this way by a blank will be below CL. If estimated concentrations below CL are flagged, then whenever the analyte is not present there are more than 19 chances in 20 of flagging the measurement as possibly not being caused by the analyte. Of course, such flagging is achievable only if the 95th percentile of blanks can be determined, which requires that thresholds be set low enough that positive noise areas are recorded for blanks.

The instrument detection limit (IDL) is the smallest concentration of analyte in a standard sample that can be distinguished reliably from instrument noise and reagent interference in the sense that 95 percent of measured concentrations on standards with a true concentration at the IDL exceed the criterion limit determined from procedural blanks. That is, 95 percent of the measurements on standards with concentration at the IDL are larger than 95 percent of the measurements on procedural blanks.

The IDL, expressed in concentration units, describes the capabilities of the instrumentation when the effects of sample preparation are ignored. It is affected by analog-to-digital converter offset, integrator slope sensitivities, and other instrument parameters. Since it does not depend on the sample matrix or include the effects of sample preparation, it must be defined in terms of blanks and standard samples of known concentration rather than environmental samples.

Sample preparation further limits reliable detection of compounds. The term "method detection limit" has been proposed by Glaser et al. (1983) to describe the additional effects of sample preparation and analytical method. The Health Physics Society (1980) has called the same quantity a "minimum detectable concentration."

The method detection limit (MDL) is the smallest concentration of analyte in a single environmental sample that can be distinguished from zero reliably in the sense that 95 percent of the measured concentrations for environmental samples with a true concentration of analyte equal to the MDL exceed the criterion limit. In other words, 95 percent of the estimated concentrations produced by environmental samples with true concentration equal to the MDL exceed 95 percent of the estimated concentrations produced by procedural blanks.

In Figure E.2.2, the first graph illustrates analyses done on pure reagents spiked with appropriate levels of the

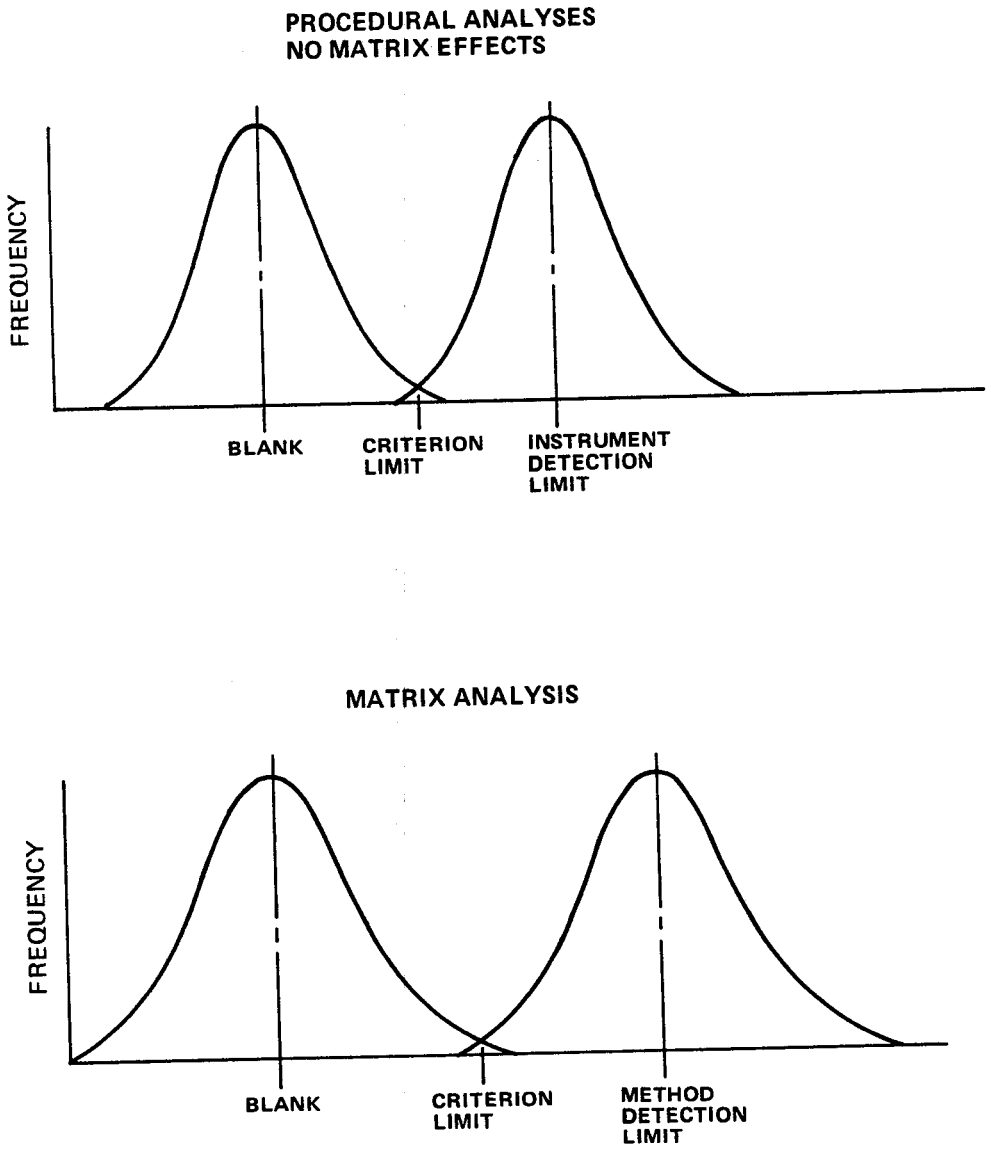



Figure E.2.2
**DETECTION LIMITS**

analyte. Note that the variability of the instrument response at a given concentration is relatively small. The second graph illustrates the increased variability from matrix effects when analyses are done on soil samples. Note that this variability increases the criterion limit and the detection limit.

The criterion limit is the instrument response (or estimated concentration) which is greater than that seen for 95 percent of analyses done on blank reagent. The instrument detection limit is that estimated concentration where 95 percent of all instrument responses are greater than 95 percent of all instrument responses seen from blanks.

The method criterion limit and method detection limit are defined by analysis of matrix (soil) spikes in which the variability of instrument response is relatively large.

The term nondetect has been avoided in the definition of MDL. In particular, the MDL is not the true concentration of environmental samples for which at most 5 percent of the measurements are nondetect when 95 percent of blank measurements are nondetect. It is usually impossible to configure GC/MS or GC/ECD instrumentation so that the percentage of nondetects produced by blanks or any low concentration of analyte is precisely controlled. If the instruments can be configured so that exactly 95 percent of all measurements on blanks are nondetect, then the MDL is the smallest concentration for which 5 percent of the measurements are nondetect.

## E.3.0 ESTIMATING DETECTION LIMITS

Estimating a detection limit is difficult because there may be no data on samples with concentrations at the detection limit, which is unknown. On the other hand, there may be data on samples with concentrations near the detection limit. If some assumptions are made about how measurements vary with concentration, then these measurements can be used to estimate the detection limit. The fewer the concentrations that are monitored, the stronger the assumptions needed to define estimates of detection limits. Each of the estimation procedures reviewed below makes different assumptions about how measurements vary with concentration. As might be expected, these assumptions lead to different detection limit estimates.

### E.3.1 CURRIE'S (1968) DETECTION LIMIT AND ESTIMATE

Currie's detection limit is applied to instrument responses (uncorrected chromotogram areas) corrected for background. That is, the instrument response for each sample measurement is corrected for instrument noise by subtracting the instrument response of an independent blank. Currie assumes the following about instrument responses and corrected responses.

- The blank and sample instrument responses are independently measured.
- No thresholds are applied to the instrument responses, so all instrument responses, no matter how small, are recorded.
- Instrument responses from samples with concentration C are normally distributed with mean $\mu_C$ and standard deviation $\sigma_C$.

In Currie's framework, a criterion limit, CL, is applied to the corrected area to control the rate of false "detects." If the corrected signal (sample instrument responses minus blank instrument responses) falls below CL, Currie recommends that "nondetect" be reported in a single sample study. CL is chosen so that when the target compound is not present, only 5 percent of the corrected areas exceed the threshold. If the target compound is not present in a sample, its instrument responses are assumed to be like the instrument responses of a blank, and its corrected sample instrument responses are therefore equivalent to the difference of the instrument responses of two independent blanks. The criterion limit is then the 95th percentile of the difference of two independent blank instrument responses. Under the above

assumptions, this difference is normally distributed with mean 0 and standard deviation $\sqrt{2}\sigma_0$, where $\sigma_0$ is the standard deviation of instrument responses area, and $CL = 1.645\sqrt{2}\sigma_0 = 2.326\sigma_0$.

The detection limit in Currie's framework is defined by the following scenario. The same sample is measured many times, giving an average corrected area $\mu_C - \mu_0$. A proportion of the measurements on the sample fall below CL, even if the target compound is present. The detection limit is the average $\mu_C - \mu_0$ for which the proportion of measurements below CL is .05. With Currie's normality assumptions, $\mu_C - \mu_0 = 2.326(\sigma_0 + \sigma_1)$ gives 5 percent of the sample corrected areas below CL.[1] That is, the detection limit is $2.326\ (\sigma_0 + \sigma_1)$. Finally, assume that the standard deviation $\sigma_1$ of raw areas for a sample that would have an average corrected area at the detection limit if it were measured many times is about the same as the standard deviation $\sigma_0$ of raw blank areas.

Then the detection limit is approximately $2(2.326\sigma_0) = 4.65\sigma_0$, which is a standard formula for the detection limit.

With Currie's assumptions, the detection limit $4.65\sigma_0$ can be estimated by $4.65s_0$, where $s_0$ is the standard deviation of n independent raw blank areas. The estimate can be calculated only if no blank sample is nondetect. Estimating the standard deviation from just the positive areas that exceed a threshold leads to an optimistic estimate of the detection limit.

Some authors have converted Currie's detection limit from area to concentration by assuming that measured concentrations are calculated by subtracting the area of a blank from the area of a sample and then multiplying the difference by a known, fixed response (calibration) factor $\beta$.

This assumption is reasonable for instrumentation with a stable response over, say, several weeks; however, GC/MS is not one of these. (The GC/MS response factors are changed every 12 hours or less, as recommended in the Love Canal Pilot Study QAPP.) The assumption also implies that internal standards are not needed since measured concentration is assumed to be area multiplied by a known factor, not area divided by internal standard area (which is random) and multiplied by a varying response factor. But if the stability assumption is satisfied and no internal standardization is needed, the detection limit can be expressed as $4.65\sigma_0$. If, in addition, no instrument thresholds on areas are active and no positive measurement is censored, then $4.65(\beta\sigma_0)$ can be estimated from the standard deviation of blanks alone.

In short, the common practice of reporting a detection limit as the standard deviation of measured concentrations on blanks multiplied by 4.65 is invalid for GC/MS data because the response factor is unstable, internal standards are used, and, typically, samples are not corrected by blanks.

## E.3.2 GLASER ET AL. ESTIMATED METHOD DETECTION LIMIT

A commonly used method is documented in Glaser, Foerst, McKee, Quave, and Budde (1981). This procedure is often applied even though it is complicated. We show here that the procedure is based on seriously flawed statistical reasoning.

Glaser et al. describe their measurement model in their section entitled "Theory" as follows:

> Measured concentrations from samples with actual concentration C are normally distributed with mean C (i.e., recovery = 100 percent and bias = 0) and standard deviation $\sigma_C$ depending on C.

In the same section, Glaser et al. write that $\sigma_C = k_0 + k_1 C$, but no use is made of this linearity. Nor do they use their suggestion to regress standard deviation on concentration or their later assumption that $k_1=0$. Therefore, we consider only the one assumption above.

The Glaser et al. normality model may hold for concentrations near the MDL but it cannot hold for concentrations close to zero. Otherwise, negative measured concentrations could be obtained from samples with actual concentration C=0. Since the estimated MDL is determined from samples with concentrations near the MDL rather than near zero, the reasonableness of the probability model for lower concentrations is not critical.

The estimated MDL of Glaser et al. has the form $t_{99} s_{MDL}$, where $s_{MDL}$ is an estimate of the standard deviation of measured concentrations at the MDL and $t_{99}$ is the 99th percentile of a t distribution. The first question is, Under what measurement model does $t_{99} s_{MDC}$ make sense as an MDL? According to the definition of an MDL (with the unimportant substitution of 99 percent for 95 percent), the null hypothesis $H_0$ that the sample is a blank should be rejected (1) for 1 percent of all blanks and (2) for 99 percent of all samples with actual concentration equal to the MDL. These two conditions can be satisfied as follows. Suppose that $H_0$ is rejected only when the measured concentration is zero and that 99 percent of blank measurements are zero. Then (1) is satisfied. To satisfy (2), the MDL must be the smallest

concentration for which 99 percent of the measured concentrations are bigger than zero. That is,

P[measured concentration > 0| true concentration=MDL]=.99.

Suppose that the 99 percent of the measurements that are positive at the MDL appear to come from a normal distribution. Then the MDL satisfies

$$P[\text{Normal}(MDL, \sigma_{MDL}) > 0] = .99,$$

which implies

$$MDL/\sigma_{MDL} = z_{99},$$

where $z_{99}$ is the 99th percentile of a normal (0,1) distribution. It follows that the MDL is defined implicitly by $MDL = z_{99}\sigma_{MDL}$. It is reasonable to conclude that this model of the measurement process justifies the Glaser et al. goal of setting MDL equal to $t_{99}s_{MDL}$.

In summary, a model of measurements that is consistent with Glaser et al. is:

- 99 percent of the measurements of blanks (actual concentration C=0) are zero, and
- For samples with actual trace concentration C>0, the positive measured concentrations have the same distribution as a normal $(C,\sigma_C)$ random variable conditioned to be larger than a positive threshold.

Under these conditions, the MDL is defined by $MDL = z_{99}\sigma_{MDL}$. Since Glaser et al. assume that the mean of measured concentrations equals the actual concentration, at the MDL the coefficient of variation of measured concentrations is $1/z_{99}$.

The MDL in this formulation has no closed form expression. But it is not difficult to develop estimates based on the idea that at the MDL the coefficient of variation is $1/z_{99}$. For example, first obtain an initial estimate of the MDL, either from an expert or by analogy with a similar analyte. Then prepare samples with concentration at the initial estimate of the MDL, measure their concentrations, and compute the mean $\bar{x}$ and standard deviation s of their measurements. If the initial MDL estimate is correct, then $\bar{x}s$ should be close to $z_{99}$. If this is not the case, either decrease or increase the concentration of the sample. For example, if $\bar{x}/s$ is too big, then reduce the concentration of the samples. Repeat the procedure until a concentration C is found for which $\bar{x}/s$ is close to C. That concentration is the estimated MDL.

Glaser et al. propose the following estimate. First, an initial estimate of the MDL is obtained. Second, a sample with concentration between one and five times the initial estimated MDL is prepared and divided into seven aliquots. The standard deviation $s_1$ of the seven replicate measurements is calculated and the initial estimate for the MDL is revised to $t_6 s_1$, where $t_6$ is the 99th percentile of a t distribution with 6 degrees of freedom. A confidence interval is then determined for the MDL based on the seven samples, and if this interval contains the initial estimate, then estimation stops. Otherwise, a new sample is taken, $s_2$ is recalculated, and sampling and estimation stop if a revised confidence interval contains the previous estimate $s_1$. Iteration continues until an estimate $s_k$ is not significantly different from the previous estimate $s_k$-1.

The Glaser et al. estimation procedure ignores the basic property of the MDL under their model: the coefficient of variation of measurements from samples with concentration at the MDL equals $z_{99}$. When sampling stops in the Glaser et al. procedure, no check is made on the coefficient of variation. Their scheme merely checks that the estimate of standard deviation from one iteration to another changes insignificantly. An obvious problem is that if the initial estimate of s leads to an estimated MDL that is far from the true MDL, then the second iteration s should be very different from the initial estimate or else the revised MDL will also be far from the true value. In brief, equality of standard deviations is irrelevant, and the coefficient of variation equalling $1/z_{99}$ is relevant. The Glaser et al. estimate of the MDL is inappropriate.

### E.3.3 HUBAUX AND VOS (1968) ESTIMATED METHOD DETECTION LIMIT

The method detection limit (MDL) is defined as follows: 95 percent of the estimated concentrations for samples with true concentration equal to the MDL are larger than 95 percent of the estimated concentrations from blanks. The Hubaux and Vos estimate of the MDL relies on the following measurement model:

> Estimated concentrations from samples with concentration C are normally distributed with mean $\beta_0 + \beta_1 C$, which is linear in C, and standard deviation $\sigma$, which is independent of C, over a range of trace concentrations.

This model does not specify how concentration is estimated, nor does it either presume or preclude subtraction of a blank signal from the sample signal. The normality assumption implies that measurements are not censored by the instrumentation. Bias in measurements is accommodated by $\beta_0$, which

is the average concentration measurement from blanks, and recovery different from 100 percent is accommodated by $\beta_1$.

The estimation procedure is as follows. To estimate $\sigma$, $\beta_0$, and $\beta_1$, a calibration experiment with standard samples of known concentration is run. The concentrations of the standard samples are estimated, and estimated concentration $Y_i$ is regressed on actual concentration $C_i$. The intercept $b_0$ of the regression line estimates bias $\beta_0$, and the slope $b_1$ estimates recovery $\beta_1$. The standard deviation $\sigma$ is estimated by the usual regression estimate $\sqrt{\Sigma(Y_1 - b_0 - b_1C_1)^2/(n-2)}$, where n is the number of samples, including replicates, analyzed in the calibration experiment.

The 95th percentile of blanks, which we call the criterion limit CL, is $\beta_0 + 1.645\sigma_0$, assuming normality. If it is important that the estimated 95th percentile of blanks be at least as large as CL, then it is not sufficient to replace $\beta_0$ and $\sigma$ in the formula for CL by $b_0$ and s, since $b_0$ and s may be smaller than $\beta_0$ and $\sigma$. The procedure incorporates estimation error in $b_0$, $b_1$, and s by adopting the classical estimate $\hat{c}1$ of a 95th percentile, which is

$$\hat{c} = b_0 + ts\left[1 + n^{-1} + \bar{c}^2\left[\Sigma(c_i-\bar{c})^2\right]^{-1}\right]$$

where t is the 95th percentile of a t distribution with n-2 degrees of freedom.

The next step is to estimate the concentration for which only 5 percent of all samples give estimated concentrations below c1. The 5th percentile of estimated concentrations from samples with an actual concentration $c_0$ is classically estimated by

$$b_0 + b_1c_0 - t_{.95,n-2}s\sqrt{1 + n^{-1} + (\bar{c}-c_0)^2/(\Sigma c_i-\bar{c})^2}$$

Therefore, the MDL is estimated by the concentration $c_0$ for which the above estimate of the 5 percentile equals c1.

The method for estimating the MDL is illustrated in Figure E.3.1 for hypothetical data for one target compound. There are 8 measured concentrations from blanks, and 3 measured concentrations on the target compound at each of the concentrations: 20 ppb, 40 ppb, and 80 ppb, giving n=17. For these data, $b_0 = 11.40$, $b_1 = .84$, and $s = 6.92$. That is, estimated measurement bias is 11.40 ppb and the estimated recovery rate is 84 percent. The outside curves show how the estimated 5th and 95th percentiles of measured concentration vary with actual concentration. The horizontal line is drawn at the 95th percentile of the measured concentrations from blanks, $\hat{c}1$, which is 24.1 ppb. The vertical line drops down to the actual concentration for which the 5th percentile of measured concentration is 24.1 ppb. This

actual concentration, which is 30.1 ppb, is the estimated MDL. In other words, the procedure estimates that 95 percent of all measurements from samples with concentration 30.1 ppb are larger than 95 percent of all blank measurements.

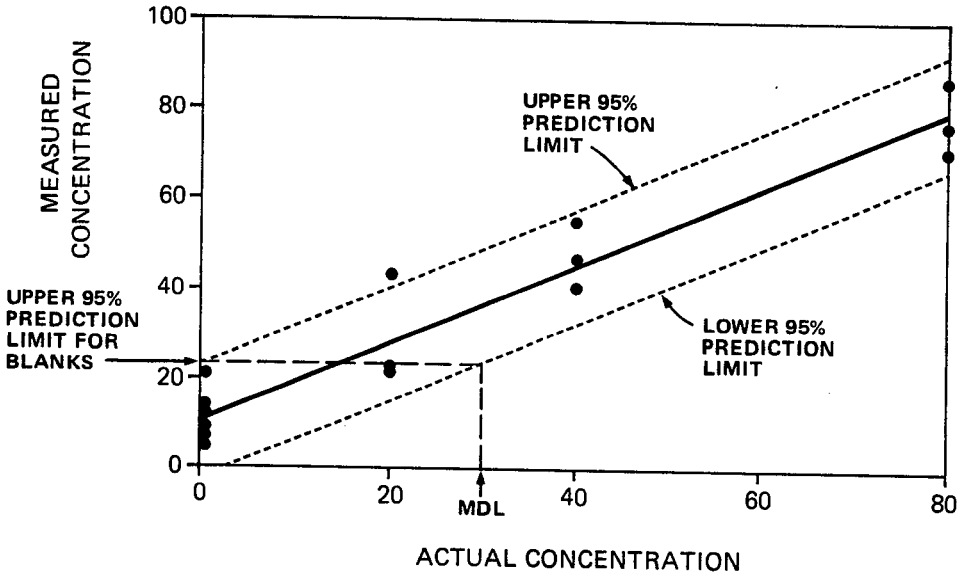



Figure E.3.1
**HUBAUX AND VOS DETECTION LIMIT**

Currie's detection limit is sometimes applied in the above context, even though it is inappropriate, because field sample measurements are not corrected by blank measurements, the calibration or response factor is not stable but is recomputed as often as every 6 hours, and internal standards are used. Even so, the standard deviation of the blank measurements multiplied by 4.65 is often reported as the detection limit. For the hypothetical data, the standard deviation of the 8 blank measurements is 5.09, which gives a Currie type estimate of 23.7. If the blank data were not changed and recovery was lowered by a factor of 3 to 28 percent, then the Hubaux and Vos estimated MDL would be about three times higher, or about 90 ppb (which is reasonable since area counts for the analyte have decreased and are therefore harder to distinguish from noise), and the Currie type estimate would be unchanged. An obvious implication is that treating instrument detection limits based on blanks as if they were method detection limits can be misleading.

An advantage to the Hubaux and Vos procedure is that it leads naturally to informal checks of the assumptions of constant standard deviation $\sigma$, constant recovery $\beta_1$, and

normality of measurements at each actual concentration. For example, the scatter plot of estimated versus actual concentration can be used to assess the extent to which variance depends on concentration, and a normal probability plot of residuals from the regression can be used to assess nonnormality. A second advantage is that it makes clear that the estimated MDL can be interpreted as an estimate of the concentration for which 95 percent of the measurements are larger than 95 percent of the measured concentrations from blanks, and this interpretation evades the issue of what is reported as nondetect. A third is that measurements are taken near the MDL rather than just from blanks, so that blanks are not assumed to behave like samples with low concentrations. A disadvantage is that the procedure needs to be modified to accommodate nondetects and nonnormality. Also, the MDL estimate may be too low because the method it uses for determining the MDL concentration on the abscissa (actual concentration) scale is biased. Whether this bias is substantial is unclear.

## E.4.0 RECOMMENDED PROCESS FOR ESTIMATING METHOD DETECTION LIMIT FOR LOVE CANAL HABITABILITY STUDY

A variant of the Hubaux and Vos method discussed above is proposed to estimate the method detection limit for the Love Canal habitability study. This method is more appropriate for the GC/MS instrumentation than either the Currie approach or the Glaser et al. approach.

The proposed method will be used only to estimate method detection limits. The criterion limit will not be estimated because of an inherent limitation in the GC/MS instrumentation. Using the GC/MS, analyses of analytes at low concentrations fail identification criteria at higher concentrations than the minimum at which quantification can occur.

The proposed method detection limit will satisfy the concerns raised by the 1980 study in that environmental samples with analyte concentrations greater than the method detection limit will have a high probability of being detected.

The proposed process for estimating the method detection limit consists of the following steps:

- Estimate a "first guess" of the MDL.
- Select a range of concentrations higher and lower than the estimated MDL, with the lowest not expected to be detected and the highest almost certain to be detected.
- Prepare spiking concentrations at three to five dilutions from the maximum concentration to the minimum concentration.
- Analyze matrix blanks and progressively higher spikes and obtain the instrument response.
- Calculate relative areas as instrument response divided by internal standard response.
- Regress the relative area on concentration.

The regression model is:

$$RA = b_0 + b_1 C + e$$

where

$$RA = \frac{\text{Area of quantitating ion peak}}{\text{Area of internal standard peak}}$$

C = Concentration of spike

e = Independent identically distributed (i.i.d.) error

The method detection limit is estimated from this model as that concentration for which the 5th percentile of the predicted RA is equal to the 95th percentile of the predicted RA at zero concentration. That is, 95 percent of the predicted RAs at the MDL concentration (and therefore the predicted concentration estimates) exceed 95 percent of the predicted RAs of blanks.

Figure E.4.1.a presents an analytical formula for calculating the MDL from statistics of the linear regression relation. Figure E.4.1.b shows the derivation of this estimator for the MDL.

The model makes several assumptions:

- The instrument always produces a response, even at zero concentration.
- The error (e) has an identical distribution regardless of the concentration.
- The response is a linear function of concentration.

These assumptions are only approximately true for the GC/MS SIM instrumentation and are being explored further. In part this is because the analysis process consists of two parts, identification and quantification; only the latter is addressed by the regression model. To understand the influence of identification on the quantification process, a short description of the physical process of GC/MS SIM analysis is needed.

The analytical process, greatly simplified, consists of several steps. First the analyte solution is injected into the instrument where it is vaporized and passed through a chromatographic column. Different chemical species pass through this column at different rates, and therefore emerge at different times.

As the analytes emerge from the gas chromatograph they pass into the mass spectrometer where molecules are broken into smaller charged ions by an electron beam. A series of "electronic windows" are then opened, each window only admitting an ion with one particular mass/charge ratio. If an ion has the correct mass/charge ratio and passes through the window, it is detected and counted.

Since only one window can be open at a time, multiple ions are counted by opening and closing the windows in a very

Figure E.4.1.a
ANALYTICAL FORMULA FOR MDL MODEL

$RA_i = aC_i + b + e_i \quad i = 1...n$

Estimate of a is $\hat{a}$, estimate of b is $\hat{b}$

n is the number of analyses

The $e_i$ are i.i.d. errors with $E(e) = 0$, $Var(e) = \sigma^2$

Let $SSC = \Sigma(C_i - \bar{C})^2$

Let $MSE = \dfrac{\Sigma RA_i^2 - \hat{b}\Sigma RA_i - \hat{a}\Sigma C_i RA_i}{(n-2)}$

Let $t = t_{(1-\alpha,\ n-2)}$ value of t statistic

Let $T = t\left[MSE\left(\dfrac{n+1}{n} + \dfrac{\bar{C}^2}{SSC}\right)\right]^{1/2}$

Then $\hat{MDL} = \dfrac{\left(2\hat{a}T - \dfrac{2t^2\ \bar{C}\ MSE}{SSC}\right)}{\left(\hat{a}^2 - \dfrac{t^2 MSE}{SSC}\right)}$

Figure E.4.1.b
DERIVATION OF MDL ESTIMATOR

Assume $\hat{RA} = \hat{a}C + \hat{b}$

At C = 0, then $\hat{RA} = \hat{b}$

At C = MDL, then $\hat{RA} = \hat{a}(MDL) + \hat{b}$

Upper (1-α)% confidence limit (predicted)

At C = 0

$$\hat{RA}_{UCL \circ C = 0} = \hat{b} + t \left[ MSE \left( \frac{n+1}{n} + \frac{\bar{C}^2}{SSC} \right) \right]^{1/2}$$

Let

$$T^2 = t^2 MSE \left( \frac{n+1}{n} + \frac{\bar{C}^2}{SSC} \right)$$

At C = MDL, lower (1-α)% confidence limit (predicted) is:

$$RA_{LCL \circ C=MDL} = \hat{a}C_{MDL} + \hat{b} - \left[ t^2 MSE \left( \frac{n+1}{n} + \frac{(C_{MDL} - \bar{C})^2}{SSC} \right) \right]^{1/2}$$

Solve for MDL = $C_{MDL} = C_m$

From definition

$$\hat{RA}_{UCL \circ C=0} = \hat{RA}_{LCL/C_m}$$

Figure E.4.1.b
(continued)

$$\hat{b} + T = \hat{a}C_m + \hat{b} - \left[t^2 MSE\left(\frac{n+1}{n} + \frac{(C_m - \bar{C})^2}{SSC}\right)\right]^{1/2}$$

$$T = \hat{a}C_m - \left[t^2 MSE\left(\frac{n+1}{n} + \frac{C_m^2}{SSC} - \frac{2C_m\bar{C}}{SSC} + \frac{\bar{C}^2}{SSC}\right)\right]^{1/2}$$

$$T = \hat{a}C_m - \left[t^2 MSE\left(\frac{n+1}{n} + \frac{\bar{C}^2}{SSC}\right) + t^2 MSE\left(\frac{C_m^2}{SSC} - \frac{2C_m\bar{C}}{SSC}\right)\right]^{1/2}$$

$$T = \hat{a}C_m - \left[T^2 + t^2 MSE\left(\frac{C_m^2}{SSC} - \frac{2C_m\bar{C}}{SSC}\right)\right]^{1/2}$$

$$\hat{a}C_m - T = \left[T^2 + t^2 MSE\left(\frac{C_m^2}{SSC} - \frac{2C_m\bar{C}}{SSC}\right)\right]^{1/2}$$

$$\hat{a}^2 C_m^2 - 2\hat{a}C_m T + T^2 = T^2 + t^2 MSE\left(\frac{C_m^2}{SSC} - \frac{2C_m\bar{C}}{SSC}\right)$$

$$\hat{a}^2 C_m - t^2 \frac{MSE\ C_m}{SSC} = 2\hat{a}T - \frac{2t^2\ \bar{C}\ MSE}{SSC}$$

$$C_m = \frac{\left(2aT - \frac{2t^2\ \bar{C}\ MSE}{SSC}\right)}{\left(\hat{a}^2 - \frac{t^2\ MSE}{SSC}\right)}$$

rapid sequence. This also means that the more ions that are sought the less time the window for each can be open, and the less sensitive the instrument is to all ions.

In the process used for Love Canal, three ions are sought for each chemical species. Theoretically the number of counts seen for each ion should occur in a known ratio. If the species elutes from the chromatographic column in the correct time and the ions are counted in the correct ratios, then the compound is considered to be positively identified.

Once identification is achieved, then the area under ion count versus time curve can be used to estimate the detected concentration. Generally the ion used for this (the quantitating ion) is the one with the greatest area of the three.

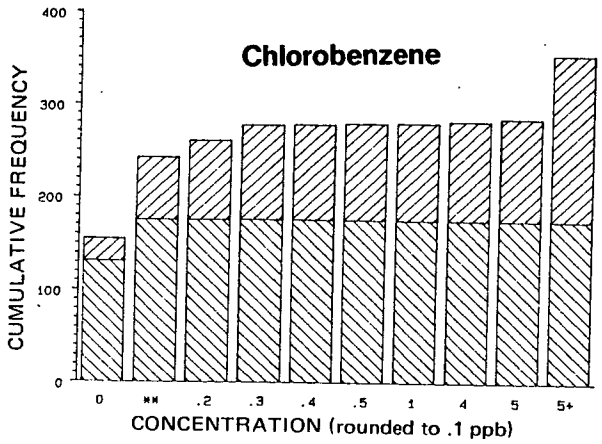
The area of the quantitating ion is adjusted by the area of the internal standard ion. The internal standard is a compound, chosen to be as similar as possible to the target compound, which is added to the analyte before injection in a known quantity. Adjusting the area of the quantitating ion by the area of the internal standard compensates for any fluctuations in the volume of analyte injected and for some drifts in the chromatographic column behavior.

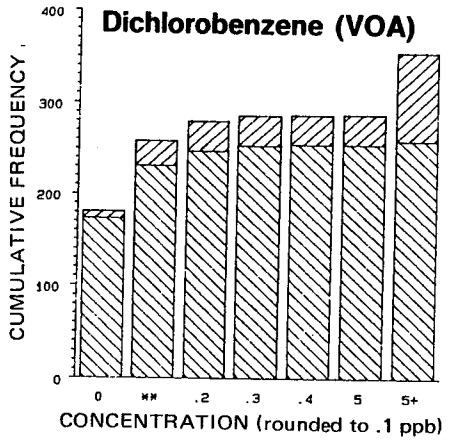
The adjusted area is the area used for the estimation of detection limits. In actual practice, the instrument will produce an area for the quantitating ion at concentration levels lower than where the identification criteria are consistently met (an identification limit). Generally concentrations estimated from these readings are not reported by the chemist or are reported with a qualifier that indicates a tentative identification.

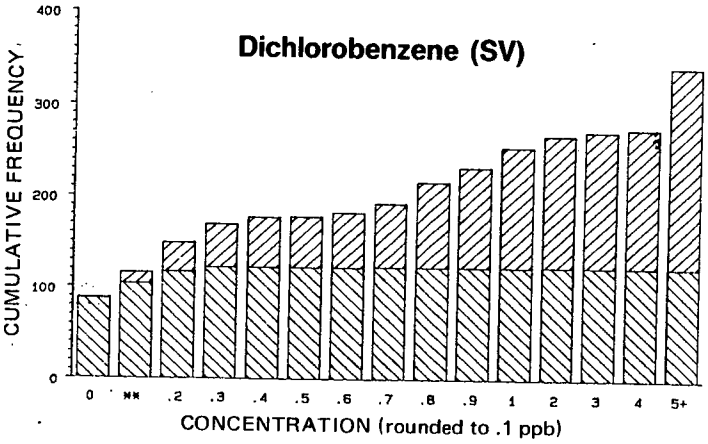
However, during the pilot study the three participating laboratories (EMS, CAA, and MGM) were requested to report data before validating and interpreting them. This enabled a comparison by concentration to be made between the data that were validated and the data that were ultimately not validated. Since the data are from unknown samples, the concentrations were estimated from the primary ion area alone.

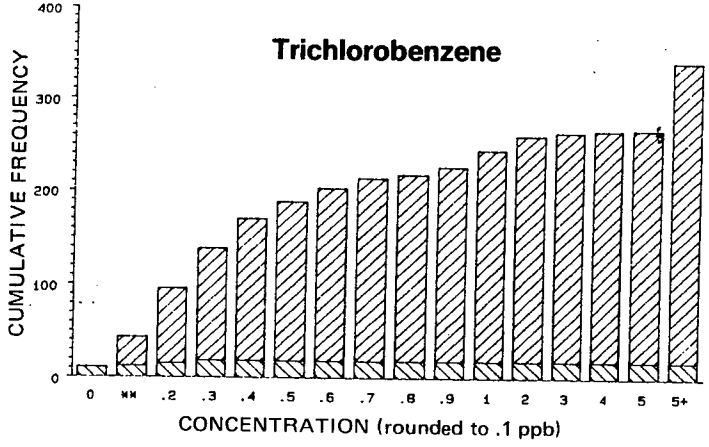
Figures E.4.2 a and b illustrate the results of this comparison in the form of a stacked bar chart. The total bar height at a concentration corresponds to the fraction of all samples analyzed that were estimated to be at that concentration or less. The lower part of the bar is the cumulative fraction of samples that failed the identification criteria.

The cumulative percentage of samples for which the identification criteria were not met tends to increase with concentration until a plateau is reached. At concentrations higher




Failed Identification Criteria

Met Identification Criteria

Figure E.4.2a
**CUMULATIVE FREQUENCY OF PILOT STUDY DATA BY CONCENTRATION**

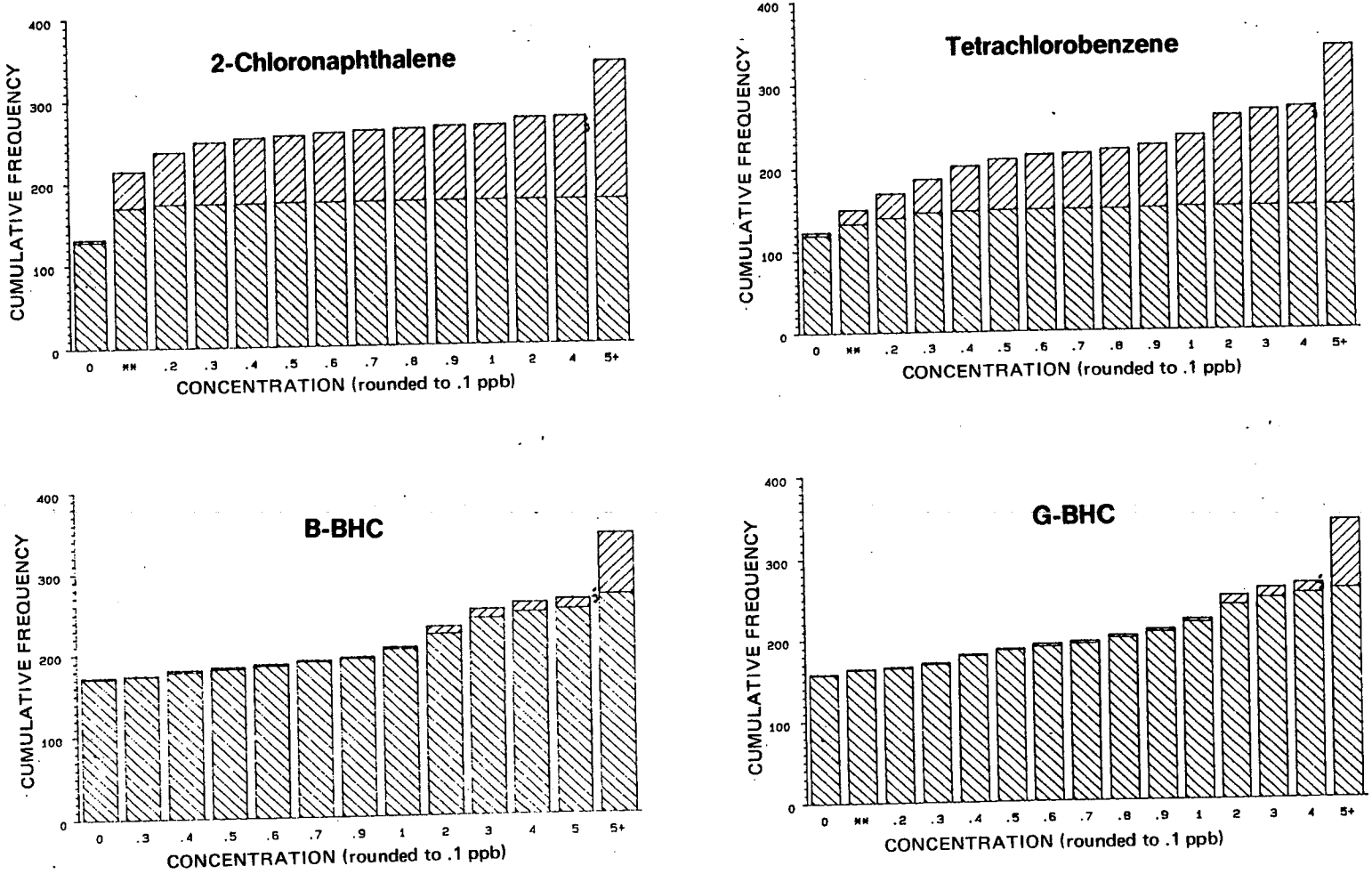



Figure E.4.2b
**CUMULATIVE FREQUENCY OF PILOT STUDY DATA BY CONCENTRATION**

than those at this plateau, almost all samples analyzed meet identification criteria. Thus, the approximate identification limit is the concentration at which the cumulative percentage of samples for which the identification criteria were not met approaches maximum.

Table E.4.1 summarizes the estimates from Figures E.4.2 through E.4.5.

Table E.4.1
APPROXIMATE IDENTIFICATION LIMIT FOR LCICs

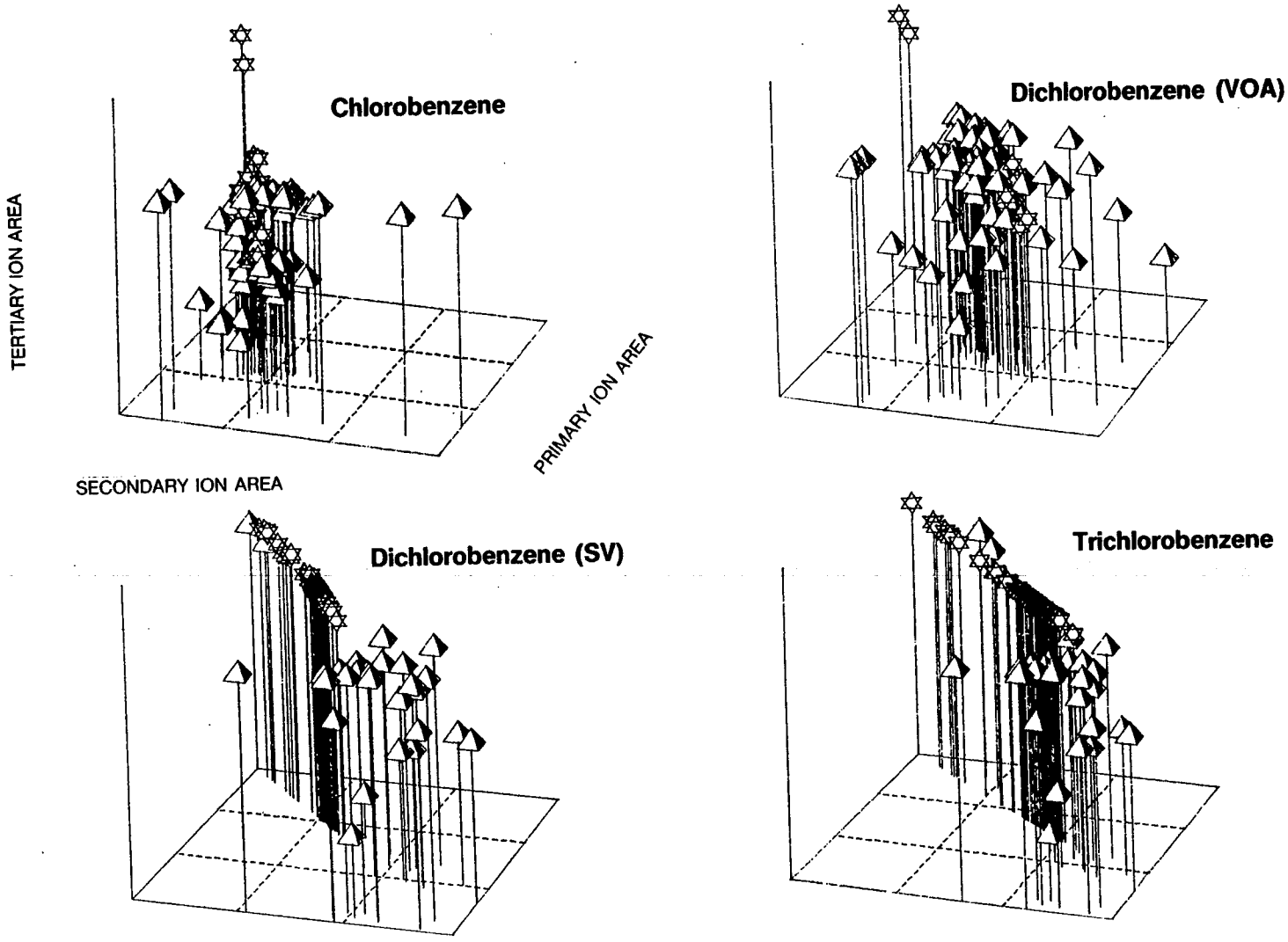
| | |
|---|---|
| Chlorobenzene | <0.1 ppb |
| Dichlorobenzene (VOA) | 0.2 - 0.3 ppb |
| Dichlorobenzene | 0.2 - 0.3 ppb |
| 1,2,3,Trichlorobenzene | 0.2 - 0.3 ppb |
| 2-Chloronaphthalene | 0.1 - 0.2 ppb |
| 1,2,3,4-Tetrachlorobenzene | 0.2 - 0.3 ppb |
| Beta-BHC | Unknown, still interference at >5 ppb |
| Gamma-BHC | Unknown, still interference at >5 ppb |

The importance of this identification limit is that it provides a lower bound on the method detection limit. Samples with analyte concentrations less than the identification limit are unlikely to have a detectable concentration reported. Unfortunately, methodology has not yet been developed to provide rigorous estimates of the identification limit beyond the empirical method presented.

Further understanding of the GC/MS process can be obtained by examining Figures E.4.3a and b through E.4.5a and b for each of the three labs. These figures present a three-dimensional diagram of the estimated concentration for each LCIC displayed as a ratio of the three ion areas.

The estimated concentrations in each plot increase as a function of the distance away from the lower righthand corner of the diagram. Estimated concentrations represented by stars were identified as the LCIC being sought. Estimated concentrations represented by pyramids failed the identification criteria.

A key element to note from these figures is that the identified LCICs lie clustered about a line out from the origin (lower right corner). The clustering about this line is very tight at high concentrations (upper left corner) and

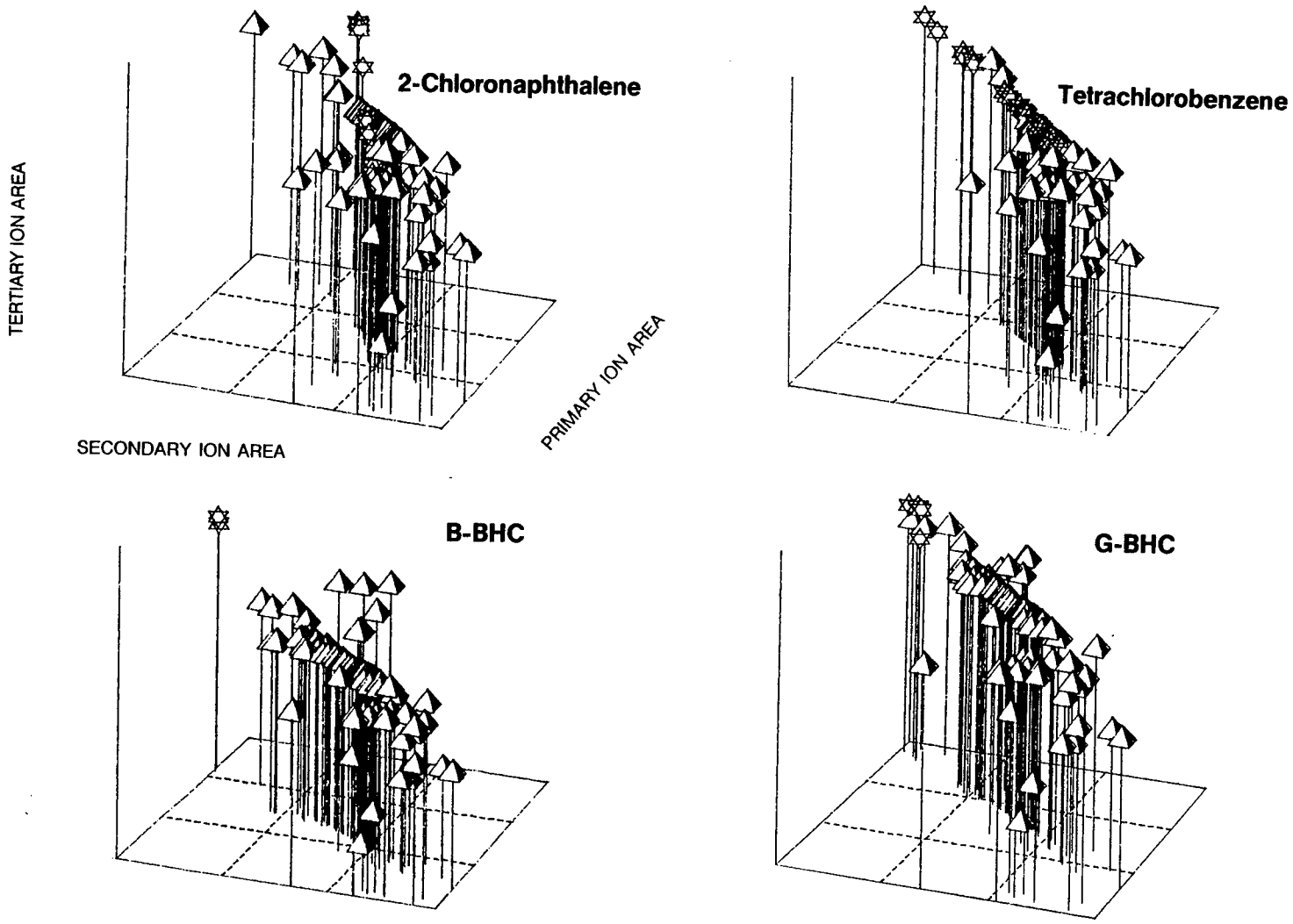



Notes: Vector length is proportional to the natural log of the concentration.

△ Failed Identification Criteria

✡ Met Identification Criteria

Figure E.4.3a
**STANDARDIZED ION AREA RATIOS**
**PILOT STUDY DATA — MGM LABORATORY**

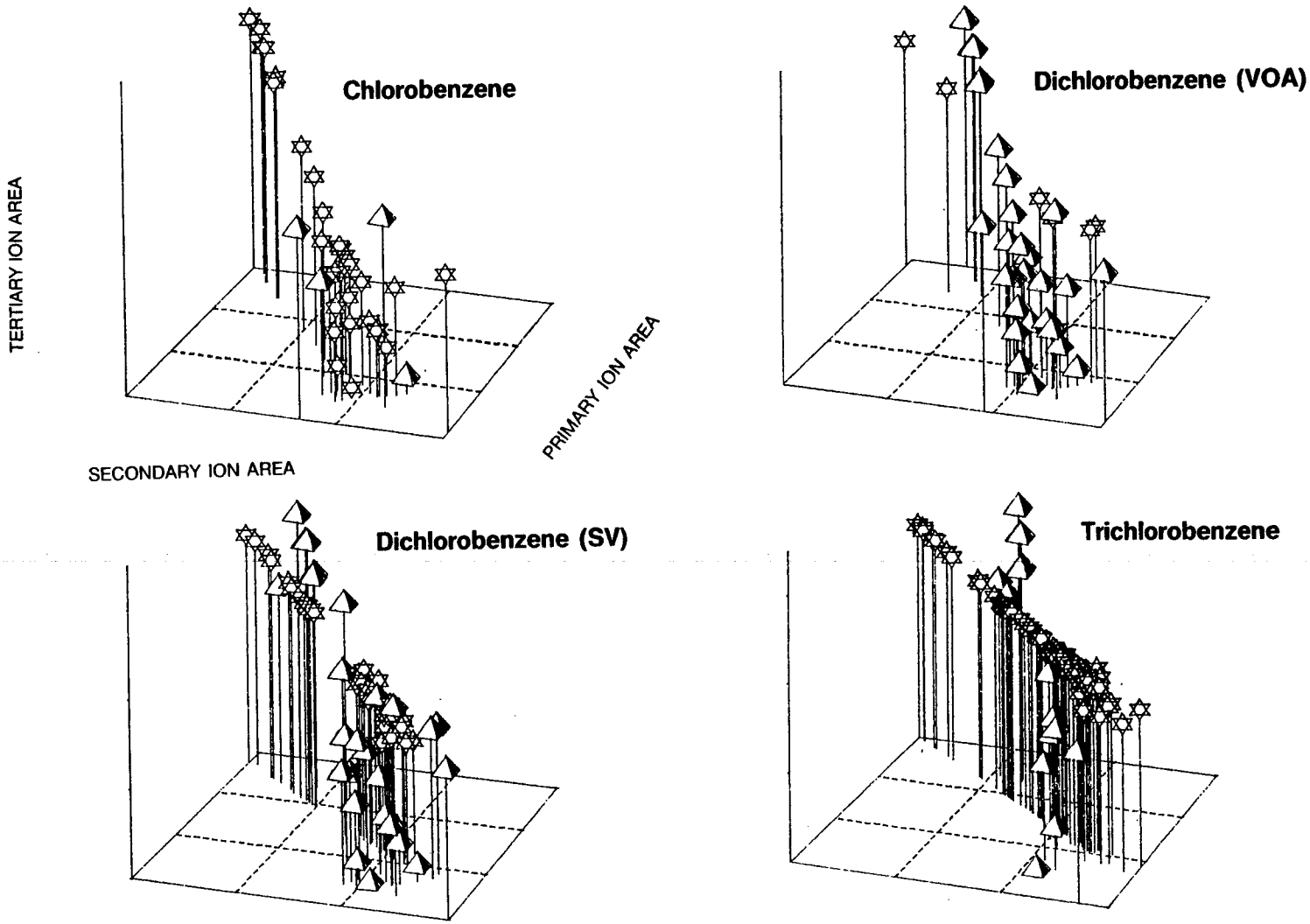



Notes: Vector length is proportional to the natural log of the concentration.

Failed Identification Criteria

Met Identification Criteria

Figure E.4.3b
**STANDARDIZED ION AREA RATIOS**
**PILOT STUDY DATA — MGM LABORATORY**

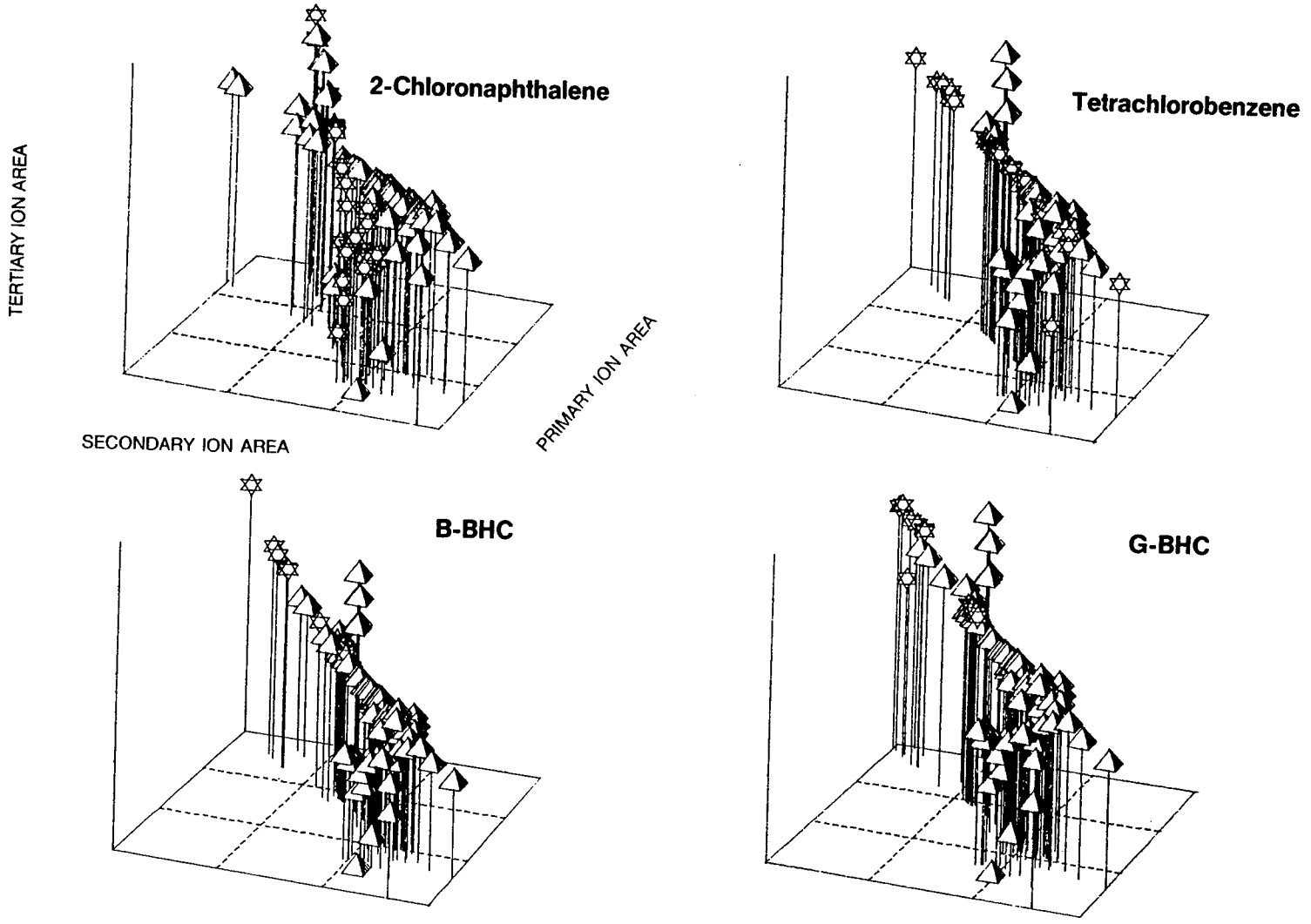



Notes: Vector length is proportional to the natural log of the concentration.

Failed Identification Criteria

Met Identification Criteria

Figure E.4.4a
**STANDARDIZED ION AREA RATIOS PILOT STUDY DATA — CAA LABORATORY**

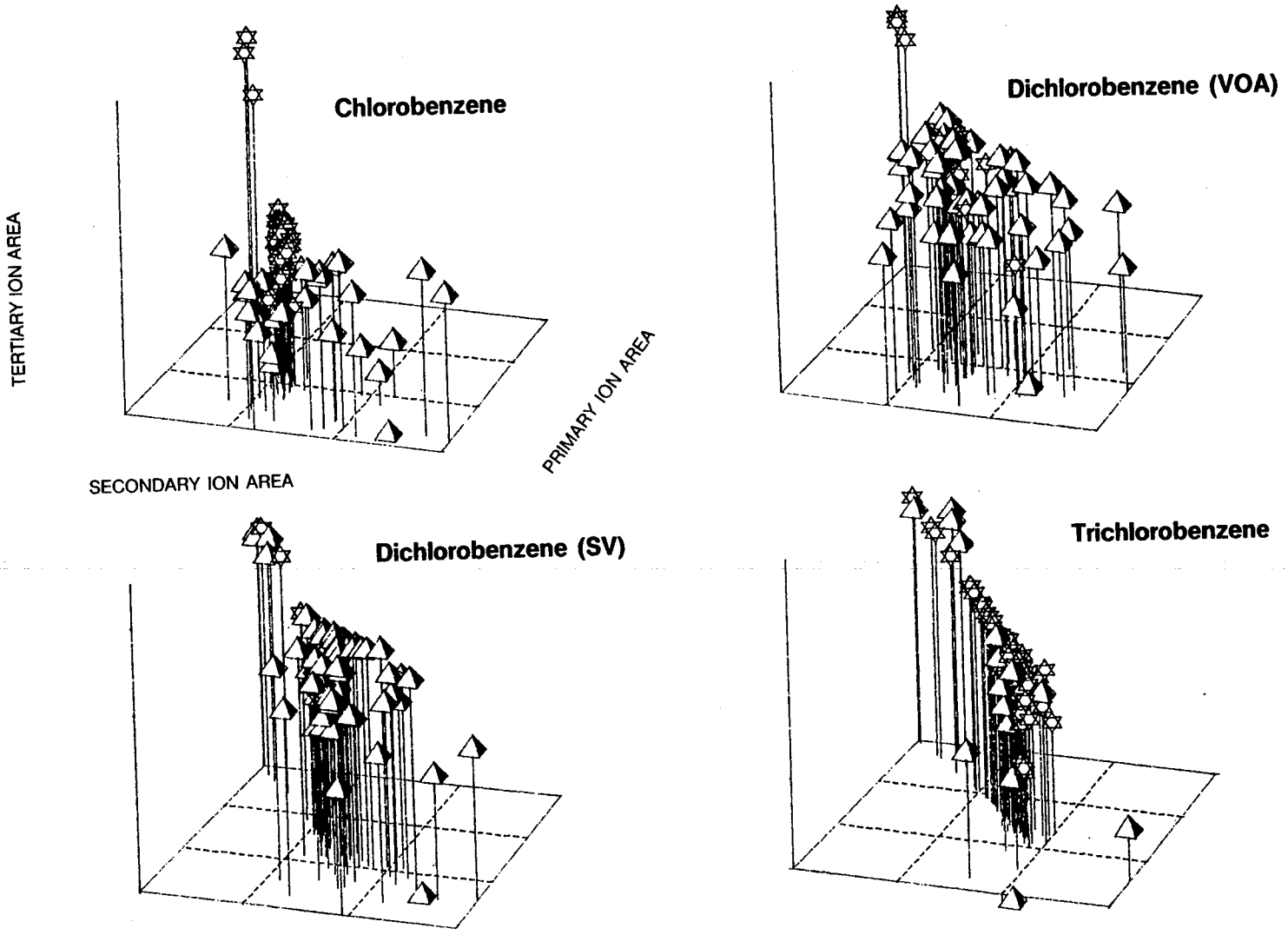



Notes: Vector length is proportional to the natural log of the concentration.

△ Failed Identification Criteria

✡ Met Identification Criteria

Figure E.4.4b
**STANDARDIZED ION AREA RATIOS**
**PILOT STUDY DATA — CAA LABORATORY**

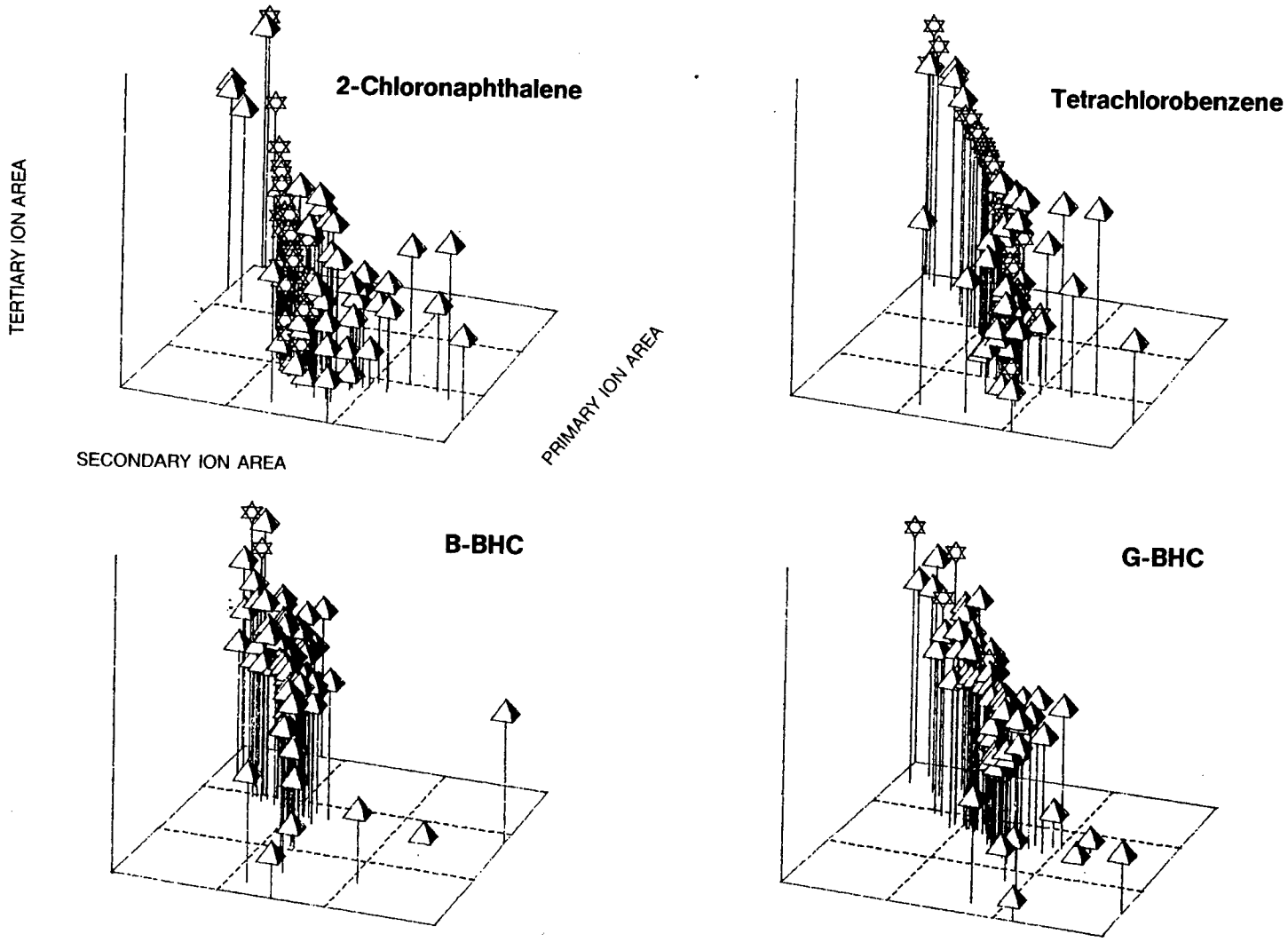



Notes: Vector length is proportional to the natural log of the concentration.

Failed Identification Criteria

Met Identification Criteria

Figure E.4.5a
**STANDARDIZED ION AREA RATIOS**
**PILOT STUDY DATA — EMS LABORATORY**




Notes: Vector length is proportional to the natural log of the concentration.

△ Failed Identification Criteria

✡ Met Identification Criteria

Figure E.4.5b
**STANDARDIZED ION AREA RATIOS**
**PILOT STUDY DATA — EMS LABORATORY**

becomes more scattered at lower concentrations. This scatter eventually results in uncertainty as to the identification.

Another source of uncertainty in identification is the presence of interfering compounds. This can be seen in the 2-chloronaphthalene diagrams. In the diagrams for all three labs it can be seen that the pyramids (non-chloronaphthalene compounds) tend to form a second line crossing the line of stars (chloronaphthalene). This may indicate the presence of another compound that has properties similar to chloronaphthalene.

## E.5.0 VERIFICATION OF PROPOSED METHOD DETECTION LIMIT ESTIMATOR

### E.5.1 EXPERIMENTAL DESIGN

The procedure for estimating the MDL was tested by requesting each of the laboratories that participated in the pilot study to perform a series of spiking experiments on Love Canal soil. EMS was unable to participate, so the spiking experiments were done by the CAA and MGM labs.

Soil was obtained from unused pilot study contingency samples, chosen by ranking concentration estimates from the pilot. The contingency samples corresponding to the samples with the lowest overall concentrations were composited and distributed to the two laboratories.

The experiment was conducted with each laboratory analyzing both the "blank" soil and progressively higher matrix (soil) spikes of 1/20, 1/10, 1/4, 1/2, and 1 dilutions of a standard solution. The spiking levels were chosen in consultation with the labs, after simulating the sensitivity of MDL estimates to spiking levels.

Each analysis was done in duplicate by both labs. The MGM lab subsequently repeated the entire experiment.

The standard solution was a concentration of 1 ppb for all volatile and semivolatile compounds (chlorobenzene, dichlorobenzene, trichlorobenzene, chloronaphthalene, and tetrachlorobenzene) except Beta BHC and Gamma BHC, in which a concentration of 5 ppb was used.

Each laboratory was requested to analyze the samples by the same protocol as was used for the pilot study, with one exception: the identification criteria were not to be strictly applied. This change in protocol allowed for quantified responses at concentrations below those at which the compound could be positively identified.

### E.5.2 RESULTS OF EXPERIMENT

The data obtained from these experiments were analyzed to estimate the method detection limits, to examine the assumptions of the MDL model, and to compare model behavior between laboratories. Figures E.5.1 through E.5.8 show the best fit linear regression line for relative area as a linear function of spike concentration for each experimental set.

Overall, the consistency was good between experimental runs at the same laboratory; however, the labs appear to have

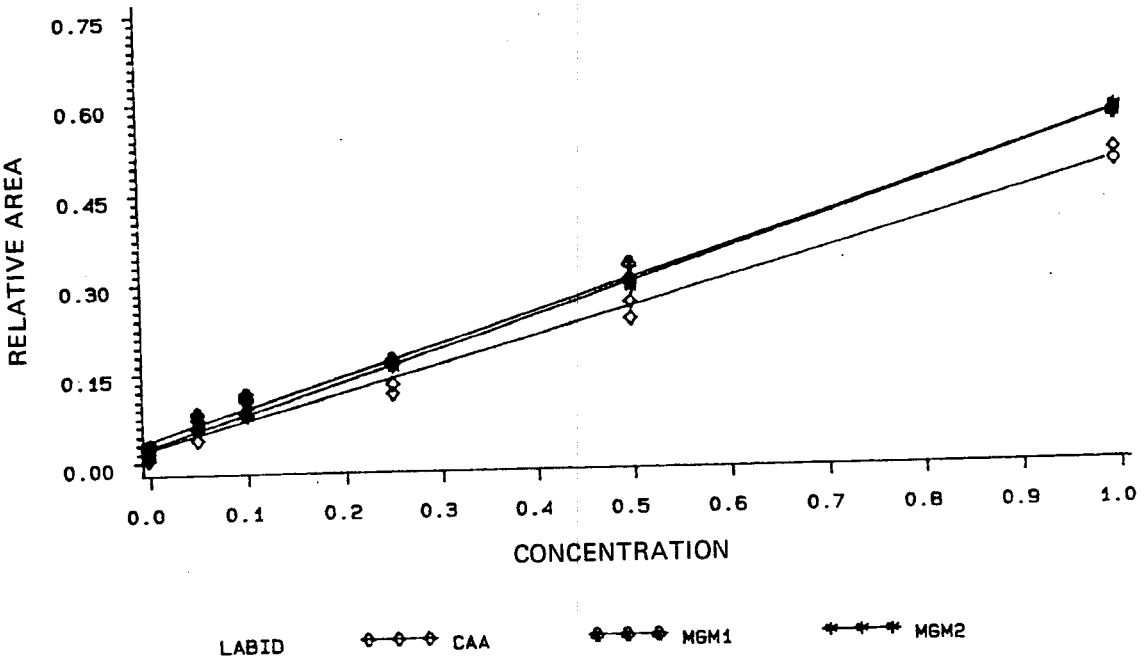



Figure E.5.1
**DETECTION LIMIT EXPERIMENT: CHLOROBENZENE**

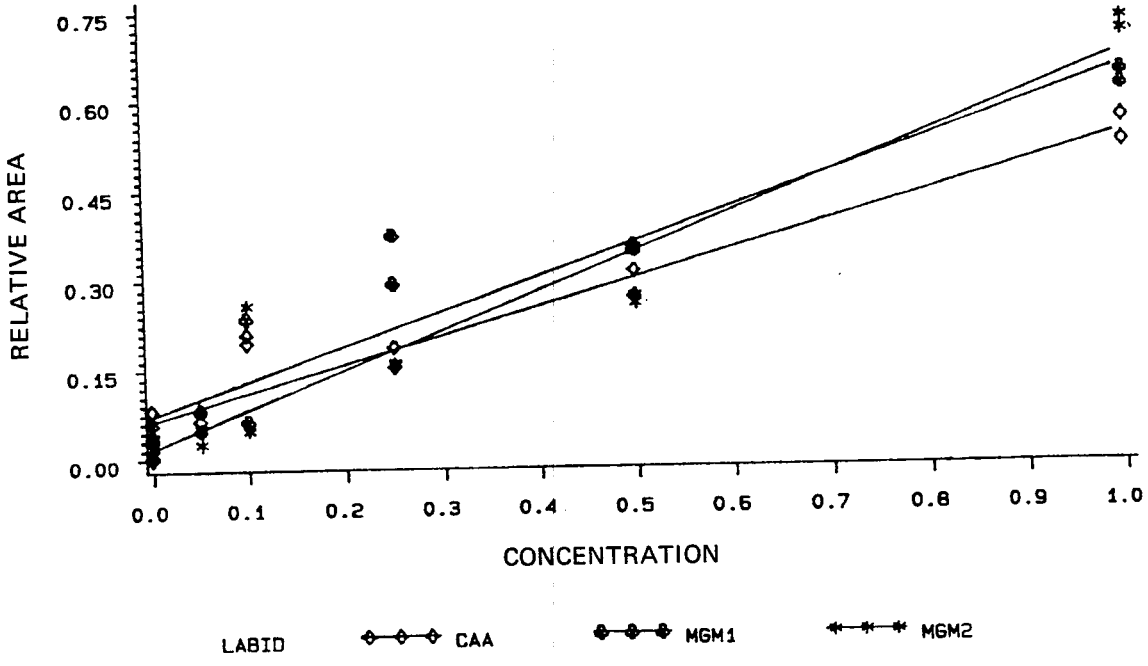



Figure E.5.2
**DETECTION LIMIT EXPERIMENT: DICHLOROBENZENE (VOA)**

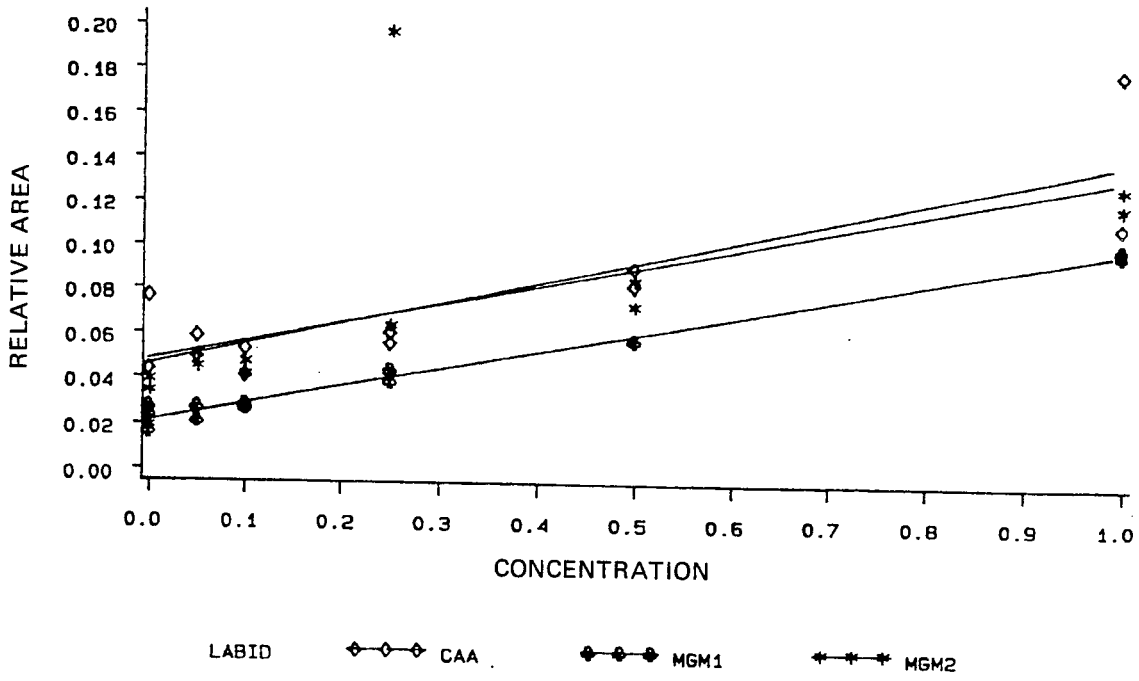



Figure E.5.3
**DETECTION LIMIT EXPERIMENT: DICHLOROBENZENE (SV)**

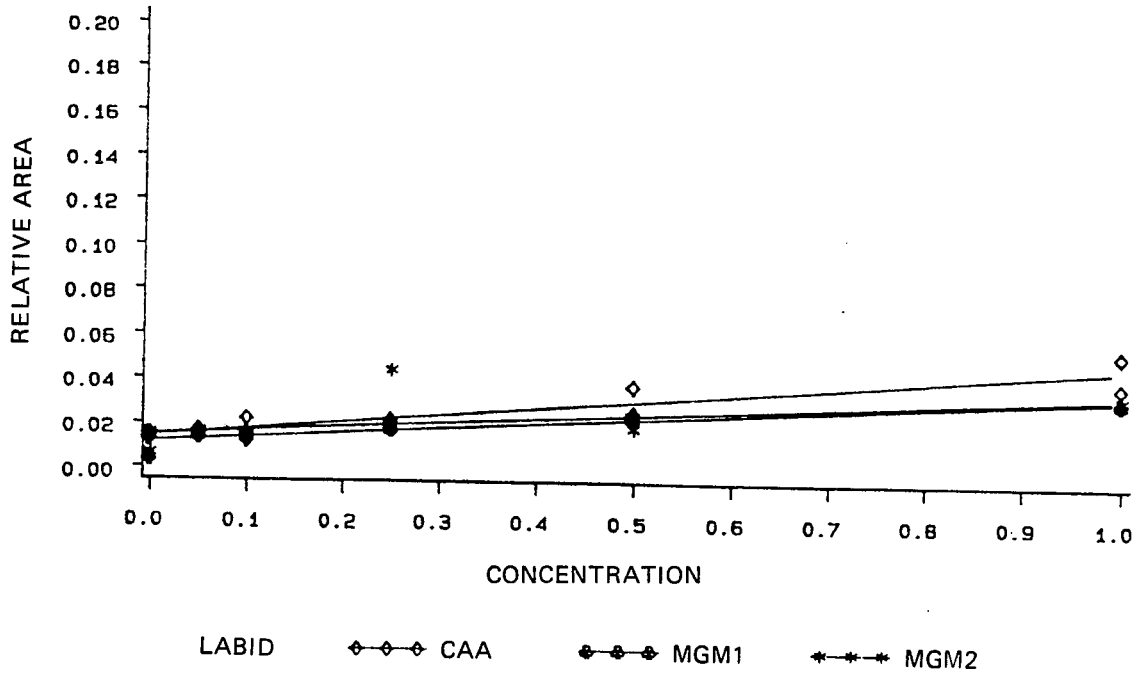



Figure E.5.4
**DETECTION LIMIT EXPERIMENT: TRICHLOROBENZENE**

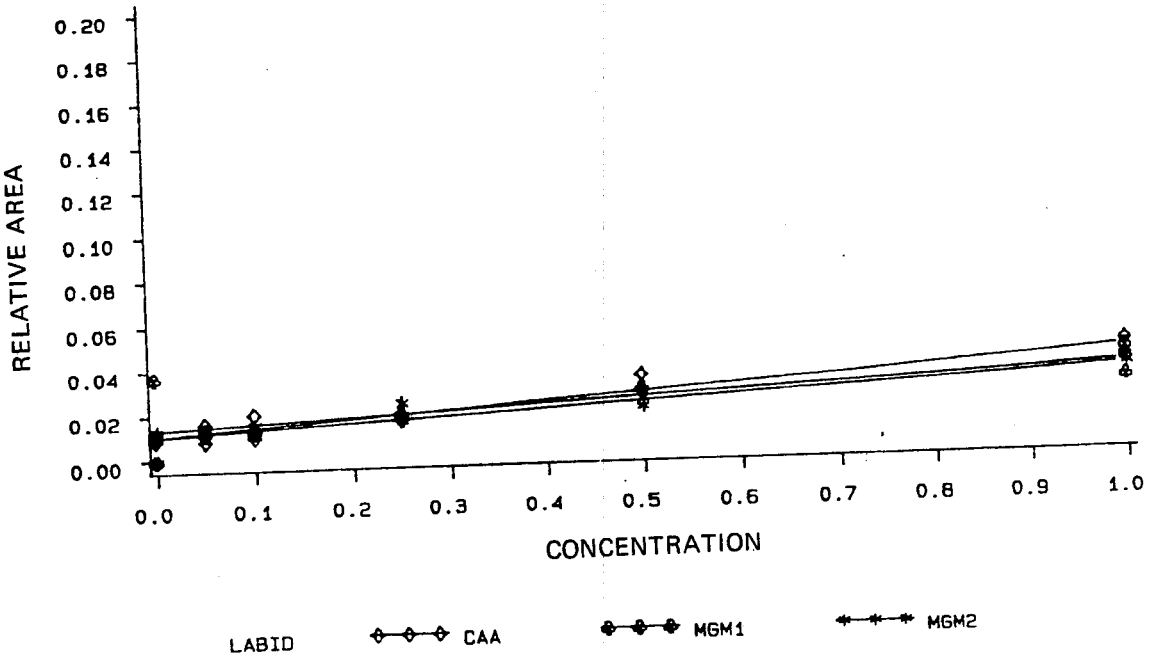



Figure E.5.5
**DETECTION LIMIT EXPERIMENT: TETRACHLOROBENZENE**

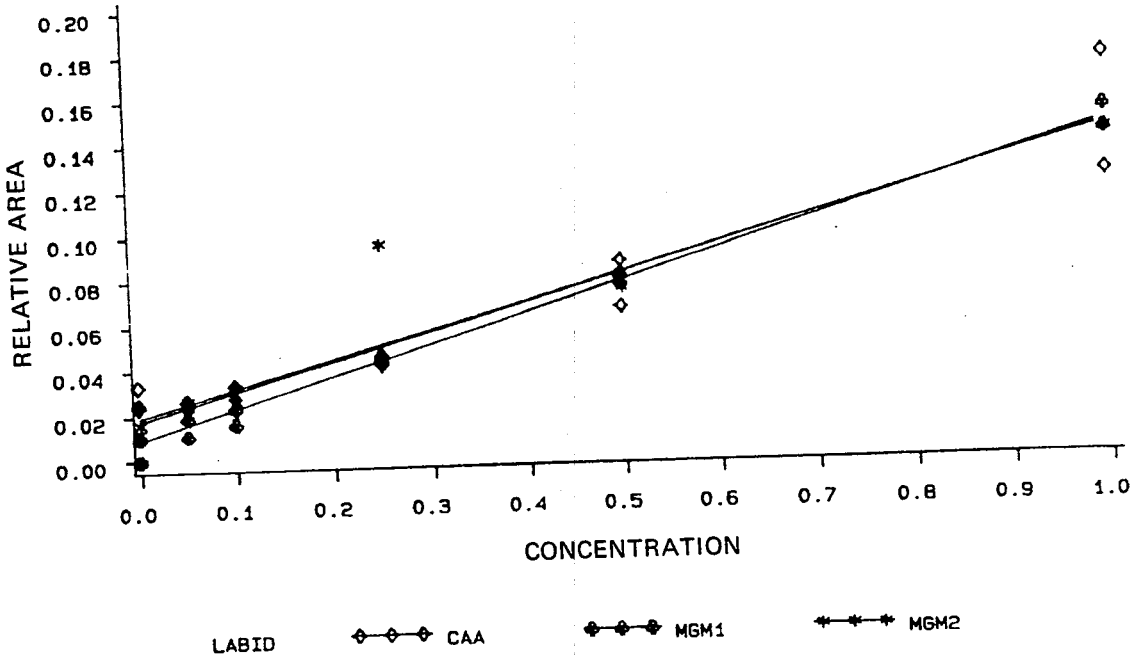



Figure E.5.6
**DETECTION LIMIT EXPERIMENT: CHLORONAPHTHALENE**

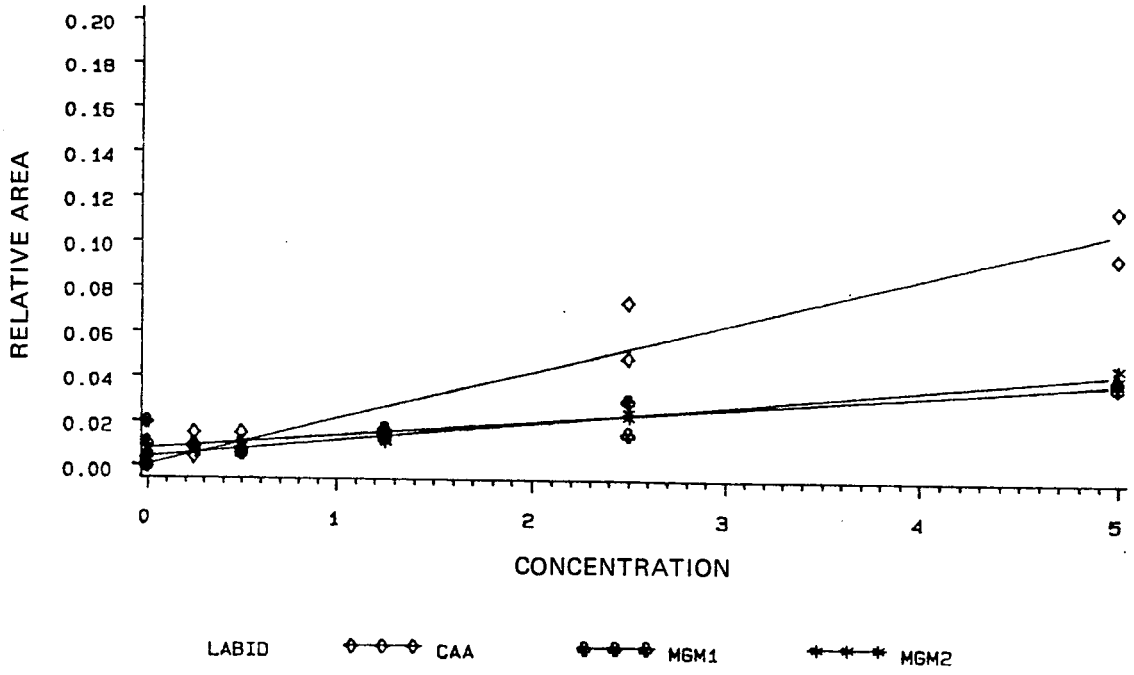



Figure E.5.7
**DETECTION LIMIT EXPERIMENT: B-BHC**

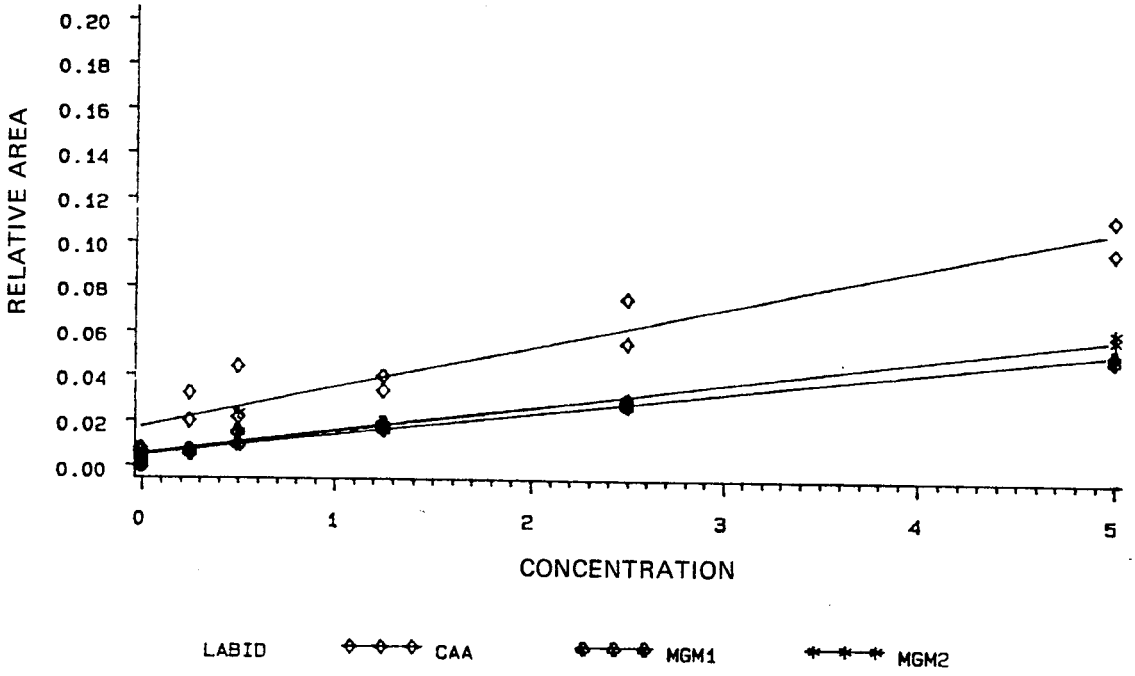



Figure E.5.8
**DETECTION LIMIT EXPERIMENT: G-BHC**

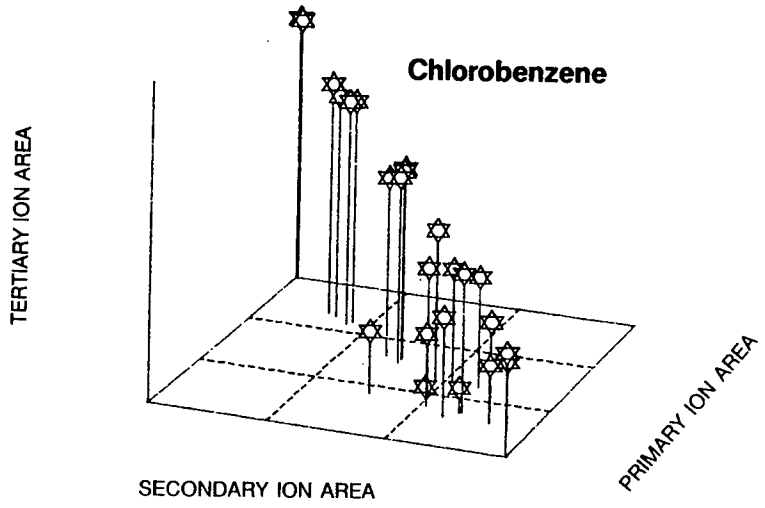
slightly differing sensitivities. Note that the relative area scale on the "Y" axis differs between the volatile compounds (chlorobenzene and dichlorobenzene) and the semivolatile compounds. This indicates that the sensitivity of the volatile analysis is greater than the sensitivity of the semivolatile analysis for spiking experiments. However, when environment samples which have contained the volatile compounds for a considerable period of time are analyzed, it appears that the semivolatile method is more sensitive. The cause of this difference between analysis of spikes and environmental samples is still under investigation, but appears to be due to the volatile extraction efficiency being less than the semivolatile.

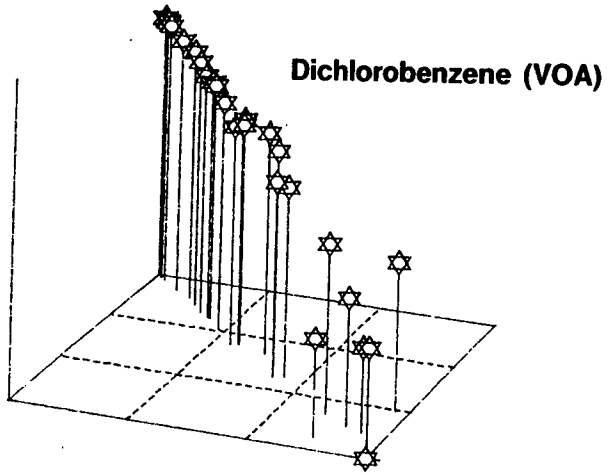
The regression lines are very sensitive to one or two "outlier" responses. For example, in Figure E.5.3, one response for a 0.25-ppb spike of 1,2-dichlorobenzene at the MGM laboratory was much higher than would be expected from the linear model. However, this was also at a concentration level where identification is uncertain. [Various robust regression techniques are being investigated to handle this problem.]

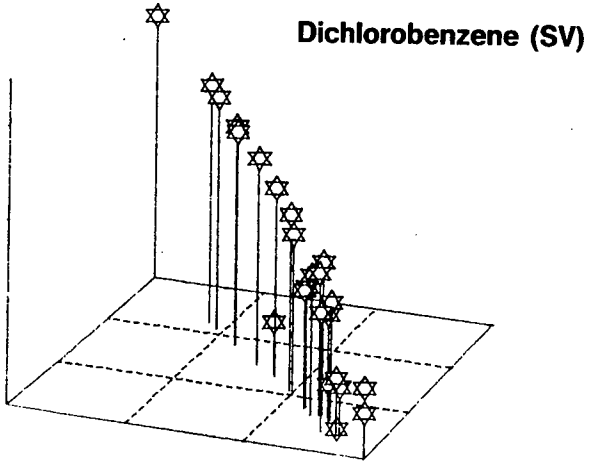
Figures E.5.9a and b and E.5.10a and b are the three-dimensional plots for the detection limit study, similar to those shown for the pilot study. In these figures, no pyramid or nonidentified values are shown because these criteria were not applied. Note the increased scatter of responses at low concentrations, particularly for the BHCs. The known spiking concentrations allow a better comparison between the LCICs and labs than the environmental samples.

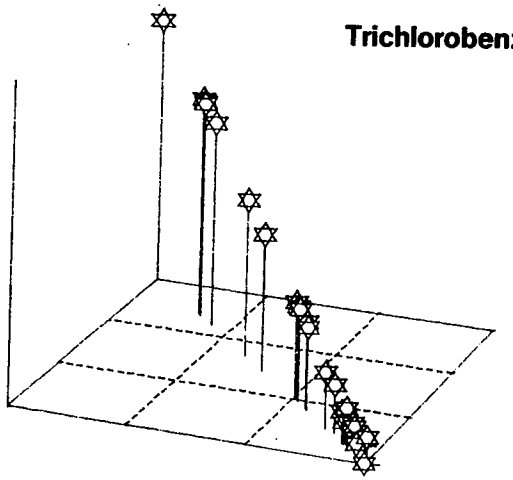
Tables E.5.1 and E.5.2 summarize the estimated method detection limits based on the proposed procedure. Table E.5.1 uses the full data set while Table E.5.2 uses the data set with some "obvious outliers" removed. Each table displays the method detection limit estimated by using each of the three ions as the quantitating ion. The MDLs are also estimated for each experiment and for the combined data from the two experiments at MGM. The last column in the table shows the average MDL as the arithmetic mean of the laboratory MDLs (e.g., CAA and MGM 1&2).

One unexpected result that is seen in these two tables is the consistency of the estimate over each of the three ions. Since the primary ion is chosen to be the ion with the largest response, the supposition would be that the third and weakest ion would have a larger estimated MDL because of additional variability at low levels. This turns out not to be the case.



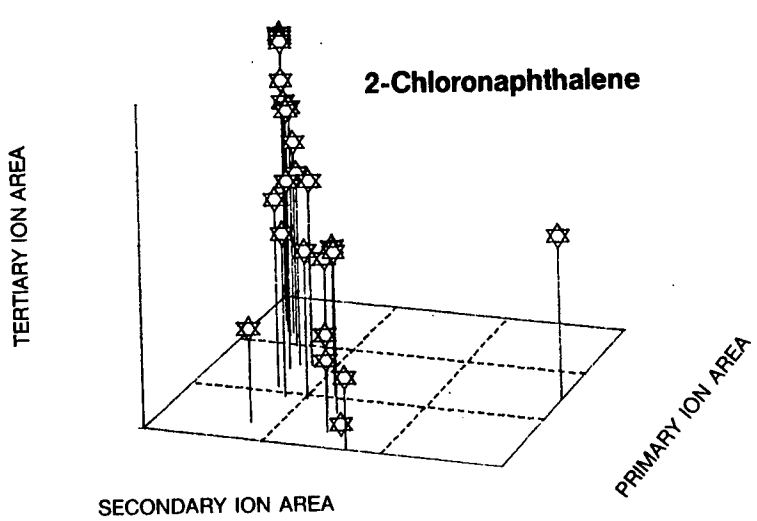



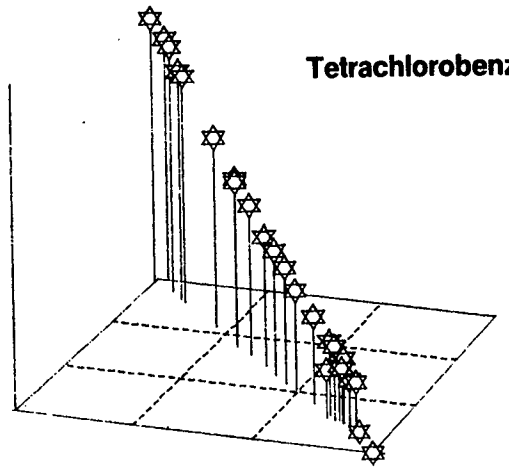



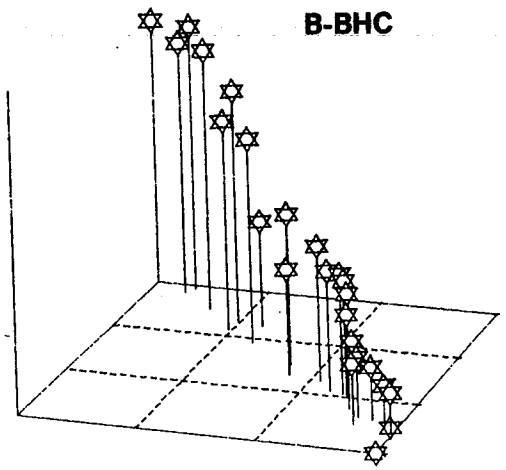

Notes: Vector length is proportional to the natural log of the concentration.

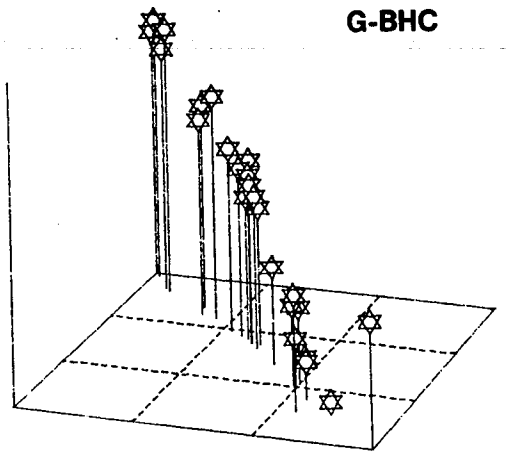
The presence of all 3 ions is the only identification criterion.

Figure E.5.9a
**STANDARDIZED ION AREA RATIOS DETECTION LIMIT DATA — MGM LABORATORY**



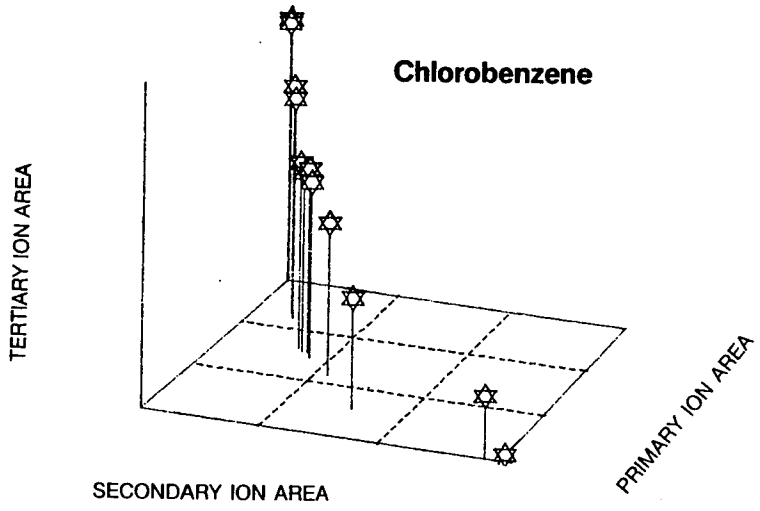



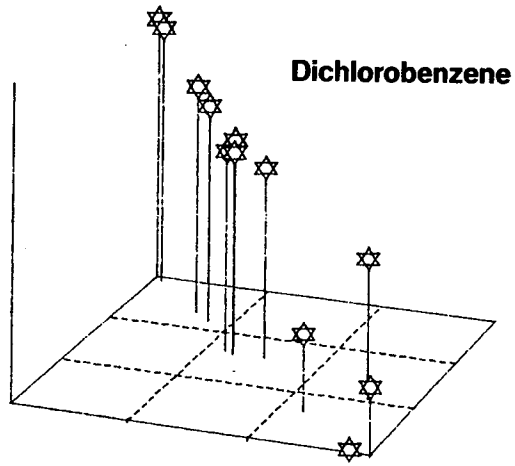



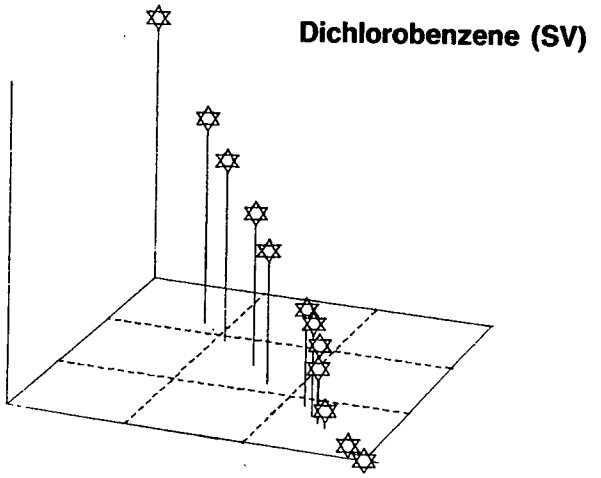

Notes: Vector length is proportional to the natural log of the concentration.

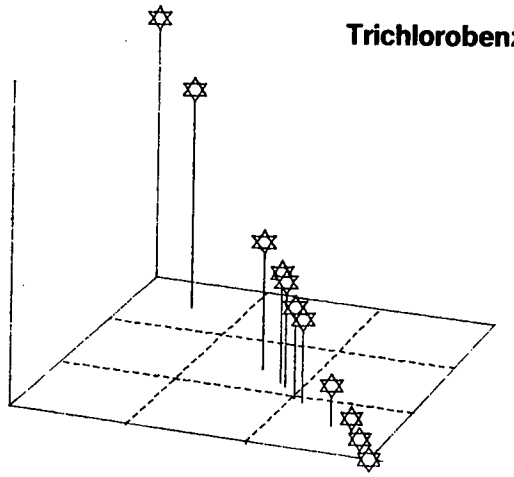
The presence of all 3 ions is the only identification criterion.

Figure E.5.9b
**STANDARDIZED ION AREA RATIOS DETECTION LIMIT DATA — MGM LABORATORY**



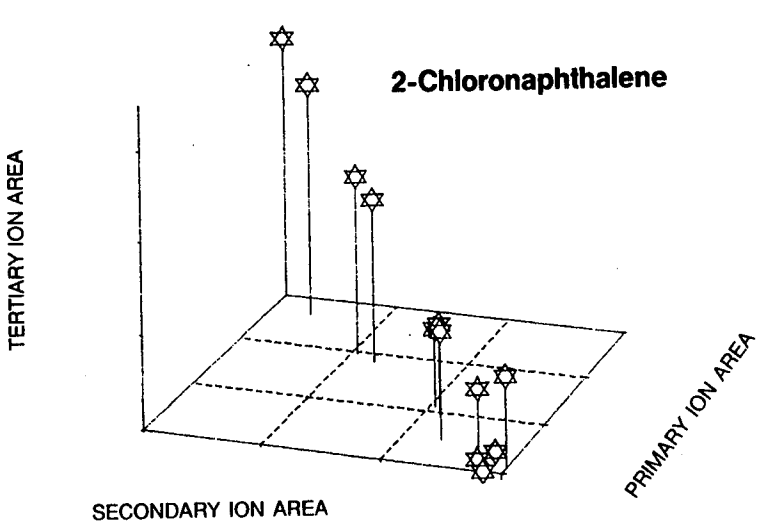



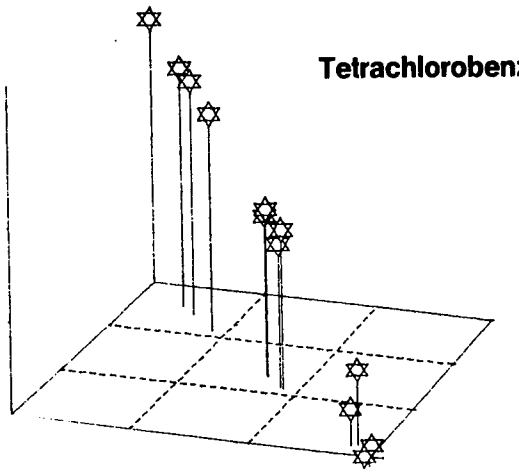



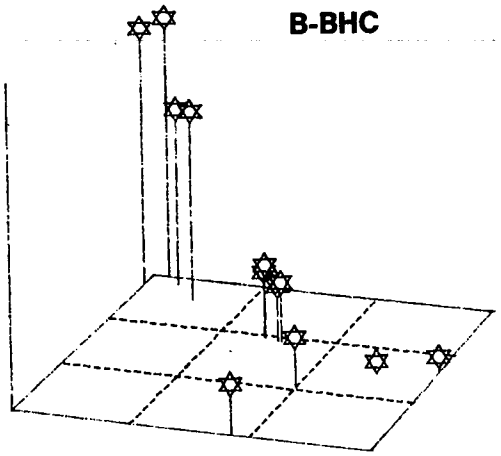

Notes: Vector length is proportional to the natural log of the concentration.

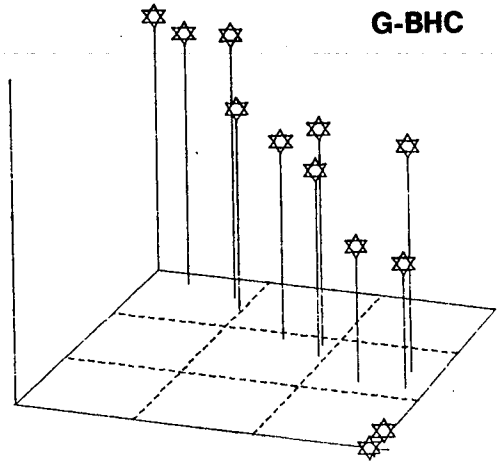
The presence of all 3 ions is the only identification criterion.

Figure E.5.10a
**STANDARDIZED ION AREA RATIOS DETECTION LIMIT DATA — CAA LABORATORY**




Notes: Vector length is proportional to the natural log of the concentration.

The presence of all 3 ions is the only identification criterion.

Figure E.5.10b
**STANDARDIZED ION AREA RATIOS DETECTION LIMIT DATA — CAA LABORATORY**

Table E.5.1
ESTIMATED DETECTION LIMIT
UNTRANSFORMED DATA
(ppb)

| LCIC | LAB/Data Set | | | | |
|---|---|---|---|---|---|
| | CAA | MGM 1 | MGM 2 | MGM 1&2 | Avg MDL |
| Chlorobenzene | | | | | |
| ion 1 | 0.22 | 0.12 | 0.05 | 0.08 | 0.15 |
| ion 2 | 0.28 | 0.19 | 0.08 | 0.14 | 0.21 |
| ion 3 | 0.20 | 0.22 | 0.15 | 0.18 | 0.19 |
| 1,2 Dichlorobenzene (VOA) | | | | | |
| ion 1 | 0.45 | 0.64 | 0.49 | 0.49 | 0.47 |
| ion 2 | 0.41 | 0.54 | 0.47 | 0.45 | 0.43 |
| ion 3 | 0.40 | 0.59 | 0.50 | 0.49 | 0.44 |
| 1,2 Dichlorobenzene | | | | | |
| ion 1 | 1.0 | 0.2 | 6.9 | 1.9 | 1.5 |
| ion 2 | 1.0 | 0.2 | 10.1 | 2.0 | 1.5 |
| ion 3 | 1.1 | 1.0 | [a] | 9.7 | 5.4 |
| 1,2,4 Trichlorobenzene | | | | | |
| ion 1 | 0.8 | 0.6 | 3.8 | 1.3 | 1.0 |
| ion 2 | 0.8 | 0.6 | 4.2 | 1.4 | 1.1 |
| ion 3 | 0.7 | 0.6 | 3.5 | 1.3 | 1.0 |
| 2 Chloronaphthalene | | | | | |
| ion 1 | 0.5 | 0.2 | 0.6 | 0.4 | 0.5 |
| ion 2 | 0.5 | 0.7 | 0.5 | 0.5 | 0.5 |
| ion 3 | 0.5 | 0.3 | 0.5 | 0.4 | 0.4 |
| 1,2,3,4 Tetrachlorobenzene | | | | | |
| ion 1 | 0.7 | 3.0 | 0.9 | 1.4 | 1.1 |
| ion 2 | 0.7 | 5.1 | 0.8 | 1.6 | 1.1 |
| ion 3 | 0.9 | 12.6 | 0.8 | 1.8 | 1.4 |
| Beta BHC | | | | | |
| ion 1 | 2.2 | 4.6 | 1.4 | 2.8 | 2.5 |
| ion 2 | 2.2 | 4.2 | 1.8 | 2.8 | 2.5 |
| ion 3 | 0.7 | 2.9 | 2.0 | 2.2 | 1.5 |
| Lindane | | | | | |
| ion 1 | 2.7 | 1.2 | 2.2 | 1.8 | 2.2 |
| ion 2 | 2.0 | 0.6 | 1.2 | 0.9 | 1.5 |
| ion 3 | 6.5 | 3.2 | 2.9 | 2.8 | 4.6 |

[a] Regression line has negative slope.

Table E.5.2
ESTIMATED DETECTION LIMIT
UNTRANSFORMED DATA
OUTLIERS REMOVED
(ppb)

| LCIC | LAB/Data Set | | | | |
|---|---|---|---|---|---|
| | CAA | MGM 1 | MGM 2 | MGM 1&2 | Avg MDL |
| Chlorobenzene | | | | | |
| ion 1 | 0.22 | 0.12 | 0.05 | 0.08 | 0.15 |
| ion 2 | 0.28 | 0.19 | 0.08 | 0.14 | 0.21 |
| ion 3 | 0.20 | 0.22 | 0.15 | 0.18 | 0.19 |
| 1,2 Dichlorobenzene (VOA) | | | | | |
| ion 1 | 0.45 | 0.64 | 0.49 | 0.49 | 0.47 |
| ion 2 | 0.41 | 0.54 | 0.47 | 0.45 | 0.43 |
| ion 3 | 0.40 | 0.59 | 0.50 | 0.49 | 0.44 |
| 1,2 Dichlorobenzene | | | | | |
| ion 1 | 0.1 | 0.2 | 0.4 | 0.6 | 0.8 |
| ion 2 | 1.0 | 0.2 | 0.4[a] | 0.6 | 0.8 |
| ion 3 | 1.1 | 1.0 | | 1.7 | 1.4 |
| 1,2,4 Trichlorobenzene | | | | | |
| ion 1 | 0.8 | 0.6 | 0.7 | 0.6 | 0.7 |
| ion 2 | 0.8 | 0.6 | 0.7 | 0.6 | 0.7 |
| ion 3 | 0.7 | 0.6 | 0.8 | 0.6 | 0.7 |
| 2 Chloronaphthalene | | | | | |
| ion 1 | 0.5 | 0.2 | 0.2 | 0.2 | 0.4 |
| ion 2 | 0.5 | 0.7 | 0.2 | 0.5 | 0.5 |
| ion 3 | 0.5 | 0.3 | 0.3 | 0.2 | 0.3 |
| 1,2,3,4 Tetrachlorobenzene | | | | | |
| ion 1 | 0.7 | 3.0 | 0.9 | 1.4 | 1.1 |
| ion 2 | 0.7 | 5.1 | 0.8 | 1.6 | 1.1 |
| ion 3 | 0.9 | 12.6 | 0.8 | 1.8 | 1.4 |
| Beta BHC | | | | | |
| ion 1 | 2.2 | 4.6 | 1.4 | 2.8 | 2.5 |
| ion 2 | 2.2 | 4.2 | 1.8 | 2.8 | 2.5 |
| ion 3 | 0.7 | 2.9 | 2.0 | 2.2 | 1.5 |
| Lindane | | | | | |
| ion 1 | 2.7 | 1.2 | 2.2 | 1.8 | 2.2 |
| ion 2 | 2.0 | 0.6 | 1.2 | 0.9 | 1.5 |
| ion 3 | 6.5 | 3.2 | 2.9 | 2.8 | 4.6 |

[a]Regression line has negative slope.

## E.5.3 MODEL ADEQUACY

The adequacy of the linear model was examined by generating a goodness of fit statistic for the regression equation for each ion and compound (Table E.5.3) (Neter and Wasserman, 1974, p. 119). This statistic is the ratio of the mean square error due to lack of fit divided by the mean square error due to pure error.

$$F = \frac{MSLF}{MSPE}$$

where

$$MSLF = SSE - SSPE = \sum_{i=1}^{N} (RA_i - RA_i)^2 - \sum_{j=1}^{C} \sum_{i=1}^{N_i} (RA_{ij} - \bar{RA}_j)^2$$

and

$$MSPE = \frac{SSPE}{N-C} \qquad C = \text{number of levels spiked}$$

This statistic will tend to be near 1.0 if the model is appropriate but will have larger values if the model is not appropriate.

Tables E.5.3 through E.5.5 present the results of this analysis for three models. Table E.5.3 is for the proposed linear model; Table E.5.4 has results for a model using the square root of the relative area; and Table E.5.5 is for a model using the log of the relative area.

The models of relative area response examined then are:

$RA = a C + b + e$ model 1

$RA = (a C + b + e)^2$ model 2

$RA = \exp(a C + b + e)$ model 3

The last column in Tables E.5.3, E.5.4, and E.5.5 is the F statistic for the hypothesis that the respective model is adequate versus the alternative that the model is not adequate. Each value of the statistic that is significant at the 95th percentile is flagged with an asterisk.

The tables contain the test statistics for a model fit to each of the three ions, for each lab, and for each compound. Of the 48 test statistics computed, 8 failed for the linear model, 18 failed for the quadratic model, and 17 failed for the exponential model. The linear model appears to perform the best overall of these alternatives; however, other variations of the regression model are being explored.

Table E.5.3
GOODNESS OF FIT
LINEAR MODEL

| Relative Factor of Ion # | Lab | Compound | Degrees of Freedom of Pure Error | Goodness of Fit 'F' Statistic |
|---|---|---|---|---|
| RA1 | CAA | Beta-BHC | 6 | 1.12065 |
| RA1 | MGM | Beta-BHC | 20 | 0.29220 |
| RA1 | CAA | ClBZ | 8 | 6.25223 * |
| RA1 | MGM | ClBZ | 21 | 0.53705 |
| RA1 | CAA | Clnapth | 6 | 0.36247 |
| RA1 | MGM | Clnapth | 20 | 0.95260 |
| RA1 | CAA | DClBZv | 8 | 6.65159 * |
| RA1 | MGM | DClBZv | 21 | 1.70832 |
| RA1 | CAA | DiCBZ | 6 | 0.46676 |
| RA1 | MGM | DiCBZ | 20 | 1.22086 |
| RA1 | CAA | Lindane | 6 | 0.83246 |
| RA1 | MGM | Lindane | 20 | 3.91509 * |
| RA1 | CAA | TetCBZ | 6 | 0.50070 |
| RA1 | MGM | TetCBZ | 20 | 0.06869 |
| RA1 | CAA | TriCBZ | 6 | 0.04468 |
| RA1 | MGM | TriCBZ | 20 | 1.70341 |
| RA2 | CAA | Beta-BHC | 6 | 1.54888 |
| RA2 | MGM | Beta-BHC | 20 | 1.06536 |
| RA2 | CAA | ClBZ | 8 | 7.41548 * |
| RA2 | MGM | ClBZ | 21 | 0.99956 |
| RA2 | CAA | Clnapth | 6 | 0.30797 |
| RA2 | MGM | Clnapth | 20 | 1.13633 |
| RA2 | CAA | DClBZv | 8 | 4.60536 * |
| RA2 | MGM | DClBZv | 21 | 1.45951 |
| RA2 | CAA | DiCBZ | 6 | 0.35042 |
| RA2 | MGM | DiCBZ | 20 | 1.25530 |
| RA2 | CAA | Lindane | 6 | 1.31472 |
| RA2 | MGM | Lindane | 20 | 2.98468 * |
| RA2 | CAA | TetCBZ | 6 | 0.45756 |
| RA2 | MGM | TetCBZ | 20 | 0.03357 |
| RA2 | CAA | TriCBZ | 6 | 0.04399 |
| RA2 | MGM | TriCBZ | 20 | 1.82291 |
| RA3 | CAA | Beta-BHC | 6 | 1.32791 |
| RA3 | MGM | Beta-BHC | 20 | 3.40032 * |
| RA3 | CAA | ClBZ | 8 | 7.40658 * |
| RA3 | MGM | ClBZ | 21 | 1.68651 |
| RA3 | CAA | Clnapth | 6 | 0.14939 |
| RA3 | MGM | Clnapth | 20 | 0.88197 |
| RA3 | CAA | DClBZv | 8 | 2.54124 |
| RA3 | MGM | DClBZv | 21 | 1.89711 |
| RA3 | CAA | DiCBZ | 6 | 0.35839 |
| RA3 | MGM | DiCBZ | 20 | 0.88583 |
| RA3 | CAA | Lindane | 6 | 0.33136 |
| RA3 | MGM | Lindane | 20 | 1.93178 |
| RA3 | CAA | TetCBZ | 6 | 0.87531 |
| RA3 | MGM | TetCBZ | 20 | 0.14483 |
| RA3 | CAA | TriCBZ | 6 | 0.10131 |
| RA3 | MGM | TriCBZ | 20 | 1.44399 |

*Statistically significant at the 95th percentile.

Table E.5.4
GOODNESS OF FIT
SQUARE ROOT TRANSFORMATION

| Square Root Relative Area of Ion # | Lab | Compound | Degrees of Freedom of Pure Error | Goodness of Fit 'F' Statistic |
|---|---|---|---|---|
| SQRTRA1 | CAA | Beta-BHC | 6 | 1.76424 |
| SQRTRA1 | MGM | Beta-BHC | 20 | 0.36469 |
| SQRTRA1 | CAA | ClBZ | 8 | 15.91910 * |
| SQRTRA1 | MGM | ClBZ | 21 | 41.03719 * |
| SQRTRA1 | CAA | Clnapth | 6 | 0.26281 |
| SQRTRA1 | MGM | Clnapth | 20 | 2.82364 * |
| SQRTRA1 | CAA | DClBZv | 8 | 3.91317 * |
| SQRTRA1 | MGM | DClBZv | 21 | 3.93559 * |
| SQRTRA1 | CAA | DiCBZ | 6 | 0.51273 |
| SQRTRA1 | MGM | DiCBZ | 20 | 1.40988 |
| SQRTRA1 | CAA | Lindane | 6 | 2.91300 |
| SQRTRA1 | MGM | Lindane | 20 | 8.24072 * |
| SQRTRA1 | CAA | TetCBZ | 6 | 0.61806 |
| SQRTRA1 | MGM | TetCBZ | 20 | 0.43324 |
| SQRTRA1 | CAA | TriCBZ | 6 | 0.12343 |
| SQRTRA1 | MGM | TriCBZ | 20 | 1.95363 |
| SQRTRA2 | CAA | Beta-BHC | 6 | 9.09186 * |
| SQRTRA2 | MGM | Beta-BHC | 20 | 0.78347 |
| SQRTRA2 | CAA | ClBZ | 8 | 10.05346 * |
| SQRTRA2 | MGM | ClBZ | 21 | 15.76009 * |
| SQRTRA2 | CAA | Clnapth | 6 | 0.16872 |
| SQRTRA2 | MGM | Clnapth | 20 | 2.33555 |
| SQRTRA2 | CAA | DClBZv | 8 | 3.41143 |
| SQRTRA2 | MGM | DClBZv | 21 | 3.77790 * |
| SQRTRA2 | CAA | DiCBZ | 6 | 0.36776 |
| SQRTRA2 | MGM | DiCBZ | 20 | 1.45905 |
| SQRTRA2 | CAA | Lindane | 6 | 11.92555 * |
| SQRTRA2 | MGM | Lindane | 20 | 6.68955 * |
| SQRTRA2 | CAA | TetCBZ | 6 | 0.56166 |
| SQRTRA2 | MGM | TetCBZ | 20 | 0.41246 |
| SQRTRA2 | CAA | TriCBZ | 6 | 0.10844 |
| SQRTRA2 | MGM | TriCBZ | 20 | 2.14862 |
| SQRTRA3 | CAA | Beta-BHC | 6 | 6.78058 * |
| SQRTRA3 | MGM | Beta-BHC | 20 | 8.28627 * |
| SQRTRA3 | CAA | ClBZ | 8 | 15.98710 * |
| SQRTRA3 | MGM | ClBZ | 21 | 13.46367 * |
| SQRTRA3 | CAA | Clnapth | 6 | 0.30409 |
| SQRTRA3 | MGM | Clnapth | 20 | 2.28659 |
| SQRTRA3 | CAA | DClBZv | 8 | 2.22332 |
| SQRTRA3 | MGM | DClBZv | 21 | 3.93560 * |
| SQRTRA3 | CAA | DiCBZ | 6 | 0.38590 |
| SQRTRA3 | MGM | DiCBZ | 20 | 0.75380 |
| SQRTRA3 | CAA | Lindane | 6 | 0.54112 |
| SQRTRA3 | MGM | Lindane | 20 | 8.01084 * |
| SQRTRA3 | CAA | TetCBZ | 6 | 0.99669 |
| SQRTRA3 | MGM | TetCBZ | 20 | 0.22080 |
| SQRTRA3 | CAA | TriCBZ | 6 | 0.20308 |
| SQRTRA3 | MGM | TriCBZ | 20 | 1.53439 |

*Statistically significant at the 95th percentile.

Table E.5.5
GOODNESS OF FIT
LOG TRANSFORMATION

| Relative Factor of Ion # | Lab | Compound | Degrees of Freedom of Pure Error | Goodness of Fit 'F' Statistic |
|---|---|---|---|---|
| LNRA1 | CAA | Beta-BHC | 6 | 2.37675 |
| LNRA1 | MGM | Beta-BHC | 20 | 1.11791 |
| LNRA1 | CAA | ClBZ | 8 | 14.3017 * |
| LNRA1 | MGM | ClBZ | 21 | 102.398 * |
| LNRA1 | CAA | Clnapth | 6 | 0.911165 |
| LNRA1 | MGM | Clnapth | 20 | 2.29978 |
| LNRA1 | CAA | DClBZv | 8 | 1.32919 |
| LNRA1 | MGM | DClBZv | 21 | 11247200 * |
| LNRA1 | CAA | DiCBZ | 6 | 0.57284 |
| LNRA1 | MGM | DiCBZ | 20 | 1.74993 |
| LNRA1 | CAA | Lindane | 6 | 7.67192 * |
| LNRA1 | MGM | Lindane | 20 | 4.66411 * |
| LNRA1 | CAA | TetCBZ | 6 | 0.711218 |
| LNRA1 | MGM | TetCBZ | 20 | 1.12216 |
| LNRA1 | CAA | TriCBZ | 6 | 0.291878 |
| LNRA1 | MGM | TriCBZ | 20 | 2.02139 |
| LNRA2 | CAA | Beta-BHC | 6 | 15316800 * |
| LNRA2 | MGM | Beta-BHC | 20 | 1.15562 |
| LNRA2 | CAA | ClBZ | 8 | 8.41227 * |
| LNRA2 | MGM | ClBZ | 21 | 31.916 * |
| LNRA2 | CAA | Clnapth | 6 | 1.22632 |
| LNRA2 | MGM | Clnapth | 20 | 2.34116 |
| LNRA2 | CAA | DClBZv | 8 | 1.42219 |
| LNRA2 | MGM | DClBZv | 21 | 11381300 * |
| LNRA2 | CAA | DiCBZ | 6 | 0.41568 |
| LNRA2 | MGM | DiCBZ | 20 | 1.82522 |
| LNRA2 | CAA | Lindane | 6 | 26890400 * |
| LNRA2 | MGM | Lindane | 20 | 4.76217 * |
| LNRA2 | CAA | TetCBZ | 6 | 0.656039 |
| LNRA2 | MGM | TetCBZ | 20 | 1.10622 |
| LNRA2 | CAA | TriCBZ | 6 | 0.259211 |
| LNRA2 | MGM | TriCBZ | 20 | 2.26815 |
| LNRA3 | CAA | Beta-BHC | 6 | 25843200 * |
| LNRA3 | MGM | Beta-BHC | 20 | 6.50349 * |
| LNRA3 | CAA | ClBZ | 8 | 18.3066 * |
| LNRA3 | MGM | ClBZ | 21 | 25.8588 * |
| LNRA3 | CAA | Clnapth | 6 | 1.46795 |
| LNRA3 | MGM | Clnapth | 20 | 2.03226 |
| LNRA3 | CAA | DClBZv | 8 | 0.930092 |
| LNRA3 | MGM | DClBZv | 21 | 6.34745 * |
| LNRA3 | CAA | DiCBZ | 6 | 0.412652 |
| LNRA3 | MGM | DiCBZ | 20 | 0.592881 |
| LNRA3 | CAA | Lindane | 6 | 0.892933 |
| LNRA3 | MGM | Lindane | 20 | 8.60795 * |
| LNRA3 | CAA | TetCBZ | 6 | 1.05883 |
| LNRA3 | MGM | TetCBZ | 20 | 0.720998 |
| LNRA3 | CAA | TriCBZ | 6 | 0.366251 |
| LNRA3 | MGM | TriCBZ | 20 | 1.53813 |

*Statistically significant at the 95th percentile.

## E.6.0 CONCLUSION AND RECOMMENDATION

In response to the concerns raised by the 1980 EPA study, several definitions and estimators of a method detection limit were investigated. A modified version of the Hubaux and Vos regression estimator is proposed for use during the Love Canal habitability study. This estimator has several advantages over the Currie or Glaser et al. methods:

- The method lends itself naturally to informal checks of the assumptions: constant standard deviation, constant recovery $\beta_1$, and normality of measurements at each actual concentration.

- The method makes it clear that the estimated MDL is an estimated concentration for which 95 percent of the measurements are greater than 95 percent of the measurements on blanks.

- The method uses measurements taken over a range of values near the MDL and so incorporates more information about the GC/MS process than either the Currie or Glaser et al. methods.

The estimator still needs further refinement, for example to better include the information provided by the identification limits of the GC/MS process. However, it appears that a modified Hubaux and Vos estimator will adequately provide an estimate of the MDL for the Love Canal habitability study.

The major recommendation of this study is that continued development be conducted on the proposed MDL estimator.

## E.7.0 REFERENCES

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