

**Chlorinated Dibenzo-*p*-dioxin  
and Dibenzofuran Residue  
Levels in Food**

Final Report

By  
John S. Stanley and Karin M. Bauer

**For the State of California  
Air Resources Board  
Research Division  
1800 15th Street  
Sacramento, California 95812**

Attn: Ralph Propper

ARB Contract No. A6-197-32  
MRI Project No. 8922-A

October 26, 1989

### DISCLAIMER

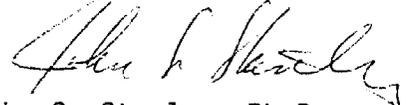
The statements and conclusions in this report are those of the contractor and not necessarily those of the State of California Air Resources Board. The material reported herein is not to be construed as actual or implied endorsement of such products.

PREFACE

This report presents the results of a study to determine the residue levels of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in foodstuffs collected within two California urban areas. This report presents the experimental design, the analytical procedures, the results of the chemical and statistical analyses, and a comparison of the compound levels determined in this study with results from analytical efforts conducted in other countries. This research effort was conducted for the State of California's Air Resources Board, Research Division, Ralph Propper, Project Officer.

The chemical analysis efforts were completed under the direction of Dr. John Stanley and Mr. Paul Cramer, with assistance from Ms. Kathy Boggess, Ms. Maurene Greene, Mr. Michael McGrath, Mr. Michael Molloy, and Mr. Kelly Thornburg. The statistical analysis efforts were completed under the direction of Ms. Karin Bauer with assistance from Ms. Jean Pelkey.

MIDWEST RESEARCH INSTITUTE

  
John S. Stanley, Ph.D.  
Program Manager

Approved:

  
John E. Going, Ph.D.  
Director  
Chemical Sciences Department

October 26, 1989

## TABLE OF CONTENTS

|            | <u>Page</u>  |
|------------|--|
| 1.0        | Summary..... 1   |
| 2.0        | Introduction..... 2  |
|            | 2.1 Statement of Work..... 2   |
|            | 2.2 Program Objectives..... 4  |
|            | 2.3 Report Organization..... 4   |
| 3.0        | Experimental Approach..... 5   |
|            | 3.1 Survey Design..... 5   |
|            | 3.2 Analytical Methods..... 9  |
| 4.0        | Results..... 17  |
|            | 4.1 Chemical Analysis Results..... 17  |
|            | 4.2 Quality Control Analysis Results..... 30   |
|            | 4.3 Statistical Analysis Results..... 44   |
| 5.0        | Discussion..... 84   |
|            | 5.1 PCDD and PCDF Residue Levels in Foodstuffs..... 84                                   |
|            | 5.2 PCDD and PCDF Intake Via Food Consumption..... 92                                    |
| 6.0        | Bibliography..... 94   |
| Appendix A | --California Air Resources Board Food Study..... A-1                                     |
| Appendix B | --Analytical Protocol for Determination of PCDDs and<br>and PCDFs in Foodstuffs..... B-1 |
| Appendix C | --Quality Assurance Program Plan (QAPP)..... C-1   |

LIST OF FIGURES

| <u>Figure</u> |   | <u>Page</u> |
|---------------|---|-------------|
| 4-1           | Reconstructed Ion Chromatograms From the HRMS Analysis of an Unspiked and a Spiked Egg Composite for TCDF and TCDD.....           | 39          |
| 4-2           | Reconstructed Ion Chromatograms From the HRMS Analysis of an Unspiked and a Spiked Egg Composite for PeCDF and PeCDD Isomers..... | 40          |
| 4-3           | Reconstructed Ion Chromatograms From the HRMS Analysis of an Unspiked and a Spiked Egg Composite for HxCDF and HxCDD Isomers..... | 41          |
| 4-4           | Reconstructed Ion Chromatograms From the HRMS Analysis of an Unspiked and a Spiked Egg Composite for HpCDF and HpCDD Isomers..... | 42          |
| 4-5           | Reconstructed Ion Chromatograms From the HRMS Analysis of an Unspiked and a Spiked Egg Composite for OCDF and OCDD.....           | 43          |

LIST OF TABLES

| <u>Table</u> |  | <u>Page</u> |
|--------------|--|-------------|
| 2-1          | Chlorinated Dioxins and Dibenzofurans of Concern.....  | 4           |
| 3-1          | Internal Standard Spiking Solutions for Determination of<br>PCDDs and PCDFs in Foodstuffs.....                                   | 12          |
| 3-2          | HRGC/HRMS Operating Conditions for PCDD/PCDF Analysis.....   | 14          |
| 3-3          | Concentration Calibration Solutions for PCDD/PCDF.....   | 15          |
| 4-1          | HRGC/HRMS Data Summaries for Fish (San Francisco).....   | 20          |
| 4-2          | HRGC/HRMS Data Summaries for Fish (Los Angeles).....   | 21          |
| 4-3          | HRGC/HRMS Data Summaries for Beef (Los Angeles).....   | 22          |
| 4-4          | HRGC/HRMS Data Summaries for Beef (San Francisco).....   | 23          |
| 4-5          | HRGC/HRMS Data Summaries for Bovine Milk (Los Angeles).....  | 24          |
| 4-6          | HRGC/HRMS Data Summaries for Bovine Milk (San Francisco)....   | 25          |
| 4-7          | HRGC/HRMS Data Summaries for Pork (Los Angeles).....   | 26          |
| 4-8          | HRGC/HRMS Data Summaries for Pork (San Francisco).....   | 27          |
| 4-9          | HRGC/HRMS Data Summaries for Chicken (Los Angeles).....  | 28          |
| 4-10         | HRGC/HRMS Data Summaries for Chicken (San Francisco).....  | 29          |
| 4-11         | HRGC/HRMS Data Summaries for Eggs (Los Angeles).....   | 31          |
| 4-12         | HRGC/HRMS Data Summaries for Eggs (San Francisco).....   | 32          |
| 4-13         | Summary of the Analysis Results for Laboratory Method<br>Blanks .....  | 33          |
| 4-14         | Method Accuracy--Fish.....   | 34          |
| 4-15         | Method Accuracy--Milk.....   | 35          |
| 4-16         | Method Accuracy--Chicken.....  | 36          |
| 4-17         | Method Accuracy--Pork.....   | 37          |
| 4-18         | Method Accuracy--Whole Egg Basis.....  | 38          |
| 4-19         | Composites Per Foodstuff and City.....   | 45          |
| 4-20         | Summary of Compositing Scheme Per Foodstuff and City.....  | 46          |
| 4-21         | Frequency of Detection of Specific PCDD and PCDF Compounds<br>in Foodstuffs Collected From Los Angeles and<br>San Francisco..... | 47          |
| 4-22         | Frequency of Detection of Specific PCDD and PCDF Compounds<br>in Saltwater Fish Composites.....                                  | 50          |

LIST OF TABLES (continued)

| <u>Table</u> |   | <u>Page</u> |
|--------------|---|-------------|
| 4-23         | Frequency of Detection of Specific PCDD and PCDF Compounds<br>in Freshwater Fish Composites.....  | 51          |
| 4-24         | Frequency of Detection of Specific PCDD and PCDF Compounds<br>in Chicken.....   | 52          |
| 4-25         | Frequency of Detection of Specific PCDD and PCDF Compounds<br>in Beef.....  | 53          |
| 4-26         | Frequency of Detection of Specific PCDD and PCDF Compounds<br>in Pork.....  | 54          |
| 4-27         | Frequency of Detection of Specific PCDD and PCDF Compounds<br>in Bovine Milk.....   | 55          |
| 4-28         | Frequency of Detection of Specific PCDD and PCDF Compounds<br>in Eggs.....  | 56          |
| 4-29         | Summary of Detects and Nondetects by City and Foodstuff<br>Across Compounds.....  | 57          |
| 4-30         | Weighted Statistical Estimates for Concentration Levels<br>Based on Food Composites With Measurable Levels of<br>Specific Compounds--Saltwater Fish.....  | 59          |
| 4-31         | Weighted Statistical Estimates for Concentration Levels<br>Based on Food Composites With Measurable Levels of<br>Specific Compounds--Freshwater Fish..... | 60          |
| 4-32         | Weighted Statistical Estimates for Concentration Levels<br>Based on Food Composites With Measurable Levels of<br>Specific Compounds--Chicken.....         | 61          |
| 4-33         | Weighted Statistical Estimates for Concentration Levels<br>Based on Food Composites With Measurable Levels of<br>Specific Compounds--Beef.....            | 62          |
| 4-34         | Weighted Statistical Estimates for Concentration Levels<br>Based on Food Composites With Measurable Levels of<br>Specific Compounds--Pork.....            | 63          |
| 4-35         | Weighted Statistical Estimates for Concentration Levels<br>Based on Food Composites With Measurable Levels of<br>Specific Compounds--Bovine Milk.....     | 64          |
| 4-36         | Weighted Statistical Estimates for Concentration Levels<br>Based on Food Composites With Measurable Levels of<br>Specific Compounds--Eggs.....            | 65          |
| 4-37         | Weighted Statistical Estimates for PCDD and PCDF<br>Concentrations in Saltwater Fish Based on All Data.....   | 67          |
| 4-38         | Weighted Statistical Estimates for PCDD and PCDF<br>Concentrations in Freshwater Fish Based on All Data.....  | 69          |

LIST OF TABLES (continued)

| <u>Table</u> |  | <u>Page</u> |
|--------------|--|-------------|
| 4-39         | Weighted Statistical Estimates for PCDD and PCDF<br>Concentrations in Chicken Based on All Data.....   | 71          |
| 4-40         | Weighted Statistical Estimates for PCDD and PCDF<br>Concentrations in Beefn Based on All Data.....   | 73          |
| 4-41         | Weighted Statistical Estimates for PCDD and PCDF<br>Concentrations in Pork Based on All Data.....  | 75          |
| 4-42         | Weighted Statistical Estimates for PCDD and PCDF<br>Concentrations in Bovine Milk Based on All Data.....                                       | 77          |
| 4-43         | Weighted Statistical Estimates for PCDD and PCDF<br>Concentrations in Eggs Based on All Data.....  | 79          |
| 4-44         | Summary of Maximum Concentration Levels for Compounds<br>Detected in at Least One Food Composite.....  | 81          |
| 4-45         | Summary of Weighted Mean Concentrations for Compounds<br>Above the Detection Level in Specific Food Composites.....                            | 82          |
| 4-46         | Summary of Weighted Mean Concentrations for All PCDD and<br>PCDF Compounds Based on All Measured Levels and<br>Estimated Detection Limits..... | 83          |
| 5-1          | Higher Chlorinated Dioxin Residues in Various Foods<br>Collected in the United States (1979-1984).....   | 86          |
| 5-2          | PCDD and PCDF Levels of Eight Cows' Milk Samples.....  | 88          |
| 5-3          | Levels of PCDD and PCDF in Food From the Federal<br>Republic of Germany.....   | 90          |
| 5-4          | Concentrations of PCDDs and PCDFs in Foods Representative<br>of the Japanese Diet.....   | 91          |
| 5-5          | Average Annual Consumption of Food Products on a National<br>and/or California Basis.....  | 93          |
| 5-6          | Average Lipid Consumption Based on Specific Food Product<br>Usage.....   | 93          |

## ABSTRACT

The chemical analysis of selected foods was conducted to provide an estimate of the residue levels of PCDDs and PCDFs. The foodstuffs included saltwater fish, freshwater fish, beef, chicken, pork, bovine milk, and eggs. The foodstuffs were collected from San Francisco and Los Angeles. Emphasis was placed on the collection of foodstuffs of California origin. Individual foods collected from multiple sites within San Francisco and Los Angeles were composited for analysis of the residue levels. Detectable levels of PCDDs and PCDFs were identified in all but the egg samples that were analyzed. Overall, the freshwater fish composites were found to have the highest incidence of detectable levels. The order of highest to lowest incidence of detection follows: freshwater fish > saltwater fish > pork and chicken > beef and milk > eggs. All data were generated from a sample size of approximately 10 g of extractable fatty materials. All data are presented to reflect lipid or fat concentrations such that extrapolation with other data bases can be achieved.



## SECTION 1.0

### SUMMARY

The research program described in this report required the random collection of multiple samples of seven specific foodstuffs from the San Francisco and Los Angeles areas. The foodstuffs included saltwater fish, freshwater fish, beef (hamburger), chicken, pork (bacon), bovine milk, and eggs. The individual food samples collected were composited for analysis of the residue levels of PCDDs and PCDFs (specifically the 2,3,7,8-substituted compounds). The composites consisted of up to 31 individually collected items, and five to eight composites were analyzed for each foodstuff. Detectable levels of specific PCDDs and PCDFs were identified in all but the egg samples that were analyzed. Overall the freshwater fish composites were found to have the highest incidence of detectable levels. The order of highest to lowest incidence of detection follows: freshwater fish > saltwater fish > pork and chicken > beef and milk > eggs.

The compounds detected in the fish samples included the 2,3,7,8-substituted tetra- through octachloro-PCDDs, but the PCDFs were limited to primarily the 2,3,7,8-TCDF. The tetrachloro compounds were not consistently detected in any of the other foodstuffs except milk. The residue levels detected in the beef, chicken, and pork were generally limited to the hexa- through octachloro compounds. Estimates of the detection limits on a sample-to-sample basis are provided in this report. These method detection limits were calculated using the observed noise signals and hence should provide an upper estimate of residue level for consideration in risk assessments.

Although many of the analyses resulted in estimated detection limits for specific compounds, there is evidence that further modifications of the methods, either increased sample size or advances in instrumentation allowing the analyst to achieve lower levels of detection, would result in measurable levels of the PCDDs and PCDFs.

The accuracy of the residue levels reported in this study is supported by the analytical data generated from quality control samples that were prepared from the specific food matrices and analyzed along with the design samples. In addition, the analysis of laboratory method blanks, including all reagents and procedures used in preparing the actual samples, demonstrated no background contribution from the laboratory. These data support the identification of the PCDDs and PCDFs in the foodstuffs at the low parts per trillion level.

## SECTION 2.0

### INTRODUCTION

Midwest Research Institute (MRI) was contracted by the State of California Air Resources Board (ARB) to determine the concentration levels of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in foods. Specific emphasis was on California-raised products. The results of this project will be used by the ARB as part of its assessment of the impact that major stationary combustion sources (municipal incinerators, hazardous waste incinerators, wire reclamation facilities, hospital incinerators, etc.) will have on the air quality and ultimately human health in the South Coast Air Basin.

This final report provides:

1. Details of the experimental design: (a) the survey design used to collect specific food products from two urban areas and (b) the analytical protocol used to provide accurate measurements of the 2,3,7,8-substituted PCDDs and PCDFs at low parts per trillion (picograms/gram, pg/g) levels.
2. The results of the chemical analysis of 50 specific food composites and the results of quality control samples analyzed.
3. The approach to statistical analysis of the analytical data and the extrapolation of the analytical data to average levels expected in California foods.
4. A comparison of the results with other specific studies that focus on the levels of the 2,3,7,8-substituted PCDDs and PCDFs in foodstuffs.

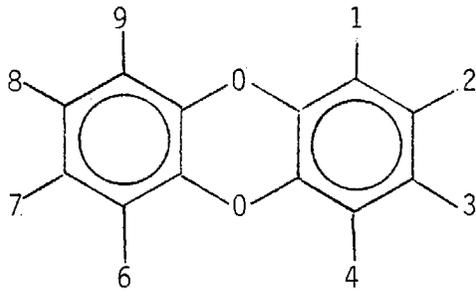
#### 2.1 Statement of Work

Through this research effort, MRI has determined polychlorinated dibenzo-*p*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) residue levels in food. The compounds of primary interest are those which contain four to eight chlorines per molecule and are substituted in the 2, 3, 7, and 8 structural positions. The specific PCDD and PCDF congeners of interest are identified in Table 2-1.

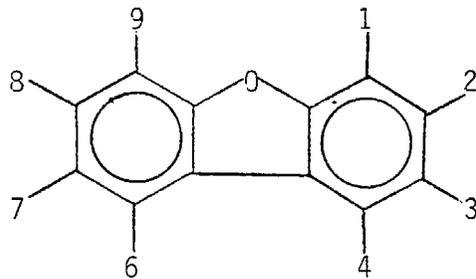
Table 2-1. Chlorinated Dioxins and Dibenzofurans of Concern

|             | <u>Dioxins</u>                            | <u>Dibenzofurans</u>                                     |
|-------------|---|--|
| Tetrachloro | 2,3,7,8                                   | 2,3,7,8  |
| Pentachloro | 1,2,3,7,8                                 | 1,2,3,7,8<br>2,3,4,7,8                                   |
| Hexachloro  | 1,2,3,4,7,8<br>1,2,3,6,7,8<br>1,2,3,7,8,9 | 1,2,3,4,7,8<br>1,2,3,6,7,8<br>1,2,3,7,8,9<br>2,3,4,6,7,8 |
| Heptachloro | 1,2,3,4,6,7,8                             | 1,2,3,4,6,7,8<br>1,2,3,4,7,8,9                           |

NOTE: The numbers indicate the position of chlorine atoms on the dioxin or dibenzofuran molecule (see diagram below).



Dibenzo-*p*-dioxin



Dibenzo-*p*-furan

## 2.2 Program Objectives

The objectives of this program were to provide the State of California ARB with a preliminary estimate of the residue levels of PCDDs and PCDFs in food, with specific emphasis on California products. This has been accomplished through a program which required prioritization of foodstuffs, field sampling, and state-of-the-art chemical analysis of selected foods.

The chemical analyses of the selected foods were conducted for specific PCDD and PCDF compounds (compounds with four to eight chlorines and substituted in the 2, 3, 7, and 8 structural positions). These data will be used by ARB to assess the relative impact of dietary concentrations of these compounds versus airborne concentrations of the compounds on body burden levels of PCDDs and PCDFs in the general California population.

The survey testing and chemical analysis were conducted to ensure the quality and reliability of the data. Of considerable importance was the need to establish data of known quality that can be compared to the airborne concentration and body burden studies that will be conducted by the ARB.

## 2.3 Report Organization

Section 3 presents the experimental approach, specifically the survey design to collect food samples based on specific food products and geographic region. This section also addresses the issue of the potential for selecting foods of California origin and the sample collection protocol. Section 3 also provides an overview of the state-of-the-art analytical methodology that was used to measure accurately the levels of PCDDs and PCDFs in foodstuffs. The chemical and statistical analysis results, as well as the supporting quality control sample results, are presented in Section 4. Section 5 presents a synopsis of other studies that have focused on the levels of PCDDs and PCDFs in foodstuffs to which the results of this ARB study of California foodstuffs may be compared. This section was prepared from a review of the existing literature on the detection of the 2,3,7,8-substituted PCDDs and PCDFs in foods. Section 6 presents a detailed bibliography of references that are pertinent to the issue of determining the PCDD and PCDF residue levels in food.

Appendix A identifies locations of food sources that were identified for collection of the priority foodstuffs (beef, pork, fish, poultry, eggs, and milk). Detailed descriptions of the analytical protocol and the QAPP are presented in Appendices B and C, respectively.

## SECTION 3.0

### EXPERIMENTAL APPROACH

This section describes the survey design and analytical methods that were used to determine PCDD and PCDF residue levels in foodstuffs from California.

#### 3.1 Survey Design

MRI collected a number of foodstuffs from commercial food sources in two California cities, Los Angeles and San Francisco. This section presents the sampling and compositing schemes that were followed.

Appendix A provides a summary of the grocers and markets that were originally identified for collection of samples and a summary of locations that were actually sampled.

##### 3.1.1 Sampling Scheme

The food collection procedure was based on a simple stratified sampling design. The two stratification variables considered were:

- Geographical location within California
- Priority food items

##### 3.1.1.1 Geographical Strata

Two urban areas, Los Angeles and San Francisco, were selected for this study. The main justification for this selection was these sites have been used for other ARB-sponsored programs for determining ambient air levels and body burden of PCDDs and PCDFs.

##### 3.1.1.2 Priority Food Item

Seven food items were selected for inclusion in the survey. These included:

- Saltwater fish
- Freshwater fish
- Pork (bacon)

- Beef (ground beef)
- Chicken
- Eggs
- Milk

The list of priority food items sampled was established based on literature search and discussions with ARB personnel. All food items were purchased fresh rather than frozen or processed.

### 3.1.1.3 Food Collection Points

The target population consisted of commercial sources (retailers and fish markets) of these foodstuffs in Los Angeles and San Francisco. A mini telephone survey of food sources in the two cities was performed to obtain information on whether the food markets carried all or some of the listed foodstuffs and on the likelihood of the products being California grown. A total of about 18 sources, including egg and milk wholesalers, pork and beef producers, meat packers, poultry specialists, the California Beef Council, and fish markets, were contacted. The following information was obtained:

- Almost all fresh saltwater fish is caught locally.
- Very little pork is from California. The major California producers are "Farmer John" and "Victor," and their source should be indicated on packaged materials.
- Most of the beef sold within the state is California grown.
- Most of the poultry is from California (four major producers supply 40 to 50 percent of all poultry consumed in California).
- Almost all eggs are California products. The packages are labeled "California Fresh Eggs."
- Almost all milk comes from California dairies. The California source is indicated on the label.

In summary, it was determined that the likelihood of finding California-source saltwater fish, eggs, and milk is very high. The chances of finding California-grown beef and poultry are high, while it will be very difficult to find California-raised fresh fish or pork in California food markets.

The mini telephone survey showed the following:

- All retail grocers carry eggs, poultry, milk, beef, and pork.
- Slightly less than half of the food markets carry fresh fish. Thus, fresh fish were purchased at fresh fish markets where possible.

#### 3.1.1.4 Targeted Number of Foodstuff Samples

MRI targeted for 30 samples of each foodstuff in Los Angeles and 20 samples of each foodstuff in San Francisco. Since the priority list of foodstuffs included seven different items, a total of 350 food samples (7 items x 50 sources) were to be collected. However, the total number of food extracts to be analyzed was 50.

#### 3.1.1.5 Number of Food Sources

Since not all retail grocers carry fresh fish, all available foodstuffs were collected from 30 retail grocers in Los Angeles and 20 in San Francisco, and the list of grocers was complemented with fresh fish markets. For example, a telephone survey to identify 20 randomly selected retail grocers in San Francisco showed that of 20 sites interviewed, only 8 carried fresh fish.

#### 3.1.2 Compositing Scheme

MRI analyzed composited samples in order to cover the broad range of commercial sources of foodstuffs. This approach has been used in previous studies related to the detection of toxic substances in biological samples (Mack and Robinson, 1985; Stanley, 1986a,b,c,d). Compositing foodstuff samples collected in a statistically meaningful manner before chemical analysis has the following advantages:

- Compositing allows a sample to be obtained that is more representative of the average level of PCDDs and PCDFs in that foodstuff.
- Compositing reduces the chemical analysis costs associated with obtaining a specified precision of the estimated levels.
- Compositing increases the amount of sample and analyte in the sample in order to increase the probability of detection of the toxic compound.

A factor that is important in the compositing scheme is the percent lipid or fatty material contained in each type of foodstuff. Although the request for proposal indicated that the required detection limits were in the range of 1 to 5 pg/g, there was no indication whether this detection limit was based on the size of the original sample or a lipid-adjusted concentration. If PCDD and PCDF concentrations in foods are correlated with the amount of lipid or fatty materials (as has been demonstrated for human body burden levels), it is deemed more advantageous to base the

analytical measurements on a minimum amount of lipid for extraction from the matrix.

The lipid or fatty content of particular foodstuffs can be readily obtained in nutritional references. Assuming that approximately 10 g of final extracted lipid material per food specimen is required for analysis, the minimum amount (weight) of a specific food sample to be collected for each food source can be determined. For example, whole milk contains about 3.2 percent fat. Thus, 1 qt of milk contains about 29 g of lipid material, sufficient for one sample extract. If milk were composited from six different locations, then 5 oz of milk would need to be collected at each location, but such a small amount would be impractical to collect. Thus the most convenient size containers were collected, and the appropriate amount of sample from each food source was measured and composited at the laboratory.

The food sampling scheme was designed to yield a total of 350 individual foodstuff samples. These were to be subdivided as follows:

- Los Angeles: 30 samples of 7 foodstuffs each
- San Francisco: 20 samples of 7 foodstuffs each

Within each geographical area, samples were composited separately for each foodstuff. Composites were not prepared across different priority food items or geographical areas. The composite schemes presented below were designated at the outset of the study.

Los Angeles

| <u>Foodstuff</u> | <u>Number of individual food samples</u> | <u>Number of samples in each composite</u> | <u>Number of composites for analysis</u> |
|------------------|--|--|--|
| Saltwater fish   | 30                                       | 10   | 3  |
| Freshwater fish  | 30                                       | 10   | 3  |
| Pork             | 30                                       | 6  | 5  |
| Beef             | 30                                       | 6  | 5  |
| Chicken          | 30                                       | 6  | 5  |
| Eggs             | 30                                       | 6  | 5  |
| Milk             | <u>30</u>                                | <u>6</u>                                   | <u>5</u>                                 |
| Total            | 210                                      |  | 31                                       |

## San Francisco

---

| <u>Foodstuff</u> | <u>Number of individual food samples</u> | <u>Number of samples in each composite</u> | <u>Number of composites for analysis</u> |
|------------------|--|--|--|
| Saltwater fish   | 20                                       | 10   | 2  |
| Freshwater fish  | 20                                       | 10   | 2  |
| Pork             | 20                                       | 7 in 2 and 6 in 1                          | 3  |
| Beef             | 20                                       | 7 in 2 and 6 in 1                          | 3  |
| Chicken          | 20                                       | 7 in 2 and 6 in 1                          | 3  |
| Eggs             | 20                                       | 7 in 2 and 6 in 1                          | 3  |
| Milk             | <u>20</u>                                | 7 in 2 and 6 in 1                          | <u>3</u>                                 |
| Total            | 140                                      |  | 19                                       |

---

### 3.2 Analytical Methods

Established analysis procedures and existing data bases for PCDD and PCDF residue levels in foods were reviewed. These reviews were based on computer-assisted literature searches and personal contacts with individuals actively participating in PCDD and PCDF research. Rapid developments in the area of sampling and analysis of biological samples (including food items) for PCDDs and PCDFs have occurred over a relatively short time frame (since approximately 1983 to the present).

MRI conducted and published a literature review (Stanley, 1984; Stanley et al., 1985) summarizing the efforts for biological matrices dating up to mid-1983. MRI also hosted a meeting of recognized experts in the area of PCDD and PCDF analyses of biological tissues. As a result of that meeting, MRI identified the basis of an analytical method and quality assurance program that has been incorporated by the Veterans Administration and the U.S. Environmental Protection Agency as a cooperative effort between the agencies (Stanley, 1986).

The most recent reviews of analytical capabilities for biological sample analyses (tissues and foods) were presented at the 6th and 7th International Dioxin Conferences in Fukuoka, Japan, September 1986, and Las Vegas, Nevada, October 1987 (Stanley et al., 1986f; Fürst et al., 1986; Ono et al., 1987; Paasivirta et al., 1987; Miyata et al., 1987; Beck et al., 1987; Mathar et al., 1987).

#### 3.2.1 Review of Sample Preparation Efforts

The review of the analytical methods used for determination of picogram-per-gram levels of PCDDs and PCDFs reveals that all the methods require the same basic preparation steps. Each method requires fortification of the samples with carbon-13 labeled PCDDs and PCDFs (internal quantitation standards) prior to extraction. These internal quantitation standards are thus carried through the entire extraction/cleanup procedure and promote the accurate quantitation of the respective PCDDs and PCDFs.

Following the extraction step, it is necessary to remove the bulk of the lipid materials via either an acid digestion or adsorption process. This is accomplished using either concentrated sulfuric acid, sulfuric acid-modified silica gel, or potassium and cesium silicates. Potentially interfering organochlorine pesticides and PCBs are removed by either alumina or Florisil chromatography. Further separation from the potential interferences is achieved by isolation of the planar PCDD and PCDF congeners on a carbon-based adsorption column. The PCDDs and PCDFs are quantitatively recovered by elution from the carbon-based column using an aromatic solvent (toluene). Some differences are noted for the various methods in the order that the sample extract is taken through the cleanup columns.

### 3.2.2 Selection of the Analytical Protocol

MRI has developed and validated an analytical method specifically for the analysis of PCDDs and PCDFs in biological tissue (Stanley et al., 1986c). The method performance has been documented to provide accurate quantitative data for the 2,3,7,8-TCDD to concentrations in the range of 1 to 10 pg/g. Method performance for this procedure has been demonstrated for each of the 2,3,7,8-substituted PCDD and PCDF congeners as well as the octachlorodibenzo-p-dioxin (OCDD) and octachlorodibenzofuran (OCDF).

The specific analytical procedures for the determination of PCDDs and PCDFs in fatty foodstuffs are presented in detail in Appendix B of this report. However, there are several deviations to the analytical procedure that should be addressed. Specifically, some modifications of the chromatographic cleanup techniques were incorporated in this study. These modifications included the use of neutral alumina versus acidic alumina columns to fractionate sample extracts and the use of a carbon-based column which consisted of AX-21 charcoal (Anderson Development Company) on silica gel versus Carbowax C on Celite as described in the protocol in Appendix B. The basis for these modifications resulted from the incorporation of these procedures in EPA's high resolution mass spectrometry (HRMS) procedure, Method 8290, for the determination of PCDDs and PCDFs in multimedia samples (Tonduer, 1987; Stanley et al., 1989).

#### 3.2.2.1 Laboratory Sample Preparation Procedures for Foodstuffs

Additional details on the preparation of each of the specific foodstuffs are described below.

##### Milk

Milk samples consisted of whole milk, half and half, and whipping cream samples. Known amounts from each sample in a composite were combined into a single sample so that each contributed equal amounts of milk fat. The goal was to approximate a total of 10 g of milk fat. For most composites, this corresponded to a volume of 70 mL.

After the sample composite was prepared, a known amount of a series of  $^{13}\text{C}$ -labeled internal quantitation standards was added

(Table 3-1), and the mixture was denatured with 3% sodium oxalate, ethanol, and diethyl ether. The sample was then extracted with three portions of hexane and the hexane combined for further cleanup.

The hexane/milk fat extract was subsequently fortified with <sup>13</sup>C-labeled dioxins and furans and subjected to an acidic silica gel slurry cleanup procedure. Specifically, 100 g of 40% sulfuric acid-impregnated silica gel was mixed with the hexane/milk fat mixture for 2 hr. Afterwards, the hexane was decanted through a funnel of sodium sulfate into a 4-g acid silica gel/1-g neutral silica gel column. The fraction collected in a Kuderna-Danish (K-D) evaporating flask. The acidic silica gel was slurried an additional two times with 50 mL of hexane for 15 min each time and the rinses placed on the column. After all the solvent from the slurry had passed through the column, an additional 50 mL of hexane was placed on the column and combined with the other eluent in the K-D flask.

The extract was reduced in volume to approximately 2 mL and applied to the top of a chromatography column comprised of 4 g sodium sulfate, 4 g neutral alumina, and 4 g sodium sulfate. The column was eluted with 10 mL of 8% dichloromethane in hexane. This portion was archived. The PCDDs and PCDFs were eluted in 15 mL of 60% dichloromethane in hexane. This fraction was collected and reduced in volume to approximately 2 mL and applied to the final column.

The final cleanup column consisted of 1 g of 5% Amoco AX-21 carbon on neutral silica gel. The column was prerinsed with 4 mL toluene, 2 mL dichloromethane/methanol/benzene (75:20:5), and 4 mL cyclohexane/dichloromethane (50:50). The fraction from the alumina column was transferred to the AX-21/silica gel column with two 1-mL rinses of hexane. The column was eluted with 10 mL of the cyclohexane/dichloromethane solution and 5 mL of the dichloromethane/methanol/benzene solution. These fractions were combined and archived. The columns were then turned over and eluted with 20 mL of toluene. The toluene was reduced in volume to approximately 100  $\mu$ L, the internal recovery standards in tridecane were then added (10  $\mu$ L, Table 3-1), and the extract further evaporated to final volume (10  $\mu$ L).

### Eggs

Two eggs from each dozen samples collected were combined to form a composite. The eggs were mixed with sodium sulfate and allowed to dry overnight. After drying, the powder was extracted with hexane, and the hexane/egg fat mix was fortified with <sup>13</sup>C mass-labeled internal quantitation standards and slurried with 150 g of acidic silica gel for 2 hr. The remaining cleanup procedure was as described for the milk samples.

Table 3-1. Internal Standard Spiking Solutions for Determination of PCDDs and PCDFs in Foodstuffs

| Compound   | Concentration (pg/ $\mu$ L) |
|--|-----------------------------|
| <u>Internal Quantitation Standards<sup>a</sup></u> |                             |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDD                 | 5                           |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDF                 | 5                           |
| $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD              | 5                           |
| $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF              | 5                           |
| $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD            | 12.5                        |
| $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDF            | 12.5                        |
| $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD          | 12.5                        |
| $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF          | 12.5                        |
| $^{13}\text{C}_{12}$ -OCDD                         | 25                          |
| <u>Internal Recovery Standard<sup>b</sup></u>      |                             |
| $^{13}\text{C}_{12}$ -1,2,3,4-TCDD                 | 50                          |
| $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD            | 125                         |

<sup>a</sup> Prepared in isooctane, 100  $\mu$ L spiked.

<sup>b</sup> Prepared in tridecane, 10  $\mu$ L spiked.

## Meats (Beef, Pork, Poultry) and Fish

All meats and fish were initially combined in equal amounts according to the composite design. The composites were then ground two to three times with dichloromethane and sodium sulfate. The dichloromethane was decanted into a round-bottom flask and the dichloromethane removed by roto-evaporation until only lipid remained. Ten (10) grams of the lipid were then dissolved in 200 mL of hexane and fortified with  $^{13}\text{C}$  mass-labeled internal quantitation standards (Table 4-1). The mixture was then processed through the cleanup procedures described previously (acid silica gel slurry, acid/neutral silica gel column, neutral alumina column, and AX-21/silica gel column).

### 3.2.2.2 HRMS Analysis Procedures

The sample extracts were analyzed using a Kratos MS-50TC high resolution mass spectrometer (HRMS). Analytical parameters for the PCDD and PCDF determination are given in Table 3-2.

A typical analysis day started with the mass calibration of the mass spectrometer, followed by the analysis of a window defining mix. This solution contains the first and last eluting isomers of a homolog group and is used to determine the ion switching points needed to switch from monitoring one homolog series to the next. This was followed by the analysis of a low level standard (2.5 pg TCDD to 12.5 pg OCDD). Relative response factors (RRFs) were calculated based on this run and were compared to those RRFs established during the initial calibration. The initial calibration curve consisted of a series of up to eight standards ranging in concentration from 1 to 200 pg/ $\mu\text{L}$  2,3,7,8-TCDD. All other 2,3,7,8-substituted PCDDs and PCDFs are included in the calibration standards.

The concentration of each congener varies with the degree of chlorination. For example, the concentration range for the octachloro congener is 5 to 1,000 pg/ $\mu\text{L}$ . Table 3-3 gives the concentration ranges for each of the isomers in the calibration standards.

Criteria for passing the daily calibration must be within  $\pm 20\%$  deviation from the initial RRFs. Daily communications between the mass spectrometer operator and the project leader ensured compliance with these criteria for 90% of the analytes before any samples were analyzed. Following the analysis of the low level standard, a solvent blank (tridecane) was analyzed, then field samples were analyzed in a random order. The day was completed with the analysis of an additional calibration standard to verify instrumental stability.

Table 3-2. HRGC/HRMS Operating Conditions for PCDD/PCDF Analysis

---

Mass Spectrometer

|                              |                                  |
|------------------------------|----------------------------------|
| Accelerating voltage:        | 8,000 V                          |
| Trap current:                | 500 $\mu$ A                      |
| Electron energy:             | 70 eV                            |
| Electron multiplier voltage: | -1,800 V                         |
| Source temperature:          | 280°C                            |
| Resolution:                  | > 10,000 (10% valley definition) |
| Overall SIM cycle time:      | 1 s                              |

Gas Chromatograph

|                          |                                  |
|--------------------------|----------------------------------|
| Column coating:          | DB 5                             |
| Film thickness:          | 0.25 $\mu$ m                     |
| Column dimensions:       | 60 m x 0.25 mm ID                |
| He linear velocity:      | ~ 25 cm/s                        |
| He head pressure:        | 1.75 kg/cm <sup>2</sup> (25 psi) |
| Injection type:          | Splitless, 45 s                  |
| Split flow:              | 30 mL/min                        |
| Purge flow:              | 6 mL/min                         |
| Injector temperature:    | 270°C                            |
| Interface temperature:   | 300°C                            |
| Injection size:          | 1-2 $\mu$ L                      |
| Initial temperature:     | 200°C                            |
| Initial time:            | 2 min                            |
| Temperature program:     | 200° to 270°C at 5°C/min         |
| Second hold time:        | 10 min                           |
| Second temperature ramp: | 270° to 330°C at 5°C/min         |
| Final hold time:         | 5 min                            |

---

Table 3-3. Concentration Calibration Solutions for PCDD/PCDF

| Compound                                  | Concentration in calibration solutions in pg/ $\mu$ L |     |     |      |     |      |      |     |
|---|---|-----|-----|------|-----|------|------|-----|
|   | CS1   | CS2 | CS3 | CS4  | CS5 | CS6  | CS7  | CS8 |
| 2,3,7,8-TCDD                              | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 2,3,7,8-TCDF                              | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 1,2,3,7,8-PeCDD                           | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 1,2,3,7,8-PeCDF                           | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 2,3,4,7,8-PeCDF                           | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 1,2,3,4,7,8-HxCDD                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,6,7,8-HxCDD                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,7,8,9-HxCDD                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,4,7,8-HxCDF                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,6,7,8-HxCDF                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,7,8,9-HxCDF                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 2,3,4,6,7,8-HxCDF                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,4,6,7,8-HpCDD                       | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,4,6,7,8-HpCDF                       | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,4,7,8,9-HpCDF                       | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| OCDD                                      | 1,000   | 500 | 250 | 125  | 50  | 25   | 12.5 | 5   |
| OCDF                                      | 1,000   | 500 | 250 | 125  | 50  | 25   | 12.5 | 5   |
| <u>Internal Quantitation</u>              |   |     |     |      |     |      |      |     |
| <u>Standards</u>                          |   |     |     |      |     |      |      |     |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDD        | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDF        | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD     | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF     | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD   | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |
| $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF   | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |
| $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |
| $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |
| $^{13}\text{C}_{12}$ -OCDD                | 250   | 250 | 250 | 250  | 250 | 250  | 250  | 250 |
| <u>Internal Recovery</u>                  |   |     |     |      |     |      |      |     |
| <u>Standard</u>                           |   |     |     |      |     |      |      |     |
| $^{13}\text{C}_{12}$ -1,2,3,4-TCDD        | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD   | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |

### 3.2.2.3 Data Reduction Procedures

Data reduction procedures were primarily conducted using a basic computer program which receives a specially formatted Incos® data file as input, and outputs an extract concentration. Then, the sample weight, percent lipid, dry weight, or other concentration or dilution factors were taken into account to arrive at a final sample concentration. Limits of detection were determined for each 2,3,7,8-substituted isomer in each sample by multiplying the median of nonmatching peaks in a retention time window by 2.5 or by reporting the concentration of a coeluting peak that did not match the qualitative ion ratio criteria for that isomer.

### 3.2.2.4 Calculation Theory

During the initial calibration, a series of up to eight standards are analyzed and relative response factors (RRFs) are determined for each native relative to the corresponding <sup>13</sup>C-labeled internal quantitation standard (IQS) and for each IQS relative to the recovery standards (RS). The average of the RRFs over all the standards is used in all succeeding calculations to determine sample amounts for a specific isomer.

As previously indicated, known amounts of IQS are added to the sample before extraction. In the data calculations, the response of the IQS, its known concentration, the response of the native, and the average RRF are used to calculate the concentration of the native isomers in the extract. Since the IQS are affected by the sample matrix and the overall extraction procedure, the calculation procedure adjusts for recovery from the sample matrix.

The recovery standards, added to the extract just prior to HRGC/HRMS analysis, are used to determine the absolute recovery of the IQS. The delivery of these two RS compounds in 10 µL of a high boiling solvent also assures the integrity of the small volume of the final extract.

## SECTION 4.0

### RESULTS

This section provides a summary of the chemical and statistical analysis results and the data from the analysis of quality control samples with the specific sample matrices.

#### 4.1 Chemical Analysis Results

The chemical analysis results for the composited foodstuff samples are presented in Tables 4-1 through 4-12. These tables provide the raw analytical data for the specific target PCDD and PCDF analytes within a particular foodstuff. The data are presented for a particular foodstuff collected within a specific urban area. The data for all sample matrices, with the exception of the egg composites, are reported on a lipid weight basis. The lipid basis was used rather than the wet weight concentration, because the analysis strategy focused on the fatty material where PCDDs and PCDFs are known to concentrate. More importantly, the reporting of concentration data on a lipid basis is essential for comparing residue levels with future program efforts to be undertaken in California.

Three footnotes in the data tables warrant some comment. In some instances, a residue level is reported but is footnoted that the ratio of the characteristic ions is outside the data quality objectives for qualitative identification. The reported values in these instances is considered valid, since the response is consistent with the determination of the particular analyte in other composites of the similar matrix.

The data reported as ND(value) indicate that the compound was not detected and the value in parentheses is the estimated method detection limit.

The third footnote of interest is found on Tables 4-1 and 4-2, which summarize the PCDD and PCDF residue levels for fish. This footnote indicates that in some instances the reported detection limit for the 1,2,3,4,7,8-HxCDF and 2,3,4,6,7,8-HxCDF is affected by interfering compounds, particularly octachlorodiphenyl ethers (ODPE). The ODPE interference gives rise to a false positive HxCDF response even though HRMS ( $R > 10,000$ ) was used for analysis because of the common chemical structure of these related compounds. The ODPE was detected as a result of the HRMS analysis strategy to document the presence or absence of this particular interference. The observation of the OPDE interference provides some indication of the potential sources for contamination in the environment. For instance, chlorinated diphenyl ethers are recognized contaminants in technical grade pentachlorophenol (Mieure et al., 1977).

Each table also includes a value termed the 2,3,7,8-TCDD toxic equivalents (TE) value. These values were generated from the TE formula (TEF) developed by the California Department of Health Services. The TE values are based on the assignment of relative toxicities of 2,3,7,8-substituted PCDDs and PCDFs to the 2,3,7,8-TCDD. Compilation of TE values allows a comparison of total PCDD and PCDF residue levels between samples. It should be noted that the TE values for the food samples are at a minimum equivalent to the highest detection limits for one of the five compounds assigned TE values of one. The OCDD and OCDF were not assigned TE values by the Department of Health Services Procedure.

| TE Formula (TEF)    |                  |                     |                  |
|---------------------|------------------|---------------------|------------------|
| PCDD                |                  | PCDF                |                  |
| Isomer              | TEF <sup>a</sup> | Isomer              | TEF <sup>a</sup> |
| 2,3,7,8-TCDD        | 1                | 2,3,7,8-TCDF        | 1                |
| 1,2,3,7,8-PeCDD     | 1                | 1,2,3,7,8-PeCDF     | 1                |
| 1,2,3,6,7,8-HxCDD   | 0.03             | 2,3,4,7,8-PeCDF     | 1                |
| 1,2,3,7,8,9-HxCDD   | 0.03             | 1,2,3,6,7,8-HxCDF   | 0.03             |
| 1,2,3,4,7,8-HxCDD   | 0.03             | 1,2,3,7,8,9-HxCDF   | 0.03             |
| 1,2,3,4,6,7,8-HpCDD | 0.03             | 1,2,3,4,7,8-HxCDF   | 0.03             |
|                     |                  | 2,3,4,6,7,8-HxCDF   | 0.03             |
|                     |                  | 1,2,3,4,6,7,8-HpCDF | 0.03             |
|                     |                  | 1,2,3,4,7,8,9-HpCDF | 0.03             |

<sup>a</sup> California Department of Health Services, 1986, "Technical Support Document on Chlorinated Dioxins and Furans. Part B. Health Effects. Appendix B. Methods for Inferring Total Potency of a Mixture of PCDDs and PCDFs" (Tables B-1 and B-2).

Specific comments on each of the foodstuffs are provided below.

#### 4.1.1 Fish (Freshwater and Saltwater)

Tables 4-1 and 4-2 provide the results for the fish sample composites collected from San Francisco and Los Angeles, respectively. The freshwater fish composites exhibited consistently more frequent detection of the PCDDs and PCDFs than were noted for the saltwater fish. The compounds detected most consistently in the fish samples were 2,3,7,8-TCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8/1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD.

The freshwater fish composites consisted of trout, catfish, or a combination of catfish and trout. It was recognized during collection that freshwater fish were not of California origin but were originally shipped from various parts of the country. For example, most of the catfish were reportedly raised in the southeastern United States, while the trout were shipped primarily from Idaho.

The origins of the saltwater fish composites, however, were more difficult to trace, although many of these samples reportedly were originally from the California coastal waters. The saltwater fish composites were comprised of sea bass, mackerel, various species of cod (ling, rock, or true), red snapper, butterfish, and kingfish.

A comparison of the PCDD and PCDF residue levels for each of the samples indicate that the freshwater fish tend to have higher lipid concentrations of the compounds than do the saltwater fish. The compound that is the exception is 2,3,7,8-TCDF, which is considerably higher in the saltwater fish than the freshwater fish composites.

#### 4.1.2 Beef

Tables 4-3 and 4-4 summarize the data for PCDDs and PCDFs in composited beef samples. All data are reported on a lipid concentration basis. The compounds detected most consistently included the 1,2,3,4,6,7,8-HpCDD and OCDD. The concentrations for these compounds are in the range of approximately 5 to 10 pg/g. As noted in the tables, there was some evidence of 2,3,7,8-TCDF, the HxCDD isomers, and 1,2,3,4,6,7,8-HpCDF, although the concentrations for the observed responses were approximately 1 pg/g.

#### 4.1.3 Bovine Milk

Tables 4-5 and 4-6 provide the analytical data summaries for the PCDD and PCDF residue levels in bovine milk. The data for all samples are reported on the extractable lipid content of each composited sample. Compounds which were frequently detected included the 2,3,7,8-TCDF, the 1,2,3,4,6,7,8-HpCDD, and OCDD. The concentrations of each of these compounds typically ranged between 1 and 5 pg/g.

#### 4.1.4 Pork

The PCDD and PCDF residue data for the pork samples are presented in Tables 4-7 and 4-8. All data are reported on a lipid concentration basis. The compounds of interest include the 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD, OCDD, and OCDF. There were some indications of the presence of the HxCDD isomers, although the frequency of detection was limited to two of seven sample extracts.

#### 4.1.5 Poultry

The poultry composite sample data are presented in Tables 4-9 and 4-10. The PCDD and PCDF residue levels for these compounds are similar to the levels noted for the beef and pork samples with the exception that some of the OCDD levels are greater than 50 pg/g. There were some indications of the presence of the 2,3,7,8-TCDD in four of the sample composites, although in these instances the sample concentrations ranged from 0.3 to 1.67 pg/g.

Table 4-1. HRGC/HRMS Data Summaries for Fish (San Francisco)

| Composite No.                     | Freshwater Fish (pg/g) |                   | Saltwater Fish (pg/g) |                   |
|-----------------------------------|------------------------|-------------------|-----------------------|-------------------|
|                                   | 15622                  | 15623             | 15620                 | 15621             |
| <u>Compounds</u>                  |                        |                   |                       |                   |
| 2,3,7,8-TCDF                      | 1.59 <sup>a</sup>      | 7.96              | 22.8                  | 19.6              |
| 2,3,7,8-TCDD                      | ND (2.2) <sup>b</sup>  | 2.8               | 1.89 <sup>a</sup>     | 0.73              |
| 1,2,3,7,8-PeCDF <sup>c</sup>      | ND (0.68)              | ND (0.51)         | ND (99.4)             | ND (2.02)         |
| 2,3,4,7,8-PeCDF                   | ND (0.62)              | ND (2.31)         | ND (4.85)             | ND (4.94)         |
| 1,2,3,7,8-PeCDD                   | 4.46                   | 1.67 <sup>a</sup> | 2.4                   | ND (2.02)         |
| 1,2,3,4,7,8-HxCDF <sup>c</sup>    | ND (4.04)              | ND (30.1)         | ND (84.2)             | ND (178)          |
| 1,2,3,6,7,8-HxCDF                 | ND (1.25)              | ND (1.16)         | ND (0.59)             | ND (1.71)         |
| 2,3,4,6,7,8-HxCDF <sup>c</sup>    | ND (1.49)              | ND (1.37)         | ND (9.76)             | ND (17)           |
| 1,2,3,7,8,9-HxCDF                 | ND (1.62)              | ND (1.5)          | ND (0.76)             | ND (2.2)          |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | 12.79                  | ND (1.34)         | 1.19                  | 1.75 <sup>a</sup> |
| 1,2,3,7,8,9-HxCDD                 | 6.74                   | ND (1.38)         | ND (0.83)             | ND (1.5)          |
| 1,2,3,4,6,7,8-HpCDF               | ND (1.1)               | 92.9 <sup>a</sup> | ND (0.84)             | 2.21 <sup>a</sup> |
| 1,2,3,4,7,8,9-HpCDF               | ND (1.51)              | 13.3              | ND (1.2)              | ND (2.59)         |
| 1,2,3,4,6,7,8-HpCDD               | 28.7                   | ND (1.49)         | ND (0.96)             | ND (1.29)         |
| OCDF                              | ND (5.46)              | ND (1.65)         | ND (0.96)             | ND (1.61)         |
| OCDD                              | 230                    | 4.37 <sup>a</sup> | 6.05                  | 12.9              |
| TE value <sup>d</sup>             | 7.50                   | 10.8              | 27.1                  | 20.4              |

<sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.

<sup>b</sup> ND = Not detected. The value in parentheses is the estimated method detection limit.

<sup>c</sup> Detection limit is influenced by the presence of polychlorinated diphenylethers.

<sup>d</sup> TE values based on the California Department of Health Services Procedure.

Table 4-2. HRGS/HRMS Data Summaries for Fish (Los Angeles)

| Composite No.                     | Freshwater Fish (pg/g) |           |           | Saltwater Fish (pg/g) |                   |                        |
|-----------------------------------|------------------------|-----------|-----------|-----------------------|-------------------|------------------------|
|                                   | 15646                  | 15647     | 15649     | 15644                 | 15648             | 15645                  |
| <u>Compounds</u>                  |                        |           |           |                       |                   |                        |
| 2,3,7,8-TCDF                      | 2.9                    | 2.87      | 0.83      | 19.7 <sup>a</sup>     | 18.8              | 28.2                   |
| 2,3,7,8-TCDD                      | 4.69 <sup>a</sup>      | 4.87      | 9.78      | 0.98                  | 1.05 <sup>a</sup> | ND (1.47) <sup>b</sup> |
| 1,2,3,7,8-PeCDF                   | ND (1.39)              | ND (1.0)  | ND (1.44) | ND (5.75)             | ND (14.9)         | ND (1.3)               |
| 2,3,4,7,8-PeCDF                   | ND (1.44)              | ND (0.91) | ND (0.56) | ND (1.01)             | ND (1.31)         | ND (1.5)               |
| 1,2,3,7,8-PeCDD                   | 6.05 <sup>a</sup>      | 13.3      | 23.6      | ND (2.18)             | ND (1.36)         | ND (1.28)              |
| 1,2,3,4,7,8-HxCDF <sup>c</sup>    | ND (12.5)              | ND (4.05) | ND (5.82) | ND (14.6)             | ND (36)           | ND (37.2)              |
| 1,2,3,6,7,8-HxCDF                 | ND (1.34)              | ND (0.67) | ND (1.33) | ND (2.26)             | ND (1.34)         | ND (1.49)              |
| 2,3,4,6,7,8-HxCDF <sup>c</sup>    | ND (1.6)               | ND (0.79) | ND (1.58) | ND (2.69)             | ND (4.37)         | ND (1.78)              |
| 1,2,3,7,8,9-HxCDF                 | ND (1.74)              | ND (0.87) | ND (1.73) | ND (2.94)             | ND (1.74)         | ND (1.94)              |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | 5.74                   | 20.0      | 84.1      | ND (2.31)             | 3.82 <sup>a</sup> | ND (3.64)              |
| 1,2,3,7,8,9-HxCDD                 | 3.91 <sup>a</sup>      | 13.4      | 38.9      | ND (1.94)             | ND (3.25)         | ND (3.76)              |
| 1,2,3,4,6,7,8-HpCDF               | ND (1.07)              | ND (1.42) | ND (1.66) | ND (7.32)             | ND (2.69)         | ND (1.96)              |
| 1,2,3,4,7,8,9-HpCDF               | ND (1.52)              | ND (2.02) | ND (2.38) | ND (10.5)             | ND (3.85)         | ND (2.8)               |
| 1,2,3,4,6,7,8-HpCDD               | 30.7                   | 49.6      | 201       | ND (3.06)             | ND (1.52)         | 3.15                   |
| OCDF                              | ND (1.4)               | ND (1.71) | ND (2.77) | ND (8.41)             | ND (3.38)         | ND (12.2)              |
| OCDD                              | 227                    | 494       | 1490      | 22.7 <sup>a</sup>     | 5.29 <sup>a</sup> | 19.9                   |
| TE value <sup>d</sup>             | 14.8                   | 23.5      | 43.9      | 20.7                  | 20.0              | 28.3                   |

Note: Data reported on a lipid weight basis.

- <sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.
- <sup>b</sup> ND = Not detected. The value in parentheses is the estimated method detection limit.
- <sup>c</sup> Detection limit is influenced by the presence of polychlorinated diphenylethers.
- <sup>d</sup> TE values based on the California Department of Health Services Procedure.

Table 4-3. HRGC/HRMS Data Summaries for Beef (Los Angeles)

| Composite No.                     | Sample Concentrating (pg/g) |                        |                   |                   |           |
|-----------------------------------|-----------------------------|------------------------|-------------------|-------------------|-----------|
|                                   | 15624                       | 15625                  | 15626             | 15627             | 15628     |
| <u>Compounds</u>                  |                             |                        |                   |                   |           |
| 2,3,7,8-TCDF                      | 0.84 <sup>a</sup>           | ND (0.57) <sup>b</sup> | ND (0.15)         | ND (0.16)         | ND (0.19) |
| 2,3,7,8-TCDD                      | ND (0.33)                   | ND (0.41)              | ND (0.12)         | ND (0.12)         | ND (0.17) |
| 1,2,3,7,8-PeCDF                   | ND (0.60)                   | ND (0.86)              | ND (0.29)         | ND (0.25)         | ND (0.64) |
| 2,3,4,7,8-PeCDF                   | ND (0.55)                   | ND (0.78)              | ND (0.26)         | ND (0.22)         | ND (0.59) |
| 1,2,3,7,8-PeCDD                   | ND (0.56)                   | ND (17.5)              | ND (0.68)         | ND (0.40)         | ND (1.1)  |
| 1,2,3,4,7,8-HxCDF                 | ND (0.73)                   | ND (1.19)              | ND (0.58)         | ND (0.38)         | ND (0.59) |
| 1,2,3,6,7,8-HxCDF                 | ND (0.71)                   | ND (1.17)              | ND (0.51)         | ND (0.37)         | ND (0.41) |
| 2,3,4,6,7,8-HxCDF                 | ND (0.85)                   | ND (1.39)              | ND (0.67)         | ND (0.44)         | ND (0.49) |
| 1,2,3,7,8,9-HxCDF                 | ND (0.93)                   | ND (1.51)              | ND (0.74)         | ND (0.48)         | ND (0.53) |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | ND (0.91)                   | ND (2.64)              | 0.72 <sup>a</sup> | 1.2               | ND (1.94) |
| 1,2,3,7,8,9-HxCDD                 | ND (0.94)                   | ND (2.72)              | ND (0.74)         | ND (0.77)         | ND (2.0)  |
| 1,2,3,4,6,7,8-HpCDF               | 1.15 <sup>a</sup>           | ND (1.99)              | 0.48              | 1.05 <sup>a</sup> | ND (2.29) |
| 1,2,3,4,7,8,9-HpCDF               | ND (0.86)                   | ND (2.84)              | ND (0.37)         | ND (0.78)         | ND (3.28) |
| 1,2,3,4,6,7,8-HpCDD               | 4.71 <sup>a</sup>           | ND (3.21)              | 3.53              | 5.84              | 6.71      |
| OCDF                              | ND (1.66)                   | ND (5.31)              | ND (0.48)         | ND (0.72)         | ND (1.46) |
| OCDD                              | 8.2                         | ND (10.7)              | 7.75              | 11.4              | 10.2      |
| TE value <sup>c</sup>             | 1.02                        | < 0.41                 | 0.14              | 0.24              | 0.20      |

Note: Data are reported on a lipid weight basis.

<sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.

<sup>b</sup> ND = Not detected. The value in parentheses is the estimated method detection limit.

<sup>c</sup> TE values based on the California Department of Health Services Procedure.

Table 4-4. HRGC/HRMS Data Summaries for Beef  
(San Francisco)

| Composite No.                     | Sample Concentrating (pg/g) |                   |                        |
|-----------------------------------|-----------------------------|-------------------|------------------------|
|                                   | 15608                       | 16509             | 15610                  |
| <u>Compounds</u>                  |                             |                   |                        |
| 2,3,7,8-TCDF                      | 1.56 <sup>a</sup>           | 0.63              | ND (0.32) <sup>b</sup> |
| 2,3,7,8-TCDD                      | ND (0.16)                   | ND (0.40)         | ND (0.38)              |
| 1,2,3,7,8-PeCDF                   | ND (0.70)                   | ND (0.10)         | ND (1.44)              |
| 2,3,4,7,8-PeCDF                   | ND (0.64)                   | ND (0.28)         | ND (1.31)              |
| 1,2,3,7,8-PeCDD                   | ND (1.0)                    | ND (1.09)         | ND (0.49)              |
| 1,2,3,4,7,8-HxCDF                 | ND (0.35)                   | ND (0.79)         | ND (0.73)              |
| 1,2,3,6,7,8-HxCDF                 | ND (0.35)                   | ND (0.77)         | ND (0.71)              |
| 2,3,4,6,7,8-HxCDF                 | ND (0.41)                   | ND (0.92)         | ND (0.85)              |
| 1,2,3,7,8,9-HxCDF                 | ND (0.45)                   | ND (1.01)         | ND (0.93)              |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | ND (1.60)                   | 3.96 <sup>a</sup> | ND (3.29)              |
| 1,2,3,6,7,8-HxCDD                 | ND (1.64)                   | ND (4.08)         | ND (3.39)              |
| 1,2,3,4,6,7,8-HpCDF               | 0.67                        | ND (1.66)         | ND (1.47)              |
| 1,2,3,4,7,8,9-HpCDF               | ND (0.78)                   | ND (2.37)         | ND (2.10)              |
| 1,2,3,4,6,7,8-HpCDD               | 4.56 <sup>a</sup>           | 5.33              | 8.95 <sup>a</sup>      |
| OCDF                              | ND (0.45)                   | ND (2.15)         | ND (1.6)               |
| OCDD                              | 8.35 <sup>a</sup>           | 11.9              | 8.03                   |
| TE value <sup>c</sup>             | 1.72                        | 0.91              | < 1.44                 |

Note: Data are reported on a lipid weight basis.

- <sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.  
<sup>b</sup> ND = Not detected. The value in parentheses is the estimated method detection limit.  
<sup>c</sup> TE values based on the California Department of Health Services Procedure.

Table 4-5. HRGC/HRMS Data Summaries for Bovine Milk (Los Angeles)

| Composite No.                     | Sample Concentrating (pg/g) |                   |                   |                   |                   |
|-----------------------------------|-----------------------------|-------------------|-------------------|-------------------|-------------------|
|                                   | 15639                       | 15640             | 15642             | 15641             | 15643             |
| <u>Compounds</u>                  |                             |                   |                   |                   |                   |
| 2,3,7,8-TCDF                      | 2.67                        | 1.30 <sup>a</sup> | 6.11 <sup>a</sup> | 3.61 <sup>a</sup> | 2.63              |
| 2,3,7,8-TCDD                      | ND (0.57) <sup>b</sup>      | ND (0.43)         | ND (1.1)          | 1.46 <sup>a</sup> | ND (0.32)         |
| 1,2,3,7,8-PeCDF                   | ND (0.51)                   | ND (0.03)         | ND (0.58)         | ND (0.35)         | ND (0.10)         |
| 2,3,4,7,8-PeCDF                   | ND (0.47)                   | ND (0.02)         | ND (0.53)         | ND (0.32)         | ND (0.32)         |
| 1,2,3,7,8-PeCDD                   | ND (0.50)                   | ND (1.05)         | ND (1.0)          | ND (0.97)         | ND (1.0)          |
| 1,2,3,4,7,8-HxCDF                 | ND (0.41)                   | ND (0.84)         | ND (0.23)         | ND (1.36)         | ND (0.72)         |
| 1,2,3,6,7,8-HxCDF                 | ND (0.40)                   | ND (0.82)         | ND (0.22)         | ND (1.34)         | ND (0.70)         |
| 2,3,4,6,7,8-HxCDF                 | ND (0.48)                   | ND (0.98)         | ND (0.27)         | ND (1.59)         | ND (0.84)         |
| 1,2,3,7,8,9-HxCDF                 | ND (0.52)                   | ND (0.96)         | ND (0.29)         | ND (1.73)         | ND (0.92)         |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | 0.59 <sup>a</sup>           | ND (0.78)         | ND (1.47)         | ND (1.31)         | ND (0.73)         |
| 1,2,3,7,8,9-HxCDD                 | ND (0.42)                   | ND (0.81)         | ND (1.52)         | ND (1.35)         | ND (0.75)         |
| 1,2,3,4,6,7,8-HpCDF               | 0.70 <sup>a</sup>           | ND (1.22)         | ND (0.5)          | ND (1.15)         | ND (0.48)         |
| 1,2,3,4,7,8,9-HpCDF               | ND (1.0)                    | ND (1.74)         | ND (0.72)         | ND (1.65)         | ND (0.64)         |
| 1,2,3,4,6,7,8-HpCDD               | 2.96 <sup>a</sup>           | 3.24 <sup>a</sup> | 3.8 <sup>a</sup>  | ND (1.03)         | 2.91 <sup>a</sup> |
| OCDF                              | ND (1.39)                   | ND (2.04)         | ND (3.64)         | ND (7.36)         | ND (1.31)         |
| OCDD                              | 2.61 <sup>a</sup>           | 6.12              | 5.35 <sup>a</sup> | 5.24 <sup>a</sup> | ND (1.32)         |
| TE value <sup>c</sup>             | 2.80                        | 1.40              | 6.22              | 5.07              | 2.72              |

Note: Data are reported on a lipid weight basis.

<sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.

<sup>b</sup> ND = Not detected. The value in parentheses is the estimated limit of detection.

<sup>c</sup> TE values based on the California Department of Health Services Procedure.

Table 4-6. HRGC/HRMS Data Summaries for Bovine Milk  
(San Francisco)

| Composite No.                     | Sample Concentrating (pg/g) |                   |                   |
|-----------------------------------|-----------------------------|-------------------|-------------------|
|                                   | 15614                       | 15615             | 15616             |
| <u>Compounds</u>                  |                             |                   |                   |
| 2,3,7,8-TCDF                      | 1.44                        | 2.16              | 2.0               |
| 2,3,7,8-TCDD                      | ND (0.63)                   | ND (0.38)         | ND (0.69)         |
| 1,2,3,7,8-PeCDF                   | ND (0.77)                   | ND (0.27)         | ND (0.45)         |
| 2,3,4,7,8-PeCDF                   | ND (0.70)                   | ND (0.24)         | ND (0.41)         |
| 1,2,3,7,8-PeCDD                   | ND (2.3)                    | ND (0.92)         | ND (0.19)         |
| 1,2,3,4,7,8-HxCDF                 | ND (0.85)                   | ND (0.51)         | ND (0.71)         |
| 1,2,3,6,7,8-HxCDF                 | ND (0.84)                   | ND (0.50)         | ND (0.69)         |
| 2,3,4,6,7,8-HxCDF                 | ND (1.0)                    | ND (0.60)         | ND (0.83)         |
| 1,2,3,7,8,9-HxCDF                 | ND (1.09)                   | ND (0.66)         | ND (0.91)         |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | ND (1.18)                   | ND (1.51)         | ND (0.47)         |
| 1,2,3,6,7,8-HxCDD                 | ND (1.21)                   | ND (1.62)         | ND (0.49)         |
| 1,2,3,4,6,7,8-HpCDF               | ND (1.93)                   | ND (0.64)         | ND (0.39)         |
| 1,2,3,4,7,8,9-HpCDF               | ND (2.76)                   | ND (0.92)         | ND (0.56)         |
| 1,2,3,4,6,7,8-HpCDD               | 4.25 <sup>a</sup>           | 2.08 <sup>a</sup> | 2.57 <sup>a</sup> |
| OCDF                              | ND (1.89)                   | ND (3.2)          | ND (0.71)         |
| OCDD                              | ND (3.41)                   | 2.23 <sup>a</sup> | 4.15 <sup>a</sup> |
| TE value <sup>c</sup>             | 1.57                        | 2.22              | 2.07              |

Note: Data are reported on a lipid weight basis.

- <sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.  
<sup>b</sup> ND = Not detected. The value in parentheses is the estimated limit of detection.  
<sup>c</sup> TE values based on the California Department of Health Services Procedure.

Table 4-7. HRGC/HRMS Data Summaries for Pork (Los Angeles)

| Composite No.                     | Sample Concentrating (pg/g) |                   |                   |                   |                   |
|-----------------------------------|-----------------------------|-------------------|-------------------|-------------------|-------------------|
|                                   | 15630                       | 15635             | 15636             | 15629             | 15637             |
| <u>Compounds</u>                  |                             |                   |                   |                   |                   |
| 2,3,7,8-TCDF                      | ND (0.24) <sup>b</sup>      | ND (0.49)         | ND (0.22)         | ND (0.29)         | ND (0.27)         |
| 2,3,7,8-TCDD                      | ND (0.52)                   | ND (0.09)         | ND (0.21)         | ND (0.07)         | ND (0.38)         |
| 1,2,3,7,8-PeCDF                   | ND (0.62)                   | ND (0.37)         | ND (0.88)         | ND (0.84)         | ND (1.4)          |
| 2,3,4,7,8-PeCDF                   | ND (0.56)                   | ND (0.33)         | ND (0.81)         | ND (0.76)         | ND (1.28)         |
| 1,2,3,7,8-PeCDD                   | ND (2.1)                    | ND (1.84)         | ND (4.36)         | ND (1.0)          | ND (2.08)         |
| 1,2,3,4,7,8-HxCDF                 | ND (3.4)                    | ND (0.62)         | ND (0.49)         | ND (0.76)         | ND (1.83)         |
| 1,2,3,6,7,8-HxCDF                 | ND (0.66)                   | ND (0.61)         | ND (0.48)         | ND (0.75)         | ND (0.81)         |
| 2,3,4,6,7,8-HxCDF                 | ND (0.78)                   | ND (0.72)         | ND (0.57)         | ND (0.89)         | ND (0.97)         |
| 1,2,3,7,8,9-HxCDF                 | ND (0.86)                   | ND (0.79)         | ND (0.62)         | ND (0.97)         | ND (1.06)         |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | 3.5 <sup>a</sup>            | ND (0.62)         | ND (0.84)         | ND (1.9)          | ND (1.12)         |
| 1,2,3,7,8,9-HxCDD                 | ND (3.6)                    | ND (0.64)         | ND (0.86)         | ND (2.0)          | ND (1.16)         |
| 1,2,3,4,6,7,8-HpCDF               | 10.6 <sup>a</sup>           | 1.57 <sup>a</sup> | 1.83 <sup>a</sup> | ND (2.4)          | 5.06 <sup>a</sup> |
| 1,2,3,4,7,8,9-HpCDF               | ND (2.32)                   | ND (2.22)         | ND (2.62)         | ND (3.43)         | ND (5.4)          |
| 1,2,3,4,6,7,8-HpCDD               | 45.5                        | 7.63              | 3.32 <sup>a</sup> | 4.07 <sup>a</sup> | 13.2              |
| OCDF                              | 9.36 <sup>a</sup>           | 1.64 <sup>a</sup> | 1.24              | ND (1.31)         | 1.58              |
| OCDD                              | 254                         | 26.7 <sup>a</sup> | 13.7              | 18.7              | 72.9              |
| TE value <sup>c</sup>             | 1.79                        | 0.28              | 0.15              | 0.12              | 0.55              |

Note: Data are reported on a lipid weight basis.

<sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.

<sup>b</sup> ND = Not detected. The value in parentheses is the estimated limit of detection.

<sup>c</sup> TE values based on the California Department of Health Services Procedure.

Table 4-8. HRGC/HRMS Data Summaries for Pork  
(San Francisco)

| Composite No.                     | Sample Concentrating (pg/g) |                   |                   |
|-----------------------------------|-----------------------------|-------------------|-------------------|
|                                   | 15611                       | 15612             | 15613             |
| <u>Compounds</u>                  |                             |                   |                   |
| 2,3,7,8-TCDF                      | ND (0.37) <sup>b</sup>      | ND (0.35)         | ND (0.54)         |
| 2,3,7,8-TCDD                      | ND (0.39)                   | ND (0.49)         | ND (0.43)         |
| 1,2,3,7,8-PeCDF                   | ND (0.58)                   | ND (0.28)         | ND (0.44)         |
| 2,3,4,7,8-PeCDF                   | ND (0.53)                   | ND (0.26)         | ND (0.40)         |
| 1,2,3,7,8-PeCDD                   | ND (2.7)                    | ND (2.37)         | ND (1.94)         |
| 1,2,3,4,7,8-HxCDF                 | ND (0.40)                   | ND (3.33)         | ND (1.5)          |
| 1,2,3,6,7,8-HxCDF                 | ND (0.39)                   | ND (0.58)         | ND (0.84)         |
| 2,3,4,6,7,8-HxCDF                 | ND (0.47)                   | ND (0.68)         | ND (1.0)          |
| 1,2,3,7,8,9-HxCDF                 | ND (0.51)                   | ND (0.75)         | ND (1.09)         |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | ND (1.47)                   | 2.83 <sup>a</sup> | ND (1.03)         |
| 1,2,3,6,7,8-HxCDD                 | ND (1.51)                   | ND (2.92)         | ND (1.06)         |
| 1,2,3,4,6,7,8-HpCDF               | 2.09 <sup>a</sup>           | 5.68 <sup>a</sup> | 2.87 <sup>a</sup> |
| 1,2,3,4,7,8,9-HpCDF               | ND (2.99)                   | ND (3.12)         | ND (1.63)         |
| 1,2,3,4,6,7,8-HpCDD               | 3.04                        | 15.3              | 12.1 <sup>a</sup> |
| OCDF                              | ND (1.41)                   | ND (2.02)         | 1.89 <sup>a</sup> |
| OCDD                              | 24.9                        | 125               | 67.4              |
| TE value <sup>c</sup>             | 0.15                        | 0.71              | 0.45              |

Note: Data are reported on a lipid weight basis.

- <sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.  
<sup>b</sup> ND = Not detected. The value in parentheses is the estimated method detection limit.  
<sup>c</sup> TE values based on the California Department of Health Services Procedure.

Table 4-9. HRGC/HRMS Data Summaries for Chicken (Los Angeles)

| Composite No.                     | Concentration (pg/g)   |                   |                   |           |                   |
|-----------------------------------|------------------------|-------------------|-------------------|-----------|-------------------|
|                                   | 15631                  | 15632             | 15633             | 15634     | 156388            |
| <u>Compounds</u>                  |                        |                   |                   |           |                   |
| 2,3,7,8-TCDF                      | ND (0.19) <sup>b</sup> | ND (.58)          | ND (0.41)         | ND (0.41) | ND (0.39)         |
| 2,3,7,8-TCDD                      | ND (0.08)              | 0.43 <sup>a</sup> | 0.31              | ND (0.56) | ND (0.13)         |
| 1,2,3,7,8-PeCDF                   | ND (0.16)              | ND (0.666)        | ND (0.39)         | ND (0.43) | ND (0.21)         |
| 2,3,4,7,8-PeCDF                   | ND (0.15)              | ND (0.60)         | ND (0.36)         | ND (0.40) | ND (0.19)         |
| 1,2,3,7,8-PeCDD                   | ND (0.37)              | ND (2.19)         | ND (0.39)         | ND (1.0)  | ND (0.19)         |
| 1,2,3,4,7,8-HxCDF                 | ND (0.37)              | ND (0.59)         | ND (0.40)         | ND (0.58) | ND (0.35)         |
| 1,2,3,6,7,8-HxCDF                 | ND (0.36)              | ND (0.56)         | ND (0.40)         | ND (0.51) | ND (0.35)         |
| 2,3,4,6,7,8-HxCDF                 | ND (0.43)              | ND (0.69)         | ND (0.47)         | ND (0.68) | ND (0.41)         |
| 1,2,3,7,8,9-HxCDF                 | ND (0.47)              | ND (0.75)         | ND (0.52)         | ND (0.74) | ND (0.45)         |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | ND (1.23)              | ND (2.08)         | ND (1.25)         | ND (1.11) | ND (1.72)         |
| 1,2,3,7,8,9-HxCDD                 | ND (1.27)              | 2.14              | ND (1.29)         | ND (1.14) | ND (1.77)         |
| 1,2,3,4,6,7,8-HpCDF               | 1.89 <sup>a</sup>      | 24.6              | 1.57 <sup>a</sup> | 3.53      | 3.42 <sup>a</sup> |
| 2,3,4,7,8,9-HpCDF                 | ND (2.04)              | ND (4.1)          | ND (1.4)          | ND (0.57) | ND (0.47)         |
| 1,2,3,4,6,7,8-HpCDD               | ND (2.14)              | 35.2              | 3.06              | 6.69      | 2.20 <sup>a</sup> |
| OCDF                              | ND (4.49)              | 26.               | ND (1.22)         | 3.79      | ND (1.09)         |
| OCDD                              | ND (3.62)              | 64                | 21.7              | 49        | 8.32              |
| TE value <sup>c</sup>             | < 0.08                 | 1.23              | 0.45              | < 0.56    | 0.17              |

Note: Data reported on a lipid weight basis.

<sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.

<sup>b</sup> ND = Not detected. The value in parentheses is the estimated method detection limit.

<sup>c</sup> TE values based on the California Department of Health Services Procedure.

Table 4-10. HRGC/HRMS Data Summaries for Chicken  
(San Francisco)

| Composite No.                     | Sample Concentrating (pg/g) |                   |                   |
|-----------------------------------|-----------------------------|-------------------|-------------------|
|                                   | 15617                       | 15618             | 15619             |
| <u>Compounds</u>                  |                             |                   |                   |
| 2,3,7,8-TCDF                      | ND (0.29) <sup>b</sup>      | ND (0.36)         | 0.67 <sup>a</sup> |
| 2,3,7,8-TCDD                      | 1.67 <sup>a</sup>           | ND (0.39)         | ND (0.47)         |
| 1,2,3,7,8-PeCDF                   | ND (0.14)                   | ND (0.12)         | ND (0.15)         |
| 2,3,4,7,8-PeCDF                   | ND (0.13)                   | ND (0.11)         | ND (0.14)         |
| 1,2,3,7,8-PeCDD                   | ND (7.4)                    | ND (1.27)         | ND (0.44)         |
| 1,2,3,4,7,8-HxCDF                 | ND (0.51)                   | ND (0.51)         | ND (0.71)         |
| 1,2,3,6,7,8-HxCDF                 | ND (0.50)                   | ND (0.14)         | ND (0.70)         |
| 2,3,4,6,7,8-HxCDF                 | ND (0.60)                   | ND (0.17)         | ND (0.84)         |
| 1,2,3,7,8,9-HxCDF                 | ND (0.65)                   | ND (0.18)         | ND (0.91)         |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | 2.29                        | ND (0.76)         | ND (1.62)         |
| 1,2,3,6,7,8-HxCDD                 | 4.30                        | ND (0.78)         | ND (1.67)         |
| 1,2,3,4,6,7,8-HpCDF               | 1.01                        | ND (0.50)         | ND (0.51)         |
| 1,2,3,4,7,8,9-HpCDF               | ND (0.75)                   | ND (0.45)         | ND (0.73)         |
| 1,2,3,4,6,7,8-HpCDD               | 11.4                        | 1.35 <sup>a</sup> | 1.1 <sup>a</sup>  |
| OCDF                              | ND (0.64)                   | ND (0.74)         | ND (0.77)         |
| OCDD                              | 96.2                        | 2.61              | 6.21 <sup>a</sup> |
| TE value <sup>c</sup>             | 2.24                        | < 1.27            | 0.70              |

Note: Data are reported on a lipid weight basis.

- <sup>a</sup> Ratio of the characteristic ions was outside the qualitative identification data quality objectives.  
<sup>b</sup> ND = Not detected. The value in parentheses is the estimated method detection limit.  
<sup>c</sup> TE values based on the California Department of Health Services Procedure.

#### 4.1.6 Eggs

The analysis of the egg sample composites (Tables 4-11 and 4-12) demonstrated no consistent responses to any of the PCDD or PCDF compounds. All data are reported as not detected with the exception of sample composite 07093 in Table 4-11. Trace levels of the 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDF, and OCDD were detected in this composite. However, the concentrations of these compounds are not appreciably different from the estimated detection levels in the other composited egg samples.

### 4.2 Quality Control Analysis Results

As part of project quality control, additional samples were analyzed to demonstrate method performance. Specifically, routine method blanks and spiked sample matrices were analyzed.

#### 4.2.1 Method Blanks

Table 4-13 presents the results from the analysis of method blanks that were prepared and analyzed along with the actual composited samples. No PCDDs or PCDFs were detected in any of the laboratory method blanks.

#### 4.2.2 Spiked Sample Matrices

The results of the spiked sample analyses are presented in Tables 4-14 to 4-18. These spiked samples were prepared from replicate aliquots of one of each of the composited samples from the study design. The sample matrices were fortified with a solution of known concentration of the specific targeted PCDDs and PCDFs. Spiked sample matrices were prepared and analyzed for all food matrices except beef. The beef composites were analyzed along with the pork composites, and only a spiked matrix sample of pork was prepared. The data presented in Tables 4-14 to 4-18 identify the specific target compounds, the approximate spike level added to the sample matrix, and the measured recovery of each of the compounds.

Figures 4-1 to 4-5 are examples of a spiked egg matrix in comparison to the unspiked matrix. These figures are presented as an example of the observed signal-to-noise rates for samples fortified at a concentration equivalent to 0.8 to 4.2 pg/g of PCDDs and PCDFs.

Table 4-11. HRGC/HRMS Data Summaries for Eggs (Los Angeles)

| Compounds             | Sample Concentrating (pg/g) |            |            |            |            |
|-----------------------|-----------------------------|------------|------------|------------|------------|
|                       | 07094                       | 07095      | 07096      | 07097      | 07097-A    |
| 2,3,7,8-TCDF          | ND (0.023) <sup>a</sup>     | ND (0.014) | ND (0.017) | ND (0.017) | ND (0.027) |
| 2,3,7,8-TCDD          | ND (0.029)                  | ND (0.019) | ND (0.012) | ND (0.018) | ND (0.027) |
| 1,2,3,7,8-PCDF        | ND (0.098)                  | ND (0.025) | ND (0.028) | ND (0.049) | ND (0.077) |
| 2,3,4,7,8-PCDF        | ND (0.035)                  | ND (0.010) | ND (0.011) | ND (0.044) | ND (0.070) |
| 1,2,3,7,8-PCDD        | ND (0.20)                   | ND (0.15)  | ND (0.058) | ND (0.15)  | ND (0.40)  |
| 1,2,3,4,7,8-HxCDF     | ND (0.14)                   | ND (0.16)  | ND (0.25)  | ND (0.25)  | ND (0.24)  |
| 1,2,3,6,7,8-HxCDF     | ND (0.14)                   | ND (0.16)  | ND (0.17)  | ND (0.31)  | ND (0.23)  |
| 2,3,4,6,7,8-HxCDF     | ND (0.16)                   | ND (0.18)  | ND (0.21)  | ND (0.52)  | ND (0.27)  |
| 1,2,3,7,8,9-HxCDF     | ND (0.18)                   | ND (0.20)  | ND (0.23)  | ND (0.58)  | ND (0.30)  |
| 1,2,3,4,7,8-HxCDD     | ND (0.44)                   | ND (0.67)  | ND (0.12)  | ND (0.14)  | ND (0.46)  |
| 1,2,3,6,7,8-HxCDD     | ND (0.36)                   | ND (0.55)  | ND (0.10)  | ND (0.12)  | ND (0.38)  |
| 1,2,3,7,8,9-HxCDD     | ND (0.37)                   | ND (0.56)  | ND (0.10)  | ND (0.12)  | ND (0.38)  |
| 1,2,3,4,6,7,8-HpCDF   | ND (0.32)                   | ND (0.068) | ND (0.062) | ND (0.081) | ND (0.77)  |
| 1,2,3,4,7,8,9-HpCDF   | ND (0.46)                   | ND (0.095) | ND (0.087) | ND (0.12)  | ND (1.1)   |
| 1,2,3,4,6,7,8-HpCDD   | ND (0.42)                   | ND (0.095) | ND (0.16)  | (0.13)     | ND (0.38)  |
| OCDF                  | ND (1.3)                    | ND (0.095) | ND (0.32)  | ND (0.35)  | ND (0.20)  |
| OCDD                  | ND (1.0)                    | ND (0.80)  | ND (0.99)  | ND (0.97)  | ND (1.6)   |
| Sample weight         | 120.4 g                     | 120.3 g    | 120 g      | 120.6 g    | 120.5 g    |
| Lipid content         | 4.1%                        | 10.7%      | 7.4%       | 4.8%       | 4.8%       |
| TE value <sup>b</sup> | < 0.20                      | < 0.15     | < 0.58     | < 0.15     | < 0.40     |

<sup>a</sup> ND = Not detected. Value in parentheses is the estimated limit of detection.

<sup>b</sup> TE values based on the California Department of Health Services Procedure.

Table 4-12. HRGC/HRMS Data Summaries for Eggs  
(San Francisco)

| Composite No.         | Sample Concentrating (pg/g) |            |            |
|-----------------------|-----------------------------|------------|------------|
|                       | 07091                       | 07092      | 07093      |
| <u>Compounds</u>      |                             |            |            |
| 2,3,7,8-TCDF          | ND (0.008) <sup>a</sup>     | ND (0.006) | 0.011      |
| 2,3,7,8-TCDD          | ND (0.019)                  | ND (0.030) | ND (0.006) |
| 1,2,3,7,8-PCDF        | ND (0.011)                  | ND (0.023) | ND (0.019) |
| 2,3,4,7,8-PCDF        | ND (0.023)                  | ND (0.021) | ND (0.017) |
| 1,2,3,7,8-PCDD        | ND (0.057)                  | ND (0.053) | ND (0.035) |
| 1,2,3,4,7,8-HxCDF     | ND (0.046)                  | ND (0.044) | ND (0.086) |
| 1,2,3,6,7,8-HxCDF     | ND (0.045)                  | ND (0.043) | ND (0.036) |
| 2,3,4,6,7,8-HxCDF     | ND (0.054)                  | ND (0.051) | ND (0.043) |
| 1,2,3,7,8,9-HxCDF     | ND (0.059)                  | ND (0.056) | ND (0.047) |
| 1,2,3,4,7,8-HxCDD     | ND (0.17)                   | ND (0.25)  | ND (0.078) |
| 1,2,3,6,7,8-HxCDD     | ND (0.13)                   | ND (0.20)  | ND (0.063) |
| 1,2,3,7,8,9-HxCDD     | ND (0.14)                   | ND (0.21)  | ND (0.065) |
| 1,2,3,4,6,7,8-HpCDF   | ND (0.069)                  | ND (0.13)  | 0.065      |
| 1,2,3,4,7,8,9-HpCDF   | ND (0.098)                  | ND (0.18)  | ND (0.036) |
| 1,2,3,4,6,7,8-HpCDD   | ND (0.13)                   | ND (0.24)  | ND (0.075) |
| OCDF                  | ND (0.21)                   | ND (0.15)  | ND (0.048) |
| OCDD                  | ND (1.05)                   | ND (0.1)   | 1.30       |
| Sample weight         | 119.2 g                     | 139.3 g    | 168 g      |
| Lipid content         | 6.9%                        | 6.0%       | 4.4%       |
| TE value <sup>b</sup> | < 0.057                     | < 0.053    | < 0.035    |

<sup>a</sup> ND = Not detected. Value in parentheses is the estimated limit of detection.

<sup>b</sup> TE values based on the California Department of Health Services Procedure.

Table 4-13. Summary of the Analysis Results for Laboratory Method Blanks

| Compound                          | Food Matrix Blank -<br>Equivalent Concentration (pg/g) |              |           |           |           |
|-----------------------------------|--|--------------|-----------|-----------|-----------|
|                                   | Fish   | Chicken/Beef | Pork      | Milk      | Egg       |
| 2,3,7,8-TCDF                      | ND (0.07) <sup>a</sup>                                 | ND (0.38)    | ND (0.17) | ND (0.04) | ND (0.05) |
| 2,3,7,8-TCDD                      | ND (0.19)  | ND (0.43)    | ND (0.36) | ND (0.07) | ND (0.16) |
| 1,2,3,7,8-PeCDF                   | ND (0.01)  | ND (0.34)    | ND (0.03) | ND (0.10) | ND (0.08) |
| 2,3,4,7,8-PeCDF                   | ND (0.01)  | ND (0.31)    | ND (0.03) | ND (0.09) | ND (0.08) |
| 1,2,3,7,8-PeCDD                   | ND (0.60)  | ND (1.02)    | ND (0.10) | ND (0.91) | ND (1.05) |
| 1,2,3,4,7,8-HxCDF                 | ND (0.09)  | ND (0.45)    | ND (0.25) | ND (0.27) | ND (0.12) |
| 1,2,3,6,7,8-HxCDF                 | ND (0.09)  | ND (0.44)    | ND (0.25) | ND (0.26) | ND (0.12) |
| 2,3,4,6,7,8-HxCDF                 | ND (0.11)  | ND (0.52)    | ND (0.29) | ND (0.31) | ND (0.15) |
| 1,2,3,7,8,9-HxCDF                 | ND (0.12)  | ND (0.57)    | ND (0.32) | ND (0.34) | ND (0.16) |
| 1,2,3,4,7,8/<br>1,2,3,6,7,8-HxCDD | ND (0.30)  | ND (6.12)    | ND (0.96) | ND (0.42) | ND (1.96) |
| 1,2,3,7,8,9-HxCDD                 | ND (0.25)  | ND (6.31)    | ND (0.99) | ND (0.35) | ND (1.64) |
| 1,2,3,4,6,7,8-HpCDF               | ND (0.16)  | ND (0.48)    | ND (0.48) | ND (0.14) | ND (0.29) |
| 1,2,3,4,7,8,9-HpCDF               | ND (0.23)  | ND (0.69)    | ND (0.68) | ND (0.20) | ND (0.42) |
| 1,2,3,4,6,7,8-HpCDD               | ND (0.57)  | ND (2.18)    | ND (2.46) | ND (0.49) | ND (1.63) |
| OCDF                              | ND (1.04)  | ND (2.02)    | ND (1.69) | ND (0.19) | ND (1.19) |
| OCDD                              | ND (0.81)  | ND (1.63)    | ND (3.37) | ND (0.27) | ND (2.48) |

<sup>a</sup> ND = Not detected. The values in parentheses are the estimated limits of detection.

Table 4-14. Method Accuracy--Fish

| Compound            | Approximate<br>Spike Level<br>(pg/g) | Recovery (%) |         |
|---------------------|--------------------------------------|--------------|---------|
|                     |                                      | Spike 1      | Spike 2 |
| 2,3,7,8-TCDF        | 20                                   | 77           | 73      |
| 2,3,7,8-TCDD        | 10                                   | 119          | 87      |
| 1,2,3,7,8-PCDF      | 20                                   | 102          | 148     |
| 2,3,4,7,8-PCDF      | 20                                   | NC           | 93      |
| 1,2,3,7,8-PCDD      | 10                                   | NC           | 78      |
| 1,2,3,4,7,8-HxCDF   | 50                                   | 74           | 100     |
| 1,2,3,6,7,8-HxCDF   | 50                                   | 88           | 77      |
| 2,3,4,6,7,8-HxCDF   | 50                                   | 97           | 93      |
| 1,2,3,7,8,9-HxCDF   | 50                                   | 77           | 72      |
| 1,2,3,4,7,8-HxCDD   | 20                                   | 129          | 153     |
| 1,2,3,6,7,8-HxCDD   | 20                                   | 95           | 93      |
| 1,2,3,7,8,9-HxCDD   | 20                                   | 121          | 121     |
| 1,2,3,4,6,7,8-HpCDF | 50                                   | 109          | 96      |
| 1,2,3,4,7,8,9-HpCDF | 50                                   | 93           | 87      |
| 1,2,3,4,6,7,8-HpCDD | 20                                   | 66           | 85      |
| OCDF                | 50                                   | 98           | 94      |
| OCDD                | 20                                   | 130          | 162     |

NC= Not calculated.

Table 4-15. Method Accuracy--Milk

| Compound            | Approximate<br>Spike Level<br>(pg/g) <sup>a</sup> | Recovery (%) |         |
|---------------------|---|--------------|---------|
|                     |   | Spike 1      | Spike 2 |
| 2,3,7,8-TCDF        | 32  | 104          | 96      |
| 2,3,7,8-TCDD        | 16  | 92           | 94      |
| 1,2,3,7,8-PCDF      | 32  | 101          | 101     |
| 2,3,4,7,8-PCDF      | 32  | 95           | 85      |
| 1,2,3,7,8-PCDD      | 16  | 96           | 119     |
| 1,2,3,4,7,8-HxCDF   | 80  | 77           | 81      |
| 1,2,3,6,7,8-HxCDF   | 80  | 76           | 79      |
| 2,3,4,6,7,8-HxCDF   | 80  | 72           | 94      |
| 1,2,3,7,8,9-HxCDF   | 80  | 65           | 76      |
| 1,2,3,4,7,8-HxCDD   | 32  | 150          | 95      |
| 1,2,3,6,7,8-HxCDD   | 32  | 122          | 82      |
| 1,2,3,7,8,9-HxCDD   | 32  | 126          | 104     |
| 1,2,3,4,6,7,8-HpCDF | 80  | 111          | 98      |
| 1,2,3,4,7,8,9-HpCDF | 80  | 94           | 85      |
| 1,2,3,4,6,7,8-HpCDD | 32  | 71           | 93      |
| OCDF                | 80  | 106          | 113     |
| OCDD                | 32  | 74           | 121     |

<sup>a</sup> Lipid adjusted concentration.

Table 4-16. Method Accuracy--Chicken

| Compound            | Approximate<br>Spike Level<br>(pg/g) | Recovery (%) |         |
|---------------------|--------------------------------------|--------------|---------|
|                     |                                      | Spike 1      | Spike 2 |
| 2,3,7,8-TCDF        | 20                                   | 81           | 90      |
| 2,3,7,8-TCDD        | 10                                   | 86           | 95      |
| 1,2,3,7,8-PCDF      | 20                                   | 88           | 93      |
| 2,3,4,7,8-PCDF      | 20                                   | 86           | 92      |
| 1,2,3,7,8-PCDD      | 10                                   | 81           | 93      |
| 1,2,3,4,7,8-HxCDF   | 50                                   | 79           | 75      |
| 1,2,3,6,7,8-HxCDF   | 50                                   | 82           | 70      |
| 2,3,4,6,7,8-HxCDF   | 50                                   | 84           | 82      |
| 1,2,3,7,8,9-HxCDF   | 50                                   | 68           | 62      |
| 1,2,3,4,7,8-HxCDD   | 20                                   | 119          | 101     |
| 1,2,3,6,7,8-HxCDD   | 20                                   | 111          | 100     |
| 1,2,3,7,8,9-HxCDD   | 20                                   | 98           | 95      |
| 1,2,3,4,6,7,8-HpCDF | 50                                   | 104          | 119     |
| 1,2,3,4,7,8,9-HpCDF | 50                                   | 97           | 92      |
| 1,2,3,4,6,7,8-HpCDD | 20                                   | 81           | 86      |
| OCDF                | 50                                   | 119          | 100     |
| OCDD                | 20                                   | 114          | 121     |

Table 4-17. Method Accuracy--Pork

| Compound            | Approximate<br>Spike Level<br>(pg/g) | Recovery (%) |
|---------------------|--------------------------------------|--------------|
| 2,3,7,8-TCDF        | 20                                   | 86           |
| 2,3,7,8-TCDD        | 10                                   | 106          |
| 1,2,3,7,8-PCDF      | 20                                   | 106          |
| 2,3,4,7,8-PCDF      | 20                                   | 83           |
| 1,2,3,7,8-PCDD      | 10                                   | 106          |
| 1,2,3,4,7,8-HxCDF   | 50                                   | 107          |
| 1,2,3,6,7,8-HxCDF   | 50                                   | 90           |
| 2,3,4,6,7,8-HxCDF   | 50                                   | 92           |
| 1,2,3,7,8,9-HxCDF   | 50                                   | 87           |
| 1,2,3,4,7,8-HxCDD   | 20                                   | 100          |
| 1,2,3,6,7,8-HxCDD   | 20                                   | 91           |
| 1,2,3,7,8,9-HxCDD   | 20                                   | 102          |
| 1,2,3,4,6,7,8-HpCDF | 50                                   | 140          |
| 1,2,3,4,7,8,9-HpCDF | 50                                   | 112          |
| 1,2,3,4,6,7,8-HpCDD | 20                                   | NC           |
| OCDF                | 50                                   | 135          |
| OCDD                | 20                                   | NC           |

NC = Not calculated.

Table 4-18. Method Accuracy--Whole Egg Basis (120 g)

| Composite No.       | Spike Level<br>(pg/g) | Recovery (%) |         |
|---------------------|-----------------------|--------------|---------|
|                     |                       | Spike 1      | Spike 2 |
| <u>Compound</u>     |                       |              |         |
| 2,3,7,8-TCDF        | 1.66                  | 93           | 100     |
| 2,3,7,8-TCDD        | 0.83                  | 101          | 97      |
| 1,2,3,7,8-PCDF      | 1.66                  | 118          | 126     |
| 2,3,4,7,8-PCDF      | 1.66                  | 106          | 108     |
| 1,2,3,7,8-PCDD      | 0.83                  | 88           | 76      |
| 1,2,3,4,7,8-HxCDF   | 4.17                  | 77           | 134     |
| 1,2,3,6,7,8-HxCDF   | 4.17                  | 76           | 179     |
| 2,3,4,6,7,8-HxCDF   | 4.17                  | 96           | 213     |
| 1,2,3,7,8,9-HxCDF   | 4.17                  | 85           | 172     |
| 1,2,3,4,7,8-HxCDD   | 1.66                  | 99           | 121     |
| 1,2,3,6,7,8-HxCDD   | 1.66                  | 104          | 97      |
| 1,2,3,7,8,9-HxCDD   | 1.66                  | 86           | 109     |
| 1,2,3,4,6,7,8-HpCDF | 4.17                  | 111          | 112     |
| 1,2,3,4,7,8,9-HpCDF | 4.17                  | 98           | 88      |
| 1,2,3,4,6,7,8-HpCDD | 1.66                  | 110          | 97      |
| OCDF                | 4.17                  | 114          | 125     |
| OCDD                | 1.66                  | 175          | 165     |

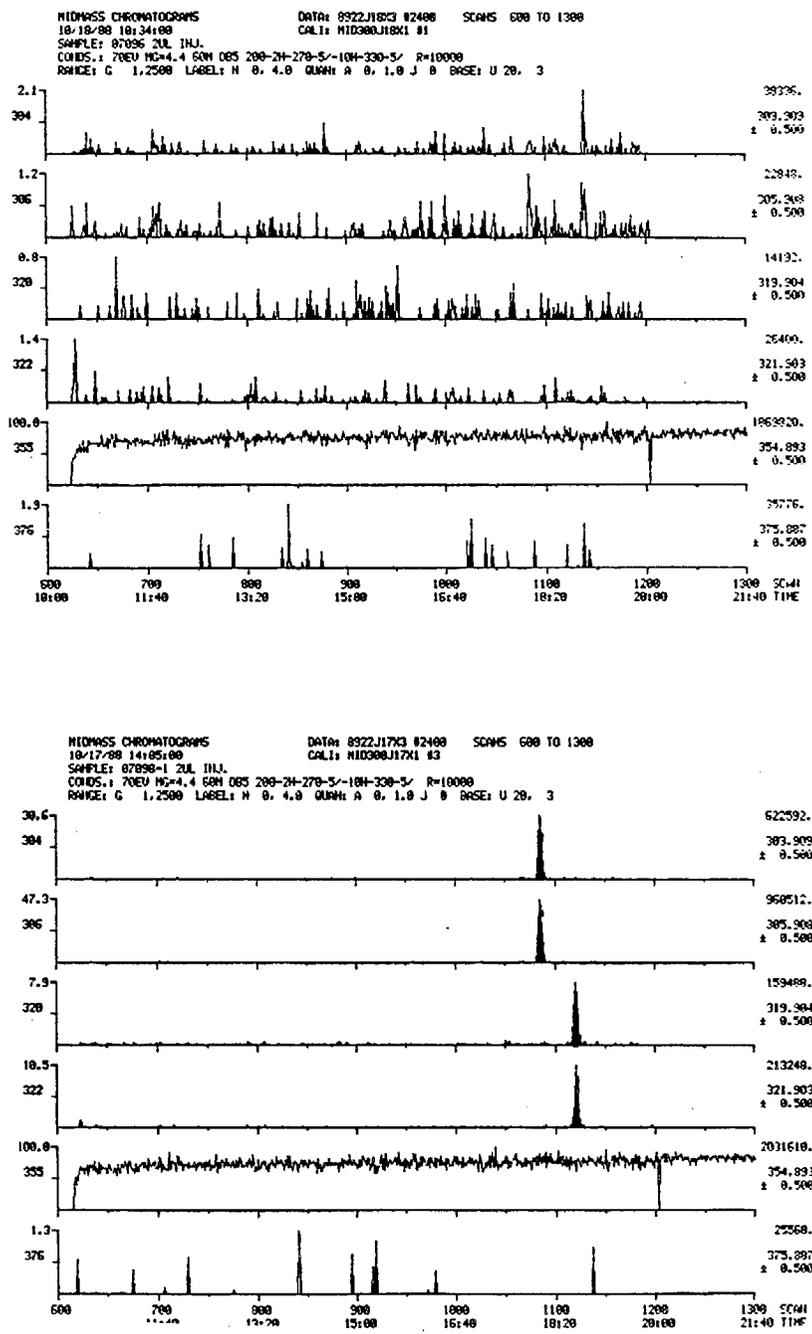


Figure 4-1. Reconstructed ion chromatograms from the HRMS analysis of an unspiked and a spiked egg composite for TCDF and TCDD. Each of the RICs reflect the responses of the characteristic ions for TCDF (m/z 304 and 306), TCDD (m/z 320 and 322), the PFK lock mass (m/z 355), and hexachlorodiphenyl ether (m/z 376). The spiked levels for 2,3,7,8-TCDF and 2,3,7,8-TCDD are equivalent to 1.7 pg/g and 0.8 pg/g, respectively.

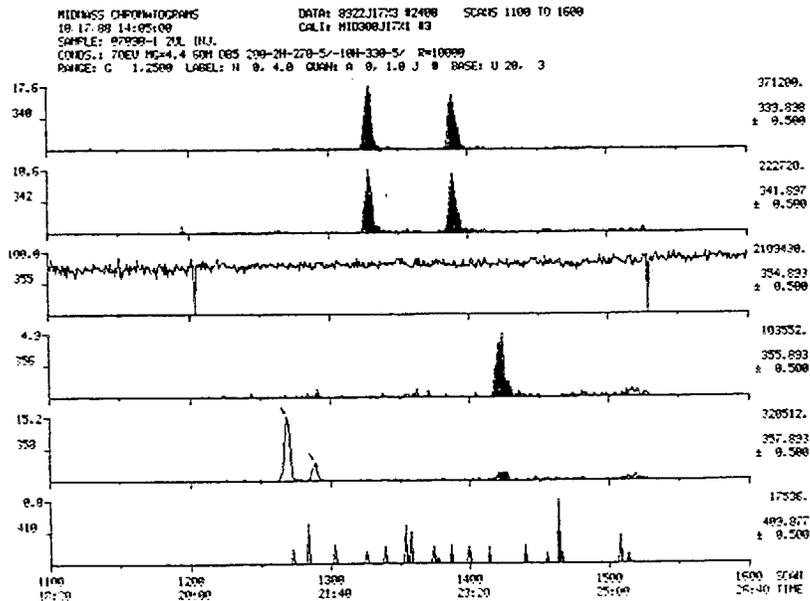
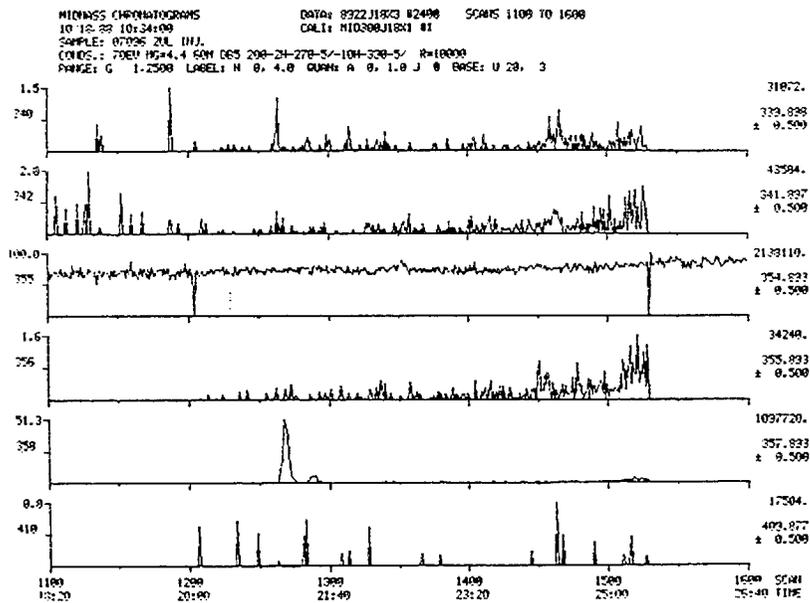


Figure 4-2. Reconstructed ion chromatograms from the HRMS analysis of an unspiked and a spiked egg composite for PeCDF and PeCDD isomers. Each of the RICs reflect the responses of the characteristic ions for the PeCDF isomers ( $m/z$  340 and 342), the PFK lock mass ( $m/z$  355), the PeCDD isomers ( $m/z$  356 and 358), and heptachlorodiphenyl ether ( $m/z$  410). The spiked levels for each of the two PeCDF isomers and the single PeCDD isomers are equivalent to 1.7  $\mu\text{g/g}$  and 0.8  $\mu\text{g/g}$ , respectively.

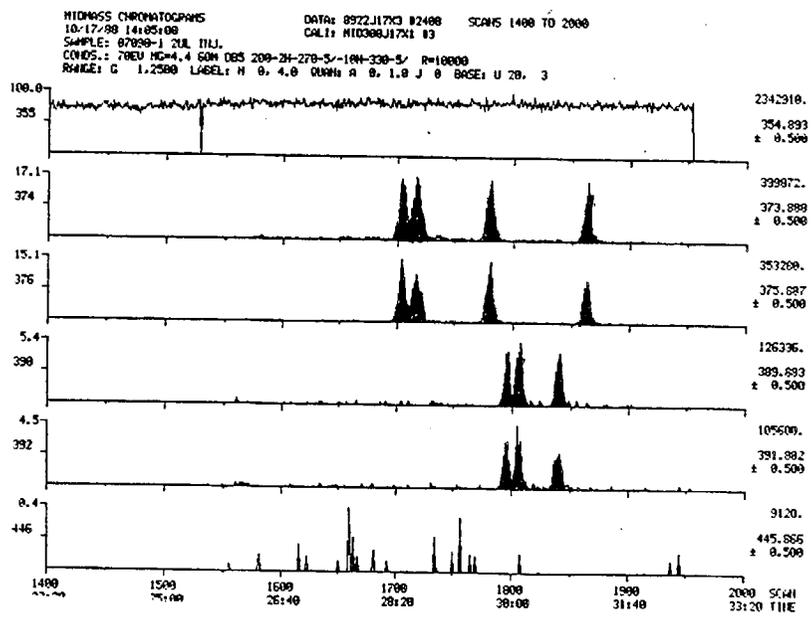
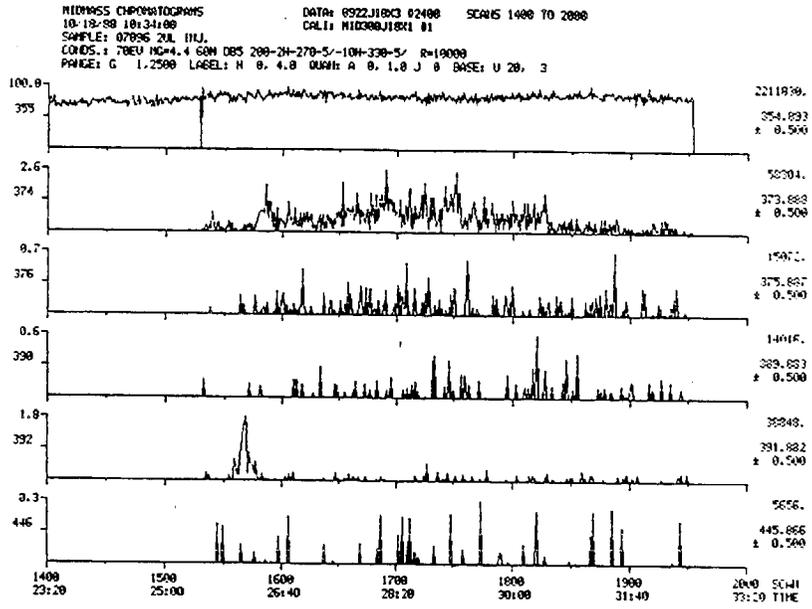


Figure 4-3. Reconstructed ion chromatograms from the HRMS analysis of an unspiked and a spiked egg composite for HxCDF and HxCDD isomers. Each of the RICs reflect the responses of the characteristic ions for the lock mass of PFK ( $m/z$  355), the HxCDF isomers ( $m/z$  374 and 376), the HxCDD isomers ( $m/z$  390 and 392) and octachlorodiphenyl ethers ( $m/z$  446). The spiked levels for each of the four HxCDF isomers and the three HxCDD isomers are equivalent to 4.2 pg/g and 1.7 pg/g, respectively.

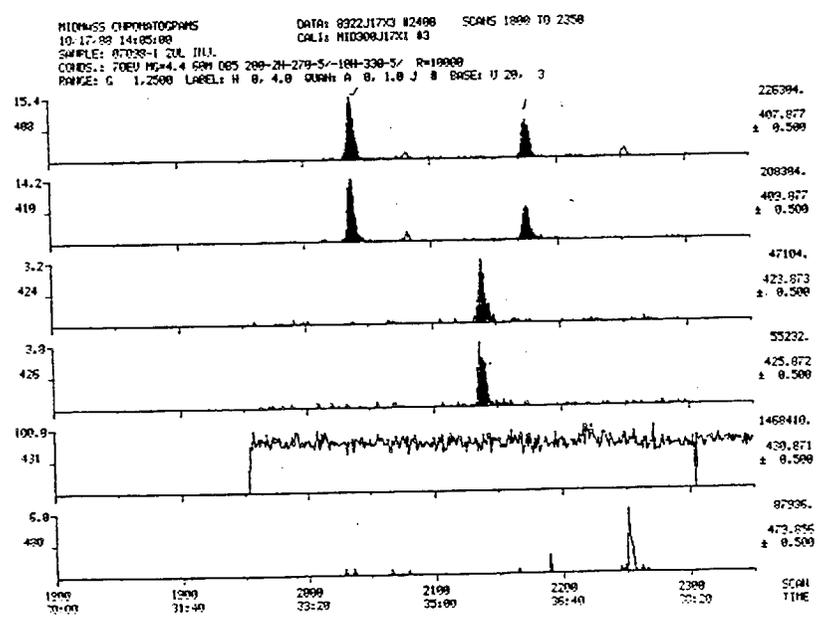
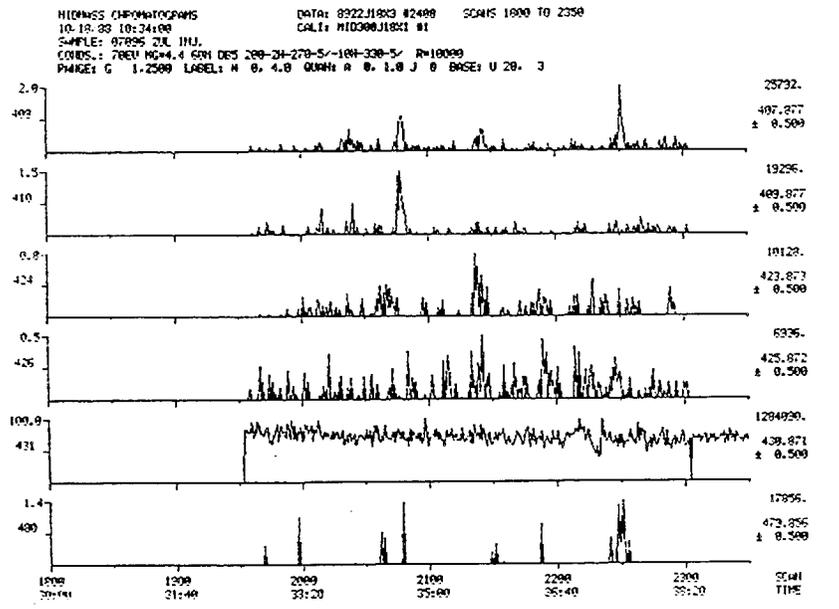


Figure 4-4. Reconstructed ion chromatograms from the HRMS analysis of an unspiked and a spiked egg composite for HpCDF and HpCDD isomers. Each set of the RICs reflect the responses of the characteristic ions for HpCDF ( $m/z$  408 and 410), HpCDD ( $m/z$  424 and 426), the lock mass for PFK at  $m/z$  431 and nonachlorodiphenyl ether at  $m/z$  480. The spiked levels for each of the two HpCDF isomers and the single HpCDD isomers are equivalent to 4.2 pg/g and 1.7 pg/g, respectively.

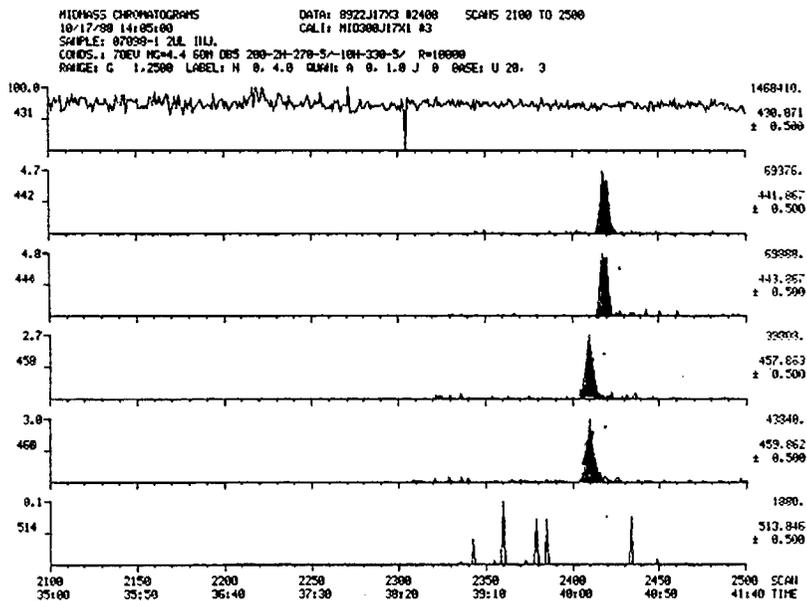
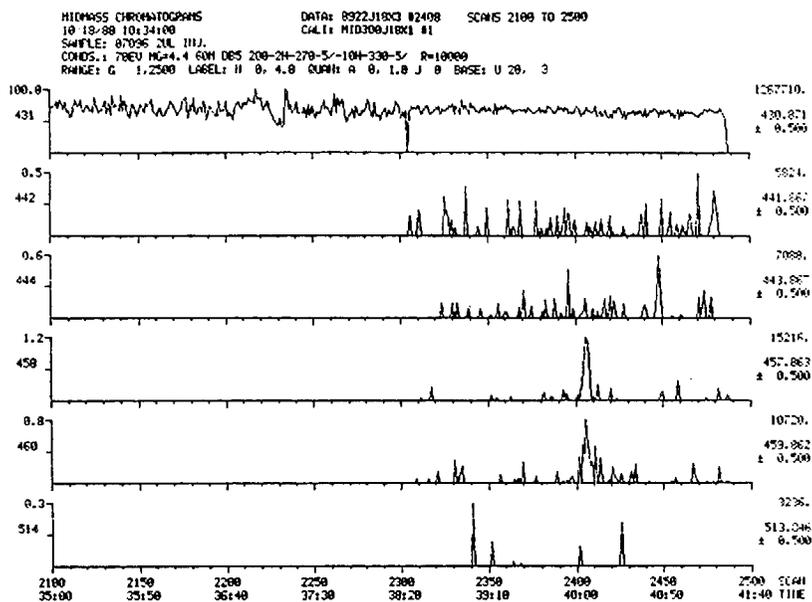


Figure 4-5. Reconstructed ion chromatograms from the HRMS analysis of an unspiked and a spiked egg composite for OCDF and OCDD. Each of the RICs reflect the responses of characteristic ions for the PFK lock mass ( $m/z$  431), the OCDF ( $m/z$  442 and 444), the OCDD ( $m/z$  458 and 460) and decachlorodiphenyl ether ( $m/z$  514). The spiked levels for OCDF and OCDD are equivalent to 4.2 pg/g and 1.7 pg/g, respectively.

### 4.3 Statistical Analysis Results

Fifty composite food samples were analyzed for the target compounds. Of the 50 composites, 31 were of foodstuff samples from Los Angeles and 19 from San Francisco. The relative size between the two sets of composites reflects approximately the relative size in population of the two cities. The distribution of the 50 composite samples across cities and foodstuff categories is shown in Table 4-19.

The individual foodstuff samples in each category were composited separately for San Francisco and Los Angeles. Approximately equal numbers of samples were used for composites in a given foodstuff category. A summary of the final compositing scheme is given in Table 4-20. The number of individual food samples reflects the number of sites at which these samples were collected. These figures were also used as weights in subsequent statistical analyses.

#### 4.3.1 Overall Results on Occurrences

The frequencies of detects and nondetects in the 50 composite samples, regardless of collection site, are summarized in Table 4-21. The table shows the number of composite samples with residue levels below ("Non Detects") or above ("Detects") the limit of detection for each of the compounds in each of the seven food categories. The last two columns show the frequencies across all foodstuff groups for both cities.

Of the target compounds, only six were not detected in any of the 50 composites. The compounds that were not detected included the PeCDF and HxCDF isomers. Also, detectable levels of 1,2,3,4,6,8,9-HpCDF were found in only one composite sample (133 pg/g in a freshwater fish composite from San Francisco). In order, the compounds with detectable levels in a number of composites are as follows:

|                               |                        |
|-------------------------------|------------------------|
| OCDD                          | in 39 (78%) composites |
| 1,2,3,4,6,7,8-HpCDD           | in 36 (72%) composites |
| 2,3,7,8-TCDF                  | in 23 (46%) composites |
| 1,2,3,4,6,7,8-HpCDF           | in 20 (40%) composites |
| 1,2,3,4,7,8/1,2,3,6,7,8-HxCDD | in 14 (28%) composites |
| 2,3,7,8-TCDD                  | in 12 (24%) composites |
| OCDF                          | in 7 (14%) composites  |
| 1,2,3,7,8-PeCDD               | in 6 (12%) composites  |
| 1,2,3,7,8,9-HxCDD             | in 6 (12%) composites  |
| 1,2,3,4,7,8,9-HpCDF           | in 1 (2%) composite    |

Table 4-19. Composites Per Foodstuff and City

|                 | Los Angeles | San Francisco | Total |
|-----------------|-------------|---------------|-------|
| Saltwater fish  | 3(31)       | 2(17)         | 5(48) |
| Freshwater fish | 3(31)       | 2(17)         | 5(48) |
| Pork            | 5(31)       | 3(20)         | 8(51) |
| Beef            | 5(31)       | 3(19)         | 8(50) |
| Chicken         | 5(31)       | 3(20)         | 8(51) |
| Egg             | 5(31)       | 3(20)         | 8(51) |
| Milk            | 5(31)       | 3(18)         | 8(49) |
| Total           | 31          | 19            | 50    |

Note: Number of sites sampled and included in the composites is indicated in parentheses.

Table 4-20. Summary of Compositing Scheme Per Foodstuff and City

| Foodstuff       | City | Composite No. | No. of Sites per Composite | No. of Sites per City | No. of Sites per Foodstuff |
|-----------------|------|---------------|----------------------------|-----------------------|----------------------------|
| Saltwater Fish  | LA   | 15644         | 10                         |                       |                            |
| Saltwater Fish  | LA   | 15645         | 11                         |                       |                            |
| Saltwater Fish  | LA   | 15648         | 10                         | 31                    |                            |
| Saltwater Fish  | SF   | 15620         | 8                          |                       |                            |
| Saltwater Fish  | SF   | 15621         | 9                          | 17                    | 48                         |
| Freshwater Fish | LA   | 15646         | 10                         |                       |                            |
| Freshwater Fish | LA   | 15647         | 11                         |                       |                            |
| Freshwater Fish | LA   | 15649         | 10                         | 31                    |                            |
| Freshwater Fish | SF   | 15622         | 8                          |                       |                            |
| Freshwater Fish | SF   | 15623         | 9                          | 17                    | 48                         |
| Pork            | LA   | 15629         | 6                          |                       |                            |
| Pork            | LA   | 15630         | 6                          |                       |                            |
| Pork            | LA   | 15635         | 6                          |                       |                            |
| Pork            | LA   | 15636         | 6                          |                       |                            |
| Pork            | LA   | 15637         | 7                          | 31                    |                            |
| Pork            | SF   | 15611         | 6                          |                       |                            |
| Pork            | SF   | 15612         | 7                          |                       |                            |
| Pork            | SF   | 15613         | 7                          | 20                    | 51                         |
| Beef            | LA   | 15624         | 6                          |                       |                            |
| Beef            | LA   | 15625         | 6                          |                       |                            |
| Beef            | LA   | 15626         | 6                          |                       |                            |
| Beef            | LA   | 15627         | 6                          |                       |                            |
| Beef            | LA   | 15628         | 7                          | 31                    |                            |
| Beef            | SF   | 15608         | 6                          |                       |                            |
| Beef            | SF   | 15609         | 7                          |                       |                            |
| Beef            | SF   | 15610         | 6                          | 19                    | 50                         |
| Chicken         | LA   | 15631         | 6                          |                       |                            |
| Chicken         | LA   | 15632         | 7                          |                       |                            |
| Chicken         | LA   | 15633         | 6                          |                       |                            |
| Chicken         | LA   | 15634         | 6                          |                       |                            |
| Chicken         | LA   | 15638         | 6                          | 31                    |                            |
| Chicken         | SF   | 15617         | 6                          |                       |                            |
| Chicken         | SF   | 15618         | 7                          |                       |                            |
| Chicken         | SF   | 15619         | 7                          | 20                    | 51                         |
| Egg             | LA   | 7097-A        | 7                          |                       |                            |
| Egg             | LA   | 7094          | 6                          |                       |                            |
| Egg             | LA   | 7095          | 6                          |                       |                            |
| Egg             | LA   | 7096          | 6                          |                       |                            |
| Egg             | LA   | 7097          | 6                          | 31                    |                            |
| Egg             | SF   | 7091          | 6                          |                       |                            |
| Egg             | SF   | 7092          | 7                          |                       |                            |
| Egg             | SF   | 7093          | 7                          | 20                    | 51                         |
| Milk            | LA   | 15639         | 7                          |                       |                            |
| Milk            | LA   | 15640         | 6                          |                       |                            |
| Milk            | LA   | 15641         | 6                          |                       |                            |
| Milk            | LA   | 15642         | 6                          |                       |                            |
| Milk            | LA   | 15643         | 6                          | 31                    |                            |
| Milk            | SF   | 15614         | 6                          |                       |                            |
| Milk            | SF   | 15615         | 6                          |                       |                            |
| Milk            | SF   | 15616         | 6                          | 18                    | 49                         |

Table 4-21. Frequency of Detection of Specific PCDD and PCDF Compounds in Foodstuffs Collected From Los Angeles and San Francisco

| COMPOUND (No.)           | LOS ANGELES AND SAN FRANCISCO COMBINED |         |             |                       |         |             |                       |         |             |                       |         |             |
|--------------------------|--|---------|-------------|-----------------------|---------|-------------|-----------------------|---------|-------------|-----------------------|---------|-------------|
|                          | SALTWATER FISH                         |         |             | FRESHWATER FISH       |         |             | FORK                  |         |             | REEF                  |         |             |
|                          | NO. OF COMPOSITES (N)                  | DETECTS | NON DETECTS | NO. OF COMPOSITES (N) | DETECTS | NON DETECTS | NO. OF COMPOSITES (N) | DETECTS | NON DETECTS | NO. OF COMPOSITES (N) | DETECTS | NON DETECTS |
| 2378-TCDF (1)            | 5                                      | 0       | 5           | 5                     | 0       | 5           | 8                     | 0       | 5           | 0                     | 5       | 3           |
| 2378-TCDD (2)            | 4                                      | 1       | 3           | 4                     | 1       | 3           | 8                     | 0       | 4           | 0                     | 4       | 0           |
| 12378-TCDF (3)           | 5                                      | 0       | 5           | 5                     | 0       | 5           | 8                     | 0       | 5           | 0                     | 5       | 0           |
| 23478-TCDF (4)           | 5                                      | 0       | 5           | 5                     | 0       | 5           | 8                     | 0       | 5           | 0                     | 5       | 0           |
| 12378-TCDD (5)           | 4                                      | 1       | 3           | 4                     | 1       | 3           | 8                     | 0       | 4           | 0                     | 4       | 0           |
| 123478-HxCDF (6)         | 5                                      | 0       | 5           | 5                     | 0       | 5           | 8                     | 0       | 5           | 0                     | 5       | 0           |
| 123678-HxCDF (7)         | 5                                      | 0       | 5           | 5                     | 0       | 5           | 8                     | 0       | 5           | 0                     | 5       | 0           |
| 234678-HxCDF (8)         | 5                                      | 0       | 5           | 5                     | 0       | 5           | 8                     | 0       | 5           | 0                     | 5       | 0           |
| 123789-HxCDF (9)         | 5                                      | 0       | 5           | 5                     | 0       | 5           | 8                     | 0       | 5           | 0                     | 5       | 0           |
| 123478/123678-HxCDD (10) | 2                                      | 3       | 1           | 4                     | 1       | 3           | 6                     | 2       | 4           | 2                     | 5       | 3           |
| 123789-HxCDD (11)        | 5                                      | 0       | 5           | 4                     | 1       | 3           | 8                     | 0       | 4           | 0                     | 4       | 0           |
| 1234678-HxCDF (12)       | 4                                      | 1       | 3           | 5                     | 0       | 4           | 1                     | 7       | 4           | 1                     | 4       | 4           |
| 1234789-HxCDF (13)       | 5                                      | 0       | 5           | 4                     | 1       | 3           | 8                     | 0       | 4           | 0                     | 4       | 0           |
| 1234678-HxCDD (14)       | 3                                      | 2       | 1           | 4                     | 1       | 3           | 0                     | 8       | 1           | 1                     | 7       | 7           |
| TCDF (15)                | 5                                      | 0       | 5           | 5                     | 0       | 5           | 3                     | 5       | 5           | 8                     | 0       | 0           |
| TCDD (16)                | 0                                      | 5       | 0           | 5                     | 0       | 5           | 0                     | 8       | 1           | 7                     | 0       | 7           |

Table 4-21 (Concluded)

| COMPOUND (No.)           | LOS ANGELES AND SAN FRANCISCO COMBINED |             |                       |             |                       |             |                       |             |                       |             |                       |             |                       |             |
|--------------------------|--|-------------|-----------------------|-------------|-----------------------|-------------|-----------------------|-------------|-----------------------|-------------|-----------------------|-------------|-----------------------|-------------|
|                          | CHICKEN                                |             |                       |             | EGG                   |             |                       |             | MILK                  |             |                       |             | ALL FOODS/BOTH CITIES |             |
|                          | NO. OF COMPOSITES (N)                  |             | NO. OF COMPOSITES (N) |             | NO. OF COMPOSITES (N) |             | NO. OF COMPOSITES (N) |             | NO. OF COMPOSITES (N) |             | NO. OF COMPOSITES (N) |             | NO. OF COMPOSITES (N) |             |
|                          | DETECTS                                | NON DETECTS | DETECTS               | NON DETECTS | DETECTS               | NON DETECTS | DETECTS               | NON DETECTS | DETECTS               | NON DETECTS | DETECTS               | NON DETECTS | DETECTS               | NON DETECTS |
| 2378-TCDF (1)            | 7                                      | 1           | 7                     | 1           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 8           | 27                    | 23          |
| 2378-TCDD (2)            | 5                                      | 3           | 8                     | 0           | 7                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 1           | 38                    | 12          |
| 12378-PCDF (3)           | 8                                      | 0           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 50                    | 0           |
| 23478-PCDF (4)           | 8                                      | 0           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 50                    | 0           |
| 12378-PCDD (5)           | 8                                      | 0           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 44                    | 6           |
| 123478-HxCDF (6)         | 8                                      | 0           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 50                    | 0           |
| 123678-HxCDF (7)         | 8                                      | 0           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 50                    | 0           |
| 234678-HxCDF (8)         | 8                                      | 0           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 50                    | 0           |
| 123789-HxCDF (9)         | 8                                      | 0           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 50                    | 0           |
| 123478/123678-HxCDD (10) | 7                                      | 1           | 8                     | 0           | 7                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 1           | 36                    | 14          |
| 123789-HxCDD (11)        | 6                                      | 2           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 44                    | 6           |
| 1234678-HxCDF (12)       | 2                                      | 6           | 7                     | 1           | 7                     | 1           | 1                     | 1           | 1                     | 1           | 1                     | 1           | 30                    | 20          |
| 1234789-HxCDF (13)       | 8                                      | 0           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 49                    | 1           |
| 1234678-HxCDD (14)       | 1                                      | 7           | 7                     | 1           | 1                     | 1           | 1                     | 1           | 1                     | 1           | 1                     | 7           | 14                    | 36          |
| OCDF (15)                | 6                                      | 2           | 8                     | 0           | 8                     | 0           | 0                     | 0           | 0                     | 0           | 0                     | 0           | 43                    | 7           |
| OCDD (16)                | 1                                      | 7           | 7                     | 1           | 2                     | 1           | 1                     | 1           | 1                     | 1           | 1                     | 6           | 11                    | 39          |

The number of composite samples with either detectable levels or levels below detection limits are further detailed in Tables 4-22 through 4-28 by type of foodstuff and by city. The last line in each table indicates the total number of chemical analyses resulting in a nondetectable or detectable level for any of the compounds. These results, expressed in percentages, are summarized in Table 4-29. Of a grand total of 800 (50 composites x 16 compounds) analytical results, about 80% showed levels below detection limits for the considered compounds in both cities (496 results for Los Angeles and 304 results for San Francisco).

Overall, freshwater fish samples had the highest incidence of detectable levels of one or more compounds, and egg samples the lowest. The order from highest to lowest incidence of any compound at a detectable level were: (1) freshwater fish, (2) saltwater fish, tie for (3) and (4) pork and chicken, tie for (5) and (6) beef and milk, and (7) egg. This pattern was also reflected in each city separately.

#### 4.3.2 Overall Results on Concentration Levels

Two approaches were taken to summarize the results in terms of actual levels (pg/g on a lipid basis). First, only those samples with levels above detection limits were included in the computations of weighted means, standard deviations, and coefficients of variation. Second, all results, both above and below detection limits, were considered.

Table 4-22. Frequency of Detection of Specific PCDD and PCDF Compounds in Saltwater Fish Composites

| FOODSTUFF: SALTWATER FISH | CITY                  |                       |                       |                       |
|---------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                           | LOS ANGELES           |                       | SAN FRANCISCO         |                       |
|                           | NO. OF COMPOSITES (N) |
|                           | NON DETECTS           | DETECTS               | NON DETECTS           | DETECTS               |
|                           | N                     | N                     | N                     | N                     |
| COMPOUND (No.)            |                       |                       |                       |                       |
| 2378-TCDF (1)             | 0                     | 3                     | 0                     | 2                     |
| 2378-TCDD (2)             | 1                     | 2                     | 0                     | 2                     |
| 12378-PeCDF (3)           | 3                     | 0                     | 2                     | 0                     |
| 23478-PeCDF (4)           | 3                     | 0                     | 2                     | 0                     |
| 12378-PeCDD (5)           | 3                     | 0                     | 1                     | 1                     |
| 123478-HxCDF (6)          | 3                     | 0                     | 2                     | 0                     |
| 123678-HxCDF (7)          | 3                     | 0                     | 2                     | 0                     |
| 1234678-HxCDF (8)         | 3                     | 0                     | 2                     | 0                     |
| 123789-HxCDF (9)          | 3                     | 0                     | 2                     | 0                     |
| 123478/123678-HxCDD (10)  | 2                     | 1                     | 0                     | 2                     |
| 123789-HxCDD (11)         | 3                     | 0                     | 2                     | 0                     |
| 1234678-HpCDF (12)        | 3                     | 0                     | 1                     | 1                     |
| 1234789-HpCDF (13)        | 3                     | 0                     | 2                     | 0                     |
| 1234678-HpCDD (14)        | 2                     | 1                     | 1                     | 1                     |
| TCDF (15)                 | 3                     | 0                     | 2                     | 0                     |
| TCDD (16)                 | 0                     | 3                     | 0                     | 2                     |
| ALL COMPOUNDS             | 38                    | 10                    | 21                    | 11                    |

Table 4-23. Frequency of Detection of Specific PCDD and PCDF Compounds in Freshwater Fish Composites

| FOODSTUFF: FRESHWATER FISH | LOS ANGELES           |         | SAN FRANCISCO         |         |
|----------------------------|-----------------------|---------|-----------------------|---------|
|                            | NO. OF COMPOSITES (N) | DETECTS | NO. OF COMPOSITES (N) | DETECTS |
| COMPOUND (No.)             |                       |         |                       |         |
| 2378-TCDF (1)              | 0                     | 3       | 0                     | 2       |
| 2378-TCDD (2)              | 0                     | 3       | 1                     | 1       |
| 12378-FeCDF (3)            | 3                     | 0       | 2                     | 0       |
| 123478-FeCDF (4)           | 3                     | 0       | 2                     | 0       |
| 12378-FeCDD (5)            | 0                     | 3       | 0                     | 2       |
| 123478-HxCDF (6)           | 3                     | 0       | 2                     | 0       |
| 123678-HxCDF (7)           | 3                     | 0       | 2                     | 0       |
| 1234678-HxCDF (8)          | 3                     | 0       | 2                     | 0       |
| 123789-HxCDF (9)           | 3                     | 0       | 2                     | 0       |
| 123478/123678-HxCDD (10)   | 0                     | 3       | 1                     | 1       |
| 123789-HxCDD (11)          | 0                     | 3       | 1                     | 1       |
| 1234678-HpCDF (12)         | 3                     | 0       | 2                     | 0       |
| 1234789-HpCDF (13)         | 3                     | 0       | 1                     | 1       |
| 1234678-HpCDD (14)         | 0                     | 3       | 1                     | 1       |
| OCDF (15)                  | 3                     | 0       | 2                     | 0       |
| OCDD (16)                  | 0                     | 3       | 0                     | 2       |
| ALL COMPOUNDS              | 27                    | 21      | 21                    | 11      |

Table 4-24. Frequency of Detection of Specific PCDD and PCDF Compounds in Chicken

| FOODSTUFF: CHICKEN       | LOS ANGELES           |                       | SAN FRANCISCO         |                       |
|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                          | NO. OF COMPOSITES (N) |
|                          | NON DETECTS           | DETECTS               | NON DETECTS           | DETECTS               |
|                          | N                     | N                     | N                     | N                     |
| COMPOUND (No.)           |                       |                       |                       |                       |
| 2378-TCDF (1)            | 5                     | 0                     | 2                     | 1                     |
| 2378-TCDD (2)            | 3                     | 2                     | 2                     | 1                     |
| 12378-FeCDF (3)          | 5                     | 0                     | 3                     | 0                     |
| 23478-FeCDF (4)          | 5                     | 0                     | 3                     | 0                     |
| 12378-FeCDD (5)          | 5                     | 0                     | 3                     | 0                     |
| 123478-HxCDF (6)         | 5                     | 0                     | 3                     | 0                     |
| 123678-HxCDF (7)         | 5                     | 0                     | 3                     | 0                     |
| 234678-HxCDF (8)         | 5                     | 0                     | 3                     | 0                     |
| 123789-HxCDF (9)         | 5                     | 0                     | 3                     | 0                     |
| 123478/123678-HxCDD (10) | 5                     | 0                     | 2                     | 1                     |
| 123789-HxCDD (11)        | 4                     | 1                     | 2                     | 1                     |
| 1234678-HPCDF (12)       | 0                     | 5                     | 2                     | 1                     |
| 1234789-HPCDF (13)       | 5                     | 0                     | 3                     | 0                     |
| 1234678-HPCDD (14)       | 1                     | 4                     | 0                     | 3                     |
| OCDF (15)                | 3                     | 2                     | 3                     | 0                     |
| OCDD (16)                | 1                     | 4                     | 0                     | 3                     |
| ALL COMPOUNDS            | 62                    | 18                    | 37                    | 11                    |

Table 4-25. Frequency of Detection of Specific PCDD and PCDF Compounds in Beef

| FOODSTUFF: BEEF          | LOS ANGELES           |                       | SAN FRANCISCO         |                       |
|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                          | NO. OF COMPOSITES (N) |
|                          | DETECTS               | NON DETECTS           | DETECTS               | NON DETECTS           |
|                          | N                     | N                     | N                     | N                     |
| COMPOUND (No.)           |                       |                       |                       |                       |
| 12378-TCDF (1)           | 4                     | 1                     | 1                     | 2                     |
| 12378-TCDD (2)           | 5                     | 0                     | 3                     | 0                     |
| 12378-PCDF (3)           | 5                     | 0                     | 3                     | 0                     |
| 123478-PCDF (4)          | 5                     | 0                     | 3                     | 0                     |
| 12378-PCDD (5)           | 5                     | 0                     | 3                     | 0                     |
| 123478-HxCDF (6)         | 5                     | 0                     | 3                     | 0                     |
| 123678-HxCDF (7)         | 5                     | 0                     | 3                     | 0                     |
| 1234678-HxCDF (8)        | 5                     | 0                     | 3                     | 0                     |
| 123789-HxCDF (9)         | 5                     | 0                     | 3                     | 0                     |
| 123478/123678-HxCDD (10) | 3                     | 2                     | 2                     | 1                     |
| 123789-HxCDD (11)        | 5                     | 0                     | 3                     | 0                     |
| 1234678-PCDF (12)        | 2                     | 3                     | 2                     | 1                     |
| 1234789-PCDF (13)        | 5                     | 0                     | 3                     | 0                     |
| 1234678-PCDD (14)        | 1                     | 4                     | 0                     | 3                     |
| PCDF (15)                | 5                     | 0                     | 3                     | 0                     |
| PCDD (16)                | 1                     | 4                     | 0                     | 3                     |
| ALL COMPOUNDS            | 66                    | 14                    | 38                    | 10                    |

Table 4-26. Frequency of Detection of Specific PCDD and PCDF Compounds in Pork

| FOODSTUFF: FORK          | LOS ANGELES           |             | SAN FRANCISCO         |             |
|--------------------------|-----------------------|-------------|-----------------------|-------------|
|                          | NO. OF COMPOSITES (N) | NON DETECTS | NO. OF COMPOSITES (N) | NON DETECTS |
| COMPOUND (No.)           |                       |             |                       |             |
| 2378-TCDF (1)            | 5                     | 0           | 3                     | 0           |
| 2378-TCDD (2)            | 5                     | 0           | 3                     | 0           |
| 12378-FeCDF (3)          | 5                     | 0           | 3                     | 0           |
| 23478-FeCDF (4)          | 5                     | 0           | 3                     | 0           |
| 12378-FeCDD (5)          | 5                     | 0           | 3                     | 0           |
| 123478-HxCDF (6)         | 5                     | 0           | 3                     | 0           |
| 123678-HxCDF (7)         | 5                     | 0           | 3                     | 0           |
| 234678-HxCDF (8)         | 5                     | 0           | 3                     | 0           |
| 123789-HxCDF (9)         | 5                     | 0           | 3                     | 0           |
| 123478/123678-HxCDD (10) | 4                     | 1           | 2                     | 1           |
| 123789-HxCDD (11)        | 5                     | 0           | 3                     | 0           |
| 1234678-HpCDF (12)       | 1                     | 4           | 0                     | 3           |
| 1234789-HpCDF (13)       | 5                     | 0           | 3                     | 0           |
| 1234678-HpCDD (14)       | 0                     | 5           | 0                     | 3           |
| OCDF (15)                | 1                     | 4           | 2                     | 1           |
| OCDD (16)                | 0                     | 5           | 0                     | 3           |
| ALL COMPOUNDS            | 61                    | 19          | 37                    | 11          |

Table 4-27. Frequency of Detection of Specific PCDD and PCDF Compounds in Bovine Milk

| FOODSTUFF: MILK          | LOS ANGELES           |                       | SAN FRANCISCO         |                       |
|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                          | NO. OF COMPOSITES (N) |
|                          | NON DETECTS           | DETECTS               | NON DETECTS           | DETECTS               |
|                          | N                     | N                     | N                     | N                     |
| COMPOUND (No.)           |                       |                       |                       |                       |
| 2378-TCDF (1)            | 0                     | 5                     | 0                     | 3                     |
| 2378-TCDD (2)            | 4                     | 1                     | 3                     | 0                     |
| 12378-PeCDF (3)          | 5                     | 0                     | 3                     | 0                     |
| 23478-PeCDF (4)          | 5                     | 0                     | 3                     | 0                     |
| 12378-PeCDD (5)          | 5                     | 0                     | 3                     | 0                     |
| 123478-HxCDF (6)         | 5                     | 0                     | 3                     | 0                     |
| 123678-HxCDF (7)         | 5                     | 0                     | 3                     | 0                     |
| 234678-HxCDF (8)         | 5                     | 0                     | 3                     | 0                     |
| 123789-HxCDF (9)         | 5                     | 0                     | 3                     | 0                     |
| 123478/123678-HxCDD (10) | 4                     | 1                     | 3                     | 0                     |
| 123789-HxCDD (11)        | 5                     | 0                     | 3                     | 0                     |
| 1234678-HPCDF (12)       | 4                     | 1                     | 3                     | 0                     |
| 1234789-HPCDF (13)       | 5                     | 0                     | 3                     | 0                     |
| 1234679-HPCDD (14)       | 1                     | 4                     | 0                     | 3                     |
| OCDF (15)                | 5                     | 0                     | 3                     | 0                     |
| OCDD (16)                | 1                     | 4                     | 1                     | 2                     |
| ALL COMPOUNDS            | 64                    | 16                    | 40                    | 8                     |

Table 4-28. Frequency of Detection of Specific PCDD and PCDF Compounds in Eggs

| FOODSTUFF: EGG           | CITY                  |                       |                       |                       |
|--------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                          | LOS ANGELES           | SAN FRANCISCO         |                       |                       |
|                          | NO. OF COMPOSITES (N) |
|                          | DETECTS               | DETECTS               | NON DETECTS           | DETECTS               |
|                          | N                     | N                     | N                     | N                     |
| COMPOUND (No.)           |                       |                       |                       |                       |
| 12378-TCDF (1)           | 5                     | 0                     | 2                     | 1                     |
| 12378-TCDD (2)           | 5                     | 0                     | 3                     | 0                     |
| 12378-PeCDF (3)          | 5                     | 0                     | 3                     | 0                     |
| 123478-PeCDF (4)         | 5                     | 0                     | 3                     | 0                     |
| 12378-FeCDD (5)          | 5                     | 0                     | 3                     | 0                     |
| 123478-HxCDF (6)         | 5                     | 0                     | 3                     | 0                     |
| 123678-HxCDF (7)         | 5                     | 0                     | 3                     | 0                     |
| 1234678-HxCDF (8)        | 5                     | 0                     | 3                     | 0                     |
| 123789-HxCDF (9)         | 5                     | 0                     | 3                     | 0                     |
| 123478/123678-HxCDD (10) | 5                     | 0                     | 3                     | 0                     |
| 123789-HxCDD (11)        | 5                     | 0                     | 3                     | 0                     |
| 1234678-HpCDF (12)       | 5                     | 0                     | 2                     | 1                     |
| 1234789-HpCDF (13)       | 5                     | 0                     | 3                     | 0                     |
| 1234678-HpCDD (14)       | 4                     | 1                     | 3                     | 0                     |
| 10CDF (15)               | 5                     | 0                     | 3                     | 0                     |
| 10CDD (16)               | 5                     | 0                     | 2                     | 1                     |
| ALL COMPOUNDS            | 79                    | 1                     | 45                    | 3                     |

Table 4-29. Summary of Detects and Nondetects by City and Foodstuff Across Compounds

|                 | Los Angeles    |             | San Francisco  |             | Both Cities         |                     |
|-----------------|----------------|-------------|----------------|-------------|---------------------|---------------------|
|                 | Nondetects (%) | Detects (%) | Nondetects (%) | Detects (%) | ND <sup>a</sup> (%) | PQ <sup>b</sup> (%) |
| Saltwater fish  | 79             | 21          | 66             | 34          | 74                  | 26                  |
| Freshwater fish | 56             | 44          | 66             | 34          | 60                  | 40                  |
| Pork            | 76             | 24          | 77             | 23          | 77                  | 23                  |
| Beef            | 83             | 18          | 79             | 21          | 81                  | 19                  |
| Chicken         | 78             | 23          | 77             | 23          | 77                  | 23                  |
| Egg             | 99             | 1           | 94             | 6           | 97                  | 3                   |
| Milk            | 80             | 20          | 83             | 17          | 81                  | 19                  |
| All Foods       | 80             | 20          | 79             | 21          | 80                  | 20                  |

Note: Percentage figures are based on the total number of analyses within each cell determined by a foodstuff-city combination.

- <sup>a</sup> ND = Not detected.  
<sup>b</sup> PQ = Positive quantifiable.

#### 4.3.2.1 Statistical Equations Used

To take into account the compositing scheme when calculating sample means, standard deviations, and coefficients of variation, the numbers of samples that made up a composite were used in all computations as explained in the statistical approach below.

Assume K samples (composites) for a given type of foodstuff were analyzed for residues. Assume that these K samples were composites of  $n_1, \dots, n_K$  individual samples, respectively. Let  $X_i$  denote the concentration of a given compound in the  $i$ th composite ( $i=1, \dots, K$ ). The basic weighted statistics are then calculated as follows:

$$\text{Weighted mean} = [n_1 * X_1 + \dots + n_K * X_K] / N$$

where  $N = n_1 + \dots + n_K$  is the total number of individual samples of a given type of foodstuff used for the K composites. For example, for saltwater fish samples from Los Angeles,  $K=3$ ,  $n_1=10$ ,  $n_2=11$ ,  $n_3=10$ , and  $N=31$ . (See Table 4-20 for number of samples making up a composite.)

$$\text{Weighted variance} = \sum_{i=1}^K \frac{n_i (S_i - \text{weighted mean})^2}{N}$$

The weighted standard deviation, STD, is obtained by taking the square root of the weighted variance.

The coefficient of variation, CV, is then computed as:

$$\text{CV}(\%) = 100 * \text{Weighted standard deviation} / \text{weighted mean}$$

#### 4.3.2.2 Statistical Treatment of Levels Below Detection Limit

Limit of detection values were available whenever a sample concentration was below detection limit. These values were used when calculating basic statistics based on all data. The tables are clearly marked in that respect.

Tables 4-30 through 4-36 provide weighted statistical estimates of concentration levels for all compounds based only on those composites with detectable levels of a particular compound. Each table is presented in two parts. The top part of each table shows the data for a given foodstuff separately for Los Angeles and San Francisco. The lower part of each table summarizes the data for both cities. Only those compounds present in composites from both cities are reported. Thus, if a compound is not shown in a table, it was not detected in any composite sample from either city.

Table 4-30. Weighted Statistical Estimates for Concentration Levels Based on Food Composites With Measurable Levels of Specific Compounds--Saltwater Fish

| FOODSTUFF: SALTWATER FISH | WEIGHTED STATISTICS BASED ON DETECTS ONLY |                    |        |         |       |               |                    |        |         |   |
|---------------------------|---|--------------------|--------|---------|-------|---------------|--------------------|--------|---------|---|
|                           | LOS ANGELES                               |                    |        |         |       | SAN FRANCISCO |                    |        |         |   |
|                           | CONCENTRATION (PG/G)                      | STANDARD DEVIATION | CV (%) | MAXIMUM | N     | MEAN          | STANDARD DEVIATION | CV (%) | MAXIMUM | N |
| COMPOUND (No.)            |   |                    |        |         |       |               |                    |        |         |   |
| 2378-TCDF (1)             | 4.30                                      | 19                 | 28.20  | 2       | 21.11 | 1.60          | 8                  | 22.80  |         |   |
| 2378-TCDD (2)             | 1.01                                      | 0.04               | 3      | 1.05    | 2     | 1.28          | 0.58               | 45     | 1.89    |   |
| 12378-PeCDD (5)           |   |                    |        | 1       | 2.40  |               |                    | 2.40   |         |   |
| 123478/123678-HxCDD (10)  | 3.82                                      |                    | 3.82   | 2       | 1.49  | 0.28          | 19                 | 1.75   |         |   |
| 1234678-HpCDF (12)        |   |                    |        | 1       | 2.21  |               |                    | 2.21   |         |   |
| 1234678-HpCDD (14)        | 3.15                                      |                    | 3.15   | 1       | 1.29  |               |                    | 1.29   |         |   |
| OCDD (16)                 | 16.09                                     | 7.54               | 47     | 22.70   | 2     | 9.68          | 3.42               | 35     | 12.90   |   |

| FOODSTUFF: SALTWATER FISH | BOTH CITIES          |       |      |                    |        |                          |                |       |      |                    |
|---------------------------|----------------------|-------|------|--------------------|--------|--------------------------|----------------|-------|------|--------------------|
|                           | CONCENTRATION (PG/G) |       |      |                    |        | CONCENTRATION (PG/G)     |                |       |      |                    |
|                           | COMPOUND (No.)       | N     | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM                  | COMPOUND (No.) | N     | MEAN | STANDARD DEVIATION |
| 2378-TCDF (1)             | 5                    | 21.96 | 3.64 | 17                 | 28.20  | 2378-TCDF (1)            | 5              | 21.96 | 3.64 | 17                 |
| 2378-TCDD (2)             | 4                    | 1.13  | 0.41 | 37                 | 1.89   | 2378-TCDD (2)            | 4              | 1.13  | 0.41 | 37                 |
| 12378-PeCDD (5)           | 1                    | 2.40  |      |                    | 2.40   | 12378-PeCDD (5)          | 1              | 2.40  |      |                    |
| 123478/123678-HxCDD (10)  | 3                    | 2.35  | 1.15 | 49                 | 3.82   | 123478/123678-HxCDD (10) | 3              | 2.35  | 1.15 | 49                 |
| 1234678-HpCDF (12)        | 1                    | 2.21  |      |                    | 2.21   | 1234678-HpCDF (12)       | 1              | 2.21  |      |                    |
| 1234678-HpCDD (14)        | 2                    | 2.31  | 0.93 | 40                 | 3.15   | 1234678-HpCDD (14)       | 2              | 2.31  | 0.93 | 40                 |
| OCDD (16)                 | 5                    | 13.82 | 7.09 | 51                 | 22.70  | OCDD (16)                | 5              | 13.82 | 7.09 | 51                 |

Table 4-31. Weighted Statistical Estimates for Concentration Levels Based on Food Composites with Measurable Levels of Specific Compounds--Freshwater Fish

| FOODSTUFF: FRESHWATER FISH | WEIGHTED STATISTICS BASED ON DETECTS ONLY |        |                    |        |         |   |                      |                    |                    |         |         |  |
|----------------------------|---|--------|--------------------|--------|---------|---|----------------------|--------------------|--------------------|---------|---------|--|
|                            | LOS ANGELES                               |        |                    |        |         |   | SAN FRANCISCO        |                    |                    |         |         |  |
|                            | CONCENTRATION (PG/G)                      |        | STANDARD DEVIATION |        | CV (%)  |   | CONCENTRATION (PG/G) |                    | STANDARD DEVIATION |         | CV (%)  |  |
| COMPOUND (No.)             | N   | MEAN   | STANDARD DEVIATION | CV (%) | MAXIMUM | N | MEAN                 | STANDARD DEVIATION | CV (%)             | MAXIMUM | MAXIMUM |  |
| 12378-TCDF (1)             | 3   | 2.22   | 0.96               | 43     | 2.90    | 2 | 4.96                 | 3.18               | 64                 | 7.96    |         |  |
| 12378-TCDD (2)             | 3   | 6.40   | 2.34               | 37     | 9.78    | 1 | 2.80                 |                    |                    | 2.80    |         |  |
| 12378-PeCDD (5)            | 3   | 14.28  | 7.09               | 50     | 23.60   | 2 | 2.98                 | 1.39               | 47                 | 4.46    |         |  |
| 123478/123678-HxCDD (10)   | 3   | 36.07  | 33.66              | 93     | 84.10   | 1 | 12.79                |                    |                    | 12.79   |         |  |
| 123789-HxCDD (11)          | 3   | 18.56  | 14.56              | 78     | 38.90   | 1 | 6.74                 |                    |                    | 6.74    |         |  |
| 1234789-HpCDF (13)         |   |        |                    |        |         | 1 | 133.00               |                    |                    | 133.00  |         |  |
| 1234678-HpCDD (14)         | 3   | 92.34  | 75.38              | 82     | 201.00  | 1 | 28.70                |                    |                    | 28.70   |         |  |
| TCDD (16)                  | 3   | 729.16 | 536.38             | 74     | 1490.00 | 2 | 110.55               | 112.62             | 102                | 230.00  |         |  |

| FOODSTUFF: FRESHWATER FISH | BOTH CITIES          |        |                    |        |         |   |                      |                    |                    |         |         |  |
|----------------------------|----------------------|--------|--------------------|--------|---------|---|----------------------|--------------------|--------------------|---------|---------|--|
|                            | CONCENTRATION (PG/G) |        |                    |        |         |   | CONCENTRATION (PG/G) |                    |                    |         |         |  |
|                            | CONCENTRATION (PG/G) |        | STANDARD DEVIATION |        | CV (%)  |   | CONCENTRATION (PG/G) |                    | STANDARD DEVIATION |         | CV (%)  |  |
| COMPOUND (No.)             | N                    | MEAN   | STANDARD DEVIATION | CV (%) | MAXIMUM | N | MEAN                 | STANDARD DEVIATION | CV (%)             | MAXIMUM | MAXIMUM |  |
| 12378-TCDF (1)             | 5                    | 3.19   | 2.43               | 76     | 7.96    |   |                      |                    |                    |         |         |  |
| 12378-TCDD (2)             | 4                    | 5.59   | 2.55               | 46     | 9.78    |   |                      |                    |                    |         |         |  |
| 12378-PeCDD (5)            | 5                    | 10.28  | 7.89               | 77     | 23.60   |   |                      |                    |                    |         |         |  |
| 123478/123678-HxCDD (10)   | 4                    | 31.29  | 31.45              | 100    | 84.10   |   |                      |                    |                    |         |         |  |
| 123789-HxCDD (11)          | 4                    | 16.14  | 13.84              | 86     | 38.90   |   |                      |                    |                    |         |         |  |
| 1234789-HpCDF (13)         | 1                    | 133.00 |                    |        | 133.00  |   |                      |                    |                    |         |         |  |
| 1234678-HpCDD (14)         | 4                    | 79.29  | 71.95              | 91     | 201.00  |   |                      |                    |                    |         |         |  |
| TCDD (16)                  | 5                    | 510.07 | 527.10             | 103    | 1490.00 |   |                      |                    |                    |         |         |  |

Table 4-32. Weighted Statistical Estimates for Concentration Levels Based on Food Composites With Measurable Levels of Specific Compounds--Chicken

| FOODSTUFF: CHICKEN       | WEIGHTED STATISTICS BASED ON DETECTS ONLY |       |                    |        |         |   |                      |                    |        |         |      |  |
|--------------------------|---|-------|--------------------|--------|---------|---|----------------------|--------------------|--------|---------|------|--|
|                          | LOS ANGELES                               |       |                    |        |         |   | SAN FRANCISCO        |                    |        |         |      |  |
|                          | CONCENTRATION (PG/G)                      |       |                    |        |         |   | CONCENTRATION (PG/G) |                    |        |         |      |  |
| COMPOUND (No.)           | N   | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM | N | MEAN                 | STANDARD DEVIATION | CV (%) | MAXIMUM |      |  |
| 2378-TCDF (1)            |   |       |                    |        |         | 1 | 0.67                 |                    |        |         | 0.67 |  |
| 2378-TCDD (2)            | 2   | 0.37  | 0.06               | 16     | 0.43    | 1 | 1.67                 |                    |        |         | 1.67 |  |
| 123478/123678-HxCDD (10) |   |       |                    |        |         | 1 | 2.29                 |                    |        |         | 2.29 |  |
| 123789-HxCDD (11)        | 1   | 2.14  |                    |        | 2.14    | 1 | 4.30                 |                    |        |         | 4.30 |  |
| 1234678-HpCDF (12)       | 5   | 7.57  | 9.23               | 122    | 24.60   | 1 | 1.01                 |                    |        |         | 1.01 |  |
| 1234678-HpCDD (14)       | 4   | 12.72 | 14.11              | 111    | 35.20   | 3 | 4.28                 | 4.66               | 109    | 11.40   |      |  |
| OCDF (15)                | 2   | 15.75 | 11.07              | 70     | 26.00   |   |                      |                    |        |         |      |  |
| OCDD (16)                | 4   | 36.88 | 22.19              | 60     | 64.00   | 3 | 31.95                | 42.09              | 132    | 96.20   |      |  |

| FOODSTUFF: CHICKEN       | BOTH CITIES          |   |      |                    |        |         |       |       |     |  |  |       |
|--------------------------|----------------------|---|------|--------------------|--------|---------|-------|-------|-----|--|--|-------|
|                          | CONCENTRATION (PG/G) |   |      |                    |        |         |       |       |     |  |  |       |
|                          | COMPOUND (No.)       | N | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |       |       |     |  |  |       |
| 2378-TCDF (1)            |                      |   |      |                    |        | 1       | 0.67  |       |     |  |  | 0.67  |
| 2378-TCDD (2)            |                      |   |      |                    |        | 3       | 0.78  | 0.60  | 77  |  |  | 1.67  |
| 123478/123678-HxCDD (10) |                      |   |      |                    |        | 1       | 2.29  |       |     |  |  | 2.29  |
| 123789-HxCDD (11)        |                      |   |      |                    |        | 2       | 3.14  | 1.08  | 34  |  |  | 4.30  |
| 1234678-HpCDF (12)       |                      |   |      |                    |        | 6       | 6.51  | 8.79  | 135 |  |  | 24.60 |
| 1234678-HpCDD (14)       |                      |   |      |                    |        | 7       | 8.97  | 11.74 | 131 |  |  | 35.20 |
| OCDF (15)                |                      |   |      |                    |        | 2       | 15.75 | 11.07 | 70  |  |  | 26.00 |
| OCDD (16)                |                      |   |      |                    |        | 7       | 34.69 | 32.66 | 94  |  |  | 96.20 |

Table 4-33. Weighted Statistical Estimates for Concentration Levels Based on Food Composites With Measurable Levels of Specific Compounds--Beef

| FOODSTUFF: BEEF          | WEIGHTED STATISTICS BASED ON DETECTS ONLY |      |                    |        |         |               |      |                    |        |         |
|--------------------------|---|------|--------------------|--------|---------|---------------|------|--------------------|--------|---------|
|                          | LOS ANGELES                               |      |                    |        |         | SAN FRANCISCO |      |                    |        |         |
|                          | N   | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM | N             | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |
| COMPOUND (No.)           |   |      |                    |        |         |               |      |                    |        |         |
| 2378-TCDF (1)            | 1   | 0.84 |                    |        | 0.84    | 2             | 1.06 | 0.46               | 44     | 1.56    |
| 123478/123678-HxCDD (10) | 2   | 0.96 | 0.24               | 25     | 1.20    | 1             | 3.96 |                    |        | 3.96    |
| 1234678-HpCDF (12)       | 3   | 0.89 | 0.30               | 33     | 1.15    | 1             | 0.67 |                    |        | 0.67    |
| 1234678-HpCDD (14)       | 4   | 5.26 | 1.21               | 23     | 6.71    | 3             | 6.23 | 1.87               | 30     | 9.95    |
| OCDD (16)                | 4   | 9.42 | 1.46               | 16     | 11.40   | 3             | 9.56 | 1.79               | 19     | 11.90   |

| FOODSTUFF: BEEF          | BOTH CITIES          |      |                    |        |         |
|--------------------------|----------------------|------|--------------------|--------|---------|
|                          | CONCENTRATION (PG/G) |      |                    |        |         |
|                          | N                    | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |
| COMPOUND (No.)           |                      |      |                    |        |         |
| 2378-TCDF (1)            | 3                    | 0.99 | 0.40               | 40     | 1.56    |
| 123478/123678-HxCDD (10) | 3                    | 2.07 | 1.46               | 71     | 3.96    |
| 1234678-HpCDF (12)       | 4                    | 0.84 | 0.27               | 33     | 1.15    |
| 1234678-HpCDD (14)       | 7                    | 5.68 | 1.61               | 28     | 9.95    |
| OCDD (16)                | 7                    | 9.48 | 1.62               | 17     | 11.90   |

Table 4-34. Weighted Statistical Estimates for Concentration Levels Based on Food Composites With Measurable Levels of Specific Compounds--Pork

| FOODSTUFF: PORK    | WEIGHTED STATISTICS BASED ON DETECTS ONLY |       |                    |        |         |               |       |                    |        |         |
|--------------------|---|-------|--------------------|--------|---------|---------------|-------|--------------------|--------|---------|
|                    | LOS ANGELES                               |       |                    |        |         | SAN FRANCISCO |       |                    |        |         |
|                    | N   | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM | N             | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM |
| COMPOUND (No.)     |   |       |                    |        |         |               |       |                    |        |         |
| 123478-HxCDD (10)  | 1   | 3.50  |                    |        | 3.50    | 1             | 2.83  |                    |        | 2.83    |
| 1234678-HpCDF (12) | 4   | 4.78  | 3.57               | 75     | 10.60   | 3             | 3.62  | 1.54               | 43     | 5.68    |
| 1234678-HpCDD (14) | 5   | 14.69 | 15.52              | 106    | 45.50   | 3             | 10.50 | 5.07               | 48     | 15.30   |
| OCCDF (15)         | 4   | 3.38  | 3.36               | 100    | 9.36    | 1             | 1.89  |                    |        | 1.89    |
| OCCDD (16)         | 5   | 77.06 | 89.39              | 116    | 254.00  | 3             | 74.81 | 40.60              | 54     | 125.00  |

| FOODSTUFF: PORK          | ROTH CITIES |       |                    |        |         |                      |      |                    |        |         |
|--------------------------|-------------|-------|--------------------|--------|---------|----------------------|------|--------------------|--------|---------|
|                          |             |       |                    |        |         | CONCENTRATION (PG/G) |      |                    |        |         |
|                          | N           | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM | N                    | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |
| COMPOUND (No.)           |             |       |                    |        |         |                      |      |                    |        |         |
| 123478/123678-HxCDD (10) | 2           | 3.14  | 0.33               | 11     | 3.50    |                      |      |                    |        |         |
| 1234678-HpCDF (12)       | 7           | 4.26  | 2.91               | 68     | 10.60   |                      |      |                    |        |         |
| 1234678-HpCDD (14)       | 8           | 13.05 | 12.67              | 97     | 45.50   |                      |      |                    |        |         |
| OCCDF (15)               | 5           | 3.05  | 3.04               | 99     | 9.36    |                      |      |                    |        |         |
| OCCDD (16)               | 8           | 76.18 | 74.19              | 97     | 254.00  |                      |      |                    |        |         |

Table 4-35. Weighted Statistical Estimates for Concentration Levels Based on Food Composites With Measurable Levels of Specific Compounds--Bovine Milk

| FOODSTUFF: MILK          | WEIGHTED STATISTICS BASED ON DETECTS ONLY |      |      |                    |        |         |               |      |                    |        |         |  |
|--------------------------|---|------|------|--------------------|--------|---------|---------------|------|--------------------|--------|---------|--|
|                          | LOS ANGELES                               |      |      |                    |        |         | SAN FRANCISCO |      |                    |        |         |  |
|                          | COMPOUND (No.)                            | N    | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM | N             | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |  |
| 2378-TCDF (1)            | 5   | 3.24 | 1.58 | 49                 | 6.11   | 3       | 1.87          | 0.31 | 17                 | 2.16   |         |  |
| 2378-TCDD (2)            | 1   | 1.46 |      |                    | 1.46   |         |               |      |                    |        |         |  |
| 123478/123678-HxCDD (10) | 1   | 0.59 |      |                    | 0.59   |         |               |      |                    |        |         |  |
| 1234678-HpCDF (12)       | 1   | 0.70 |      |                    | 0.70   |         |               |      |                    |        |         |  |
| 1234678-HpCDD (14)       | 4   | 3.22 | 0.35 | 11                 | 3.80   | 3       | 2.97          | 0.93 | 31                 | 4.25   |         |  |
| OCDD (16)                | 4   | 4.74 | 1.37 | 29                 | 6.12   | 2       | 3.19          | 0.96 | 30                 | 4.15   |         |  |

| FOODSTUFF: MILK          | BOTH CITIES          |      |      |                    |        |         |                      |      |                    |        |         |  |
|--------------------------|----------------------|------|------|--------------------|--------|---------|----------------------|------|--------------------|--------|---------|--|
|                          | CONCENTRATION (PG/B) |      |      |                    |        |         | CONCENTRATION (PG/B) |      |                    |        |         |  |
|                          | COMPOUND (No.)       | N    | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM | N                    | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |  |
| 2378-TCDF (1)            | 8                    | 2.74 | 1.43 | 52                 | 6.11   |         |                      |      |                    |        |         |  |
| 2378-TCDD (2)            | 1                    | 1.46 |      |                    | 1.46   |         |                      |      |                    |        |         |  |
| 123478/123678-HxCDD (10) | 1                    | 0.59 |      |                    | 0.59   |         |                      |      |                    |        |         |  |
| 1234678-HpCDF (12)       | 1                    | 0.70 |      |                    | 0.70   |         |                      |      |                    |        |         |  |
| 1234678-HpCDD (14)       | 7                    | 3.11 | 0.67 | 22                 | 4.25   |         |                      |      |                    |        |         |  |
| OCDD (16)                | 6                    | 4.24 | 1.45 | 34                 | 6.12   |         |                      |      |                    |        |         |  |

Table 4-36. Weighted Statistical Estimates for Concentration Levels Based on Food Composites With Measurable Levels of Specific Compounds--Eggs

| FOODSTUFF: EGG     | WEIGHTED STATISTICS BASED ON DETECTS ONLY |      |                    |        |         |                      |       |                    |        |         |
|--------------------|---|------|--------------------|--------|---------|----------------------|-------|--------------------|--------|---------|
|                    | LOS ANGELES                               |      |                    |        |         | SAN FRANCISCO        |       |                    |        |         |
|                    | CONCENTRATION (PG/G)                      |      |                    |        |         | CONCENTRATION (PG/G) |       |                    |        |         |
| COMPOUND (No.)     | N   | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM | N                    | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM |
| 2378-TCDF (1)      |   |      |                    |        |         | 1                    | 0.10  |                    |        | 0.10    |
| 1234678-HPCDF (12) |   |      |                    |        |         | 1                    | 0.59  |                    |        | 0.59    |
| 1234678-HPCDD (14) | 1   | 1.76 |                    |        | 1.76    |                      |       |                    |        |         |
| OCDD (16)          |   |      |                    |        |         | 1                    | 11.71 |                    |        | 11.71   |

| FOODSTUFF: EGG     | BOTH CITIES          |       |                    |        |         |   |      |                    |        |         |
|--------------------|----------------------|-------|--------------------|--------|---------|---|------|--------------------|--------|---------|
|                    | CONCENTRATION (PG/G) |       |                    |        |         |   |      |                    |        |         |
|                    | N                    | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM | N | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |
| COMPOUND (No.)     |                      |       |                    |        |         |   |      |                    |        |         |
| 2378-TCDF (1)      | 1                    | 0.10  |                    |        |         |   |      |                    |        | 0.10    |
| 1234678-HPCDF (12) | 1                    | 0.59  |                    |        |         |   |      |                    |        | 0.59    |
| 1234678-HPCDD (14) | 1                    | 1.76  |                    |        | 1.76    |   |      |                    |        | 1.76    |
| OCDD (16)          | 1                    | 11.71 |                    |        | 11.71   |   |      |                    |        | 11.71   |

The concentration statistics of interest are (1) N, the number of composites with detectable levels of a particular compound, (2) the weighted mean, (3) the weighted standard deviation, (4) the weighted coefficient of variation, a measure of the variability of the data, and (5) the maximum level of a particular compound found in a composite.

Tables 4-37 through 4-43 present these same statistics based on all data. When a particular compound was below the detection limit, limit of detection values were used. Except for the fish samples, N (the number of composites considered in the calculations) is always 5 for Los Angeles and 3 for San Francisco. A number of results for the 1,2,3,4,7,8-HxCDF and 2,3,4,6,7,8-HxCDF from both saltwater and freshwater fish samples were deleted from the computations because of interference to the presence of polychlorodiphenyl ether.

Because of small sample sizes (5 composites for Los Angeles and 3 for San Francisco), the average concentrations were not compared between the two cities by means of a t-test. For the same reason, upper confidence limits were not computed for concentration levels. Rather, the maximum concentration level of a compound found in a foodstuff category is given for each city.

For ease of comparison, three summary tables have been generated:

1. Table 4-44 lists the maximum concentration levels of those compounds detected in at least one composite food sample, regardless of sampling site. Only 10 compounds are listed. If a compound is not shown in the first column of this table, then it was not detected in any of the 50 composites.
2. Table 4-45 lists the weighted mean concentrations for all compound/foodstuff combinations where levels were above detection limits.
3. Table 4-46 lists the same statistics as Table 4-45 with the exception that levels below detection limits have been replaced by the actual detection limit values. Thus all compounds are listed. However, no data were available for 1,2,3,4,7,8-HxCDF in saltwater fish because of interferences arising from an octachlorodiphenyl ether.

Table 4-37. Weighted Statistical Estimates for PCDD and PCDF Concentrations in Saltwater Fish  
Based on All Data (LOD values used for nondetects)

| FOODSTUFF: SALTWATER FISH | WEIGHTED STATISTICS BASED ON ALL DATA--LOD VALUES USED FOR NONDETECTS |       |      |                    |        |         |               |      |                    |        |         |  |
|---------------------------|---|-------|------|--------------------|--------|---------|---------------|------|--------------------|--------|---------|--|
|                           | LOS ANGELES   |       |      |                    |        |         | SAN FRANCISCO |      |                    |        |         |  |
|                           | COMPOUND (No.)  | N     | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM | N             | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |  |
| 12378-TCDF (1)            | 3   | 22.43 | 4.30 | 19                 | 28.20  | 2       | 21.11         | 1.60 | 8                  | 22.80  |         |  |
| 12378-TCDD (2)            | 3   | 1.18  | 0.22 | 19                 | 1.47   | 2       | 1.28          | 0.58 | 45                 | 1.89   |         |  |
| 12378-PeCDF (3)           | 1   | 1.30  |      |                    | 1.30   | 1       | 2.02          |      |                    | 2.02   |         |  |
| 123478-PeCDF (4)          | 3   | 1.28  | 0.20 | 16                 | 1.50   | 0       |               |      |                    |        |         |  |
| 12378-PeCDD (5)           | 3   | 1.60  | 0.40 | 25                 | 2.18   | 2       | 2.20          | 0.19 | 9                  | 2.40   |         |  |
| 123478-HxCDF (6)          | 0   |       |      |                    |        | 0       |               |      |                    |        |         |  |
| 123678-HxCDF (7)          | 3   | 1.69  | 0.40 | 24                 | 2.26   | 2       | 1.18          | 0.56 | 47                 | 1.71   |         |  |
| 123478-HxCDF (8)          | 3   | 2.91  | 1.08 | 37                 | 4.37   | 0       |               |      |                    |        |         |  |
| 123789-HxCDF (9)          | 3   | 2.20  | 0.52 | 24                 | 2.94   | 2       | 1.52          | 0.72 | 47                 | 2.20   |         |  |
| 123478/123678-HxCDD (10)  | 3   | 3.27  | 0.67 | 20                 | 3.82   | 2       | 1.49          | 0.28 | 19                 | 1.75   |         |  |
| 123789-HxCDD (11)         | 3   | 3.01  | 0.77 | 25                 | 3.76   | 2       | 1.18          | 0.33 | 28                 | 1.50   |         |  |
| 1234678-HxCDF (12)        | 3   | 2.31  | 0.30 | 13                 | 2.69   | 2       | 1.57          | 0.68 | 44                 | 2.21   |         |  |
| 1234789-HxCDF (13)        | 2   | 3.30  | 0.52 | 16                 | 3.85   | 2       | 1.94          | 0.69 | 36                 | 2.59   |         |  |
| 1234678-HPCDD (14)        | 3   | 2.60  | 0.74 | 29                 | 3.15   | 2       | 1.13          | 0.16 | 15                 | 1.29   |         |  |
| 10CDF (15)                | 3   | 8.13  | 3.63 | 45                 | 12.20  | 2       | 1.30          | 0.32 | 25                 | 1.61   |         |  |
| 10CDD (16)                | 3   | 16.09 | 7.54 | 47                 | 22.70  | 2       | 9.68          | 3.42 | 35                 | 12.90  |         |  |

(CONTINUED)

Table 4-37 (Concluded)

| FOODSTUFF: SALTWATER FISH | BOTH CITIES          |                    |           |         |         |
|---------------------------|----------------------|--------------------|-----------|---------|---------|
|                           | CONCENTRATION (PG/G) | STANDARD DEVIATION | CV (%)    | MAXIMUM |         |
| COMPOUND (No.)            | N                    | MEAN               | DEVIATION | CV (%)  | MAXIMUM |
| 12378-TCDF (1)            | 5                    | 21.96              | 3.64      | 17      | 28.20   |
| 12378-TCDD (2)            | 5                    | 1.21               | 0.39      | 32      | 1.89    |
| 12378-FeCDF (3)           | 2                    | 1.62               | 0.36      | 22      | 2.02    |
| 123478-FeCDF (4)          | 3                    | 1.28               | 0.20      | 16      | 1.50    |
| 12378-FeCDD (5)           | 5                    | 1.81               | 0.45      | 25      | 2.40    |
| 123478-HxCDF (6)          | 0                    |                    |           |         |         |
| 123678-HxCDF (7)          | 5                    | 1.51               | 0.52      | 35      | 2.26    |
| 123478-HxCDF (8)          | 3                    | 2.91               | 1.08      | 37      | 4.37    |
| 123789-HxCDF (9)          | 5                    | 1.96               | 0.68      | 35      | 2.94    |
| 123478/123678-HxCDD (10)  | 5                    | 2.64               | 1.02      | 39      | 3.82    |
| 123789-HxCDD (11)         | 5                    | 2.36               | 1.09      | 46      | 3.76    |
| 1234678-HpCDF (12)        | 5                    | 2.05               | 0.59      | 29      | 2.69    |
| 1234789-HpCDF (13)        | 4                    | 2.69               | 0.91      | 34      | 3.85    |
| 1234678-HpCDD (14)        | 5                    | 2.08               | 0.92      | 44      | 3.15    |
| 10CDF (15)                | 5                    | 5.71               | 4.38      | 77      | 12.20   |
| 10CDD (16)                | 5                    | 13.82              | 7.09      | 51      | 22.70   |

Table 4-38. Weighted Statistical Estimates for PCDD and PCDF Concentrations in Freshwater Fish Based on All Data (LOD values used for nondetects)

| FOODSTUFF: FRESHWATER FISH | WEIGHTED STATISTICS BASED ON ALL DATA--LOD VALUES USED FOR NONDETECTS |        |                    |        |         |   |                      |                    |        |         |  |  |
|----------------------------|---|--------|--------------------|--------|---------|---|----------------------|--------------------|--------|---------|--|--|
|                            | LOS ANGELES   |        |                    |        |         |   | SAN FRANCISCO        |                    |        |         |  |  |
|                            | CONCENTRATION (PG/G)  |        |                    |        |         |   | CONCENTRATION (PG/G) |                    |        |         |  |  |
| COMPOUND (No.)             | N   | MEAN   | STANDARD DEVIATION | CV (%) | MAXIMUM | N | MEAN                 | STANDARD DEVIATION | CV (%) | MAXIMUM |  |  |
| 2378-TCDF (1)              | 3   | 2.22   | 0.96               | 43     | 2.90    | 2 | 4.96                 | 3.18               | 64     | 7.96    |  |  |
| 2378-TCDD (2)              | 3   | 6.40   | 2.34               | 37     | 9.78    | 2 | 2.52                 | 0.30               | 12     | 2.80    |  |  |
| 12378-PCDF (3)             | 3   | 1.27   | 0.20               | 16     | 1.44    | 2 | 0.62                 | 0.05               | 9      | 0.68    |  |  |
| 123478-PCDF (4)            | 3   | 0.97   | 0.36               | 37     | 1.44    | 2 | 1.51                 | 0.84               | 56     | 2.31    |  |  |
| 12378-PCDD (5)             | 3   | 14.28  | 7.09               | 50     | 23.60   | 2 | 2.98                 | 1.39               | 47     | 4.46    |  |  |
| 123478-HxCDF (6)           | 2   | 4.89   | 0.88               | 18     | 5.82    | 1 | 4.04                 |                    |        | 4.04    |  |  |
| 123678-HxCDF (7)           | 3   | 1.10   | 0.32               | 29     | 1.34    | 2 | 1.20                 | 0.04               | 4      | 1.25    |  |  |
| 234678-HxCDF (8)           | 3   | 1.31   | 0.38               | 29     | 1.60    | 2 | 1.43                 | 0.06               | 4      | 1.49    |  |  |
| 123789-HxCDF (9)           | 3   | 1.43   | 0.41               | 29     | 1.74    | 2 | 1.56                 | 0.06               | 4      | 1.62    |  |  |
| 123478/123678-HxCDD (10)   | 3   | 36.07  | 33.66              | 93     | 84.10   | 2 | 6.73                 | 5.72               | 85     | 12.79   |  |  |
| 123789-HxCDD (11)          | 3   | 18.56  | 14.56              | 78     | 38.90   | 2 | 3.90                 | 2.68               | 69     | 6.74    |  |  |
| 1234678-HpCDF (12)         | 3   | 1.38   | 0.24               | 17     | 1.66    | 1 | 1.10                 |                    |        | 1.10    |  |  |
| 1234789-HpCDF (13)         | 3   | 1.97   | 0.35               | 18     | 2.38    | 2 | 71.15                | 65.60              | 92     | 133.00  |  |  |
| 1234678-HpCDD (14)         | 3   | 92.34  | 75.38              | 82     | 201.00  | 2 | 14.29                | 13.58              | 95     | 28.70   |  |  |
| TCDF (15)                  | 3   | 1.95   | 0.58               | 30     | 2.77    | 2 | 3.44                 | 1.90               | 55     | 5.46    |  |  |
| TCDD (16)                  | 3   | 729.16 | 536.38             | 74     | 1490.00 | 2 | 110.55               | 112.62             | 102    | 230.00  |  |  |

Table 4-38 (Concluded)

| FOODSTUFF: FRESHWATER FISH |   | BOTH CITIES          |                    |        |         |  |
|----------------------------|---|----------------------|--------------------|--------|---------|--|
|                            |   | CONCENTRATION (PG/G) |                    |        |         |  |
| COMPOUND (No.)             | N | MEAN                 | STANDARD DEVIATION | CV (%) | MAXIMUM |  |
| 2378-TCDF (1)              | 5 | 3.19                 | 2.43               | 76     | 7.96    |  |
| 2378-TCDD (2)              | 5 | 5.02                 | 2.65               | 53     | 9.78    |  |
| 12378-FeCDF (3)            | 5 | 1.04                 | 0.35               | 34     | 1.44    |  |
| 23478-FeCDF (4)            | 5 | 1.16                 | 0.63               | 55     | 2.31    |  |
| 12378-FeCDD (5)            | 5 | 10.28                | 7.89               | 77     | 23.60   |  |
| 123478-HxCDF (6)           | 3 | 4.66                 | 0.84               | 18     | 5.82    |  |
| 123678-HxCDF (7)           | 5 | 1.14                 | 0.26               | 23     | 1.34    |  |
| 234678-HxCDF (8)           | 5 | 1.35                 | 0.32               | 23     | 1.60    |  |
| 123789-HxCDF (9)           | 5 | 1.47                 | 0.34               | 23     | 1.74    |  |
| 123478/123678-HxCDD (10)   | 5 | 25.68                | 30.66              | 119    | 84.10   |  |
| 123789-HxCDD (11)          | 5 | 13.37                | 13.74              | 103    | 38.90   |  |
| 1234678-HpCDF (12)         | 4 | 1.33                 | 0.24               | 18     | 1.66    |  |
| 1234789-HpCDF (13)         | 5 | 26.47                | 51.17              | 193    | 133.00  |  |
| 1234678-HpCDD (14)         | 5 | 64.70                | 71.61              | 111    | 201.00  |  |
| OCDF (15)                  | 5 | 2.48                 | 1.42               | 57     | 5.46    |  |
| OCDD (16)                  | 5 | 510.07               | 527.10             | 103    | 1490.00 |  |

Table 4-39. Weighted Statistical Estimates for PCDD and PCDF Concentrations in Chicken Based on All Data (LOD values used for nondetects)

| FOODSTUFF: CHICKEN       | WEIGHTED STATISTICS BASED ON ALL DATA--LOD VALUES USED FOR NONDETECTS |       |                    |                      |         |   |                      |                    |        |                      |   |      |                    |        |         |
|--------------------------|---|-------|--------------------|----------------------|---------|---|----------------------|--------------------|--------|----------------------|---|------|--------------------|--------|---------|
|                          | LOS ANGELES   |       |                    |                      |         |   | SAN FRANCISCO        |                    |        |                      |   |      |                    |        |         |
|                          | CONCENTRATION (PG/G)  |       |                    | CONCENTRATION (PG/G) |         |   | CONCENTRATION (PG/G) |                    |        | CONCENTRATION (PG/G) |   |      |                    |        |         |
| COMPOUND (No.)           | N   | MEAN  | STANDARD DEVIATION | CV (%)               | MAXIMUM | N | MEAN                 | STANDARD DEVIATION | CV (%) | MAXIMUM              | N | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |
| 2378-TCDF (1)            | 5   | 0.40  | 0.13               | 31                   | 0.58    | 3 | 0.45                 | 0.17               | 37     | 0.67                 |   |      |                    |        |         |
| 2378-TCDD (2)            | 5   | 0.31  | 0.18               | 58                   | 0.56    | 3 | 0.80                 | 0.57               | 71     | 1.67                 |   |      |                    |        |         |
| 12378-FeCDF (3)          | 5   | 0.38  | 0.18               | 48                   | 0.66    | 3 | 0.14                 | 0.01               | 9      | 0.15                 |   |      |                    |        |         |
| 23478-FeCDF (4)          | 5   | 0.35  | 0.17               | 47                   | 0.60    | 3 | 0.13                 | 0.01               | 10     | 0.14                 |   |      |                    |        |         |
| 12378-FeCDD (5)          | 5   | 0.87  | 0.76               | 87                   | 2.19    | 3 | 2.82                 | 3.02               | 107    | 7.40                 |   |      |                    |        |         |
| 123478-HxCDF (6)         | 5   | 0.46  | 0.11               | 23                   | 0.59    | 3 | 0.58                 | 0.10               | 16     | 0.71                 |   |      |                    |        |         |
| 123678-HxCDF (7)         | 5   | 0.46  | 0.10               | 23                   | 0.58    | 3 | 0.44                 | 0.24               | 53     | 0.70                 |   |      |                    |        |         |
| 234678-HxCDF (8)         | 5   | 0.54  | 0.12               | 23                   | 0.69    | 3 | 0.53                 | 0.28               | 53     | 0.84                 |   |      |                    |        |         |
| 123789-HxCDF (9)         | 5   | 0.59  | 0.13               | 22                   | 0.75    | 3 | 0.58                 | 0.31               | 54     | 0.91                 |   |      |                    |        |         |
| 123478/123678-HxCDD (10) | 5   | 1.50  | 0.38               | 25                   | 2.08    | 3 | 1.52                 | 0.62               | 41     | 2.29                 |   |      |                    |        |         |
| 123789-HxCDD (11)        | 5   | 1.54  | 0.39               | 25                   | 2.14    | 3 | 2.15                 | 1.46               | 68     | 4.30                 |   |      |                    |        |         |
| 1234678-HpCDF (12)       | 5   | 7.57  | 9.23               | 122                  | 24.60   | 3 | 0.66                 | 0.23               | 35     | 1.01                 |   |      |                    |        |         |
| 1234789-HpCDF (13)       | 5   | 1.79  | 1.37               | 76                   | 4.10    | 3 | 0.64                 | 0.14               | 22     | 0.75                 |   |      |                    |        |         |
| 1234678-HpCDD (14)       | 5   | 10.68 | 13.35              | 125                  | 35.20   | 3 | 4.28                 | 4.66               | 109    | 11.40                |   |      |                    |        |         |
| OCDF (15)                | 5   | 7.92  | 9.85               | 124                  | 26.00   | 3 | 0.72                 | 0.05               | 8      | 0.77                 |   |      |                    |        |         |
| OCDD (16)                | 5   | 30.45 | 23.87              | 78                   | 64.00   | 3 | 31.95                | 42.09              | 132    | 96.20                |   |      |                    |        |         |

(CONTINUED)

Table 4-39 (Concluded)

| FOODSTUFF: CHICKEN       | BOTH CITIES          |       |                    |        |         |
|--------------------------|----------------------|-------|--------------------|--------|---------|
|                          | CONCENTRATION (PG/G) |       |                    |        |         |
| COMPOUND (No.)           | N                    | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM |
| 12378-TCDF (1)           | 8                    | 0.42  | 0.14               | 34     | 0.67    |
| 12378-TCDD (2)           | 8                    | 0.50  | 0.45               | 90     | 1.67    |
| 12378-FeCDF (3)          | 8                    | 0.28  | 0.18               | 65     | 0.66    |
| 12378-FeCDF (4)          | 8                    | 0.26  | 0.17               | 64     | 0.60    |
| 12378-FeCDD (5)          | 8                    | 1.64  | 2.20               | 134    | 7.40    |
| 123478-HxCDF (6)         | 8                    | 0.51  | 0.12               | 23     | 0.71    |
| 123678-HxCDF (7)         | 8                    | 0.45  | 0.17               | 37     | 0.70    |
| 1234678-HxCDF (8)        | 8                    | 0.54  | 0.20               | 38     | 0.84    |
| 123789-HxCDF (9)         | 8                    | 0.59  | 0.22               | 38     | 0.91    |
| 123478/123678-HxCDD (10) | 8                    | 1.51  | 0.49               | 32     | 2.29    |
| 123789-HxCDD (11)        | 8                    | 1.78  | 1.01               | 57     | 4.30    |
| 1234678-HpCDF (12)       | 8                    | 4.86  | 7.95               | 164    | 24.60   |
| 1234789-HpCDF (13)       | 8                    | 1.34  | 1.21               | 90     | 4.10    |
| 12346789-HpCDD (14)      | 8                    | 8.17  | 11.25              | 138    | 35.20   |
| 10CDF (15)               | 8                    | 5.10  | 8.45               | 166    | 26.00   |
| 10CDD (16)               | 8                    | 31.03 | 32.27              | 104    | 96.20   |

Table 4-40. Weighted Statistical Estimates for PCDD and PCDF Concentrations in Beef  
Based on All Data (LOD values used for nondetects)

| FOODSTUFF: BEEF          | WEIGHTED STATISTICS BASED ON ALL DATA--LOD VALUES USED FOR NONDETECTS |      |      |                    |        |         |      |               |                    |        |         |  |  |  |
|--------------------------|---|------|------|--------------------|--------|---------|------|---------------|--------------------|--------|---------|--|--|--|
|                          | LOS ANGELES   |      |      |                    |        |         |      | SAN FRANCISCO |                    |        |         |  |  |  |
|                          | COMPOUND (No.)  | N    | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM | N    | MEAN          | STANDARD DEVIATION | CV (%) | MAXIMUM |  |  |  |
| 2378-TCDF (1)            | 5   | 0.38 | 0.28 | 73                 | 0.84   | 3       | 0.83 | 0.51          | 62                 | 1.56   |         |  |  |  |
| 2378-TCDD (2)            | 5   | 0.23 | 0.12 | 51                 | 0.41   | 3       | 0.32 | 0.11          | 34                 | 0.40   |         |  |  |  |
| 12378-PeCDF (3)          | 5   | 0.53 | 0.23 | 43                 | 0.86   | 3       | 0.71 | 0.55          | 78                 | 1.44   |         |  |  |  |
| 123478-PeCDF (4)         | 5   | 0.48 | 0.21 | 43                 | 0.78   | 3       | 0.72 | 0.43          | 60                 | 1.31   |         |  |  |  |
| 12378-PeCDD (5)          | 5   | 3.95 | 6.64 | 168                | 17.50  | 3       | 0.87 | 0.26          | 30                 | 1.09   |         |  |  |  |
| 123478-HxCDF (6)         | 5   | 0.69 | 0.27 | 39                 | 1.19   | 3       | 0.63 | 0.19          | 31                 | 0.79   |         |  |  |  |
| 123678-HxCDF (7)         | 5   | 0.64 | 0.29 | 45                 | 1.17   | 3       | 0.62 | 0.18          | 30                 | 0.77   |         |  |  |  |
| 234678-HxCDF (8)         | 5   | 0.76 | 0.34 | 45                 | 1.39   | 3       | 0.74 | 0.22          | 30                 | 0.92   |         |  |  |  |
| 123789-HxCDF (9)         | 5   | 0.83 | 0.37 | 45                 | 1.51   | 3       | 0.81 | 0.25          | 30                 | 1.01   |         |  |  |  |
| 123478/123678-HxCDD (10) | 5   | 1.50 | 0.71 | 47                 | 2.64   | 3       | 3.00 | 0.99          | 33                 | 3.96   |         |  |  |  |
| 123789-HxCDD (11)        | 5   | 1.45 | 0.79 | 54                 | 2.72   | 3       | 3.09 | 1.03          | 33                 | 4.08   |         |  |  |  |
| 1234678-HpCDF (12)       | 5   | 1.42 | 0.67 | 47                 | 2.29   | 3       | 1.29 | 0.43          | 33                 | 1.66   |         |  |  |  |
| 1234789-HpCDF (13)       | 5   | 1.68 | 1.21 | 72                 | 3.28   | 3       | 1.78 | 0.69          | 39                 | 2.37   |         |  |  |  |
| 1234678-HpCDD (14)       | 5   | 4.86 | 1.35 | 28                 | 6.71   | 3       | 6.23 | 1.87          | 30                 | 8.95   |         |  |  |  |
| OCDF (15)                | 5   | 1.91 | 1.72 | 90                 | 5.31   | 3       | 1.44 | 0.71          | 49                 | 2.15   |         |  |  |  |
| OCDD (16)                | 5   | 9.67 | 1.41 | 15                 | 11.40  | 3       | 9.56 | 1.79          | 19                 | 11.90  |         |  |  |  |

Table 4-40 (Concluded)

| FOODSTUFF; BEEF          | BOTH CITIES          |      |                    |        |         |  |
|--------------------------|----------------------|------|--------------------|--------|---------|--|
|                          | CONCENTRATION (PG/G) |      |                    |        |         |  |
| COMPOUND (No.)           | N                    | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |  |
| 2378-TCDF (1)            | 8                    | 0.55 | 0.44               | 81     | 1.56    |  |
| 2378-TCDD (2)            | 8                    | 0.26 | 0.12               | 46     | 0.41    |  |
| 12378-PeCDF (3)          | 8                    | 0.60 | 0.39               | 64     | 1.44    |  |
| 12378-PeCDF (4)          | 8                    | 0.57 | 0.33               | 58     | 1.31    |  |
| 12378-PeCDD (5)          | 8                    | 2.78 | 5.44               | 196    | 17.50   |  |
| 123478-HxCDF (6)         | 8                    | 0.67 | 0.24               | 37     | 1.19    |  |
| 123678-HxCDF (7)         | 8                    | 0.63 | 0.25               | 40     | 1.17    |  |
| 234678-HxCDF (8)         | 8                    | 0.75 | 0.30               | 40     | 1.39    |  |
| 123789-HxCDF (9)         | 8                    | 0.82 | 0.33               | 40     | 1.51    |  |
| 123478/123678-HxCDD (10) | 8                    | 2.07 | 1.10               | 53     | 3.96    |  |
| 123789-HxCDD (11)        | 8                    | 2.08 | 1.19               | 57     | 4.08    |  |
| 1234678-HxCDF (12)       | 8                    | 1.37 | 0.59               | 43     | 2.29    |  |
| 1234789-HxCDF (13)       | 8                    | 1.72 | 1.04               | 61     | 3.28    |  |
| 1234678-HxCDD (14)       | 8                    | 5.38 | 1.71               | 32     | 8.95    |  |
| OCDF (15)                | 8                    | 1.73 | 1.44               | 83     | 5.31    |  |
| OCDD (16)                | 8                    | 9.63 | 1.57               | 16     | 11.90   |  |

Table 4-41. Weighted Statistical Estimates for PCDD and PCDF Concentrations in Pork  
Based on All Data (LOD values used for nondetects)

| FOODSTUFF: FORK          | WEIGHTED STATISTICS BASED ON ALL DATA--LOD VALUES USED FOR NONDETECTS |       |       |                    |        |         |               |       |                    |        |         |  |  |
|--------------------------|---|-------|-------|--------------------|--------|---------|---------------|-------|--------------------|--------|---------|--|--|
|                          | LOS ANGELES   |       |       |                    |        |         | SAN FRANCISCO |       |                    |        |         |  |  |
|                          | COMPOUND (No.)  | N     | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM | N             | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM |  |  |
| 12378-TCDF (1)           | 5   | 0.30  | 0.10  | 32                 | 0.49   | 3       | 0.42          | 0.09  | 20                 | 0.54   |         |  |  |
| 12378-TCDD (2)           | 5   | 0.26  | 0.17  | 66                 | 0.52   | 3       | 0.44          | 0.04  | 9                  | 0.49   |         |  |  |
| 12378-FeCDF (3)          | 5   | 0.84  | 0.35  | 42                 | 1.40   | 3       | 0.43          | 0.12  | 28                 | 0.58   |         |  |  |
| 123478-FeCDF (4)         | 5   | 0.77  | 0.32  | 42                 | 1.28   | 3       | 0.39          | 0.11  | 28                 | 0.53   |         |  |  |
| 12378-FeCDD (5)          | 5   | 2.27  | 1.10  | 48                 | 4.36   | 3       | 2.32          | 0.31  | 13                 | 2.70   |         |  |  |
| 123478-HxCDF (6)         | 5   | 1.43  | 1.08  | 76                 | 3.40   | 3       | 1.81          | 1.20  | 66                 | 3.33   |         |  |  |
| 123678-HxCDF (7)         | 5   | 0.67  | 0.12  | 17                 | 0.81   | 3       | 0.61          | 0.18  | 30                 | 0.84   |         |  |  |
| 1234678-HxCDF (8)        | 5   | 0.79  | 0.14  | 18                 | 0.97   | 3       | 0.73          | 0.22  | 30                 | 1.00   |         |  |  |
| 123789-HxCDF (9)         | 5   | 0.87  | 0.15  | 18                 | 1.06   | 3       | 0.80          | 0.24  | 30                 | 1.09   |         |  |  |
| 123478/123678-HxCDD (10) | 5   | 1.58  | 1.03  | 65                 | 3.50   | 3       | 1.79          | 0.78  | 44                 | 2.83   |         |  |  |
| 123789-HxCDD (11)        | 5   | 1.64  | 1.06  | 65                 | 3.60   | 3       | 1.85          | 0.81  | 44                 | 2.92   |         |  |  |
| 1234678-HpCDF (12)       | 5   | 4.32  | 3.34  | 77                 | 10.60  | 3       | 3.62          | 1.54  | 43                 | 5.68   |         |  |  |
| 1234789-HpCDF (13)       | 5   | 3.27  | 1.22  | 37                 | 5.40   | 3       | 2.56          | 0.68  | 27                 | 3.12   |         |  |  |
| 1234678-HpCDD (14)       | 5   | 14.69 | 15.52 | 106                | 45.50  | 3       | 10.50         | 5.07  | 48                 | 15.30  |         |  |  |
| OCDF (15)                | 5   | 2.98  | 3.13  | 105                | 9.36   | 3       | 1.79          | 0.26  | 14                 | 2.02   |         |  |  |
| OCDD (16)                | 5   | 77.06 | 89.39 | 116                | 254.00 | 3       | 74.81         | 40.60 | 54                 | 125.00 |         |  |  |

(CONTINUED)

Table 4-41 (Concluded)

| FOODSTUFF: PORK          | BOTH CITIES          |       |                    |        |         |
|--------------------------|----------------------|-------|--------------------|--------|---------|
|                          | CONCENTRATION (PG/G) |       |                    |        |         |
| COMPOUND (No.)           | N                    | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM |
| 2378-TCDF (1)            | 8                    | 0.35  | 0.11               | 31     | 0.54    |
| 2378-TCDD (2)            | 8                    | 0.33  | 0.16               | 49     | 0.52    |
| 12378-FeCDF (3)          | 8                    | 0.68  | 0.35               | 51     | 1.40    |
| 23478-FeCDF (4)          | 8                    | 0.62  | 0.32               | 52     | 1.28    |
| 12378-FeCDD (5)          | 8                    | 2.29  | 0.88               | 38     | 4.36    |
| 123478-HxCDF (6)         | 8                    | 1.58  | 1.14               | 72     | 3.40    |
| 123678-HxCDF (7)         | 8                    | 0.65  | 0.15               | 23     | 0.84    |
| 234678-HxCDF (8)         | 8                    | 0.77  | 0.18               | 23     | 1.00    |
| 123789-HxCDF (9)         | 8                    | 0.84  | 0.19               | 23     | 1.09    |
| 123478/123678-HxCDD (10) | 8                    | 1.66  | 0.95               | 57     | 3.50    |
| 123789-HxCDD (11)        | 8                    | 1.72  | 0.98               | 57     | 3.60    |
| 1234678-HpCDF (12)       | 8                    | 4.04  | 2.80               | 69     | 10.60   |
| 1234789-HpCDF (13)       | 8                    | 2.99  | 1.10               | 37     | 5.40    |
| 1234678-HpCDD (14)       | 8                    | 13.05 | 12.67              | 97     | 45.50   |
| OCDF (15)                | 8                    | 2.51  | 2.51               | 100    | 9.36    |
| OCDD (16)                | 8                    | 76.18 | 74.19              | 97     | 254.00  |

Table 4-42. Weighted Statistical Estimates for PCDD and PCDF Concentrations in Bovine Milk  
Based on All Data (LOD values used for nondetects)

| FOODSTUFF: MILK          | WEIGHTED STATISTICS BASED ON ALL DATA--LOD VALUES USED FOR NONDETECTS |      |                    |        |         |   |                      |                    |        |         |  |  |
|--------------------------|---|------|--------------------|--------|---------|---|----------------------|--------------------|--------|---------|--|--|
|                          | LOS ANGELES   |      |                    |        |         |   | SAN FRANCISCO        |                    |        |         |  |  |
|                          | CONCENTRATION (PG/G)  |      |                    |        |         |   | CONCENTRATION (PG/G) |                    |        |         |  |  |
| COMPOUND (No.)           | N   | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM | N | MEAN                 | STANDARD DEVIATION | CV (%) | MAXIMUM |  |  |
| 2378-TCDF (1)            | 5   | 3.24 | 1.58               | 49     | 6.11    | 3 | 1.87                 | 0.31               | 17     | 2.16    |  |  |
| 2378-TCDD (2)            | 5   | 0.77 | 0.43               | 56     | 1.46    | 3 | 0.57                 | 0.13               | 24     | 0.69    |  |  |
| 12378-FeCDF (3)          | 5   | 0.32 | 0.22               | 68     | 0.58    | 3 | 0.50                 | 0.21               | 42     | 0.77    |  |  |
| 23478-FeCDF (4)          | 5   | 0.34 | 0.18               | 52     | 0.53    | 3 | 0.45                 | 0.19               | 42     | 0.70    |  |  |
| 12378-FeCDD (5)          | 5   | 0.89 | 0.21               | 24     | 1.05    | 3 | 1.14                 | 0.87               | 77     | 2.30    |  |  |
| 123478-HxCDF (6)         | 5   | 0.70 | 0.39               | 55     | 1.36    | 3 | 0.69                 | 0.14               | 20     | 0.85    |  |  |
| 123678-HxCDF (7)         | 5   | 0.69 | 0.38               | 56     | 1.34    | 3 | 0.68                 | 0.14               | 21     | 0.84    |  |  |
| 234678-HxCDF (8)         | 5   | 0.82 | 0.45               | 55     | 1.59    | 3 | 0.81                 | 0.16               | 20     | 1.00    |  |  |
| 123789-HxCDF (9)         | 5   | 0.87 | 0.49               | 56     | 1.73    | 3 | 0.89                 | 0.18               | 20     | 1.09    |  |  |
| 123478/123678-HxCDD (10) | 5   | 0.96 | 0.35               | 36     | 1.47    | 3 | 1.07                 | 0.46               | 43     | 1.57    |  |  |
| 123789-HxCDD (11)        | 5   | 0.95 | 0.41               | 43     | 1.52    | 3 | 1.11                 | 0.47               | 42     | 1.62    |  |  |
| 1234678-HxCDF (12)       | 5   | 0.81 | 0.31               | 39     | 1.22    | 3 | 0.99                 | 0.67               | 68     | 1.93    |  |  |
| 1234789-HxCDF (13)       | 5   | 1.15 | 0.44               | 38     | 1.74    | 3 | 1.41                 | 0.96               | 68     | 2.76    |  |  |
| 1234678-HxCDD (14)       | 5   | 2.79 | 0.92               | 33     | 3.80    | 3 | 2.97                 | 0.93               | 31     | 4.25    |  |  |
| OCDF (15)                | 5   | 3.09 | 2.25               | 73     | 7.36    | 3 | 1.93                 | 1.02               | 53     | 3.20    |  |  |
| OCDD (16)                | 5   | 4.08 | 1.83               | 45     | 6.12    | 3 | 3.26                 | 0.79               | 24     | 4.15    |  |  |

(CONTINUED)

Table 4-42 (Concluded)

| FOODSTUFF: MILK          | BOTH CITIES |      |                    |        |         |
|--------------------------|-------------|------|--------------------|--------|---------|
|                          | N           | MEAN | STANDARD DEVIATION | CV (%) | MAXIMUM |
| CONFOUND (No.)           |             |      |                    |        |         |
| 2378-TCDF (1)            | 8           | 2.74 | 1.43               | 52     | 6.11    |
| 2378-TCDD (2)            | 8           | 0.69 | 0.36               | 52     | 1.46    |
| 12378-FeCDF (3)          | 8           | 0.39 | 0.23               | 60     | 0.77    |
| 23478-FeCDF (4)          | 8           | 0.38 | 0.19               | 50     | 0.70    |
| 12378-FeCDD (5)          | 8           | 0.98 | 0.57               | 58     | 2.30    |
| 123478-HxCDF (6)         | 8           | 0.70 | 0.32               | 46     | 1.36    |
| 123678-HxCDF (7)         | 8           | 0.68 | 0.32               | 46     | 1.34    |
| 234678-HxCDF (8)         | 8           | 0.82 | 0.37               | 46     | 1.59    |
| 123789-HxCDF (9)         | 8           | 0.88 | 0.40               | 46     | 1.73    |
| 123478/123678-HxCDD (10) | 8           | 1.00 | 0.39               | 39     | 1.57    |
| 123789-HxCDD (11)        | 8           | 1.01 | 0.44               | 43     | 1.62    |
| 1234678-HpCDF (12)       | 8           | 0.87 | 0.49               | 56     | 1.93    |
| 1234789-HpCDF (13)       | 8           | 1.25 | 0.69               | 56     | 2.76    |
| 1234678-HpCDD (14)       | 8           | 2.86 | 0.93               | 32     | 4.25    |
| OCDF (15)                | 8           | 2.67 | 1.97               | 74     | 7.36    |
| OCDD (16)                | 8           | 3.78 | 1.58               | 42     | 6.12    |

Table 4-43. Weighted Statistical Estimates for PCDD and PCDF Concentrations in Eggs  
Based on All Data (LOD values used for nondetects)

| FOODSTUFF: EGG           | WEIGHTED STATISTICS BASED ON ALL DATA--LOD VALUES USED FOR NONDETECTS |       |                    |        |         |   |                      |                    |        |         |  |  |
|--------------------------|---|-------|--------------------|--------|---------|---|----------------------|--------------------|--------|---------|--|--|
|                          | LOS ANGELES   |       |                    |        |         |   | SAN FRANCISCO        |                    |        |         |  |  |
|                          | CONCENTRATION (PG/G)  |       |                    |        |         |   | CONCENTRATION (PG/G) |                    |        |         |  |  |
| COMPOUND (No.)           | N   | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM | N | MEAN                 | STANDARD DEVIATION | CV (%) | MAXIMUM |  |  |
| 12378-TCDF (1)           | 5   | 0.27  | 0.09               | 33     | 0.42    | 3 | 0.09                 | 0.01               | 7      | 0.10    |  |  |
| 12378-TCDD (2)           | 5   | 0.29  | 0.10               | 35     | 0.42    | 3 | 0.23                 | 0.15               | 67     | 0.42    |  |  |
| 12378-PCDF (3)           | 5   | 0.76  | 0.39               | 52     | 1.20    | 3 | 0.21                 | 0.08               | 40     | 0.32    |  |  |
| 123478-PCDF (4)          | 5   | 0.50  | 0.37               | 74     | 1.09    | 3 | 0.23                 | 0.06               | 26     | 0.29    |  |  |
| 12378-PCDD (5)           | 5   | 2.82  | 1.96               | 69     | 6.25    | 3 | 0.56                 | 0.18               | 33     | 0.74    |  |  |
| 123478-HxCDF (6)         | 5   | 2.80  | 0.74               | 26     | 3.75    | 3 | 0.64                 | 0.11               | 17     | 0.77    |  |  |
| 123678-HxCDF (7)         | 5   | 2.75  | 0.99               | 36     | 4.19    | 3 | 0.47                 | 0.12               | 24     | 0.60    |  |  |
| 1234678-HxCDF (8)        | 5   | 3.63  | 1.85               | 51     | 7.03    | 3 | 0.56                 | 0.14               | 24     | 0.71    |  |  |
| 123789-HxCDF (9)         | 5   | 4.04  | 2.07               | 51     | 7.84    | 3 | 0.62                 | 0.15               | 24     | 0.78    |  |  |
| 123478/123678-HxCDD (10) | 5   | 9.45  | 5.80               | 61     | 17.94   | 3 | 3.63                 | 2.09               | 58     | 6.25    |  |  |
| 123789-HxCDD (11)        | 5   | 4.33  | 2.65               | 61     | 8.23    | 3 | 1.69                 | 0.98               | 58     | 2.92    |  |  |
| 1234678-HPCDF (12)       | 5   | 4.00  | 4.48               | 112    | 12.03   | 3 | 1.07                 | 0.55               | 51     | 1.81    |  |  |
| 1234789-HPCDF (13)       | 5   | 5.73  | 6.41               | 112    | 17.19   | 3 | 1.32                 | 0.92               | 70     | 2.50    |  |  |
| 1234678-HPCDD (14)       | 5   | 3.27  | 1.97               | 60     | 5.94    | 3 | 1.84                 | 1.14               | 62     | 3.33    |  |  |
| OCDF (15)                | 5   | 5.61  | 5.12               | 91     | 15.85   | 3 | 1.58                 | 0.85               | 54     | 2.33    |  |  |
| OCDD (16)                | 5   | 14.84 | 5.55               | 37     | 25.00   | 3 | 8.09                 | 4.91               | 61     | 11.71   |  |  |

(CONTINUED)

Table 4-43 (Concluded)

| FOODSTUFF: EGG           | BOTH CITIES          |       |                    |        |         |
|--------------------------|----------------------|-------|--------------------|--------|---------|
|                          | CONCENTRATION (PG/G) |       |                    |        |         |
| COMPOUND (No.)           | N                    | MEAN  | STANDARD DEVIATION | CV (%) | MAXIMUM |
| 2378-TCDF (1)            | 8                    | 0.20  | 0.11               | 56     | 0.42    |
| 2378-TCDD (2)            | 8                    | 0.27  | 0.13               | 48     | 0.42    |
| 12378-PeCDF (3)          | 8                    | 0.54  | 0.41               | 76     | 1.20    |
| 23478-PeCDF (4)          | 8                    | 0.39  | 0.32               | 81     | 1.09    |
| 12378-PeCDD (5)          | 8                    | 1.93  | 1.89               | 98     | 6.25    |
| 123478-HxCDF (6)         | 8                    | 1.95  | 1.20               | 62     | 3.75    |
| 123678-HxCDF (7)         | 8                    | 1.86  | 1.36               | 73     | 4.19    |
| 234678-HxCDF (8)         | 8                    | 2.43  | 2.08               | 86     | 7.03    |
| 123789-HxCDF (9)         | 8                    | 2.70  | 2.32               | 86     | 7.84    |
| 123478/123678-HxCDD (10) | 8                    | 7.17  | 5.50               | 77     | 17.94   |
| 123789-HxCDD (11)        | 8                    | 3.29  | 2.51               | 76     | 8.23    |
| 1234678-HpCDF (12)       | 8                    | 2.85  | 3.79               | 133    | 12.03   |
| 1234789-HpCDF (13)       | 8                    | 4.00  | 5.47               | 137    | 17.19   |
| 1234678-HpCDD (14)       | 8                    | 2.71  | 1.83               | 68     | 5.94    |
| OCDF (15)                | 8                    | 4.03  | 4.49               | 111    | 15.85   |
| OCDD (16)                | 8                    | 12.19 | 6.25               | 51     | 25.00   |

Table 4-44. Summary of Maximum Concentration Levels for Compounds Detected in at Least One Food Composite

| COMPOUND (No.)           | MAXIMUM CONCENTRATIONS OF DETECTS ONLY |              |              |              |              |              |              |              |              |              |              |              |
|--------------------------|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
|                          | SALTWATER FRESHWATER FISH              |              | FORK         |              | REEF         |              | CHICKEN      |              | EGG          |              | MILK         |              |
|                          | CONC. (PB/G)                           | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) | CONC. (PB/G) |
|                          | MAXIMUM                                | MAXIMUM      | MAXIMUM      | MAXIMUM      | MAXIMUM      | MAXIMUM      | MAXIMUM      | MAXIMUM      | MAXIMUM      | MAXIMUM      | MAXIMUM      | MAXIMUM      |
| 2378-TCDF (1)            | 28.20                                  | 7.96         |              |              | 1.56         |              | 0.67         |              | 0.10         |              |              | 6.11         |
| 2378-TCDD (2)            | 1.89                                   | 9.78         |              |              |              |              | 1.67         |              |              |              |              | 1.46         |
| 12378-PCDD (5)           | 2.40                                   | 23.60        |              |              |              |              |              |              |              |              |              |              |
| 123478/123678-HxCDD (10) | 3.82                                   | 84.10        | 3.50         |              | 3.96         |              | 2.29         |              |              |              |              | 0.59         |
| 123789-HxCDD (11)        |  | 38.90        |              |              |              |              | 4.30         |              |              |              |              |              |
| 1234678-HpCDF (12)       | 2.21                                   |              | 10.60        |              | 1.15         |              | 24.60        |              | 0.59         |              |              | 0.70         |
| 1234789-HpCDF (13)       |  | 133.00       |              |              |              |              |              |              |              |              |              |              |
| 1234678-HpCDD (14)       | 3.15                                   | 201.00       | 45.50        |              | 8.95         |              | 35.20        |              | 1.76         |              |              | 4.25         |
| OCDF (15)                |  |              | 9.36         |              |              |              | 26.00        |              |              |              |              |              |
| OCDD (16)                | 22.70                                  | 1490.00      | 254.00       |              | 11.90        |              | 96.20        |              | 11.71        |              |              | 6.12         |

Table 4-45. Summary of Weighted Mean Concentrations for Compounds Above the Detection Level in Specific Food Composites

| COMPOUND (No.)           | WEIGHTED MEAN CONCENTRATIONS BASED ON DETECTS ONLY |      |                 |      |              |      |              |      |              |      |              |      |              |      |
|--------------------------|--|------|-----------------|------|--------------|------|--------------|------|--------------|------|--------------|------|--------------|------|
|                          | SALTWATER FISH                                     |      | FRESHWATER FISH |      | PORK         |      | BEEF         |      | CHICKEN      |      | EGG          |      | MILK         |      |
|                          | CONC. (PB/G)                                       | MEAN | CONC. (PB/G)    | MEAN | CONC. (PB/G) | MEAN | CONC. (PB/G) | MEAN | CONC. (PB/G) | MEAN | CONC. (PB/G) | MEAN | CONC. (PB/G) | MEAN |
| 237B-TCDF (1)            | 21.96  |      | 3.19            |      |              |      | 0.99         |      | 0.67         |      | 0.10         |      | 2.74         |      |
| 237B-TCDD (2)            | 1.13   |      | 5.59            |      |              |      |              |      | 0.78         |      |              |      | 1.46         |      |
| 1237B-PeCDD (5)          | 2.40   |      | 10.28           |      |              |      |              |      |              |      |              |      |              |      |
| 12347B/12367B-HxCDD (10) | 2.35   |      | 31.29           |      | 3.14         |      | 2.07         |      | 2.29         |      |              |      | 0.59         |      |
| 123789-HxCDD (11)        |  |      | 16.14           |      |              |      |              |      | 3.14         |      |              |      |              |      |
| 123467B-HpCDF (12)       | 2.21   |      |                 |      | 4.26         |      | 0.84         |      | 6.51         |      | 0.59         |      | 0.70         |      |
| 1234789-HpCDF (13)       |  |      | 133.00          |      |              |      |              |      |              |      |              |      |              |      |
| 123467B-HpCDD (14)       | 2.31   |      | 79.29           |      | 13.05        |      | 5.68         |      | 8.97         |      | 1.76         |      | 3.11         |      |
| OCDF (15)                |  |      |                 |      | 3.05         |      |              |      | 15.75        |      |              |      |              |      |
| OCDD (16)                | 13.82  |      | 510.07          |      | 76.18        |      | 9.40         |      | 34.69        |      | 11.71        |      | 4.24         |      |

Table 4-46. Summary of Weighted Mean Concentrations for All PCDD and PCDF Compounds Based on All Measured Levels and Estimated Detection Limits

| COMPOUND (No.)           | WEIGHTED MEAN CONCENTRATIONS BASED ON ALL DATA--LOD VALUES USED FOR NONDETECTS |                 |       |      |         |       |      |              |              |              |              |              |
|--------------------------|--|-----------------|-------|------|---------|-------|------|--------------|--------------|--------------|--------------|--------------|
|                          | SALTWATER FISH   | FRESHWATER FISH | FORK  | REEF | CHICKEN | EGG   | MILK | CONC. (PG/G) |
|                          | MEAN   | MEAN            | MEAN  | MEAN | MEAN    | MEAN  | MEAN | MEAN         | MEAN         | MEAN         | MEAN         | MEAN         |
| 2378-TCDF (1)            | 21.96  | 3.19            | 0.35  | 0.55 | 0.42    | 0.20  | 2.74 |              |              |              |              |              |
| 2378-TCDD (2)            | 1.21   | 5.02            | 0.33  | 0.26 | 0.50    | 0.27  | 0.69 |              |              |              |              |              |
| 12378-PeCDF (3)          | 1.62   | 1.04            | 0.68  | 0.60 | 0.28    | 0.54  | 0.39 |              |              |              |              |              |
| 23478-PeCDF (4)          | 1.28   | 1.16            | 0.62  | 0.57 | 0.26    | 0.39  | 0.38 |              |              |              |              |              |
| 12378-PeCDD (5)          | 1.81   | 10.28           | 2.29  | 2.78 | 1.64    | 1.93  | 0.98 |              |              |              |              |              |
| 123478-HxCDF (6)         |  | 4.66            | 1.58  | 0.67 | 0.51    | 1.95  | 0.70 |              |              |              |              |              |
| 123678-HxCDF (7)         | 1.51   | 1.14            | 0.65  | 0.63 | 0.45    | 1.86  | 0.68 |              |              |              |              |              |
| 234678-HxCDF (8)         | 2.91   | 1.35            | 0.77  | 0.75 | 0.54    | 2.43  | 0.82 |              |              |              |              |              |
| 123789-HxCDF (9)         | 1.96   | 1.47            | 0.84  | 0.82 | 0.59    | 2.70  | 0.88 |              |              |              |              |              |
| 123478/123678-HxCDD (10) | 2.64   | 25.68           | 1.66  | 2.07 | 1.51    | 7.17  | 1.00 |              |              |              |              |              |
| 123789-HxCDD (11)        | 2.36   | 13.37           | 1.72  | 2.08 | 1.78    | 3.29  | 1.01 |              |              |              |              |              |
| 1234678-HpCDF (12)       | 2.05   | 1.33            | 4.04  | 1.37 | 4.86    | 2.85  | 0.87 |              |              |              |              |              |
| 1234789-HpCDF (13)       | 2.69   | 26.47           | 2.99  | 1.72 | 1.34    | 4.00  | 1.25 |              |              |              |              |              |
| 1234678-HpCDD (14)       | 2.08   | 64.70           | 13.05 | 5.38 | 8.17    | 2.71  | 2.86 |              |              |              |              |              |
| OCDF (15)                | 5.71   | 2.48            | 2.51  | 1.73 | 5.10    | 4.03  | 2.67 |              |              |              |              |              |
| OCDD (16)                | 13.82  | 510.07          | 76.18 | 9.63 | 31.03   | 12.19 | 3.78 |              |              |              |              |              |

## SECTION 5.0

### DISCUSSION

In order to fully assess the importance of the PCDD and PCDF residue data generated under this study, it is necessary to consider the results from other existing data bases and to assess the potential for bioaccumulation of PCDDs and PCDFs through consideration of intake through dietary practices. This section presents a synopsis of other data bases on PCDD and PCDF residue for studies conducted on both the national and international level. Information is also presented on the average consumption (by the average Californian or U.S. citizen) of the general foodstuffs analyzed in this study.

The information presented in this section will be useful in developing a model for the estimation of the impact of food consumption on the total body burden of the general California population. It is beyond the scope of this effort to develop the specific model.

#### 5.1 PCDD and PCDF Residue Levels in Foodstuffs

A literature search was conducted to compile PCDD and PCDF residue levels in foods and to review the state-of-the-art methods of analysis for PCDDs and PCDFs. The literature search was conducted via an automated computer compilation of citations from *Chemical Abstracts* generally from 1980 through 1988. However, much of the current information on the residue levels of PCDDs and PCDFs in foodstuffs is not readily found in the open literature.

The most useful references on the PCDD and PCDF levels in foods are found in the Proceedings of American Chemical Society national symposia on dioxins in the environment. Preliminary data on the PCDD and PCDF residue levels in food were presented at the 6th and 7th International Dioxin Conferences which were held in 1986 (Fukuoka, Japan) and in 1987 (Las Vegas, Nevada). Unfortunately, the data on the PCDD and PCDF levels in foods from the various studies presented at these conferences have not been published at this time. References to the studies are presented in the discussions of food levels, and some information has been gleaned from the review of the extended abstracts from the international conference program listings.

The most extensive information on PCDD and PCDF residue levels in food are described in the literature as results from efforts conducted within the United States (Firestone et al., 1986), Japan (Ono et al., 1987; Takizawa and Muto, 1987; Ogaki et al., 1987), and the Federal Republic of Germany (Beck et al., 1987; Mathar et al., 1987; Beck et al., 1988). A survey of the PCDD and PCDF residue levels in food has also been conducted in Canada (OMAF/MOE,

1988; Birmingham et al., 1988). Other studies regarding PCDD and PCDF residue levels in U.S. foods are currently under way in the State of Vermont (personal communication, B. Fitzgerald, Air Pollution Control Division) and EPA Region V. These studies are being conducted to evaluate the impacts of emissions from a resource recovery facility and a hazardous waste site, respectively.

The food item that is most often cited in the literature with respect to the analysis for PCDDs and PCDFs is fish (Firestone et al., 1986; Kaczmar et al., 1985; Rappe et al., 1985; Stalling et al., 1982; Ryan et al., 1983). The U.S. Food and Drug Administration (FDA) report (Firestone et al., 1986) also summarized the results from the analysis of a number of different species of fish. The impetus for the analysis of these samples was to determine the effects of contamination resulting from highly industrialized areas surrounding a geographical region or from releases from hazardous waste sites.

Some experiments have been conducted to determine if there is a need for concern for uptake of PCDDs in vegetation (fruits and vegetables). Although the investigations have not been extensive, the results have indicated that there is no significant uptake of PCDDs, particularly 2,3,7,8-TCDD (NRCC, 1981; Isensee and Jones, 1971; Cocucci, 1979; Wipf et al., 1982; Pocchiari et al., 1983; Sundstrom et al., 1979; Crosby and Wong, 1977; Jensen et al., 1983; Mathar et al., 1987).

#### 5.1.1 U.S. Food and Drug Administration Market Basket Study

Results of the FDA Market Basket Surveys are an extremely important source of data. Various foods are examined by the FDA for residues of pentachlorophenol (PCP) as part of the agency's Total Diet Program. Individual foods or food ingredients found to contain over 0.05 µg PCP/g are examined for higher chlorinated PCDD residues. In addition, portions of ground beef, pork chops, chicken, egg, and beef liver from the FDA market basket are analyzed specifically for residues of PCDD regardless of PCP residues in the products.

The results of analyses of various foods collected by the FDA in a 5-year period beginning in 1979 are reported by Firestone et al. (1986). Table 5-1 is a summary of these findings.

Low levels (300 pg/g) of hepta- and octachlorodibenzo-*p*-dioxins were found in bacon, chicken, pork chops, and beef liver. Hexachlorodibenzo-*p*-dioxins were not detected in any of the foods at the detection limits achieved by the FDA laboratories (10-40 pg/g).

In the FDA study, several beef livers had higher levels of OCDD residues, and one beef liver contained about 400 and 3,800 pg/g of 1,2,3,4,5,7,8-HpCDD and OCDD, respectively. No PCDDs (limit of detection 10-40 pg/g) were found in ground beef.

Table 5-1. Higher Chlorinated Dioxin Residues in Various Foods Collected in the United States (1979-1984)

| Food          | No. of Products | FDA Collecting District <sup>a</sup> | PCP (µg/g) | pg/g <sup>b</sup>   |                     |           |
|---------------|-----------------|--------------------------------------|------------|---------------------|---------------------|-----------|
|               |                 |                                      |            | 1,2,3,4,6,7,9-HpCDD | 1,2,3,4,6,7,8-HpCDD | OCDD      |
| Bacon         | 1               | MIN                                  | 0.06       | ND                  | 46                  | 160       |
| Blue crab     | 1               | NSV                                  | -          | ND                  | ND                  | ND        |
| Crab          | 1               | NOL                                  | 0.0        | ND                  | ND                  | ND        |
| Catfish       | 1               | NOL                                  | 0.18       | ND                  | ND                  | ND        |
| Trout         | 1               | NOL                                  | 0.14       | ND                  | ND                  | ND        |
| Ground beef   | 16              | c                                    | -          | ND                  | ND                  | ND        |
| Peanut butter | 1               | SAN                                  | 0.10       | ND                  | ND                  | ND        |
| Milk          | 58              | c                                    | 0.01-0.05  | ND                  | ND                  | ND        |
| Chicken       | 14              | c                                    | -          | ND                  | ND                  | ND        |
| Chicken       | 1               | MIN                                  | 0.17       | 42                  | 28                  | 252       |
| Chicken       | 1               | NSV                                  | -          | ND                  | ND                  | 76        |
| Chicken       | 1               | SEA                                  | -          | ND                  | ND                  | 29        |
| Eggs          | 17              | c                                    | -          | ND                  | ND                  | ND        |
| Eggs          | 1               | HOU                                  | 0.29       | 39                  | 21                  | 304       |
| Eggs          | 6               | HOU                                  | 0.19-0.24  | ND                  | ND                  | 80-205    |
| Eggs          | 5               | NOL <sup>d</sup>                     | 0.3-1.2    | 40-60               | 88-588              | 295-1,610 |
| Eggs          | 6               | NOL <sup>e</sup>                     | 0.1-1.4    | ND-60               | 44-303              | 105-940   |
| Pork chops    | 16              | c                                    | -          | ND                  | ND                  | ND        |
| Pork chops    | 2               | SAN, SEA                             | -          | ND                  | ND                  | 53, 27    |
| Liver, calf   | 1               | HFD                                  | -          | ND                  | ND                  | 133       |
| Liver, beef   | 3               | c                                    | -          | ND                  | ND                  | ND        |
| Liver, beef   | 1               | SEA                                  | 0.1        | ND                  | 428                 | 3,830     |
| Liver, beef   | 1               | ORL                                  | 0.07       | ND                  | 168                 | 614       |
| Liver, beef   | 1               | SEA                                  | 0.05       | ND                  | 136                 | 818       |
| Liver, beef   | 22              | c                                    | -          | ND-37               | ND-64               | ND-197    |

Source: Firestone et al., 1986.

<sup>a</sup> HFD = Hartford; HOU = Houston; MIN = Minneapolis; NOL = New Orleans; NSV = Nashville; SAN = San Francisco; SEA = Seattle.

<sup>b</sup> ND, not measured; limit of measurement about 10-40 pg/g; presence of dioxin residues not routinely confirmed by GC/MS. Values corrected for recovery (70-90%).

<sup>c</sup> Samples collected at various locations in the United States.

<sup>d</sup> Samples collected from farms in Mena, Arkansas, area in 1983.

<sup>e</sup> Samples collected from farms in Mena, Arkansas, area in 1984.

A survey of milk for higher chlorinated dioxin residues was conducted in 1981-1983. No PCDDs (limit of detection 5-15 pg/g) were found in 58 milk samples collected in different parts of the United States. No PCDDs were found in 17 egg products collected in various parts of the United States. PCP and PCDD residues in eggs from the Houston, Texas, and Mena, Arkansas, areas collected in 1982 and 1983-1984, respectively, were due to local PCP contamination problems in the area.

As noted in Table 5-1 the FDA study included notations indicating that several of the food products were collected in the San Francisco area. It is not clear, however, how many individual food groups were analyzed and at what frequency.

#### 5.1.2 Canada

Two specific studies for the determination of PCDD and PCDF residue levels in Canadian foodstuffs have been reported (Davies, 1988; OMAF/MOE, 1988; Birmingham et al., 1988). The study described by Davies (1988) included the analysis of food composites consisting of five categories: fresh meat and eggs, root vegetables, fresh fruit, leafy vegetables, and bovine milk. The results reported by Davies presented quantitative data on PCDDs and PCDFs for each of the food groups, and it was concluded that fruit (apples) provided the route of exposure through dietary intake. These conclusions were challenged and discounted in a follow-on study conducted as a collaborative effort between Ontario's Ministry of Agriculture and Food and the Ministry of Environment (OMAF/MOE, 1988; Birmingham et al., 1988). The general conclusions of the OMAF/MOE study were that fruit and vegetable samples were substantially free of PCDD and PCDF residues; that animal products contained residues of PCDDs and PCDFs, and the data are consistent with values from efforts conducted in the United States and the Federal Republic of Germany; and that the data generated under the OMAF/MOE study are significantly lower than the residue levels reported by Davies (1988).

#### 5.1.3 Federal Republic of Germany

Two studies have been reported regarding efforts in the Federal Republic of Germany to correlate body burden levels of PCDDs and PCDFs to food intake. Beck et al. (1987) reported on the concentration of the 2,3,7,8-substituted PCDDs and PCDFs in bovine milk. Table 5-2 provides a summary of the residue levels of the 2,3,7,8-substituted congeners in eight different milk samples collected as composites from different dairies supplying Berlin. The data reported in Table 5-2 range in concentration from 0.2 to 1.1 pg/g based on the fat content of the samples rather than total sample weight.

Mathar et al. (1987) reported at the 7th International Dioxin Conference that the scope of the study presented by Beck et al. (1987) had been expanded to encompass the determination of PCDDs and PCDFs in a variety of foodstuffs that had been collected from markets in Berlin. This study included the analysis of fruits, vegetables, fish (specifically cod), milk and other dairy products, beef, pork, poultry, and eggs. The

Table 5-2. PCDD and PCDF Levels of Eight Cows' Milk Samples (pg/g; fat weight basis)

|                     | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | $\bar{X}$ | Det. Limit |
|---------------------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|------------|
| 2,3,7,8-TCDF        | < 0.1 | 0.29  | 0.28  | 1.1   | 1.0   | 1.4   | 1.4   | 0.27  | 0.7       | 0.1        |
| 2,3,7,8-TCDD        | 0.33  | < 0.2 | < 0.2 | < 0.2 | N.D.  | < 0.2 | N.D.  | N.D.  | 0.2       | 0.2        |
| 1,2,3,7,8-PCDF      | N.D.  | 0.4   | N.D.  | 0.26  | 0.24  | N.D.  | 0.39  | < 0.2 | 0.2       | 0.2        |
| 2,3,4,7,8-PCDF      | 1.3   | 0.91  | 1.1   | 1.6   | 1.5   | 1.3   | 2.9   | 0.8   | 1.4       | 0.2        |
| 1,2,3,7,8-PCDD      | 1.0   | 0.72  | N.D.  | 0.81  | 0.6   | 0.78  | 1.2   | < 0.5 | 0.7       | 0.5        |
| 1,2,3,4,7,8-HxCDF   | 0.93  | 0.67  | 0.70  | 0.85  | < 0.3 | 0.84  | 1.9   | 0.57  | 0.9       | 0.3        |
| 1,2,3,6,7,8-HxCDF   | 0.73  | 0.58  | 0.57  | 0.85  | < 0.3 | 0.73  | 2.1   | 0.41  | 0.8       | 0.3        |
| 2,3,4,6,7,8-HxCDF   | 0.65  | 0.48  | 0.53  | 0.68  | N.D.  | 0.64  | 1.8   | 0.37  | 0.7       | 0.3        |
| 1,2,3,4,7,8-HxCDD   | 0.33  | 0.34  | < 0.3 | < 0.3 | < 0.3 | 0.36  | 0.33  | < 0.3 | 0.3       | 0.3        |
| 1,2,3,6,7,8-HxCDD   | 1.3   | 1.2   | 1.0   | 0.82  | 0.32  | 1.7   | 1.9   | 0.80  | 1.1       | 0.3        |
| 1,2,3,7,8,9-HxCDD   | < 0.3 | 0.34  | 0.36  | 0.39  | N.D.  | 0.55  | 0.48  | < 0.3 | 0.4       | 0.3        |
| 1,2,3,4,6,7,8-HpCDF | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5     | *          |
| 1,2,3,4,6,7,8-HpCDD | < 2   | < 2   | < 2   | < 2   | < 2   | < 2   | < 2   | < 2   | < 2       | *          |
| OCDF                | < 10  | < 10  | < 10  | < 10  | < 10  | < 10  | < 10  | < 10  | < 10      | *          |
| OCDF                | < 1   | < 1   | < 1   | < 1   | < 1   | < 1   | < 1   | < 1   | < 1       | *          |

Source: Beck, H., K. Eckart, M. Kellert, W. Mathar, Ch.-S. Rühl, and R. Wittkowski. 1987. *Chemosphere*, 16, 1977-1982.

\* = not significantly higher than blanks.

$\bar{X}$  = mean value (N.D. values were calculated with half value of detection limit).

< = detected with 5:1 signal-to-noise ratio (detection limit).

ND = not detectable.

data from this study were recently published (Beck et al., 1988). The analytical efforts reported by Mathar et al. (1987) and Beck et al. (1988) demonstrated that the 2,3,7,8-substituted PCDDs and PCDFs were not detected in fruits, vegetables, or vegetable oils. Detection limits for these food products averaged 20 ppq (parts per quadrillion,  $10^{-15}$  g/g). Measurable residue levels of the 2,3,7,8-substituted PCDDs and PCDFs were determined in all other products. The highest concentrations were detected in the fish samples. Table 5-3 provides a synopsis of the PCDD and PCDF residue levels in foodstuffs reported by Beck et al. (1988).

#### 5.1.4 Japan

Three different studies on the levels of PCDDs and PCDFs in foods of Japanese origin were reported at the 6th International Dioxin Conference. Ono et al. (1987) described the results of the analysis of foods representative of the Japanese diet (see Table 5-4). These included vegetables, cooking oils, rice and wheat, fish, beef, pork, poultry, and eggs that were collected in Matsuyama during 1986. Ono et al. detected tetra- through octachloro-substituted PCDDs in the various foodstuffs. The highest concentrations were detected in poultry (chicken and eggs). Ono et al. have estimated that the typical Japanese diet leads to an intake of approximately 5,200 pg/day of total PCDDs, which is equivalent to 63 pg of 2,3,7,8-TCDD.

A review of the data in Table 5-4, however, reveals that the 2,3,7,8-substituted PCDDs are not the predominant congeners. Also, it is important to note that OCDD, which has typically been reported as the major contaminant in most environmental and human tissue samples, was not consistently detected in the food products. It is possible that the approach for sample preparation, particularly the digestion of the meat and egg samples in an alcoholic potassium hydroxide solution, resulted in the dechlorination of the OCDD.

Ryan et al. (1987) have studied the alcoholic potassium hydroxide digestion procedure and have concluded that this procedure leads to the formation of alternate PCDD compounds with non-2,3,7,8-substitution. The presence of the 1,3,6,8- and 1,3,7,9-tetrachloro congeners and the 1,2,3,6,8-pentachloro congeners indicates potential background contribution from sources other than the foodstuffs (Heller et al., 1985; Stanley and Sack, 1986).

Additional data on a variety of other foodstuffs from Japan (Akita and Osaka) were reported by Takizawa and Muto (1987) and Ogaki et al. (1987). Each of these studies also approached the analysis by first using the alcoholic saponification digestion procedure. The data in these studies are reported as total concentration per degree of chlorination, and no isomer is specifically indicated. As a result, it is difficult to assess the validity of the data and to ascertain how the data can be extrapolated for valid comparison to other studies.

Table 5-3. Levels of PCDD and PCDF in Food From the Federal Republic of Germany (in ppt/fat)

| Isomer            | Cow's Milk | Butter | Beef  | Pork | Sheep | Herring | Cod |
|-------------------|------------|--------|-------|------|-------|---------|-----|
| 2,3,7,8-TCDF      | 0.7        | 0.15   | < 0.3 | 0.11 | < 0.6 | 57      | 98  |
| 2,3,7,8-TCDD      | 0.2        | 0.08   | 0.6   | 0.03 | ND    | 4.7     | 23  |
| 1,2,3,7,8-PeCDF   | 0.2        | 0.09   | ND    | ND   | ND    | 16      | 48  |
| 2,3,4,7,8-PeCDF   | 1.4        | 0.45   | 1.5   | 0.08 | 0.4   | 29      | 3.1 |
| 1,2,3,7,8-PeCDD   | 0.7        | 0.41   | 0.8   | 0.12 | 0.5   | 12      | 1.3 |
| 1,2,3,4,7,8-HxCDF | 0.9        | 0.43   | 0.8   | 0.15 | 0.9   | 30      | 6.9 |
| 1,2,3,6,7,8-HxCDF | 0.8        | 0.44   | 0.6   | 0.07 | 1.2   | 4.2     | 13  |
| 2,3,4,6,7,8-HxCDF | 0.7        | 0.31   | 1.3   | 0.05 | 1.5   | 3.6     | 8.2 |
| 1,2,3,4,7,8-HxCDD | 0.3        | 0.15   | 0.6   | 0.21 | 0.3   | 1.2     | ND  |
| 1,2,3,6,7,8-HxCDD | 1.1        | 0.95   | 1.9   | 0.29 | 1.5   | 5.8     | 17  |
| 1,2,3,7,8,9-HxCDD | 0.4        | 0.26   | 0.6   | 0.06 | 0.4   | 1.0     | 5.2 |

Source: Beck et al. 1987. *Biomedical and Environmental Mass Spectrometry*, 16, 161-165.

Table 5-4. Concentrations (pg/g on wet weight basis) of PCDDs and PCDFs in Foods Representative of the Japanese Diet

|  | Vegetable | Oil       | Rice<br>and<br>Wheat | Fish  | Beef  | Pork  | Chicken | Egg   |
|--|-----------|-----------|----------------------|-------|-------|-------|---------|-------|
| 1,3,6,8-T <sub>4</sub> CDD                                       | 0.8       | < 0.2     | 0.4                  | 1.0   | 1.2   | 0.8   | 3.9     | 2.3   |
| 1,3,7,9-T <sub>4</sub> CDD                                       | 0.7       | < 0.2     | 0.3                  | 0.8   | 0.5   | 0.5   | 1.5     | 1.0   |
| Total T <sub>4</sub> CDD   | 1.5       | -         | 0.7                  | 1.8   | 1.7   | 1.3   | 5.4     | 3.3   |
| 1,2,3,6,8-P <sub>5</sub> CDD                                     | 0.1       | < 0.1     | < 0.1                | < 0.3 | < 0.3 | < 0.3 | 1.3     | 0.9   |
| Total P <sub>5</sub> CDD   | 0.1       | -         | -                    | -     | -     | -     | 1.3     | 0.9   |
| 1,2,4,6,7,9-/<br>1,2,4,6,8,9-/<br>1,2,3,4,6,8-H <sub>6</sub> CDD | < 0.1     | < 0.5     | < 0.3                | < 1.1 | < 0.8 | < 1.2 | 1.6     | 2.3   |
| 1,2,3,6,7,9-/<br>1,2,3,6,8,9-H <sub>6</sub> CDD                  | < 0.1     | < 0.5     | < 0.3                | < 1.1 | < 0.8 | < 1.2 | 7.3     | 6.2   |
| 1,2,3,6,7,8-H <sub>6</sub> CDD                                   | < 0.1     | < 0.5     | < 0.3                | < 1.1 | < 0.8 | < 1.2 | 8.1     | 5.7   |
| 1,2,3,7,8,9-H <sub>6</sub> CDD                                   | < 0.1     | < 0.5     | < 0.3                | < 1.1 | < 0.8 | < 1.2 | 2.7     | 1.8   |
| Total H <sub>6</sub> CDD   | -         | -         | -                    | -     | -     | -     | 19.7    | 16.0  |
| 1,2,3,4,6,7,9-H <sub>7</sub> CDD                                 | < 0.2     | Tr. (0.8) | < 0.6                | < 2.2 | < 1.4 | < 1.4 | 2.9     | 2.9   |
| 1,2,3,4,6,7,8-H <sub>7</sub> CDD                                 | < 0.2     | Tr. (0.8) | < 0.6                | < 2.2 | < 1.4 | 2.9   | 4.6     | 4.6   |
| Total H <sub>7</sub> CDD   | -         | -         | -                    | -     | -     | 2.9   | 7.5     | 7.5   |
| O <sub>8</sub> CDD   | < 0.3     | 4.4       | < 1.3                | < 5.0 | < 4.5 | 11.9  | < 4.0   | < 4.0 |
| Total PCDDs  | 1.6       | 6.1       | 0.7                  | 1.8   | 1.7   | 16.1  | 33.9    | 27.7  |
| 2,3,7,8-T <sub>4</sub> CDF                                       | < 0.02    | < 0.1     | < 0.05               | 1.1   | < 0.2 | < 0.2 | < 0.3   | < 0.2 |
| Total T <sub>4</sub> CDF   | -         | -         | -                    | 1.1   | -     | -     | -       | -     |
| 2,3,4,8,9-P <sub>5</sub> CDF                                     | < 0.03    | < 0.1     | 0.2                  | < 0.2 | < 0.6 | < 0.3 | < 0.6   | < 0.3 |
| Total P <sub>5</sub> CDF   | -         | -         | 0.2                  | -     | -     | -     | -       | -     |
| Total PCDFs  | -         | -         | 0.2                  | 1.1   | -     | -     | -       | -     |

Source: Ono et al., 1987.

## 5.2 PCDD and PCDF Intake Via Food Consumption

Dietary intake of PCDDs and PCDFs can be estimated based on consumption of specific food products for the average person. In order to determine the dietary intake for the average Californian or U.S. citizen, several different agricultural and food organizations were contacted. These sources included the California Egg Commission, the California Beef Council, the California Milk Advisory Board, the California Pork Producers, the California Department of Food and Agriculture, the National Pork Producers Association, the National Livestock and Meat Board, and the U.S. Department of Agriculture. In most instances, the data on food consumption were traced back to the USDA information sources on national averages. Additional detail beyond the USDA estimates for regional or state usages would require conduct of specific surveys. Data generated from the USDA sources are typically based on documented production and imports divided by the total population. Table 5-5 provides a summary of the consumption information gathered. Some comparisons of estimates from specific California agencies are provided with the USDA statistics.

In addition to identifying the total consumption of specific food products, it is also necessary to estimate the average intake of lipophilic materials which the PCDDs and PCDFs are expected to be associated. Table 5-6 provides a summary of the expected lipid consumption based on specific food products. The data presented were taken from a publication of the National Livestock and Meat Board (Breidenstein and Williams) or estimated from the percentage of lipid extractable materials as determined by the laboratory procedures of this study.

Table 5-5. Average Annual Consumption of Food Products on a National and/or California Basis

| Food product | Retail | Edible | Units/Year  | Information Source        |
|--------------|--------|--------|-------------|---------------------------|
| Beef         | 72.7   | 48.7   | 1b/person   | USDA (1988)               |
| Pork         | 63.1   | 42.3   | 1b/person   | USDA (1988)               |
| Chicken      | 64.1   | 44.2   | 1b/person   | USDA (1988)               |
| Fish         | 15.4   | 15.4   | 1b/person   | USDA (1988)               |
|              | 20     | 20     | 1b/person   | California Seafood        |
| Milk         | 228    | 228    | 1b/person   | USDA (1987)               |
|              | 228    | 228    | 1b/person   | California Milk Board     |
| Egg          | 243    | 243    | eggs/person | USDA (1988)               |
|              | 240    | 240    | eggs/person | California Egg Commission |

Table 5-6. Average Lipid Consumption Based on Specific Food Product Usage

| Food Product | Lipid Consumption     | Information Source                     |
|--------------|-----------------------|--|
| Beef         | 1,230 g/person/year   | Breidenstein and Williams <sup>a</sup> |
| Pork         | 807 g/person/year     | Breidenstein and Williams              |
| Milk         | ~ 5,000 g/person/year | CARB Project A6-197-32.                |
| Eggs         | ~ 600 g/person/year   | CARB Project A6-197-32                 |

<sup>a</sup> "Contribution of Red Meat to the U.S. Diet," National Livestock and Meat Board.

## SECTION 6.0

### BIBLIOGRAPHY

- Beck, H., K. Eckart, M. Kellert, W. Mathar, Ch.-S. Rühl, and R. Wittkowski. 1987. "Levels of PCDFs and PCDDs in Samples of Human Origin and Food in the Federal Republic of Germany," *Chemosphere*, 16, 1977-1982.
- Beck, H., K. Eckart, W. Mathar, Ch.-S. Rühl, and R. Wittkowski. 1988. "Isomer Specific Determination of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin and Related Compounds in Human Fat and Food," *J. Biomedical and Environmental Mass Spectrometry*, 16, 161-165.
- Birmingham, B. 1988. "Dietary Intake of PCDD and PCDF from Food in Ontario," Presented at the 8th International Symposium on Chlorinated Dioxins and Related Compounds, August, Umea, Sweden.
- Breidenstein, B. C., and J. C. Williams. "Contribution of Red Meat to the U.S. Diet," National Livestock and Meat Board.
- Cocucci, S., F. Di Gerolamo, A. Verderio, et al. 1979. "Absorption and Translocation of Tetrachlorodibenzo-*p*-dioxin by Plants from Polluted Soil," *Experientia*, 35(4):482-484.
- Connett, P., and T. Webster. 1987. "Critical Factors in the Assessment of Food Chain Contamination by PCDD/PCDF from Incinerators," Presented at the 7th International Symposium on Chlorinated Dioxins and Related Compounds, October 4-9, Las Vegas, Nevada.
- Crosby, D. G., and A. S. Wong. 1977. "Environmental Degradation of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)," *Science*, 195:1337-1338.
- Davies, K. 1988. "Concentrations and Dietary Intake of Selected Organochlorines, Including PCBs, PCDDs, and PCDFs in Fresh Food Composites Grown in Ontario, Canada," *Chemosphere*, 17(2):263-276.
- Firestone, D., R. A. Niemann, L. F. Schneider, J. R. Gridley, and D. E. Brown. 1986. "Dioxin Residues in Fish and Other Foods," in *Chlorinated Dioxins and Dibenzofurans in Perspective*, C. Rappe, G. Choudhary, L. H. Keith, Eds., Lewis Publishers, Inc., Chelsea, Michigan, pp. 355-365.
- Heller, J. S., D. G. Patterson, L. R. Alexander, D. F. Groce, R. P. O'Connor, and C. R. Lapeza. 1985. "Control of Artifacts and Contamination in the Development of a Dioxin Analytical Program," Presented at the 33rd Annual Conference on Mass Spectrometry and Allied Topics, San Diego, California.

Isensee, A. R. 1978. "Bioaccumulation of 2,3,7,8-Tetrachlorodibenzo-p-dioxin," *Ecol. Bull.*, C. Ramel, Ed., 27:255-262.

Isensee, A. R., and G. E. Jones. 1971. "Absorption and Translocation of Root and Foliage Applied 2,4-Dichlorophenol, 2,7-Dichlorodibenzo-p-dioxin, and 2,3,7,8-Tetrachlorodibenzo-p-dioxin," *J. Agric. Food Chem.*, 19:1210-1214.

Isensee, A. R., and G. E. Jones. 1975. "Distribution of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) in Aquatic Model Ecosystem," *Environ. Sci. Technol.*, 9:668-672.

Jensen, D. J., and R. A. Hummel. 1982. "Secretion of TCDD in Milk and Cream Following the Feeding of TCDD to Lactating Dairy Cows," *Bull. Environ. Contam. Toxicol.*, 29:440-446.

Jensen, D. J., R. A. Hummel, N. H. Mahle, C. W. Kocher, and H. S. Higgins. 1981. "Residue Study on Beef Cattle Consuming 2,3,7,8-Tetrachlorodibenzo-p-dioxin," *J. Agric. Food Chem.*, 29(2):265-268.

Jensen, D. J., M. E. Getzendaner, R. A. Hummel, and J. Turley. 1983. "Residue Study for (2,4,5-Trichlorophenoxy) Acetic Acid and 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Grass and Rice," *J. Agric. Food Chem.*, 31:118-122.

Kaczmar, S. W., M. J. Zabik, and F. M. D'Itri. 1985. "Part Per Trillion Residues of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Michigan Fish," in *Chlorinated Dioxins and Dibenzofurans in the Total Environment II*, L. H. Keith, C. Rappe, and G. Choudhary, Eds., Butterworth Publishers, Boston, Massachusetts, pp. 103-110.

LeBel, G. L., D. T. Williams, J. J. Ryan, and B. P.-Y. Lau. 1986. "Evaluation of XAD-2 Resin Cartridge for Concentration/Isolation of Chlorinated Dibenzofurans and Furans from Drinking Water at the Parts-per-Quadrillion Level," in *Chlorinated Dioxins and Dibenzofurans in Perspective*, C. Rappe, G. Choudhary, and L. H. Keith, Eds., Lewis Publishers, Inc., Chelsea, Michigan, pp. 329-342.

Mack, G. A., and P. E. Robinson. 1985. "Use of Compositated Samples to Increase the Precision and Probability of Detection of Toxic Chemicals," ACS Symposium Series 292, Environmental Applications of Chemometrics, J. J. Breen and P. E. Robinson, Eds., American Chemical Society, Washington, DC, pp. 174-183.

Mathar, W., H. Beck, K. Eckart, Ch.-S. Rühl, and R. Wittkowski. 1987. "Body Burden with PCDDs and PCDFs from Food Intake in Germany," Presented at the 7th International Symposium on Chlorinated Dioxins and Related Compounds, October 4-9, Las Vegas, Nevada.

Mitchell, M. F., H. A. McLeod, and J. R. Roberts. 1984. "Polychlorinated Dibenzofurans: Criteria for Their Effects on Humans and the Environment," Associate Committee on Scientific Criteria for Environmental Quality, NRCC No. 22846.

Miyata, H., K. Takayama, J. Ogaki, T. Kashimoto, and S. Fukushima. 1987. "Monitoring of PCDDs in Osaka Bay Using Blue Mussel," *Chemosphere*, **16**, 1817-1822.

Nostrom, R. J., D. J. Hallett, M. Simon, and M. J. Mulvihill. 1982. "Analysis of Great Lakes Herring Gull Eggs for Tetrachlorodibenzo-*p*-dioxins," in *Chlorinated Dioxins and Related Compounds*, O. Hutzinger, R. W. Frei, E. Merian, and F. Pocchiari, Eds., Pergamon Press, New York, pp. 173-182.

NRCC National Research Council of Canada. 1981. "Polychlorinated Dibenzo-*p*-dioxins: Criteria for Their Effects on Man and His Environment," Associate Committee on Scientific Criteria for Environmental Quality, NRCC No. 18574.

OMAF/MOE, Ontario Ministry of Agriculture and Food/Ministry of Environment. 1988. "Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans and Other Organochlorine Contaminants in Food," ISBN-0-7229-4608-6, August 1988.

Ono, M., Y. Kashima, T. Wakimoto, and R. Tatsukawa. 1987. "Daily Intake of PCDDs and PCDFs by Japanese Through Food," *Chemosphere*, **16**, 1823-1828.

Paasivirta, J., J. Tarhanen, B. Juvonen, and P. Vuorinen. 1987. "Dioxins and Related Aromatic Chloroethers in Baltic Wildlife," *Chemosphere*, **16**, 1787-1790.

Pocchiari, F., A. DiDomenico, V. Silano, and G. Zapponi. 1983. "Environmental Impact of the Accidental Release of Tetrachlorodibenzo-*p*-dioxin (TCDD) at Seveso (Italy)," in *Accidental Exposure to Dioxins: Human Health Aspects*, F. Coulston and F. Pocchiari, Eds., Academic Press, New York, pp. 5-35.

Rappe, C., P.-A. Bergquist, and S. Marklund. 1985. "Analysis of Polychlorinated Dibenzofurans and Dioxins in Ecological Samples," in *Chlorinated Dioxins and Dibenzofurans in the Total Environment II*, L. H. Keith, C. Rappe, and G. Choudhary, Eds., Butterworth Publishers, Boston, Massachusetts, pp. 125-138.

Rappe, C., M. Nygren, G. Lindström, H. R. Buser, O. Blaser, and C. Wütrich, "Polychlorinated Dibenzofurans and Dibenzo-*p*-dioxins and Other Chlorinated Contaminants in Cow Milk from Various Locations in Sweden." 1987. *Environ. Sci. Technology*.

Ryan J. J., P.-Y. Lau, J. C. Pilon, and D. Lewis. 1983. "2,3,7,8-Tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-Tetrachlorodibenzofuran Residues in Great Lakes Commercial and Sport Fish," in *Chlorinated Dioxins and Dibenzofurans in the Total Environment*, G. Choudhary, L. H. Keith, and C. Rappe, Eds., Butterworth Publishers, Boston, Massachusetts, pp. 87-98.

Ryan, J. J., and J. C. Pilon. 1982. "Chlorinated Dibenzodioxins and Dibenzofurans in Chicken Litter and Livers Arising from Pentachlorophenol Contamination of Wood Shavings," in *Chlorinated Dioxins and Related Compounds*, O. Hutzinger, R. W. Frei, E. Merian, and F. Pocchiari, Eds., Pergamon Press, New York, New York, pp. 183-190.

Ryan, J. J., R. Lizotte, L. G. Panopio, B. P.-Y. Lau, W. F. Sun, and Y. Masuda. 1987. "The Effect of Strong Alkali on the Determination of PCDDs and PCDFs in Biological Samples," Presented at the 7th International Symposium on Chlorinated Dioxins and Related Compounds, October 4-9, Las Vegas, Nevada.

Schechter, A., R. Kooka, P. Serne, K. Olie, and J. Constable. 1987. "Chlorinated Dioxin and Dibenzofuran Levels in Food Samples Collected in 1984-87 in the North and South of Vietnam," Presented at the 7th International Symposium on Chlorinated Dioxins and Related Compounds, October 4-9, Las Vegas, Nevada.

Stanley, J. S. 1988. "Chlorinated Dibenzo-*p*-dioxin and Dibenzofuran Residue Levels in Food," Phase I Interim Report Prepared for the California Air Resources Board, March 7, 1988.

Stanley, J. S. 1986a. "Broad Scan Analysis of the FY82 National Human Adipose Tissue Survey Specimen, Volume I, Executive Summary," EPA Publication No. EPA-560/5-86-035.

Stanley, J. S. 1986b. "Broad Scan Analysis of the FY82 National Human Adipose Tissue Survey Specimen, Volume II, Volatile Organic Compounds," EPA Publication No. EPA-560/5-86-036.

Stanley, J. S. 1986c. "Broad Scan Analysis of the FY82 National Human Adipose Tissue Survey Specimen, Volume III, Semivolatile Organic Compounds," EPA Publication No. EPA-560/5-86-037.

Stanley, J. S. 1986d. "Broad Scan Analysis of the FY82 National Human Adipose Tissue Survey Specimens, Volume IV, Polychlorinated Dibenzo-*p*-dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF)," EPA Publication No. EPA-560/5-86-038.

Stanley, J. S., and R. A. Stockton. 1986. "Broad Scan Analysis of the FY82 National Human Adipose Tissue Survey Specimen, Volume V, Trace Elements," EPA Publication No. EPA-560/5-86-039.

Stanley, J. S. 1984. "Methods of Analysis for Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Biological Matrices - Literature Review and Preliminary Recommendations," EPA Publication No. EPA-560/5-84-001.

Stanley, J. S., J. E. Going, D. P. Redford, F. W. Kutz, and A. L. Young. 1985. "Analytical Methods for Measurement of Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Human Adipose Tissue," in: *Chlorinated Dioxins and Dibenzofurans in the Total Environment*, Volume II, G. Choudhary, L. H. Keith, and C. Rappe, Eds., Butterworth Publishers, Woburn, Massachusetts, pp. 181-196.

Stanley, J. S., and T. M. Sack. 1986. "Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxins by High Resolution Gas Chromatography/High Resolution Mass Spectrometry," EPA Publication No. EPA-600/4-86-004, NTIS Publication No. P886 161361.

Stanley, J. S., K. Boggess, J. Onstot, T. Sack, J. Remmers, J. Breen, F. W. Kutz, P. Robinson, and G. Mack. 1986a. "PCDDs and PCDFs in Human Adipose Tissues from the EPA FY82 NHATS Repository," *Chemosphere*, 15, 1605-1612.

Stanley, J. S., K. Boggess, J. E. Going, G. A. Mack, J. Remmers, J. Breen, F. W. Kutz, J. Carra, and P. Robinson. 1986b. "Broad Scan Analysis of Human Adipose Tissue from the EPA FY82 NHATS Repository," Chapter 14 in *Environmental Epidemiology*, F. C. Kopfler, G. F. Craun, Eds., Lewis Publishers, Inc., Chelsea, Michigan, pp. 161-1979.

Stanley, J. S., R. E. Ayling, K. M. Bauer, M. J. McGrath, T. M. Sack, and K. R. Thornburg. 1986c. "Analysis for Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Human Adipose Tissue: Method Evaluation Study," EPA Publication No. EPA-560/5-85-022.

Stanley, J. S., R. E. Ayling, K. M. Bauer, M. J. McGrath, T. M. Sack, K. R. Thornburg, J. C. Remmers, J. Breen, M. Frankenberry, C. Stroup, B. M. Shepard, and H. K. Kang. 1986e. "Evaluation of an Analytical Method for the EPA/VA Human Adipose Tissue Study," 6th International Symposium on Chlorinated Dioxins and Related Compounds, September 16-19, Fukuoka, Japan.

Stephens, R. D., D. Hayward, L. Goldman, and P. Papenek. 1987. "PCDD and PCDF in Breast Milk as Correlated with Fish Consumption," Presented at the 7th International Symposium on Chlorinated Dioxins and Related Compounds, October 4-9, Las Vegas, Nevada.

Sundstrom, G., S. Jensen, B. Jansson, and K. Erne. 1979. "Chlorinated Phenoxyacetic Acid Derivatives and Tetrachlorodibenzo-*p*-dioxin in Foliage After Application of 2,4,5-Trichlorophenoxyacetic Acid Esters," *Arch. Environ. Contam. Toxicol.*, 8(4):441-448.

Takizawa, Y., and H. Muto. 1987. "PCDDs and PCDFs Carried to the Human Body from the Diet," *Chemosphere*, 16, 1971-1976.

Wipf, H. K., E. Homberger, N. Neimer, U. B. Ranalder, W. Vetter, and J. P. Vuilleumeier. 1982. "TCDD Levels in Soil and Plant Samples from the Seveso Area," in *Chlorinated Dioxins and Related Compounds: Impact on the Environment*, O. Hutzinger et al., Eds., Pergamon Press, New York, pp. 115-126.

APPENDIX A

CALIFORNIA AIR RESOURCES BOARD FOOD STUDY

SAN FRANCISCO SAMPLING SITES

SAN FRANCISCO SAMPLING SITES

| RETAIL TARGETS                               | ZIP CODE | EGGS | MILK/BUTTER | POULTRY | BEEF | PORK | FRESH FISH | SALTWATER FISH |
|--|----------|------|-------------|---------|------|------|------------|----------------|
| ARGUELLO MARKET<br>782 ARGUELLO BLVD         | ?        | -    | -           | -       | -    | -    | -          | -              |
| BELL MKTS, INC.<br>3950 24TH                 | 94114    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| C&E GROCERY AND DELI<br>506 BUSH             | 94108    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| CLEVELAND MKT<br>744 BRAZIL AVE              | 94112    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| EXCELSIOR FARMERS MKT<br>4575 MISSION        | D        |      |             |         |      |      |            |                |
| EUREKA VALLEY MEAT MKT<br>2283 MARKET STREET | 94114    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| GR MARKET AND DELI<br>2601 SUTTER            | 94115    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| JC SUPERMARKET<br>920 CORTLAND AVE           | 94110    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| JERRY'S MKT<br>1001 STANYAN                  | 94110    | Y    | Y           | Y       | Y    | Y    | Y          | Y              |
| LOMBARD HEIGHTS MKT<br>1877 STOCKTON         | 94133    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| LUCKY STORES, INC.<br>1100 EDDY              | D        |      |             |         |      |      |            |                |
| MISSION PLAZA MKT<br>2023 MISSION            | 94110    | Y    | Y           | Y       | Y    | Y    | Y          | Y              |
| NINTH AND MORAGA MKT<br>1701 NINTH AVE       | 94122    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| O'LOONEY'S MKT<br>588 HAIGHT                 | -        | Y    | Y           | N       | N    | N    | N          | N              |
| PETE'S GROCERY<br>581 VALENCIA               | D        |      |             |         |      |      |            |                |
| PRIDE SUPERETTE<br>3086 24TH                 | D        |      |             |         |      |      |            |                |
| SAFEWAY STORE<br>3350 MISSION                | 94110    | Y    | Y           | Y       | Y    | Y    | N          | N              |

|   |       |   |   |   |   |   |   |   |
|---|-------|---|---|---|---|---|---|---|
| SAFEWAY STORE<br>2020 MARKET              | 94114 | Y | Y | Y | Y | Y | N | N |
| SUPER FAIR MKT<br>201 LELAND              | 94134 | Y | Y | Y | Y | Y | N | N |
| TERMINAL MKT<br>1925 JERROLD AVE          | 94124 | Y | Y | Y | Y | Y | N | N |
| V-J GROCERY AND DELI<br>1139 CLAY         | 94108 | Y | Y | Y | Y | Y | N | N |
| VALLEY SUPERMARKET<br>65 LELAND AVE       | 94134 | Y | Y | Y | Y | Y | N | N |
| WELDON'S GROCERY/DELI<br>1931 SUTTER      | 94115 | Y | Y | Y | Y | Y | N | N |
| YOUR FRIENDLY MKT<br>1999 GOLDEN GATE AVE | ?     |   |   |   |   |   |   |   |
|   |       |   |   |   |   |   |   |   |
| CAL-MART MKT<br>3585 CALIFORNIA           | 94118 | Y | Y | Y | Y | Y | Y | Y |
| CANTON MARKET<br>1135 STOCKTON            | 94133 | N | N | Y | N | N | Y | Y |
| LICK SUPER MARKET<br>350 7TH AVE          | 94118 | Y | Y | Y | Y | Y | Y | Y |
| SAFEWAY STORE<br>1830 OCEAN AVE           | 94112 | Y | Y | Y | Y | Y | Y | Y |
| SUN DUCK MKT<br>1107 STOCKTON             | 94133 | N | N | Y | N | N | Y | Y |
|   |       |   |   |   |   |   |   |   |
| THRIFTWAY<br>2174 UNION ST                | 94123 | Y | Y | Y | Y | Y | Y | Y |
| FARMER'S MARKET<br>100 ALEMANY BLVD       | 94110 | Y | Y | Y | Y | Y | Y | Y |
| ROSSI'S MKT<br>527 VALLEJO                | 94133 | Y | Y | Y | Y | Y | N | N |

|  |       |   |   |   |   |   |   |   |
|--|-------|---|---|---|---|---|---|---|
| D'ANGELO BROS<br>2339 NORIEGA              | 94122 | N | N | N | N | N | Y | Y |
| DOM'S FISH MKT<br>4735 MISSION             | 94112 | N | N | N | N | N | Y | Y |
| EXCELSIOR FISH & POULTRY<br>4555 MISSION   | 94112 | N | N | Y | N | N | Y | Y |
| JOE'S FISH GROTTO<br>4435 MISSION          | 94112 | N | N | N | N | N | Y | Y |
| MISSION MKT FISH-POULTRY<br>2590 MISSION   | 94110 | N | N | Y | N | N | Y | Y |
| SAN FRANCISCO SEAFOOD MKT<br>2423 MISSION  | 94110 | N | N | N | N | N | Y | Y |
| UNITED FISH AND POULTRY<br>2055 MCALLISTER | 94118 | N | N | Y | N | N | Y | Y |
| FRANK'S FISH MKT<br>771 CLAY               | D     |   |   |   |   |   |   |   |
| GOOD LIFE GROCERY<br>1524 20TH             | 94122 | N | N | Y | N | N | Y | Y |
| PJ'S FOOD MKT<br>1609 VALLEJO              | 94123 | N | N | N | N | N | Y | Y |
| PUCCINI MEATS<br>2323 CHESTNUT             | 94123 | N | N | Y | Y | Y | Y | Y |
| SEAFOOD CIRCUS<br>5029 3RD STREET          | 94124 | N | N | N | N | N | Y | Y |
| SEAWIN FISH CO.<br>2701 JENNINGS           | D     |   |   |   |   |   |   |   |
| TOKYO FISH MKT<br>1908 FILLMORE            | ?     | - | - | - | - | - | - | - |

? = UNABLE TO OBTAIN INFORMATION  
D = DISCONNECTED TELEPHONE  
- = NOT A TARGET SITE

LOS ANGELES SAMPLING SITES

LOS ANGELES SAMPLING SITES

| RETAIL TARGETS                           | ZIP CODE | EGGS | MILK/BUTTER | POULTRY | BEEF | PORK | FRESH FISH | SALTWATER FISH |
|--|----------|------|-------------|---------|------|------|------------|----------------|
| EL MERCADO GROCERY<br>3425 E. 1ST        | 90063    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| FOOD BARGAIN<br>4208 HUNTINGTON DRIVE S. | 90032    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| HODPER MKT<br>8301 HODPER AVE            | 90001    | Y    | Y           | Y       | Y    | Y    | Y          | Y              |
| LA SUPERIOR MEAT MKT<br>1320 W 11TH      | ?        | -    | -           | -       | -    | -    | -          | -              |
| LA SUPERIOR MEAT MKT<br>1053 W 23RD      | ?        | -    | -           | -       | -    | -    | -          | -              |
| LA SUPERIOR MEAT MKT<br>1671 W 11TH      | D        |      |             |         |      |      |            |                |
| MASON'S MKT<br>8400 S FIGUERDA           | 90003    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| PENNY FOOD MART<br>8515 S CENTRAL        | 90001    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| RAUL'S MARKET<br>1939 NADEAU             | 90019    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| TRIANGLE MKT<br>1900 CAHUENGA            | 90068    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| WEAVER'S MKT<br>4851 LONG BEACH AVE W    | 90058    | Y    | Y           | Y       | Y    | Y    | N          | N              |
| ALPHA BETA CO<br>5461 N FIGUEROA         | 90042    | Y    | Y           | Y       | Y    | Y    | Y          | Y              |
| BEMBI'S MEAT AND GROCERY<br>1831 W 7TH   | D        |      |             |         |      |      |            |                |
| BOY'S MKT INC<br>5080 RODEO DRIVE        | 90035    | Y    | Y           | Y       | Y    | Y    | Y          | Y              |
| BRADLEY'S MKT<br>4800 S SAN PEDRO        | 90011    | Y    | Y           | Y       | Y    | Y    | N          | N              |

|   |       |   |   |   |   |   |   |   |
|---|-------|---|---|---|---|---|---|---|
| CANYON COUNTRY STORE<br>2108 LAUREL CANYON BLVD | 90046 | Y | Y | Y | Y | Y | N | N |
| EL CANEY MEAT MKT<br>4600 MAPLEWOOD AVE         | ?     | - | - | - | - | - | - | - |
| ERNIE'S MKT<br>7516 AVALON BLVD                 | D     |   |   |   |   |   |   |   |
| FAIRFAX GROCERY<br>517 N FAIRFAX AVE            | -     |   |   |   |   |   |   |   |
| FIFTY FIFTH STREET MKT<br>5428 HOOPER AVE       | 90011 | Y | Y | Y | Y | Y | N | N |
| GENE'S MKT<br>3535 S NORMANDIE AVE              | 90007 | Y | Y | Y | Y | Y | N | N |
| GLASSMAN'S DELI-SUPERMKT<br>1070 N WESTERN AVE  | ?     | - | - | - | - | - | - | - |
| GRAND CENTRAL PUBLIC MKT<br>317 S BROADWAY      | 90013 | Y | Y | Y | Y | Y | Y | Y |
| H&F MKT<br>152 S FRESNO                         | -     | Y | Y | N | Y | N | N | N |
| HENRY'S MKT<br>3701 MONTEREY RD                 | -     | Y | Y | N | N | N | N | N |
| HUGHES MKT<br>5311 SANTA MONICA BLVD            | 90029 | Y | Y | Y | Y | Y | Y | Y |
| JS GROCERY MKT<br>3216 W SUNSET BLVD            | -     | Y | Y | N | N | N | N | N |
| JOHNNIE'S GROCERY/MEATS<br>2017 N EASTERN AVE   | ?     | - | - | - | - | - | - | - |
| JURGENSEN'S GROCERY<br>133 N LARCHMONT BLVD     | 90004 | Y | Y | Y | Y | Y | Y | Y |
| KAY'S FOOD MART<br>7005 N FIGUEROA              | -     | Y | Y | N | N | N | N | N |
| LOUIE'S MKT<br>908 E JEFFERSON BLVD             | 90011 | Y | Y | Y | Y | Y | N | N |
| LYDIA'S MKT<br>2942 E 4TH                       | -     | Y | Y | N | N | N | N | N |
| MARKET GROCERY<br>968 S SAN PEDRO               | -     | Y | Y | N | N | N | N | N |
| MODERN FOOD MART<br>3500 WHITTIER BLVD          | ?     |   |   |   |   |   |   |   |

|  |       |   |   |   |   |   |   |   |
|--|-------|---|---|---|---|---|---|---|
| NEW ORLEANS FISH MKT<br>2101 W VERNON AVE        | -     | N | N | N | N | N | Y | Y |
| OLYMPIC SUPERMARKET<br>100 S WESTERN AVE         | -     | Y | Y | N | N | N | N | N |
| PALMS SUPER MKT<br>3568 MOTOR AVE                | D     |   |   |   |   |   |   |   |
| PAT'S GROCERY/DELI<br>4957 BUCHANAN              | -     | Y | Y | N | N | N | N | N |
| PIONEER SUPERMARKET<br>1601 W SUNSET BLVD        | 90026 | Y | Y | Y | Y | Y | Y | Y |
| POPEYE MKT<br>1062 S BROADWAY                    | -     | Y | Y | N | N | N | N | N |
| RALPH'S GROCERY CO<br>7257 W SUNSET BLVD         | 90046 | Y | Y | Y | Y | Y | Y | Y |
| ROYALTY MKT<br>6200 S SAN PEDRO                  | 90003 | Y | Y | Y | Y | Y | N | N |
| SAFEWAY STORES INC<br>1430 S FAIRFAX AVE         | 90019 | Y | Y | Y | Y | Y | Y | Y |
| SAFEWAY STORES INC<br>3461 W 3RD                 | D     |   |   |   |   |   |   |   |
| ST FRANCIS GROCERY<br>1710 GARFIELD PLACE        | ?     |   |   |   |   |   |   |   |
| 71ST AND MAIN MKT<br>7025 S MAIN                 | ?     |   |   |   |   |   |   |   |
| SUNRISE MKT<br>4307 GRIFFIN AVE                  | -     | Y | Y | N | N | N | N | N |
| SUNSET GROCERY<br>1289 W SUNSET BLVD             | D     |   |   |   |   |   |   |   |
| SUPERIOR WAREHOUSE GRCRS<br>7316 COMPTON AVE     | 90001 | Y | Y | Y | Y | Y | Y | Y |
| THRIFTMART<br>2500 S VERMONT AVE                 | D     |   |   |   |   |   |   |   |
| TRANS SUPER MKT<br>1411 W WASHINGTON BLVD        | 90007 | Y | Y | Y | Y | Y | Y | Y |
| UNIVERSAL GROCERY/DELI<br>5021 SANTA MONICA BLVD | -     | N | N | N | N | N | N | N |

|  |       |   |   |   |   |   |   |   |
|--|-------|---|---|---|---|---|---|---|
| A & D FISH MKT<br>8475 S CENTRAL AVE           | 90001 | N | N | N | N | N | Y | Y |
| ALL SEAS FISH MKT<br>4320 S VERMONT AVE        | 90037 | N | N | N | N | N | Y | Y |
| BOB'S FISH MKT<br>415 N FAIRFAX AVE            | 90048 | N | N | N | N | N | Y | Y |
| COLLINS FISH MKT<br>4873 W ADAMS BLVD          | 90016 | N | N | N | N | N | Y | Y |
| CRENSHAW FISH MKT<br>3407 CRENSHAW BLVD        | 90016 | N | N | N | N | N | Y | Y |
| DOCK AND CARRY FISH MKT<br>1025 W CENTURY BLVD | 90044 | N | N | N | N | N | Y | Y |
| THE FISH HOUSE<br>3440 W SLAUSON AVE           | 90043 | N | N | N | N | N | Y | Y |
| FISHERMAN'S OUTLET MKT<br>529 S CENTRAL        | 90013 | N | N | N | N | N | N | Y |
| GW FISH AND POULTRY<br>572 N SPRING            | 90012 | N | N | N | N | N | Y | Y |
| BORDEN'S FRESH PACIFIC<br>9116 W PICO BLVD     | 90035 | N | N | N | N | N | Y | Y |
| BOSS SEAFOOD MKT<br>5055 S VERMONT AVE         | 90044 | N | N | N | N | N | Y | Y |
| HOOK LINE AND SINKER<br>10402 S NORMANDIE AVE  | 90044 | N | N | N | N | N | Y | Y |
| HYDE PARK FISH MKT<br>6216 CRENSHAW BLVD       | 90043 | N | N | N | N | N | Y | Y |
| ISLAND FISH MKT<br>2412 W SLAUSON AVE          | 90043 | N | N | N | N | N | Y | Y |
| LADAY FISH MKT<br>10720 S VERMONT AVE          | ?     |   |   |   |   |   |   |   |
| MERCADO DEL MAR<br>3209 N BROADWAY             | 90031 | N | N | N | N | N | ? | ? |
| NICK'S FISH MKT<br>9229 W SUNSET BLVD          | -     |   |   |   |   |   |   |   |

|   |       |   |   |   |   |   |   |   |
|---|-------|---|---|---|---|---|---|---|
| PACIFIC AMERICAN FISH CO<br>838 E 6TH             | 90021 | N | N | N | N | N | Y | Y |
| PACIFIC SEAFOOD<br>902 MATED                      | ?     |   |   |   |   |   |   |   |
| PHIL'S FISH AND POULTRY<br>124 N LARCHMONT        | 90004 | N | N | N | N | N | Y | Y |
| RICK'S FISH AND SEAFOOD<br>4750 W WASHINGTON BLVD | 90016 | N | N | N | N | N | N | Y |
| SAX FISH AVE<br>370 N FAIRFAX AVE                 | -     |   |   |   |   |   |   |   |
| UNITED POULTRY CO<br>736 N BROADWAY               | 90012 | N | N | N | N | N | Y | Y |
| BOY'S MARKET INC<br>841 S WESTERN AVE             | 90005 | Y | Y | Y | Y | Y | Y | Y |
| EARLE'S MKT<br>2636 W JEFFERSON BLVD              | -     | Y | Y | N | N | N | N | N |
| ED AND JOE'S GROCERY<br>4868 SANTA MONICA BLVD    | D     |   |   |   |   |   |   |   |
| HILLTOP FOOD CENTER<br>10526 S WESTERN AVE        | 90047 | Y | Y | Y | Y | Y | N | N |
| HUNGRY BOY MKT<br>1414 W SUNSET BLVD              | D     |   |   |   |   |   |   |   |
| JEWEL T DISCOUNT GROCERY<br>3965 CRENSHAW BLVD    | D     |   |   |   |   |   |   |   |
| MARY'S MKT<br>3245 CITY TERRACE DR                | ?     | - | - | - | - | - | - | - |
| RALPH'S GROCERY CO<br>8575 W 3RD                  | 90048 | Y | Y | Y | Y | Y | Y | Y |
| SAFEWAY STORES INC<br>7211 N FIGUEROA             | 90041 | Y | Y | Y | Y | Y | Y | Y |
| VENICE GROCERY<br>1563 VENICE BLVD                | -     | Y | Y | N | N | N | N | N |

|                    |   |   |   |   |   |   |   |   |
|--------------------|---|---|---|---|---|---|---|---|
| WESTERN GROCERY    |   |   |   |   |   |   |   |   |
| 3725 S WESTERN AVE | - | Y | Y | N | N | N | N | N |

|              |   |  |  |  |  |  |  |  |
|--------------|---|--|--|--|--|--|--|--|
| Y & Y MARKET |   |  |  |  |  |  |  |  |
| 1601 W 12TH  | D |  |  |  |  |  |  |  |

|                   |       |   |   |   |   |   |   |   |
|-------------------|-------|---|---|---|---|---|---|---|
| ADLONG GROCERIES  |       |   |   |   |   |   |   |   |
| 1550 W ADAMS BLVD | 90007 | Y | Y | Y | Y | Y | N | N |

|                 |       |   |   |   |   |   |   |   |
|-----------------|-------|---|---|---|---|---|---|---|
| BIG SAVER FOODS |       |   |   |   |   |   |   |   |
| 3000 N BROADWAY | 90031 | Y | Y | Y | Y | Y | Y | Y |

|                      |   |   |   |   |   |   |   |   |
|----------------------|---|---|---|---|---|---|---|---|
| CUT RATE FOOD MART   |   |   |   |   |   |   |   |   |
| 236 W MANCHESTER AVE | - | Y | Y | N | N | N | N | N |

|                   |       |   |   |   |   |   |   |   |
|-------------------|-------|---|---|---|---|---|---|---|
| DAILY FOOD MARKET |       |   |   |   |   |   |   |   |
| 1300 VENICE BLVD  | 90006 | Y | Y | Y | Y | Y | Y | Y |

|                    |       |   |   |   |   |   |   |   |
|--------------------|-------|---|---|---|---|---|---|---|
| DOUBLE M FOOD MART |       |   |   |   |   |   |   |   |
| 6655 N FIGUEROA    | 90042 | Y | Y | Y | Y | Y | Y | Y |

|                 |       |   |   |   |   |   |   |   |
|-----------------|-------|---|---|---|---|---|---|---|
| TONY'S MARKET   |       |   |   |   |   |   |   |   |
| 6901 S FIGUEROA | 90003 | Y | Y | Y | Y | Y | N | N |

|               |       |   |   |   |   |   |   |   |
|---------------|-------|---|---|---|---|---|---|---|
| VIVIAN MARKET |       |   |   |   |   |   |   |   |
| 1447 W 3RD    | 90017 | Y | Y | Y | Y | Y | N | N |

? = UNABLE TO OBTAIN INFORMATION  
D = DISCONNECTED TELEPHONE  
- = NOT A TARGET SITE

## APPENDIX B

### ANALYTICAL PROTOCOL FOR DETERMINATION OF PCDDs AND PCDFs IN FOODSTUFFS

(The analytical protocol for foodstuffs is derived from a method for determining PCDDs and PCDFs in Human Adipose Tissue. Ref. Stanley et al., 1986, EPA 560/5-86-020. Modification to this method for analyses conducted on ARB Contract No. A6-197-32 has been described in Section 3.2 of the technical report.)

TABLE OF CONTENTS

| <u>Section</u> | <u>Description</u>  | <u>Page</u> |
|----------------|---|-------------|
| 1              | Scope and Application . . . . .   | B-3         |
| 2              | Summary of Method . . . . .   | B-3         |
| 3              | Definitions . . . . .   | B-6         |
| 4              | Interferences . . . . .   | B-7         |
| 5              | Safety. . . . .   | B-7         |
| 6              | Apparatus and Equipment . . . . .   | B-8         |
| 7              | Reagents and Standard Solutions . . . . .   | B-11        |
| 8              | High Resolution Gas Chromatography/Mass Spectrometry<br>Performance Criteria. . . . . | B-13        |
| 9              | Quality Control Procedures. . . . .   | B-31        |
| 10             | Sample Preservation and Handling. . . . .   | B-33        |
| 11             | Sample Extraction . . . . .   | B-33        |
| 12             | Cleanup Procedures. . . . .   | B-35        |
| 13             | Analytical Procedures . . . . .   | B-38        |
| 14             | Data Reduction. . . . .   | B-43        |
| 15             | Reporting and Documentation . . . . .   | B-50        |

ANALYTICAL PROTOCOL FOR DETERMINATION OF PCDDs AND PCDFs  
IN HUMAN ADIPOSE TISSUE

1. SCOPE AND APPLICATION

- 1.1 This method provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) at concentrations ranging from 1 to 100 pg/g for the tetrachloro congeners up to 5 to 500 pg/g for the octachloro congeners in 10-g aliquots of human adipose tissue.
- 1.2 The minimum measurable concentration is estimated to range from 1 pg/g (1 part per trillion) for 2,3,7,8-TCDD and 2,3,7,8-TCDF up to 5 pg/g for OCDD and OCDF. However, these detection limits depend on the kinds and concentrations of interfering compounds in the sample matrix and the absolute method recovery.
- 1.3 The method will be used to determine PCDDs and PCDFs, particularly congeners with chlorine substitution in the 2,3,7,8 positions. Table 1 lists the specific PCDDs and PCDFs and target method detection limits.

2. SUMMARY OF METHOD

Figure 1 presents a schematic of the analytical procedures for determination of PCDDs and PCDFs in human adipose tissue. The analytical method requires extraction and isolation of lipid materials from human adipose samples. This is accomplished using sample sizes ranging up to 10 g. The tissue is spiked with known amounts of the carbon-13 labeled PCDDs and PCDFs (e.g., 500 pg of  $^{13}\text{C}_{12}$ -TCDD/F to 2,500 pg of  $^{13}\text{C}_{12}$ -OCDD/F) as internal quantitation standards. Extraction and homogenization are accomplished using methylene chloride and a Tekmar Tissuemizer®. The extract is filtered through anhydrous sodium sulfate to remove water. The extraction procedure is repeated (three to five times) until the tissue sample has been thoroughly homogenized. The final extract is adjusted to a known volume (100 mL) and the extractable lipid is determined using a minimum of 1% of the final volume. The methylene chloride in the remaining extract is concentrated until only an oily residue remains. The residue is diluted with hexane (~ 200 mL), and 100 g of sulfuric acid modified silica gel (40% w/w) is added to the solution with stirring. The mixture is stirred for approximately 2 h, and the supernatant is decanted and filtered through anhydrous sodium sulfate. The adsorbent is washed with at least two additional aliquots of hexane.

The combined hexane extracts are eluted through a column consisting of a layer of sulfuric acid modified silica gel, and a layer of unmodified silica gel. The eluate is concentrated to approximately 1 mL and added to a column of acidic alumina. The PCDDs and PCDFs are eluted from the alumina using 20% methylene chloride/hexane. This eluate is concentrated to approximately 0.5 mL and is added to a 500-mg Caropak C/Celite column. The PCDDs and PCDFs are eluted from the column using 20 mL of toluene.

Table 1. Target PCDD and PCDF Congeners and Target Method Detection Limits

| Compound            | CAS no. <sup>a</sup> | Target method detection limit (pg/g) <sup>b</sup> |
|---------------------|----------------------|---|
| 2,3,7,8-TCDD        | 1746-01-6            | 1.0   |
| 2,3,7,8-TCDF        | 51207-31-9           | 1.0   |
| 1,2,3,7,8-PeCDD     | 40321-76-4           | 1.0   |
| 1,2,3,7,8-PeCDF     | 57117-41-6           | 1.0   |
| 2,3,4,7,8-PeCDF     | 57117-31-4           | 1.0   |
| 1,2,3,4,7,8-HxCDD   | 39227-28-6           | 2.5   |
| 1,2,3,6,7,8-HxCDD   | 57653-85-7           | 2.5   |
| 1,2,3,7,8,9-HxCDD   | 19408-74-3           | 2.5   |
| 1,2,3,4,7,8-HxCDF   | 70648-29-9           | 2.5   |
| 1,2,3,6,7,8-HxCDF   | 57117-44-9           | 2.5   |
| 1,2,3,7,8,9-HxCDF   | 72918-21-9           | 2.5   |
| 2,3,4,6,7,8-HxCDF   | 60851-34-5           | 2.5   |
| 1,2,3,4,6,7,8-HpCDD | 35822-46-9           | 2.5   |
| 1,2,3,4,6,7,8-HpCDF | 67562-39-4           | 2.5   |
| 1,2,3,4,7,8,9-HpCDF | 55673-89-7           | 2.5   |
| OCDD                | 3268-87-9            | 5.0   |
| OCDF                | 39001-02-0           | 5.0   |

<sup>a</sup>Chemical Abstract Services number.

<sup>b</sup>pg/g = parts per trillion.

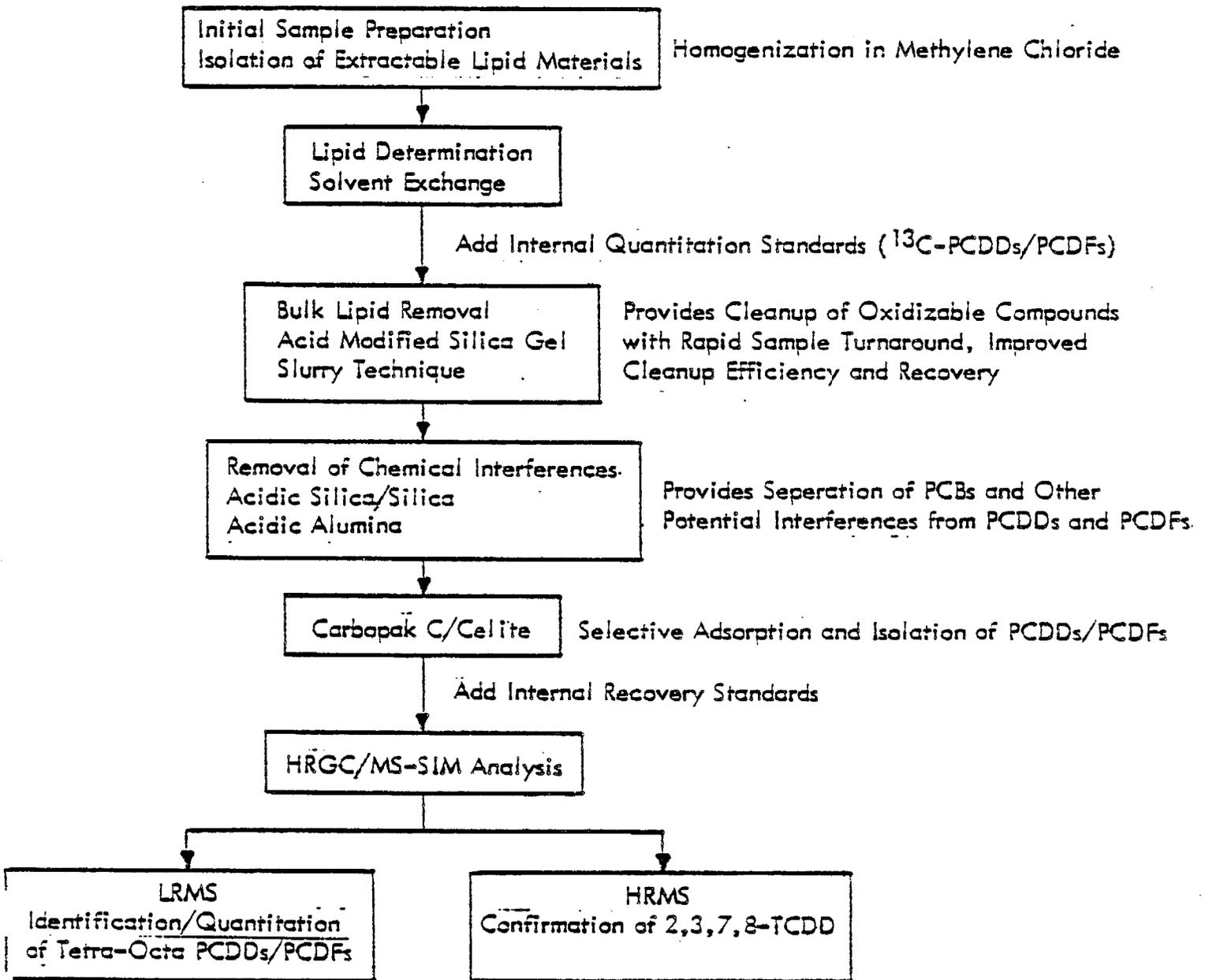


Figure 1. Schematic of the sample preparation and instrumental analysis procedures for determination of PCDDs and PCDFs in human adipose tissue.

The toluene is concentrated to less than 1 mL and transferred to conical vials. Tridecane (10  $\mu$ L) containing 500 pg of an internal recovery standard is added as a keeper, and the extract is concentrated to final volume.

The HRGC/MS analysis is completed in the selected ion monitoring mode (SIM). Analysis of the tetra- through octachloro PCDD and PCDF congeners is achieved using low resolution mass spectrometry. Separation of the tetra- through octachloro PCDD and PCDF congeners is achieved using a 60-m DB-5 column. Verification of the 2,3,7,8-TCDD is achieved using either a 50-m CP Sil 88 column or 60-m SP-2330 column and HRGC/MS-SIM analysis in the high resolution mode ( $R = 10,000$ ).

### 3. DEFINITIONS

- 3.1 Concentration calibration solutions -- Solutions containing known amounts of the native analytes (unlabeled 2,3,7,8-substituted PCDDs and PCDFs), the internal quantitation standards (Carbon-13 labeled PCDDs and PCDFs), and the recovery standard,  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. These calibration solutions are used to determine instrument response of the analytes relative to the internal quantitation standards and of the internal quantitation standards relative to the internal recovery standard.
- 3.2 Internal quantitation standards -- Carbon-13 labeled PCDDs and PCDFs, which are added to every sample and are present at the same concentration in every method blank and quality control sample. These are added to the adipose tissue and are used to measure the concentration of each analyte. The concentration of each internal quantitation standard is measured in every sample, and percent recovery is determined using the internal recovery standard.
- 3.3 Internal recovery standard --  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD which is added to every sample extract just before the final concentration step and HRGC/MS-SIM analysis.
- 3.4 Laboratory method blank -- This blank is prepared in the laboratory through performing all analytical procedures except addition of a sample aliquot to the extraction vessel. A minimum of one laboratory method blank will be analyzed with each batch of samples.
- 3.5 HRGC column performance check mixture -- A mixture containing known amounts of selected TCDD standards; it is used to demonstrate continued acceptable performance of the capillary column, to separate ( $\leq 25\%$  valley on a 50-m CP Sil 88 or 60-m SP-2330 HRGC column and 30 to 60% for a 60-m DB-5 HRGC column) 2,3,7,8-TCDD isomer from all other 21 TCDD isomers, and to define the TCDD retention time window.
- 3.6 Relative response factor -- Response of the mass spectrometer to a known amount of an analyte relative to a known amount of an internal standard (quantitation or recovery).

- 3.7 Mass resolution check -- Standard method used to demonstrate static resolution of 10,000 minimum (10% valley definition).
- 3.8 Sample batch -- A sample batch consists of up to 10 human adipose tissue samples, one method blank, 2 internal quality control (QC) samples (spiked and unspiked), and an external performance audit sample (blind spike).

#### 4. INTERFERENCES

Chemicals which elute from the HRGC column with  $\pm 10$  scans of the internal and/or recovery standards and which produce within the retention time window ions at any of the masses used to detect or quantify PCDDs, PCDFs, or the internal quantitation and recovery standards are potential interferences. Most frequently encountered potential interferences are other sample components that are extracted along with the PCDDs and PCDFs, e.g., PCBs, chlorinated methoxybiphenyls, chlorinated hydroxydiphenyl ethers, chlorinated benzylphenyl ethers, chlorinated naphthalenes, DDE, DDT, etc. The actual incidence of interference by these chemicals depends also upon relative concentrations, mass spectrometric resolution, and chromatographic conditions. Because very low levels (pg/g) of PCDDs and PCDFs are anticipated, the elimination of interferences is essential. High purity reagents and solvents must be used and all equipment must be scrupulously cleaned. Laboratory method blanks must be analyzed to demonstrate absence of contamination that would interfere with measurement of the PCDDs and PCDFs. Column chromatographic procedures are used to remove coextracted sample components; these procedures must be performed carefully to minimize loss of PCDDs and PCDFs during attempts to increase their concentration relative to other sample components.

#### 5. SAFETY

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The 2,3,7,8-TCDD is a known teratogen, mutagen, and carcinogen. Ingestion of microgram quantities can result in toxic effects. The other 2,3,7,8-substituted PCDDs and PCDFs may exhibit teratogenic, mutagenic, and carcinogenic effects. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. Only experienced personnel will be allowed to work with these chemicals.
- 5.2 All laboratory personnel will be required to wear laboratory coats or coveralls, gloves, and safety glasses. The neat standards, stock, and working solutions will be handled only in a Class A fume hood or glove box. When manipulating stock standards or working solutions, the analyst is advised to place the solution vials in a secure holder (sample block or glass beaker) to prevent accidental spills.

- 5.3 If these standards are spilled, absorb as much as possible with absorbent paper and place in a container clearly labeled as PCDD or PCDF waste. Solvent-wash all contaminated surfaces with toluene and absorbent paper followed by washing with a strong soap and water solution. Dispose of all contaminated materials in sealed steel containers labeled as contaminated with PCDD and/or PCDF residue and indicate the approximate level of contamination. As a final precaution, prepare a wipe sample of the exposed surface area and include the wipe as part of the sample analysis batch. This will be used to confirm that the work area is free of contamination.
- 5.4 If handling of these compounds results in skin contact, immediately remove all contaminated clothing and wash the affected skin areas with soap and water for at least 15 min.
- 5.5 Disposal of laboratory wastes -- All laboratory wastes (solvents and absorbents) will be disposed of as hazardous wastes. The laboratory personnel should take care to dispose of the sodium sulfate, silica gel, and alumina in separate containers. Excess solvents should be disposed of in gallon polyethylene jugs containing a layer of activated charcoal. Excess solvent that is known to be contaminated with PCDDs or PCDFs should be kept at a minimum by evaporating the solvent with a stream of air.

## 6. APPARATUS AND EQUIPMENT

### 6.1 High Resolution Gas Chromatograph/Mass Spectrometer/Data System (HRGC/HRMS/DS)

6.1.1 The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. When using this method, a 1- $\mu$ L injection volume is used. The injection volumes for all extracts, blanks, calibration solutions, and the performance check sample must be consistent.

### 6.1.2 High Resolution Gas Chromatograph-Mass Spectrometer Interface

The HRGC/MS interface is directly coupled to the mass spectrometer ion source. All components of the interface should be glass or glass-lined stainless steel. The interface components should be compatible with 300°C temperatures. The HRGC/MS interface must be appropriately designed so that the separation of the PCDDs and PCDFs which is achieved in the gas chromatographic column is not appreciably degraded. Cold spots and/or active surfaces (adsorption sites) in the HRGC/MS

interface can cause peak tailing and peak broadening. It is recommended that the HRGC column be fitted directly into the MS ion source. Graphite ferrules should be avoided in the HRGC injection port since they may absorb PCDDs or PCDFs. Vespel or equivalent ferrules are recommended.

#### 6.1.3 Mass Spectrometer

The mass spectrometer must be capable of maintaining a minimum resolution of 10,000 (10% valley) for high resolution confirmation analysis. The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with total cycle time (including voltage reset time) of 1 s or less.

#### 6.1.4 Data System

A dedicated hardware or data system is required to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each m/z (characteristic ion) being monitored as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights.

### 6.2 HRGC Columns

For isomer-specific determinations of 2,3,7,8-TCDD, the following fused silica capillary columns are recommended: a 50-m CP-Sil 88 column and a 60-m SP-2330 (SP-2331) column. However, any capillary column which separates 2,3,7,8-TCDD from all other TCDDs may be used for such analyses, provided that the minimum acceptance criteria in Section 8 are met.

### 6.3 Miscellaneous Equipment

- 6.3.1 Nitrogen evaporation apparatus with variable flow rate.
- 6.3.2 Balance capable of accurately weighing to  $\pm 0.01$  g.
- 6.3.3 Balance capable of accurately weighing to  $\pm 0.0001$  g.
- 6.3.4 Water bath -- equipped with concentric ring cover and capable of being temperature-controlled.
- 6.3.5 Stainless steel spatulas or spoons.
- 6.3.6 Magnetic stirrers and stir bars.
- 6.3.7 High speed tissue homogenizer -- Tekmar Tissuemizer® equipped with an EN-8 probe or equivalent.
- 6.3.8 Vacuum dessicator.

## 6.4 Glassware

- 6.4.1 Erlenmeyer flask -- 500 mL.
- 6.4.2 Kuderna-Danish apparatus -- 500-mL evaporating flask, 15-mL graduated concentrator tubes with ground-glass stoppers, and three-ball macro Snyder column (Kontes K-570001-0500, K-503000-0121, and K-569001-0219 or equivalent).
- 6.4.3 Minivials -- 1-mL borosilicate glass with conical-shaped reservoir and screw caps lined with Teflon®-faced silicone disks.
- 6.4.4 Powder funnels -- glass.
- 6.4.5 Chromatographic columns for the silica and alumina chromatography -- 1 cm ID x 10 cm long and 1 cm ID x 30 cm long with 250-mL reservoir and equipped with TFE stopcocks.
- 6.4.6 Chromatographic column for the Carboapak cleanup -- disposable 5-mL graduated glass pipets, 6 to 7 mm ID.
- 6.4.7 Glass rods.
- 6.4.8 Carborundum boiling chips -- Extracted for 6 hr in a Soxhlet apparatus with benzene and air dried.
- 6.4.9 Glass wool, silanized (Supelco) -- Extract with methylene chloride and hexane and air dry before use.
- 6.4.10 Glassware cleaning procedure -- All glassware used for these analyses will be cleaned via the following procedure. Wash the glassware in soap and water, rinse with copious amounts of tap water, distilled water, and distilled-in-glass acetone, in that order. Immediately prior to use, the glassware should be rinsed with distilled-in-glass quality solvents: methylene chloride, toluene, and hexane. The glassware should be allowed to dry fully.

As an added precaution, all glassware will be marked with a unique code that should be noted in the extraction and cleanup procedures for each sample. This glassware tracking will allow background results from specific glassware to be documented.

After use, each piece of glassware should be rinsed with the last solvent used in it, followed by a rinse with toluene, then acetone, before transferring it to the glassware washing facility.

## 7. REAGENTS AND STANDARD SOLUTIONS

### 7.1 Column Chromatography Reagents

- 7.1.1 Alumina, acidic (Biorad, AG-4) -- Extract the alumina in a Soxhlet apparatus with methylene chloride for 18 h (minimum of two cycles per hour). Air dry and activate it by heating in a foil-covered glass container for 24 h at 190°C.
- 7.1.2 Silica gel -- High purity grade, type 60, 70-230 mesh; extract the silica gel in a Soxhlet apparatus with methylene chloride for 10 h (minimum of 2 cycles per hour). Air dry and activate it by heating in a foil-covered glass container for 24 h at 130°C.
- 7.1.3 Silica gel impregnated with 40% (by weight) sulfuric acid -- Add two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated) (e.g., 40 g of H<sub>2</sub>SO<sub>4</sub> plus 60 g of silica gel) in a glass screw-cap bottle. Tumble for 5 to 6 h, shaking occasionally until free of lumps.
- 7.1.4 Sulfuric acid, concentrated -- ACS grade, specific gravity 1.84.
- 7.1.5 Graphitized carbon black (Carbopack C, Supelco), surface of approximately 12 m<sup>2</sup>/g, 80/100 mesh -- Mix thoroughly 3.6 g of Carbopack C and 16.4 g of Celite 545® in a 40-mL vial. Activate at 130°C for 6 h. Store in a desiccator.
- 7.1.6 Celite 545® (Fischer Scientific), reagent grade, or equivalent.
- 7.2 Desiccating agents -- Sodium sulfate; granular, anhydrous. Before use extract with methylene chloride for 16 h (minimum of two cycles per hour), air dry and then muffle for ≥ 4 h in a shallow tray at 400°C. Let it cool in a desiccator and store in oven at 130°C.
- 7.3 Solvents -- High purity, distilled in glass: methylene chloride, toluene, benzene, cyclohexane, methanol, acetone, hexane; reagent grade: tridecane. High purity solvents are dispensed from Teflon® squirt bottles.
- 7.4 Concentration Calibration Solutions (Table 2)

Eight tridecane solutions containing native calibration standards, <sup>13</sup>C<sub>12</sub>-labeled internal quantitation standards, and two internal recovery standards are required. The complete compound list is

Table 2. Concentration Calibration Solutions

| Compound<br>Native                        | Concentration in calibration solutions in pg/ $\mu$ L |     |     |      |     |      |      |     |
|---|---|-----|-----|------|-----|------|------|-----|
|   | CS1   | CS2 | CS3 | CS4  | CS5 | CS6  | CS7  | CS8 |
| 2,3,7,8-TCDD                              | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 2,3,7,8-TCDF                              | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 1,2,3,7,8-PeCDD                           | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 1,2,3,7,8-PeCDF                           | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 2,3,4,7,8-PeCDF                           | 200   | 100 | 50  | 25   | 10  | 5    | 2.5  | 1   |
| 1,2,3,4,7,8-HxCDD                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,6,7,8-HxCDD                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,7,8,9-HxCDD                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,4,7,8-HxCDF                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,6,7,8-HxCDF                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,7,8,9-HxCDF                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 2,3,4,6,7,8-HxCDF                         | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,4,6,7,8-HpCDD                       | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,4,6,7,8-HpCDF                       | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| 1,2,3,4,7,8,9-HpCDF                       | 500   | 250 | 125 | 62.5 | 25  | 12.5 | 6.25 | 2.5 |
| OCDD                                      | 1,000   | 500 | 250 | 125  | 50  | 25   | 12.5 | 5   |
| OCDF                                      | 1,000   | 500 | 250 | 125  | 50  | 25   | 12.5 | 5   |
| <u>Internal Quantitation Standards</u>    |   |     |     |      |     |      |      |     |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDD        | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDF        | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD     | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF     | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD   | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |
| $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF   | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |
| $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |
| $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |
| $^{13}\text{C}_{12}$ -OCDD                | 250   | 250 | 250 | 250  | 250 | 250  | 250  | 250 |
| <u>Internal Recovery Standard</u>         |   |     |     |      |     |      |      |     |
| $^{13}\text{C}_{12}$ -1,2,3,4-TCDD        | 50  | 50  | 50  | 50   | 50  | 50   | 50   | 50  |
| $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD   | 125   | 125 | 125 | 125  | 125 | 125  | 125  | 125 |

given in Table 2. The native 2,3,7,8-TCDD is supplied as a certified standard solution from the U.S. EPA QA Reference Materials Branch. All other native compounds were supplied in crystalline form by Cambridge Isotope Laboratories (Woburn, MA).  $^{13}\text{C}_{12}$ -Labeled internal quantitation standards were supplied in solution in *n*-nonane by Cambridge Isotope Laboratories. Portions of the native standards were accurately weighed to the nearest 0.001 mg with a Cahn 27 electrobalance and dissolved in toluene.

#### 7.5 Column Performance Check Mixture

The column performance check mixture consists of several TCDD isomers which will be used to document the separation of 2,3,7,8-TCDD from all other isomers. This solution will contain TCDDs (A) eluting closely to 2,3,7,8-TCDD, and the first- (F) and last-eluting (L) TCDDs.

| <u>Analyte</u>                     | <u>Approximate amount per ampule</u> |
|------------------------------------|--------------------------------------|
| Unlabeled 2,3,7,8-TCDD             | 10 ng                                |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDD | 10 ng                                |
| 1,2,3,4-TCDD (A)                   | 10 ng                                |
| 1,4,7,8-TCDD (A)                   | 10 ng                                |
| 1,2,3,7-TCDD (A)                   | 10 ng                                |
| 1,2,3,8-TCDD (A)                   | 10 ng                                |
| 1,3,6,8-TCDD (F)                   | 10 ng                                |
| 1,2,8,9-TCDD (L)                   | 10 ng                                |

#### 7.6 Spiking Solutions

Three solutions are prepared using the same stock as in Section 7.4. A native standard solution and a  $^{13}\text{C}_{12}$  internal quantitation standard solution are prepared in isooctane (Tables 3 and 4). A recovery standard solution is prepared in tridecane (Table 4). Samples are spiked with 100  $\mu\text{L}$  of internal quantitation standard solution and final sample extracts are spiked with 10  $\mu\text{L}$  of internal recovery standard solution.

### 8. HIGH RESOLUTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY PERFORMANCE CRITERIA

Samples and standards are analyzed by using a Carlo Erba MFC500 gas chromatography (GC) coupled to a Kratos MS50TC double-focusing mass spectrometer (MS) to be operated in the electron impact mode. The HRGC/MS interface is simply a direct connection of the fused silica HRGC column to the ion source of the MS via a heated interface oven. Data acquisition and processing are controlled by a Finnigan-MAT Incos 2300 data system.

Table 3. Native Spiking Solution<sup>a</sup>

| Compound            | Concentration<br>(pg/ $\mu$ L) |
|---------------------|--------------------------------|
| 2,3,7,8-TCDD        | 5                              |
| 2,3,7,8-TCDF        | 5                              |
| 1,2,3,7,8-PeCDD     | 5                              |
| 1,2,3,7,8-PeCDF     | 5                              |
| 2,3,4,7,8-PeCDF     | 5                              |
| 1,2,3,4,7,8-HxCDD   | 12.5                           |
| 1,2,3,6,7,8-HxCDD   | 12.5                           |
| 1,2,3,7,8,9-HxCDD   | 12.5                           |
| 1,2,3,4,7,8-HxCDF   | 12.5                           |
| 1,2,3,6,7,8-HxCDF   | 12.5                           |
| 1,2,3,7,8,9-HxCDF   | 12.5                           |
| 2,3,4,6,7,8-HxCDF   | 12.5                           |
| 1,2,3,4,6,7,8-HpCDD | 12.5                           |
| 1,2,3,4,6,7,8-HpCDF | 12.5                           |
| 1,2,3,4,7,8,9-HpCDF | 12.5                           |
| OCDD                | 25                             |
| OCDF                | 25                             |

<sup>a</sup>Prepared in isooctane.

Table 4. Internal Standard Spiking Solutions

| Compound   | Concentration<br>(pg/ $\mu$ L) |
|--|--------------------------------|
| <u>Internal Quantitation Standards<sup>a</sup></u> |                                |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDD                 | 5                              |
| $^{13}\text{C}_{12}$ -2,3,7,8-TCDF                 | 5                              |
| $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD              | 5                              |
| $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF              | 5                              |
| $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD            | 12.5                           |
| $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF            | 12.5                           |
| $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD          | 12.5                           |
| $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF          | 12.5                           |
| $^{13}\text{C}_{12}$ -OCDD                         | 25                             |
| <u>Internal Recovery Standard<sup>b</sup></u>      |                                |
| $^{13}\text{C}_{12}$ -1,2,3,4-TCDD                 | 50                             |
| $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD            | 125                            |

<sup>a</sup>Prepared in isooctane.

<sup>b</sup>Prepared in tridecane.

## 8.1 HRGC/MS Analysis of PCDD/PCDF

Single run selected ion monitoring (SIM) analysis of the tetra-chloro through octachloro-dioxins and furans is carried out with the instrumental conditions and parameters outlined in Table 5. For each HRGC/MS run, five distinct groups of ions, which correspond to each chlorine level, are sequentially monitored. These ion descriptors are shown in Table 6. The masses of the two most abundant ions in the molecular ion cluster of each dioxin and furan and isotopically labeled standard are monitored. In addition, the masses corresponding to the molecular ions of the hexachloro through decachlorodiphenyl ethers (PCDEs) are monitored to aid in the confirmation of positive furan results. Interference from the presence of PCDE is noted by coincident response to the characteristic ions for PCDFs. A lock mass,  $m/z$  381 from PFK (per-fluorokerosene), is used to observe and correct any magnet/instrument drift during the analysis.

### 8.1.1 Tuning and Mass Calibration

The mass spectrometer is tuned on a daily basis to yield optimum sensitivity and peak shape using an ion peak ( $m/z$  381) from PFK. The resolution is visually monitored and maintained at  $\geq 3,000$  (10% valley definition) to provide adequate noise rejection while maintaining good ion transmission.

Mass calibration of the mass spectrometer for the HRGC/MS analysis of PCDD/PCDF is carried out on a daily basis. The magnetic field is adjusted to pass  $m/z$  300 at full accelerating voltage. PFK is admitted to the MS and an accelerating voltage scan from 8,000 to 4,000 V is acquired by the data system. This corresponds to an effective mass range of 301 to 593 amu. Upon completion of a successful calibration step, the five ion descriptors shown in Table 6 are updated to reflect the new mass calibration.

### 8.1.2 Ion Descriptor Switching

The ion descriptors shown in Table 6 are sequentially monitored during a PCDD/PCDF analysis to cover the retention windows of each chlorination level. The retention windows and hence the descriptor switch points are determined initially and whenever a new HRGC column is installed by injection of a mixture of PCDD and PCDF congeners. Daily adjustment of the descriptor switch times are performed when careful monitoring of the standard retention times shows this to be necessary. The descriptors are designed to ensure acquisition of all isomers of each homolog.

Table 5. HRGC/LRMS Operating Conditions for PCDD/PCDF Analysis

---

Mass spectrometer

|                              |                                      |
|------------------------------|--------------------------------------|
| Accelerating voltage:        | 8,000 V                              |
| Trap current:                | 500 $\mu$ A                          |
| Electron energy:             | 70 eV                                |
| Electron multiplier voltage: | -1,800 V                             |
| Source temperature:          | 280°C                                |
| Resolution:                  | $\geq$ 3,000 (10% valley definition) |
| Overall SIM cycle time:      | 1 s                                  |

Gas chromatograph

|                        |                                  |
|------------------------|----------------------------------|
| Column coating:        | DB-5                             |
| Film thickness:        | 0.25 $\mu$ m                     |
| Column dimensions:     | 60 m x 0.25 mm ID                |
| He linear velocity:    | $\sim$ 25 cm/sec                 |
| He head pressure:      | 1.75 kg/cm <sup>2</sup> (25 psi) |
| Injection type:        | Splitless, 45 s                  |
| Split flow:            | 30 mL/min                        |
| Purge flow:            | 6 mL/min                         |
| Injector temperature:  | 270°C                            |
| Interface temperature: | 300°C                            |
| Injection size:        | 1-2 $\mu$ L                      |
| Initial temperature:   | 200°C                            |
| Initial time:          | 2 min                            |
| Temperature program:   | 200°C to 330°C at 5°C/min        |

---

Table 6. Ions Monitored for HRGC/MS of PCDD/PCDF

| Descriptor | ID                          | Mass    | Nominal dwell time (sec) |
|------------|-----------------------------|---------|--------------------------|
| A1         | TCDF                        | 303.902 | 0.090                    |
|            |                             | 305.899 | 0.090                    |
|            | $^{13}\text{C}_{12}$ -TCDF  | 315.942 | 0.090                    |
|            |                             | 317.939 | 0.090                    |
|            | TCDD                        | 319.897 | 0.090                    |
|            |                             | 321.894 | 0.090                    |
|            | $^{13}\text{C}_{12}$ -TCDD  | 331.937 | 0.090                    |
|            |                             | 333.934 | 0.090                    |
|            | HxCDFE                      | 373.840 | 0.090                    |
|            | PFK (lock mass)             | 380.976 | 0.090                    |
| A2         | TCDF                        | 303.902 | 0.045                    |
|            |                             | 305.899 | 0.045                    |
|            | TCDD                        | 319.897 | 0.045                    |
|            |                             | 321.894 | 0.045                    |
|            | PeCDF                       | 337.863 | 0.045                    |
|            |                             | 339.860 | 0.045                    |
|            | $^{13}\text{C}_{12}$ -PeCDF | 349.903 | 0.045                    |
|            |                             | 351.900 | 0.045                    |
|            | PeCDD                       | 353.858 | 0.045                    |
|            |                             | 355.855 | 0.045                    |
|            | $^{13}\text{C}_{12}$ -PeCDD | 365.898 | 0.045                    |
|            |                             | 367.895 | 0.045                    |
|            | PFK (lock mass)             | 380.976 | 0.035                    |
|            | HpCDFE                      | 407.801 | 0.035                    |
| A3         | HxCDF                       | 373.821 | 0.080                    |
|            |                             | 375.818 | 0.080                    |
|            | PFK (lock mass)             | 380.976 | 0.080                    |
|            | $^{13}\text{C}_{12}$ -HxCDF | 385.861 | 0.080                    |
|            |                             | 387.858 | 0.080                    |
|            | HxCDD                       | 389.816 | 0.080                    |
|            |                             | 391.813 | 0.080                    |
|            | $^{13}\text{C}_{12}$ -HxCDD | 401.856 | 0.080                    |
|            | 403.853                     | 0.080   |                          |
|            | OCDPE                       | 443.759 | 0.080                    |

Table 6 (continued)

| Descriptor | ID                                   | Mass    | Nominal dwell<br>time (sec) |
|------------|--------------------------------------|---------|-----------------------------|
| A4         | PFK (lock mass)                      | 380.976 | 0.040                       |
|            | HxCDD                                | 389.816 | 0.040                       |
|            |                                      | 391.813 | 0.040                       |
|            | HpCDF                                | 407.782 | 0.040                       |
|            |                                      | 409.779 | 0.040                       |
|            | <sup>13</sup> C <sub>12</sub> -HpCDF | 419.822 | 0.040                       |
|            |                                      | 421.819 | 0.040                       |
|            | HpCDD                                | 423.777 | 0.040                       |
|            |                                      | 425.774 | 0.040                       |
|            | <sup>13</sup> C <sub>12</sub> -HpCDD | 435.817 | 0.040                       |
|            |                                      | 437.814 | 0.040                       |
|            | <sup>37</sup> Cl <sub>4</sub> -HpCDD | 429.768 | 0.040                       |
|            |                                      | 431.765 | 0.040                       |
| NCDPE      | 477.720                              | 0.040   |                             |
| A5         | PFK (lock mass)                      | 380.976 | 0.06                        |
|            | OCDF                                 | 441.743 | 0.07                        |
|            |                                      | 443.740 | 0.07                        |
|            | <sup>13</sup> C <sub>12</sub> -OCDF  | 453.783 | 0.07                        |
|            |                                      | 455.780 | 0.07                        |
|            | OCDD                                 | 457.738 | 0.07                        |
|            |                                      | 459.735 | 0.07                        |
|            | <sup>13</sup> C <sub>12</sub> -OCDD  | 469.779 | 0.07                        |
|            | 471.776                              | 0.07    |                             |
| DCDPE      | 511.681                              | 0.06    |                             |

### 8.1.3 HRGC Column Performance (60-m DB-5)

The HRGC column performance must be demonstrated at the start of each 12-h analysis period.

8.1.3.1 Inject 1  $\mu\text{L}$  of the column performance check solution (Section 7.5) and acquire selected ion monitoring (SIM) data for  $m/z$  320, 322, 332, and 334.

8.1.3.2 The chromatographic peak separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers should be resolved with a valley of 30-60%, where

$$\text{Valley \%} = (x/y)(100)$$

x = measured height of the valley between the chromatographic peak corresponding to 2,3,7,8-TCDD and the peak of the nearest TCDD isomer; and

y = the peak height of 2,3,7,8-TCDD.

Figure 2 is an example of the separation of a TCDD isomer mixture and the calculation of isomer resolution.

It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The column performance check solution also contains the TCDD isomers eluting first and last under the analytical conditions specified in this protocol, thus defining the retention time window for total TCDD determination. Any individual selected ion current profile or the reconstructed total ion current ( $m/z$  320 +  $m/z$  322) constitutes an acceptable form of data presentation.

### 8.1.4 Initial Calibration for PCDD/PCDF Analysis

Initial calibration is required before any samples are analyzed for PCDD/PCDF. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Section 8.1.7.

8.1.4.1 Tune and calibrate the instrument with PFK as outlined in Section 8.1.1.

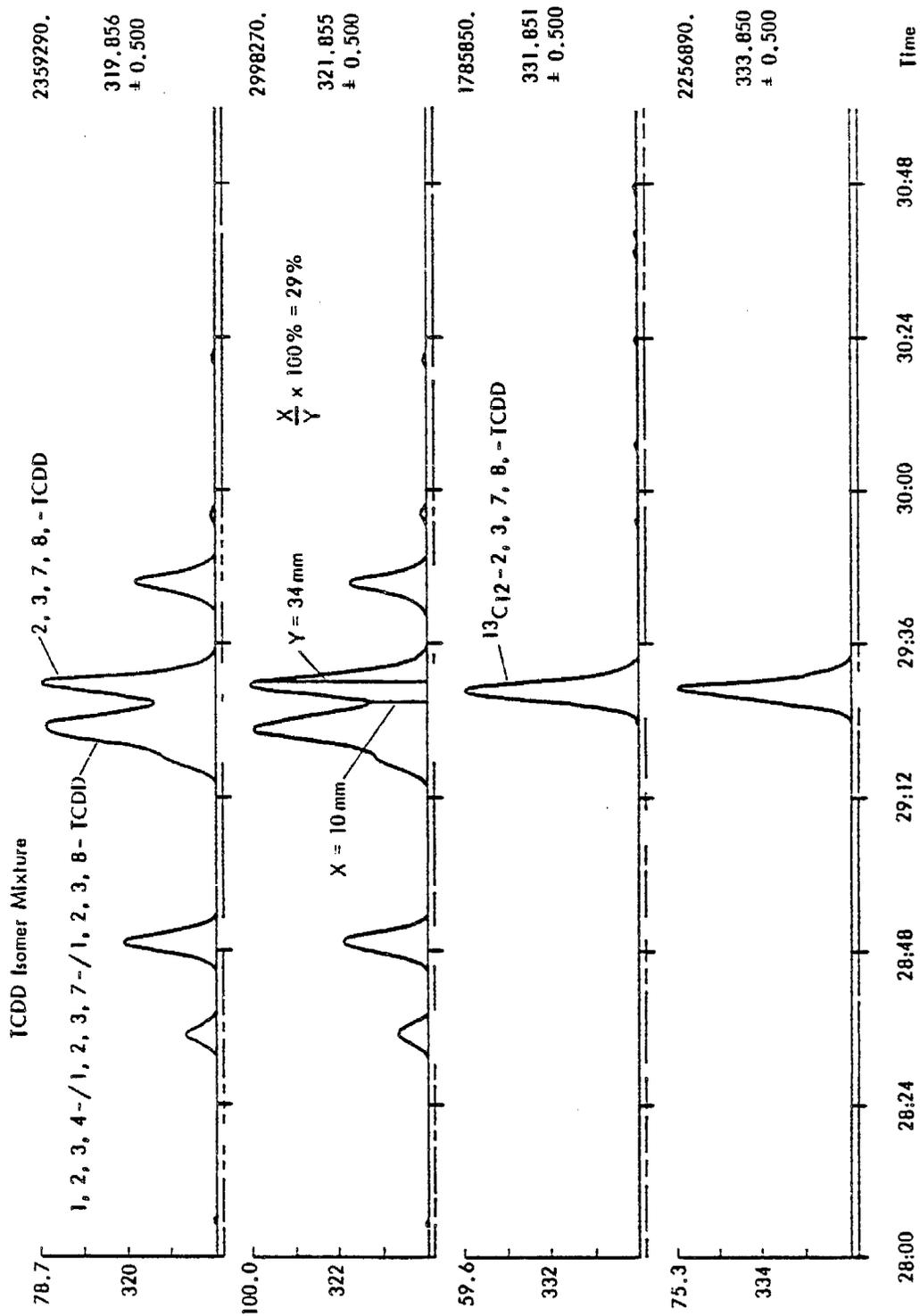


Figure 2. Example of the separation of 2,3,7,8-TCDD from other TCDD isomers on a 60 m DB-5 column.

- 8.1.4.2 Six of the eight concentration calibration solutions listed in Table 2 will be analyzed for the initial calibration phase. These must include solutions CS4 through CS8 (Table 2). The analyst may select any of the remaining solutions for demonstrating calibration at the upper concentration range.
- 8.1.4.3 Using the HRGC and MS conditions in Table 5 and the SIM monitoring descriptors in Table 6, analyze a 1- $\mu$ L aliquot of each of the six concentration calibration solutions in triplicate.
- 8.1.4.4 Compute the relative response factors (RRFs) for each analyte in the concentration calibration solution using the criteria for positive identification of PCDD/PCDF's given in Section 14.1 and the computational methods in Section 14.2.
- 8.1.4.5 Compute the means and their respective relative standard deviations (% RSD) for the RRFs from each triplicate analysis for each analyte in the standard.
- 8.1.4.6 Calculate the grand means ( $\overline{RRF}$ ) and their respective RSDs using the six mean RRFs for each analyte.
- 8.1.5 Criteria for Acceptable Initial Calibration
- 8.1.5.1 The % RSD for the response factors for each triplicate analysis of a single concentration calibration standard for each analyte must be less than  $\pm 30\%$  except for the TCDD and TCDF, which must be less than  $\pm 20\%$ .
- 8.1.5.2 The variation of the mean RRFs for the six concentration calibrated standards (Section 8.1.5.1) must be less than 30% except for the TCDD and TCDF which must be less than 20%.
- 8.1.5.3 The SIM traces for all ions used for quantitation must present a signal-to-noise (S/N) ratio of  $\geq 2.5$ . This includes analytes and isotopically labeled standards.

8.1.5.4 Isotopic ratios must be within  $\pm 20\%$  of the theoretical values (see Table 7).

NOTE: If the criteria for acceptable calibration listed above have been met, the RRF can be considered independent of the analyte quantity for the calibration concentration range. The grand mean RRF from the initial calibration for unlabeled PCDD/PCDFs and for the isotopically labeled standards will be used for all calculations until routine calibration criteria (Section 8.1.7) are no longer met. At such time, new mean RRFs will be calculated from a new set of six triplicate determinations.

#### 8.1.6 Routine Calibrations

Routine calibrations must be performed at the beginning of every day before actual sample analyses are performed and as the last injection of every day.

8.1.6.1 Inject 1  $\mu\text{L}$  of the concentration calibration solution CS 7 (see Table 2) as the initial calibration check on each analysis day. It is recommended that the analyst select a concentration calibration solution that brackets the sample concentrations observed on a single analysis date as the last injection of each analysis date.

8.1.6.2 Compute the RRFs for each analyte in the concentration calibration solution using the criteria for positive identification of PCDD/Fs given in Section 14.1 and the computational methods in Section 14.2.

#### 8.1.7 Criteria for Acceptable Routine Calibration

8.1.7.1 The measured RRF for all analytes must be within  $\pm 30\%$  of the grand mean values established by triplicate analysis of the calibration concentration solutions, except for TCDD and TCDF, which must be within  $\pm 20\%$  of the mean values established in the initial calibration step.

8.1.7.2 Isotopic ratios must be within  $\pm 20\%$  of the theoretical value for each analyte and isotopically labeled standard (see Table 7).

Table 7. Ion Ratios for HRGC/LRMS Analysis of PCDD/PCDF

| Compound                             | Ions monitored | Theoretical ratio | Acceptable range |
|--------------------------------------|----------------|-------------------|------------------|
| TCDF                                 | 304/306        | 0.76              | 0.61 - 0.91      |
| <sup>13</sup> C <sub>12</sub> -TCDF  | 316/318        | 0.76              | 0.61 - 0.91      |
| TCDD                                 | 320/322        | 0.76              | 0.61 - 0.91      |
| <sup>13</sup> C <sub>12</sub> -TCDD  | 332/334        | 0.76              | 0.61 - 0.91      |
| PeCDF                                | 338/340        | 0.61              | 0.49 - 0.73      |
| <sup>13</sup> C <sub>12</sub> -PeCDF | 350/352        | 0.61              | 0.49 - 0.73      |
| PeCDD                                | 354/356        | 0.61              | 0.49 - 0.73      |
| <sup>13</sup> C <sub>12</sub> -PeCDD | 366/368        | 0.61              | 0.49 - 0.73      |
| HxCDF                                | 374/376        | 1.22              | 0.98 - 1.46      |
| <sup>13</sup> C <sub>12</sub> -HxCDF | 386/388        | 1.22              | 0.98 - 1.46      |
| HxCDD                                | 390/392        | 1.22              | 0.98 - 1.46      |
| <sup>13</sup> C <sub>12</sub> -HxCDD | 402/404        | 1.22              | 0.98 - 1.46      |
| HpCDF                                | 408/410        | 1.02              | 0.82 - 1.22      |
| <sup>13</sup> C <sub>12</sub> -HpCDF | 420/422        | 1.02              | 0.82 - 1.22      |
| HpCDD                                | 424/426        | 1.02              | 0.82 - 1.22      |
| <sup>13</sup> C <sub>12</sub> -HpCDD | 436/438        | 1.02              | 0.82 - 1.22      |
| OCDF                                 | 442/444        | 0.87              | 0.70 - 1.04      |
| <sup>13</sup> C <sub>12</sub> -OCDF  | 454/456        | 0.87              | 0.70 - 1.04      |
| OCDD                                 | 458/460        | 0.87              | 0.70 - 1.04      |
| <sup>13</sup> C <sub>12</sub> -OCDD  | 470/472        | 0.87              | 0.70 - 1.04      |

- 8.1.7.3 If any of the above criteria is not met, a second attempt may be made before repeating the entire initialization process.

## 8.2 HRGC/HRMS Analysis (Isomer Specific TCDD Analysis)

Isomer specific analysis for 2,3,7,8-TCDD is carried out with the instrumental conditions and parameters shown in Table 8. In addition to monitoring the masses of the most abundant molecular ions of TCDD, an ion corresponding to the loss of COCl from the molecular ion is monitored for verification purposes. Mass spectrometer resolution is maintained at or above 10,000 (10% valley definition) in order to increase the specificity of the analysis.

### 8.2.1 Tuning and Mass Calibration

- 8.2.1.1 The mass spectrometer must be operated in the electron (impact) ionization mode. Static resolving power of at least 10,000 (10% valley) must be demonstrated before any analysis of a set of samples is performed. Static resolution checks must be performed at the beginning and at the end of each 12-h period of operation. However, it is recommended that a visual check (i.e., not documented) of the static resolution be made before and after each analysis.
- 8.2.1.2 The MS shall be tuned daily using PFK to yield a resolution of at least 10,000 (10% valley) and optimal response at  $m/z$  254.986. This step is followed by calibration of an accelerating voltage scan of PFK beginning at  $m/z$  254 (typical calibration range is 255 to 493 amu). Other voltage scans from the same data file are used to establish and document both the resolution at  $m/z$  316.983 and the mass measurement accuracy at  $m/z$  330.979.
- 8.2.1.3 Following calibration, the SIM experiment descriptor is updated to reflect the new calibration. Six masses (see Table 8) are monitored by scanning  $\sim m/10,000$  amu (atomic mass units) over each mass. The total cycle time is kept to 1 s. The  $m/z$  280.983 ion from PFK is used as a lock mass because it is the most abundant PFK ion within the range of  $m/z$  255 to 334 and therefore permits the use of low partial pressures of PFK, which minimizes PFK interferences at the analytical masses.

Table 8. HRGC/HRMS Operating Conditions

Mass spectrometer

Accelerating voltage: 8,000 V  
 Trap current: 500  $\mu$ A  
 Electron energy: 70 eV  
 Electron multiplier voltage: 2,000 V  
 Source temperature: 280°C  
 Resolution: 10,000 (10% valley definition)

SIM Parameters

| <u>Identity</u>                     | <u>Mass</u> | <u>Nominal dwell times (s)</u> |
|-------------------------------------|-------------|--------------------------------|
| TCDD-COCl                           | 258.930     | 0.15                           |
| TCDD                                | 319.897     | 0.15                           |
| TCDD                                | 321.894     | 0.15                           |
| <sup>13</sup> C <sub>12</sub> -TCDD | 331.937     | 0.15                           |
| <sup>13</sup> C <sub>12</sub> -TCDD | 333.934     | 0.15                           |
| PFK (lock mass)                     | 280.983     | 0.10                           |

Overall SIM cycle time = 1 s

Gas chromatograph

Column coating: CP-Sil 88  
 Film Thickness: 0.2  $\mu$ m  
 Column dimensions: 50 m x 0.22 mm ID

Helium linear velocity: ~ 25 cm/s  
 Helium head pressure: 1.75 kg/cm<sup>2</sup> (25 psi)

Injection type: Splitless, 45 s  
 Split flow: 30 mL/min  
 Purge flow: 6 mL/min  
 Injector temperature: 270°C  
 Interface temperature: 240°C  
 Injection size: 2  $\mu$ L  
 Initial temperature: 200°C  
 Initial time: 1 min  
 Temperature program: 200°C to 240°C at 4°C/min

## 8.2.2 Mass Measurement and Resolution Check

Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10% valley) at  $m/z$  254.986 (or any other mass reasonably close to  $m/z$  259). Calibrate the voltage sweep at least across the mass range  $m/z$  259 to  $m/z$  334 and verify that  $m/z$  330.979 from PFK (or any other mass close to  $m/z$  334) is measured within  $\pm 5$  ppm (i.e., 1.7 mmu, if  $m/z$  331 is chosen) using  $m/z$  254.986 as a reference. Documentation of the mass resolution must then be accomplished by recording the peak profile of the PFK reference peak  $m/z$  318.979 (or any other reference peak at a mass close to  $m/z$  320/322). The format of the peak profile representation must allow manual determination of the resolution; i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The results of the peak width measurement (performed at 5% of the maximum which corresponds to the 10% valley definition) must appear on the hard copy and cannot exceed 100 ppm (or 31.9 mmu if  $m/z$  319 is the chosen reference ion).

## 8.2.3 HRGC Column Performance (50-m CP Sil 88/60-m SP-2330)

Prior to any HRGC/HRMS analysis of calibration solutions or samples for 2,3,7,8-TCDD, the resolution of the HRGC columns must be documented to be within allowable limits in order to provide conditions adequate for unambiguous isomer-specific analysis of 2,3,7,8-TCDD. This column performance check must be demonstrated at the start of each 12-h analysis period.

8.2.3.1 Inject 2  $\mu$ L of the column performance check solution and acquire selected ion monitoring (SIM) data for  $m/z$  258.930, 319.897, 321.894, 331.937, and 333.934 within a total cycle time of  $\leq 1$  s (Table 8).

8.2.3.2 The chromatographic peak separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of  $\leq 25\%$ , where

$$\text{Valley \%} = (x/y)(100)$$

x = measured height of the valley between the chromatographic peak corresponding to 2,3,7,8-TCDD and the peak of the nearest TCDD isomer; and

y = the peak height of 2,3,7,8-TCDD.

- 8.2.3.3 If the above resolution requirement is not met, corrective action must be taken and acceptable resolution documented prior to any further analyses. Corrective action may include removal of the first meter of the HRGC column, replacement or clearing of the injector port, or complete replacement of the GC column.
- 8.2.3.4 The column performance check solution also contains the TCDD isomers eluting first and last under the analytical conditions specified in this protocol, thus defining the retention time window for total TCDD determination. The peaks representing 2,3,7,8-TCDD and the first and the last eluting TCDD isomer should be labeled and identified as such on the chromatograms (F and L, respectively). Any individual selected ion current profile or the reconstructed total ion current ( $m/z$  259 +  $m/z$  320 +  $m/z$  322) constitutes an acceptable form of data presentation.
- 8.2.4 Initial Calibration for HRGC/HRMS 2,3,7,8-TCDD Analysis
- Initial calibration is required before any samples are analyzed for 2,3,7,8-TCDD. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Section 8.2.6.
- 8.2.4.1 At least six of the concentration calibration solutions listed in Table 2 must be utilized for the initial calibration. These must include solutions CS4 through CS8. The analyst may select any of the remaining solutions for demonstrating calibration at the upper concentration range.
- 8.2.4.2 Tune and calibrate the instrument with PFK as described in Section 8.2.1.
- 8.2.4.3 Inject 1  $\mu$ L of the column performance check solution (Section 8.2.3) and acquire SIM mass spectra data for  $m/z$  258.930, 319.897, 321.894, 331.937, and 333.934 using a total cycle time of  $\leq 1$  s (see Table 8). The laboratory must not perform any further analysis until it has been demonstrated and documented that the criterion listed in Section 8.2.3.2 has been met.

- 8.2.4.4 Using the same GC and MS conditions (Table 8) that produced acceptable results with the column performance check solution, analyze a 1- $\mu$ L aliquot of each of the six concentration calibration solutions in triplicate.
- 8.2.4.5 Calculate the RRFs for unlabeled 2,3,7,8-TCDD relative to  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and the RRF for  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD relative to  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD using the criteria for positive identification of TCDD by HRGC/HRMS given in Section 14.1 and the computational methods in Section 14.2.
- 8.2.4.6 Calculate the six means (RRFs) and their respective relative standard deviations (% RSD) for the response factors from each of the triplicate analyses for both unlabeled and  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD.
- 8.2.4.7 Calculate the grand mean RRFs and their respective relative standard deviations (% RSD) using the six mean RRFs.
- 8.2.5 Criteria for Acceptable Initial Calibration
- The criteria listed below for acceptable calibration must be met before analysis of any sample is performed.
- 8.2.5.1 The percent relative standard deviation (RSD) for the response factors from each of the triplicate analyses of a single concentration calibration standard for both unlabeled and  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD must be less than 20%.
- 8.2.5.2 The variation of the mean RRFs from the six concentration calibration standards unlabeled and  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD must be less than 20% RSD.
- 8.2.5.3 SIM traces for 2,3,7,8-TCDD must present a signal-to-noise ratio of  $\geq 2.5$  for m/z 258.930, m/z 319.897, and m/z 321.894.
- 8.2.5.4 SIM traces for  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD must present a signal-to-noise ratio  $\geq 2.5$  for m/z 331.937 and m/z 333.934.
- 8.2.5.5 Isotopic ratios for 320/322 and 332/334 must be within the allowed range (0.61 to 0.91).

NOTE: If the criteria for acceptable calibration listed above have been met, the RRF can be considered independent of the analyte quantity for the calibration concentration range. The grand mean RRF from the initial calibration for unlabeled 2,3,7,8-TCDD and for  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD will be used for all calculations until routine calibration criteria (Section 8.2.6) are no longer met. At such time, new mean RRFs will be calculated from a new set of six triplicate determinations.

#### 8.2.6 Routine Calibrations

Routine calibrations must be performed at the beginning of a 12-h period after successful mass resolution and HRGC column performance check runs and before analysis of actual samples. The response factor calibration must also be verified at the end of each analysis date.

8.2.6.1 Inject 1  $\mu\text{L}$  of the concentration calibration solution (CS7, Table 2) which contains 2.5  $\text{pg}/\mu\text{L}$  of unlabeled 2,3,7,8-TCDD, 50.0  $\text{pg}/\mu\text{L}$  of  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, and 50  $\text{pg}/\mu\text{L}$  of  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. Using the same HRGC/MS/DS conditions as used in Table 8, determine and document acceptable calibration as provided below.

#### 8.2.7 Criteria for Acceptable Routine Calibration

The following criteria must be met before further analysis is performed. If these criteria are not met, corrective action must be taken and the instrument must be recalibrated.

8.2.7.1 The measured RRF for unlabeled 2,3,7,8-TCDD must be within 20% of the mean values established in the initial calibration by triplicate analyses of concentration calibration solutions.

8.2.7.2 The measured RRF for  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD must be within 20% of the mean value established by triplicate analysis of the concentration calibration solutions during the initial calibration.

- 8.2.7.3 Isotopic ratios must be within the allowed range (0.61 to 0.90).
- 8.2.7.4 If one of the above criteria is not satisfied, a second attempt can be made before repeating the entire initialization process.

NOTE: An initial calibration must be carried out whenever the routine calibration solution is replaced by a new one from a different lot.

## 9. QUALITY CONTROL PROCEDURES

### 9.1 Summary of QC Analyses

9.1.1 Initial and routine calibration and instrument performance checks.

9.1.2 Analysis of a batch of samples with accompanying QC analyses:

Sample batch -- 10 NHATS adipose tissue samples plus additional QC analyses including 1 method blank, a control tissue and a spiked tissue sample.

"Blind" QC (external QC) samples may be submitted by an external source (quality assurance group or independent laboratory) and included among the batch of samples. Blind samples include spiked samples, unidentified duplicates, and performance evaluation samples.

9.2 Performance Evaluation Solutions -- Included among the samples in every third batch will be a solution provided by the quality control coordinator containing known amounts of unlabeled 2,3,7,8-TCDD and/or other PCDD/PCDF isomers. The accuracy of measurements for performance evaluation samples should be in the range of 70-130%.

### 9.3 Column Performance Check Solutions

9.3.1 At the beginning of each 12-h period during which samples are to be analyzed, an aliquot of the HRGC column performance check solution shall be analyzed to demonstrate adequate HRGC resolution for selected TCDD isomers.

## 9.4 Method Blanks

9.4.1 A minimum of one method blank is generated with each batch of samples. A method blank is generated by performing all steps detailed in the analytical procedure using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis, but omit addition of the adipose tissue.

9.4.1.1 The method blank must contain the same amounts of Carbon-13 labeled internal quantitation standards that are added to samples before bulk lipid cleanup.

9.4.1.2 An acceptable method blank exhibits no positive response for any of the characteristic ions monitored.

9.4.1.2.1 If the above criterion is not met, solvents, reagents, spiking solutions, apparatus, and glassware are checked to locate and eliminate the source of contamination before any samples are extracted and analyzed.

9.4.1.2.2 If new batches of reagents or solvents contain interfering contaminants, purify or discard them.

9.5 Control Samples -- Control samples are prepared from a bulk sample(s) of human adipose tissue or similar matrix (e.g., porcine fat). This material is prepared by blending the tissue with methylene chloride, drying the extract by eluting through anhydrous sodium sulfate, and removing the methylene chloride using rotoevaporation at elevated temperatures (80°C). The evaporation process should be extended to ensure all traces of the extraction solvent have been removed. The resulting oily matrix (lipid) is subdivided into 10-g aliquots which are analyzed with each sample batch. The results of the individual analysis will be used to give a measure of precision from batch to batch over an entire program. Sufficient tissue should be extracted to provide a homogeneous lipid matrix that can be used over the total analysis program. Enough lipid matrix is necessary to prepare the spiked samples describe in Section 9.6.

9.6 Spiked Samples -- Spiked lipid samples are prepared using a portion of the homogenized lipid described in Section 9.5. Sufficient spiked lipid matrix is prepared to provide a minimum of one spiked sample per sample batch. It is recommended that a minimum

of three spiked levels of the matrix are prepared ranging from 10 to 50 times the estimated limit of detection for each compound. Each analysis of spiked sample must be accompanied by analysis of a control sample in order to make the necessary corrections for background contribution before determining the accuracy of the method (Equation 9-1).

$$\text{Accuracy (\%)} = 100\% \times \frac{\text{Conc. spiked sample} - \text{conc. control sample}}{\text{Spike level}} \quad \text{Eq. 9-1}$$

- 9.7 Duplicate Sample Analysis -- When possible a duplicate analysis of specific samples is included in the sample batch as an additional measure of method precision. It is suggested that the total tissue sample is extracted to isolate lipids material and then subdivided for duplicate analysis. Precision is calculated as relative percent difference (RPD) where the differences in the duplicate measurements (for each analyte) is divided by the average of the two measurements and multiplied by 100%.
- 9.8 External Samples -- Samples submitted as blinds to the analyst may consist of either performance solutions of PCDD and PCDF congeners or spiked sample matrices. These performance solutions or samples should be submitted by a source external to the analytical program (QA unit of analysis laboratory or independent laboratory). Performance audit solutions are intended to evaluate instrument calibration and quantitation procedures. Spiked blind samples must be accompanied by the corresponding unspiked samples to correct concentrations for background concentration. The blind spiked samples are intended to evaluate the total analytical procedure. The analyst must keep in mind that it is necessary to compare differences in standard sources for each type of external sample.

## 10. SAMPLE PRESERVATION AND HANDLING

All adipose tissue samples must be maintained at less than -20°C from time of collection. The analyst should instruct the collaborator collecting the sample(s) to avoid the use of chlorinated materials. Samples are handled using stainless steel forceps, spatulas, or scissors. Aliquots of samples removed from sample bottles not used for analysis are disposed rather than returned to the sample vial. All sample bottles (glass) are cleaned as specified in Section 6.4.10. Teflon®-lined caps should be used. As with any biological sample, the analyst should avoid any undue exposure.

## 11. SAMPLE EXTRACTION

### 11.1 Extraction of Adipose Tissue

- 11.1.1 Accurately weigh to the nearest 0.01 g a 10-g portion of a frozen adipose tissue sample into a culture tube (2.2 x 15 cm).

Note: Sample size may be smaller, depending on availability.

### 11.1.2 Addition of internal quantitation standards

Allow the adipose tissue specimen to reach room temperature and then add the carbon-13 internal quantitation spiking solution (Section 7.6) such that it delivers 500 to 2,500 pg of each of the surrogates specified in Table 4 in a 100- $\mu$ L volume.

11.1.3 Add 10 mL of methylene chloride and homogenize the mixture for approximately 1 min with a Tekmar Tissuemizer®.

11.1.4 Allow the mixture to separate and decant the methylene chloride extract from the residual solid material using a disposable pipette. The methylene chloride is eluted through a filter funnel containing a plug of clean glass wool and 5 to 10 g of anhydrous sodium sulfate. The dried extract is collected in a 100-mL volumetric flask.

11.1.5 A second 10-mL aliquot of methylene chloride is added to the sample and homogenized for 1 min. The methylene chloride is decanted, dried, and transferred to the 100-mL volumetric flask as specified in Section 11.1.3

11.1.6 The culture tube is rinsed with at least two additional aliquots (10 mL each) of methylene chloride, and the entire contents are transferred to the filter funnel containing the anhydrous sodium sulfate. The filter funnel and contents are rinsed with additional methylene chloride (20 to 40 mL). The total eluent from the filter funnel is collected in the 100-mL volumetric flask. Discard the sodium sulfate.

11.1.7 The final volume of the extract for each sample is adjusted to 100 mL in the volumetric flask using methylene chloride.

## 11.2 Lipid Determination

11.2.1 Preweigh a clean 1-dram glass vial to the nearest 0.0001 g using an analytical balance tared to zero.

11.2.2 Accurately transfer 1.0 mL of the final extract (100 mL) from Section 11.1.7 to the 1-dram vial. Reduce the volume of methylene chloride from the extract using a water bath (50-60°C) gentle stream of purified nitrogen until an oil residue remains.

- 11.2.3 Accurately weigh the 1-dram vial and residue to the nearest 0.0001 g and calculate the weight of lipid present in the vial based on difference. Nitrogen blow-down is continued until a constant weight is achieved.
- 11.2.4 Calculate the percent lipid content of the original sample to the nearest 0.1% as shown in Equation 11-1.

$$\text{Lipid content, LC (\%)} = \frac{W_{LR} \times V_{EXT}}{W_{AT} \times V_{AL}} \times 100\% \quad \text{Eq. 11-1}$$

- where:  $W_{LR}$  = weight of the lipid residue to the nearest 0.0001 g calculated from Section 11.2.3;
- $V_{EXT}$  = total volume of the extract in mL from Section 11.1.6 (100.0 mL);
- $W_{AT}$  = weight of the original adipose tissue samples to the nearest 0.01 g from Section 11.1.1; and
- $V_{AL}$  = volume of the aliquot of the final extract in mL used for the quantitative measure of the lipid residue (1.0 mL).

- 11.2.5 Record the lipid residue measured in Section 11.2.3 and the percent lipid content calculated from Section 11.2.4.

### 11.3 Extract Concentration

- 11.3.1 Quantitatively transfer the remaining extract volume (99.0 mL) to a 500-mL Erlenmeyer flask. Rinse the volumetric flask with 20 to 30 mL of additional methylene chloride to ensure quantitative transfer.
- 11.3.2 Place the Erlenmeyer flask on a hot plate at 40°C to remove solvent until an oily residue remains.

## 12. CLEANUP PROCEDURES

### 12.1 Bulk Lipid Removal

- 12.1.1 Add a total of 200 mL of n-hexane to the spiked lipid residue in the 500-mL Erlenmeyer flask.

- 12.1.2 Slowly add, with stirring, 100 g of the 40% w/w sulfuric acid impregnated silica gel (Section 7.1.3). Stir with a magnetic stir-plate for 2 h.
- 12.1.3 Allow solids to settle and decant liquid through a powder funnel containing 20 g of anhydrous sodium sulfate and collect in a 500-mL sample bottle.
- 12.1.4 Rinse solids with two 50-mL portions of hexane. Stir each rinse for 15 min, decant, and dry by elution through sodium sulfate combining the hexane extracts from Section 12.1.3.
- 12.1.5 After the rinses have gone through the sodium sulfate, rinse the sodium sulfate with an additional 25 mL of hexane and combine with the hexane extracts from Section 12.1.4.
- 12.1.6 Prepare an acidic silica column as follows: Pack a 1 cm x 10 cm chromatographic column with a glass wool plug, add approximately 25 mL of hexane, add 1.0 g of silica gel (Section 7.1.2) and allow to settle, then add 4.0 g of 40% w/w sulfuric acid impregnated silica gel (Section 7.1.3) and allow to settle. Pack a second chromatographic column (1 cm x 30 cm) with a glass wool plug, add approximately 25 mL of hexane, add 6.0 g of acidic alumina (Section 7.1.1), and allow to settle and then top with a 1-cm layer of sodium sulfate (Section 7.2). Elute the excess hexane solvent through the columns until the solvent level reaches the top of the chromatographic packing. Inspect columns to ensure they are free of channels and air bubbles. Wash the alumina column with 40 mL of 50% v/v methylene chloride/hexane. Remove the methylene chloride from the adsorbent by eluting the column with an additional 100 mL of hexane. Elute the excess solvent from the column until the solvent level reaches the top of the sodium sulfate layer.
- 12.1.7 Quantitatively transfer the hexane extract from the Erlenmeyer flask (Sections 12.1.3 through 12.1.5) to the silica gel column reservoir. Allow the hexane extract to percolate through the column and collect in a KD concentrator.
- 12.1.8 Complete the elution of the extract from the silica gel column with 50 mL of hexane in the KD concentrator. Concentrate the eluate to approximately 1.0 mL, using nitrogen blow-down as necessary.

Note: If the 40% sulfuric acid/silica gel is noted to be highly discolored throughout the length of the adsorbent bed it is necessary to repeat the cleaning procedure beginning with Section 12.1.1.

## 12.2 Separation of Chemical Interferences

- 12.2.1 Transfer the concentrate (1.0 mL) to the top of the alumina column. Rinse the K-D assembly with two 1.0-mL portions of hexane and transfer the rinses to the top of the alumina column. Elute the alumina column with 18 mL of hexane until the hexane level is just below the top of the sodium sulfate. Discard the eluate. Columns must not be allowed to reach dryness (i.e., a solvent "head" must be maintained).
- 12.2.2 Place 30 mL of 20% (v/v) methylene chloride in hexane on top of the alumina and elute the TCDDs from the column. Collect this fraction in a 50-mL culture tube.
- 12.2.3 Prepare an 18% Carbopak C/Celite 545® mixture by thoroughly mixing 3.6 g of Carbopak C (80/100 mesh) and 16.4 g of Celite 545® in a 40-mL vial. Activate at 130°C for 6 h. Store in a desiccator. Cut off a clean 5-mL disposable glass pipet (6 to 7 mm ID) at the 4-mL mark. Insert a plug of glass wool and push to the 2-mL mark. Add 500 mg of the activated Carbopak/Celite mixture followed by another glass wool plug. Using two glass rods, push both glass wool plugs simultaneously towards the Carbopak/Celite mixture and gently compress the Carbopak/Celite plug to a length of 3 to 3.5 cm. Pre-elute the column with 2 mL of toluene followed by 1 mL of 75:20:5 methylene chloride/methanol/ benzene, 1 mL of 1:1 cyclohexane in methylene chloride, and 2 mL of hexane. The flow rate should be less than 0.5 mL/min. While the column is still wet with hexane, add the entire eluate (30 mL) from the alumina column (Section 12.2.2) to the top of the column. Rinse the culture tube which contained the extract twice with 1 mL of hexane and add the rinsates to the top of the column. Elute the column sequentially with two 1-mL aliquots of hexane, 1 mL of 1:1 cyclohexane in methylene chloride, and 1 mL of 75:20:5 methylene chloride/methanol/benzene. Turn the column upside down and elute the PCDD/PCDF fraction with 20 mL of toluene into 6-dram vial.
- 12.2.4 Using a stream of nitrogen, reduce the toluene volume to approximately 1 mL. Carefully transfer the concentrate into a 1-mL minivial and reduce the volume to about 200 µL using a stream of nitrogen.

- 12.2.5 Rinse the concentrator tube with three washings using 500  $\mu\text{L}$  of 1% toluene in methylene chloride. Concentrate to 200-500  $\mu\text{L}$  and add 10  $\mu\text{L}$  of the tridecane solution containing the internal recovery standard and store the sample in a refrigerator until HRGC/MS analysis.
- 12.2.6 Immediately prior to analysis, using a gentle stream of nitrogen at room temperature, remove toluene and methylene chloride. Submit sample to HRGC/MS once a stable 10  $\mu\text{L}$  volume of tridecane is attained.

### 13. ANALYTICAL PROCEDURES

#### 13.1 HRGC/MS Analysis for PCDD/PCDF

- 13.1.1 Once routine calibration criteria are met, the instrument is ready for sample analysis. Prior to the first sample, a blank injection of tridecane should be analyzed to document system cleanliness. If any evidence of system contamination is found, corrective action must be taken and another tridecane blank analyzed.

The typical daily sequence of injections is shown in Table 9 and Figure 3.

Note: Syringe Technique -- Congeners of PCDD/PCDF in the syringes used for HRGC/MS analysis can be problematic unless the syringes are properly handled between samples. The following procedure has been found to be very effective for PCDD/PCDF removal from contaminated syringes and will be used throughout these analyses.

- Rinse the syringe 10 times with isooctane.
- Fill the syringe with toluene and sonicate syringe and plunger in toluene for 5 min and repeat at least twice.
- Rinse the syringe 10 times with tridecane and pull up 1  $\mu\text{L}$  of clean tridecane.
- Syringe is ready for use.

At no time should air be introduced into the HRGC column by using an air plug in the syringe. The oxygen present in the air plug will quickly degrade a nonbonded GC phase.

- 13.1.2 Inject a 1- $\mu\text{L}$  aliquot of the extract into the GC, operated under the conditions previously used (Section 8.1) to produce acceptable results with the performance check solution.

Table 9. Typical Daily Sequence for PCDD/PCDF Analysis

- 
1. Tune and calibrate mass scale versus perfluorokerosene (PFK).
  2. Inject column performance mixture.
  3. Inject concentration calibration solution 2.5 to 12.5 pg/ $\mu$ L (CS-7) solution.
  4. Inject blank (tridecane).
  5. Inject samples 1 through "N".
  6. Inject concentration calibration solution 2.5 to 12.5 pg/ $\mu$ L (CS-7) solution or other concentration calibration solutions CS1 to CS8 to bracket observed sample concentration.
-

# INSTRUMENTAL ANALYSIS

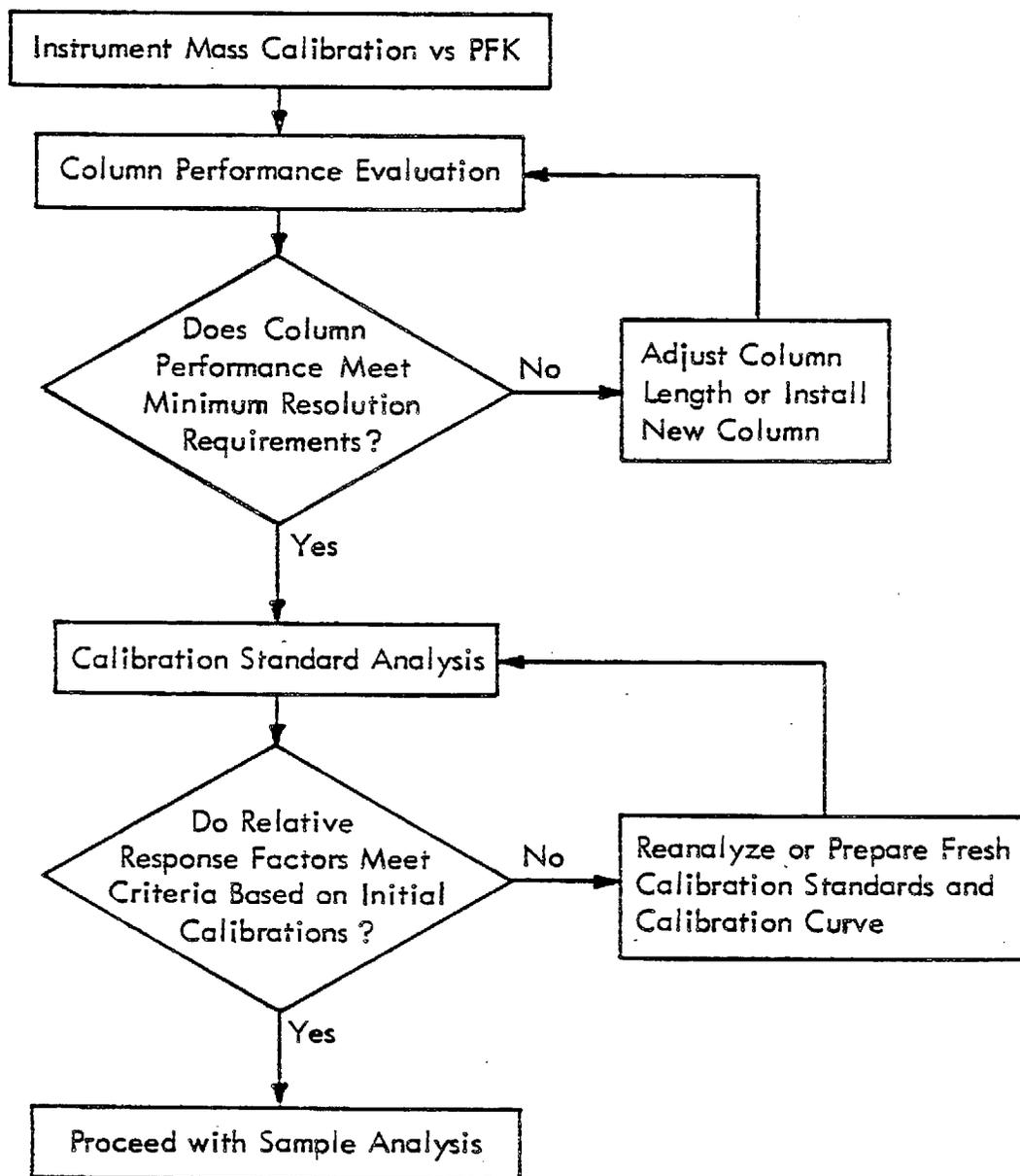


Figure 3. Daily QA procedures for proceeding with sample analysis.

- 13.1.3 Acquire SIM data according to the same acquisition and MS operating conditions previously used (Section 8.1) to determine the relative response factors.
- 13.1.3.1 Acquire SIM data for the characteristic ions designated in Table 6.
- 13.1.3.2 Instrument performance shall be monitored by examining and recording the peak areas for the recovery standard,  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. If this area should decrease to less than 50% of the calibration standard, sample analyses shall be stopped until the problem is found and corrected.

### 13.2 HRGC/HRMS Confirmation of 2,3,7,8-TCDD

The presence of 2,3,7,8-TCDD observed through the general PCDD and PCDF procedure should be confirmed using HRGC/HRMS (resolution 10,000).

- 13.2.1 Once the daily criteria of mass calibration, mass resolution, HRGC performance, and routine calibration are met and documented, the instrument is ready for sample analysis. Prior to the first sample, a blank injection of tridecane will be made to document system cleanliness.

The typical daily schedule for HRGC/HRMS analysis of TCDD is shown in Table 10 and Figure 3.

- 13.2.2 Inject a 1- $\mu\text{L}$  aliquot of the extract into the GC, operated under the conditions previously used (Section 8.2) to produce acceptable results with the column performance check solution.
- 13.2.3 Acquire SIM data according to Section 8.2.4.3. Use the same acquisition and MS operating conditions previously used to determine the relative response factors.

- 13.2.3.1 Acquire SIM data for the following selected characteristic ions:

| <u>m/z</u> | <u>Compound</u>   |
|------------|---|
| 258.930    | TCDD - COC1   |
| 319.897    | Unlabeled TCDD  |
| 321.894    | Unlabeled TCDD  |
| 331.937    | $^{13}\text{C}_{12}$ -2,3,7,8-TCDD,<br>$^{13}\text{C}_{12}$ -1,2,3,4-TCDD |
| 333.934    | $^{13}\text{C}_{12}$ -2,3,7,8-TCDD,<br>$^{13}\text{C}_{12}$ -1,2,3,4-TCDD |

Table 10. Typical Daily Schedule for HRGC/HRMS Analysis of TCDD

---

1. Tune and calibrate mass scale.
  2. Perform mass measurement check and mass resolution check.
  3. Inject column performance check solution.
  4. Inject the routine concentration calibration solution (CS7) and confirm response factor consistency.
  5. Inject tridecane blank.
  6. Inject samples 1 through "N".
  7. Inject concentration calibration solution and confirm response factor consistency.
  8. Mass resolution check.
-

## 14. DATA REDUCTION

In this section, the procedures for the data reduction are outlined for the analysis of data from both the HRGC/MS method for PCDD/PCDF and the HRGC/HRMS method for 2,3,7,8-TCDD. Figure 4 presents a schematic of the qualitative criteria for identifying PCDDs and PCDFs.

### 14.1 Qualitative Identification

- 14.1.1 The ion current responses for each mass for a particular PCDD/PCDF analyte must be within  $\pm 1$  s to attain positive identification of that analyte. For example, m/z 338 and m/z 340 must have maximum peak responses that are within  $\pm 1$  s to be positively identified as a pentachlorodibenzofuran.
- 14.1.2 The ion current intensities for a particular PCDD/PCDF must be  $\geq 2.5$  times the noise level ( $S/N \geq 2.5$ ) for positive identification of that isomer.
- 14.1.3 The integrated ion current ratios of the analytical masses for a particular PCDD/PCDF must fall within the ranges shown in Table 7.
- 14.1.4 The recovery of the internal quantitation standards should be between 50 and 115%.

### 14.2 Quantitative Calculations

- 14.2.1 Relative response factors for native PCDD and PCDF analytes (RRF). RRFs are calculated from the data obtained during the analysis of concentration calibration solutions using the following formula:

$$RRF = \frac{A_{STD} \cdot C_{IS}}{A_{IS} \cdot C_{STD}} \quad \text{Eq. 14-1}$$

where  $A_{STD}$  = the sum of the areas of the integrated ion abundances for the analyte in question. For example, for TCDD,  $A_{STD}$  would be the sum of the integrated ion abundances for m/z 320 and 322;

$A_{IS}$  = the sum of the areas of the integrated ion abundances for the labeled PCDD/F used as the internal quantitation standard for the above analyte. For example, for  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD,  $A_{IS}$  would be the sum of the integrated ion abundance for m/z 332 and 334.

$C_{STD}$  = concentration of the analyte in pg/ $\mu\text{L}$ ;

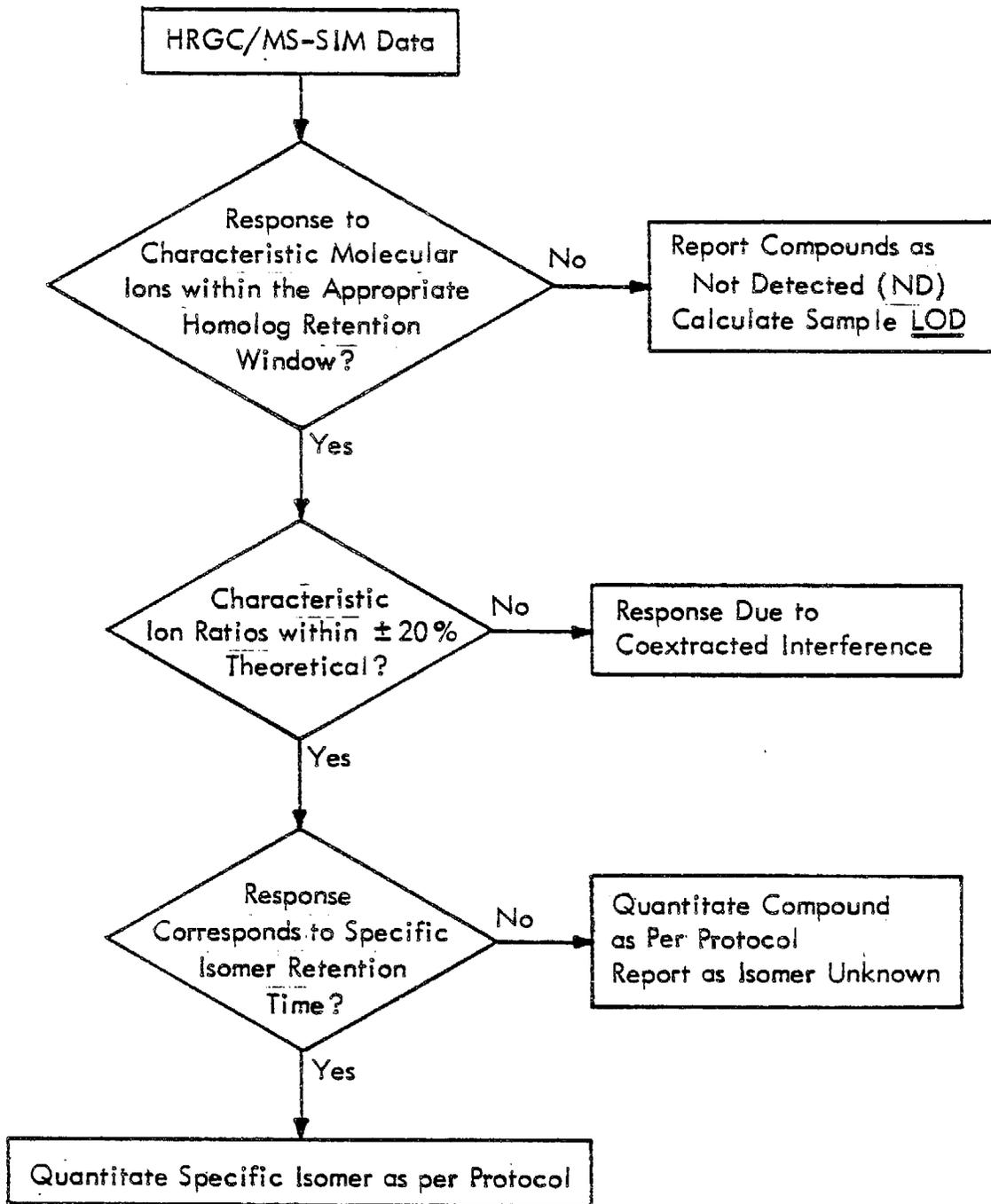


Figure 4. Qualitative criteria for identifying PCDDs and PCDFs.

$C_{IS}$  = concentration of the internal quantitation standard in pg/ $\mu$ L; and

Table 11 provides the pairing of target analytes to internal quantitation standards for determining RRF values for PCDD and PCDF compounds.

14.2.2 Relative response factors for the internal quantitation standards ( $RRF_{IS}$ ). The  $RRF_{IS}$  values are calculated from data obtained during the analysis of concentration calibration solutions using the following formula.

$$RRF_{IS} = \frac{A_{IS} \times C_{RS}}{A_{RS} \times C_{IS}} \quad \text{Eq. 14-2}$$

where  $A_{IS}$  and  $C_{IS}$  are defined as given in Section 14.2.1 and

$C_{RS}$  = concentrations of the internal recovery standard in pg/ $\mu$ L; and

$A_{RS}$  = the sum of the areas of the integrated ion abundances for the labeled PCDD ( $^{13}C_{12}$ -1,2,3,4-TCDD or  $^{13}C_{12}$ -1,2,3,7,8,9-HxCDD). For example, for  $^{13}C_{12}$ -1,2,3,4-TCDD,  $A_{RS}$  would be the sum of the integrated ion abundance for m/z 332 and 334.

Refer to Table 11 for pairing of the internal quantitation standards with the appropriate internal recovery standard.

14.2.3 Concentrations of sample components. Figure 5 presents a schematic for quantitation of PCDDs and PCDFs which meet the criteria specified in Section 14.1. Calculate the concentration of PCDD/Fs in sample extracts using the formula:

$$C_{\text{sample}} = \frac{A_{\text{sample}} \cdot Q_{IS} \cdot 100}{A_{IS} \cdot RRF \cdot W_{AT} \cdot LC} \quad \text{Eq. 14-3}$$

where  $C_{\text{sample}}$  = the lipid adjusted concentration of PCDD or PCDF congener in pg/g;

$A_{\text{sample}}$  = sum of the integrated ion abundances determined for the PCDD/PCDF in question;

$A_{IS}$  = sum of the integrated ion abundances determined for the labeled PCDD/F used as the internal quantitation standard for the above analyte;

Table 11. Target Analyte/Internal Quantitation Standard and Internal Quantitation Standard/Internal Recovery Standard Pairs

| Target analyte      | Internal standards                        |   |
|---------------------|---|---|
|                     | Quantitation                              | Recovery                                |
| 2,3,7,8-TCDD        | $^{13}\text{C}_{12}$ -2,3,7,8-TCDD        | $^{13}\text{C}_{12}$ -1,2,3,4-TCDD      |
| 2,3,7,8-TCDF        | $^{13}\text{C}_{12}$ -2,3,7,8-TCDF        | $^{13}\text{C}_{12}$ -1,2,3,4-TCDD      |
| 1,2,3,7,8-PeCDF     | $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF     | $^{13}\text{C}_{12}$ -1,2,3,4-TCDD      |
| 2,3,4,7,8-PeCDF     | $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF     | $^{13}\text{C}_{12}$ -1,2,3,4-TCDD      |
| 1,2,3,7,8-PeCDD     | $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD     | $^{13}\text{C}_{12}$ -1,2,3,4-TCDD      |
| 1,2,3,4,7,8-HxCDF   | $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF   | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,6,7,8-HxCDF   | $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF   | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 2,3,4,6,7,8-HxCDF   | $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF   | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,7,8,9-HxCDF   | $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF   | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,4,7,8-HxCDD   | $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD   | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,6,7,8-HxCDD   | $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD   | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,7,8,9-HxCDD   | $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD   | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,4,6,7,8-HpCDF | $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,4,7,8,9-HpCDF | $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,4,6,7,8-HpCDD | $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| OCDF                | $^{13}\text{C}_{12}$ -OCDD                | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| OCDD                | $^{13}\text{C}_{12}$ -OCDD                | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |

# QUANTITATION

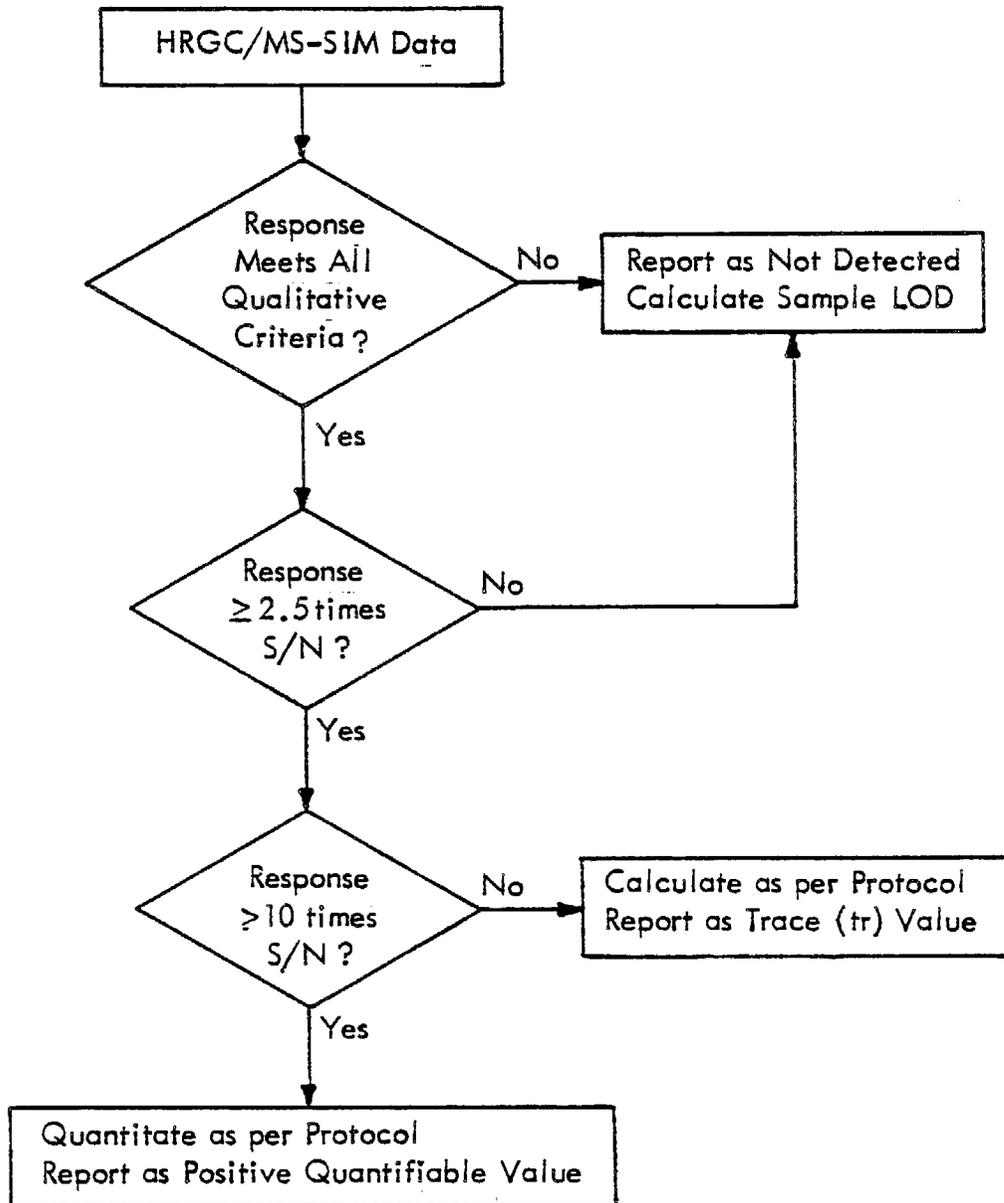


Figure 5. Procedure for quantitation of PCDDs and PCDFs in human adipose tissue.

$Q_{IS}$  = the amount (total pg) of the labeled internal quantitation standard added to the sample prior to extraction;

RRF = relative response factor of the above analyte relative to its labeled internal quantitation standard determined from the initial triplicate calibration;

$W_{AT}$  = weight (g) of original adipose tissue sample; and

LC = percent extractable lipid determined from Eq. 11-1.

Refer to Table 11 for pairing of target analytes with the appropriate internal quantitation standard.

Quantitative data should be classified to indicate the intensity of the signal response. Suggested qualifiers include: not detected, ND (signal-to-noise ratio is less than 2.5); trace, TR (signal-to-noise ratio is greater than or equal to 2.5 but less than 10); and positive quantifiable, PQ (signal-to-noise ratio is greater than or equal to 10).

14.2.4 Recovery of internal quantitation standards. Calculate the recovery of the labeled internal quantitation standards measured in the final extract using the formula:

$$\text{Internal Quant. Std.} = \frac{A_{IS} \cdot Q_{RS}}{A_{RS} \cdot Q_{IS} \cdot \text{RRF}} \cdot 100 \quad \text{Eq. 14.4}$$

Percent Recovery

where  $A_{IS}$  = sum of the integrated ion abundances determined for the labeled PCDD/PCDF internal quantitation standard in question;

$A_{RS}$  = sum of the integrated ion abundances determined for m/z 332 and m/z 334 of  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD or m/z 390 and m/z 392 of  $^{13}\text{C}_{13}$ -1,2,3,7,8,9-HxCDD (recovery standards)

$Q_{RS}$  = amount (pg) of the respective recovery standard, added to the final extract;

$Q_{IS}$  = amount (pg) the labeled internal quantitation standard added to the sample prior to extraction; and

$RRF_{IS}$  = relative response factor for the labeled internal quantitation standard in question relative to the internal recovery standard. This value shall be the RRF determined from the initial calibration.

Refer to Table 11 for pairing of the internal quantitation standards with the appropriate target analytes.

Note: The result of calculations as presented in Section 14.2 may be off by as much as 1% due to the fact that 1 mL of the final 100 mL volume from the extraction was used for lipid determination.

### 14.3 Estimated Method Detection Limit

Estimated method detection limits must be calculated in situations where (1) no response is noted for a specific congener; (2) a response is noted but ion ratios are incorrect; and (3) where a response is quantitated as a trace value.

14.3.1 For samples in which no unlabeled PCDD or PCDF is detected, calculate the estimated minimum detectable concentration. The background area is determined by integrating the ion abundances for the characteristic ions in the appropriate region and relating the product area to an estimated concentration that would produce that product area.

Use the formula:

$$C_E = \frac{2.5 \cdot A_{\text{sample}} \cdot Q_{IS}}{A_{IS} \cdot \overline{RRF} \cdot W_{AT}} \quad \text{Eq. 14-5}$$

where  $C_E$  = estimated concentration of unlabeled PCDD or PCDF required to produce  $A_{\text{sample}}$ ;

$A_{\text{sample}}$  = sum of integrated ion abundances or peak heights for the characteristic ions of the unlabeled PCDD or PCDF isomer in the same group of  $\geq 5$  scans used to measure  $A_{IS}$ ; and

$A_{IS}$  = sum of integrated ion abundances for the appropriate ions characteristic of the respective internal quantitation standard.

$Q_{IS}$ ,  $\overline{RRF}$ , and  $W_{AT}$  retain the definitions previously stated in Section 14.2. Alternatively, if peak height measurements are used for quantification, measure the estimated detection limit by the peak height of the noise in the 2,3,7,8-TCDD RT window.

- 14.3.2 For samples for which a response at the retention time of a specific PCDD or PCDF congener is noted, but the qualitative criteria for ion ratios are outside the acceptable range (Table 7), the estimated detection level is calculated as given in Eq. 14.3 except the values are qualified as not detected, ND, and the concentration is reported in parenthesis.
- 14.3.3 If a response for a specific PCDD or PCDF congener is qualified as a trace, TR, value (signal to noise is greater than or equal to 2.5 but less than 10) the analyst must also provide an estimated method detection limit. This is accomplished by using the observed signal to noise on either side of the response and calculating as given in Eq. 14-5.

## 15. REPORTING AND DOCUMENTATION

All data should be reported on an individual sample basis using the data report format shown in Figure 6. The analyst is required to maintain all raw data, calculations, and control charts in a format as to allow a complete external data review. Suggested data formats for tracing calculations are provided in Figure 7.

State of California  
Air Resources Board  
Sacramento, CA 95812

ARB  
Body Burden Study  
PCDD/F Analysis Form

|                       |     |                    |   |   |    |
|-----------------------|-----|--------------------|---|---|----|
| Sample Code           | ... | Analysis Date LRMS | / | / | 87 |
| Lab Number            |     | Analysis Date HRMS | / | / | 87 |
| Batch Number          |     | Reviewed by:       |   |   |    |
| Wet Tissue Weight (g) |     |                    |   |   |    |
| % Extractable Lipid   |     |                    |   |   |    |

| Native Compounds    | Data Qualifier (1) | LOD (pg/g) (2) | Concentration (pg/g) (2) | Internal Quantitation Standard | Spiked Level (pg) | Percent (%) Recovery |
|---------------------|--------------------|----------------|--------------------------|--------------------------------|-------------------|----------------------|
| 2378-TCDF (3)       |                    |                |                          | 13C12-2378-TCDF                | 500               |                      |
| 2378-TCDD (3)       |                    |                |                          | 13C12-2378-TCDD                | 500               |                      |
| 12378-PeCDF         |                    |                |                          | 13C12-12378-PeCDF              | 500               |                      |
| 23478-PeCDF         |                    |                |                          | 13C12-12378-PeCDD              | 500               |                      |
| 12378-PeCDD         |                    |                |                          | 13C12-123478-HxCDF             | 1250              |                      |
| 123478-HxCDF        |                    |                |                          | 13C12-123678-HxCDD             | 1250              |                      |
| 123678-HxCDF        |                    |                |                          | 13C12-1234678-HpCDF            | 1250              |                      |
| 234678-HxCDF        |                    |                |                          | 13C12-1234678-HpCDD            | 1250              |                      |
| 123789-HxCDF        |                    |                |                          | 13C12-OCDD                     | 2500              |                      |
| 123478/123678-HxCDD |                    |                |                          |                                |                   |                      |
| 123789-HxCDD        |                    |                |                          |                                |                   |                      |
| 1234678-HpCDF       |                    |                |                          |                                |                   |                      |
| 1234789-HpCDF       |                    |                |                          |                                |                   |                      |
| 1234678-HpCDD       |                    |                |                          |                                |                   |                      |
| OCDF                |                    |                |                          |                                |                   |                      |
| OCDD                |                    |                |                          |                                |                   |                      |

Remarks

(1) ND - Not detected above Limit of Detection (LOD); TR - Trace; PQ - Positive Quantifiable.  
 (2) Concentration based on total extractable lipid (g).  
 (3) From High Resolution Mass Spectrometry Data

Figure 6. Analysis report form.

RAW DATA SUMMARY FOR DETERMINATION OF 1,2,3,7,8-PeCDD IN HUMAN ADIPOSE TISSUE

| Sample no. | Sample weight (xx.xx g) | Extractable lipid content (xx.x %) | Analysis date | <sup>13</sup> C <sub>12</sub> -PeCDD Amount (pg) | <sup>13</sup> C <sub>12</sub> -PeCDD m/z 332 | <sup>13</sup> C <sub>12</sub> -PeCDD m/z 334 | Ion ratio 366/368 | 1,2,3,7,8-PeCDD m/z 354 | 1,2,3,7,8-PeCDD m/z 356 | Ion ratio 354/356 | 1,2,3,7,8-PeCDD <sup>a</sup> conc. (pg/g) |
|------------|-------------------------|------------------------------------|---------------|--|--|--|-------------------|-------------------------|-------------------------|-------------------|---|
|            |                         |                                    |               |  |  |  |                   |                         |                         |                   |   |

<sup>a</sup> Value reported as concentration in extractable lipid.

Figure 7. Example of raw data summary format for the determination of 1,2,3,7,8-PeCDD in human adipose tissue.

Section No: 1.0  
Revision No: 0  
Date: 2/12/88  
Page: 1 of 1

APPENDIX C

QUALITY ASSURANCE PROGRAM PLAN (QAPP)

ARB Contract No. A6-197-33  
Task No. I

SECTION 1.0

CHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS  
CONTAMINATION OF THE FOOD CHAIN

Section No: 2.0  
Revision No: 0  
Date: 2/12/88  
Page: 1 of 1

SECTION 2.0  
TABLE OF CONTENTS

| <u>Section</u> | <u>Heading</u>                                      | <u>Pages</u> | <u>Revision</u> | <u>Date</u> |
|----------------|---|--------------|-----------------|-------------|
| 1.0            | Title Page  | 1            | 0               | 02/12/88    |
| 2.0            | Table of Contents                                   | 1            | 0               | 02/12/88    |
| 3.0            | Project Description                                 | 2            | 0               | 02/12/88    |
| 4.0            | Project Organization and Management                 | 4            | 0               | 02/12/88    |
| 5.0            | Personnel Qualifications                            | 3            | 0               | 02/12/88    |
| 6.0            | Facilities, Equipment, Consumables,<br>and Services | 4            | 0               | 02/12/88    |
| 7.0            | Data Generation                                     | 7            | 0               | 02/12/88    |
| 8.0            | Data Reduction and Analysis                         | 4            | 0               | 02/12/88    |
| 9.0            | Data Quality Assessment                             | 4            | 0               | 02/12/88    |
| 10.0           | Corrective Action                                   | 2            | 0               | 02/12/88    |
| 11.0           | Documentation and Reporting                         | 2            | 0               | 02/12/88    |

## SECTION 3.0

### PROJECT DESCRIPTION

Midwest Research Institute (MRI) has been contracted by the State of California Air Resources Board (ARB) to determine the concentration levels of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in foods with specific emphasis on California-raised products. The results of this project will be used by the ARB as part of their assessment of the impact that major stationary combustion sources (municipal incinerators, hazardous waste incinerators, wire reclamation facilities, hospital incinerators, etc.) will have on the air quality in the South Coast Air Basin.

The objectives of the proposed program are to provide the State of California ARB with a preliminary estimate of the residue levels of PCDDs and PCDFs in food, with specific emphasis on California products. This will be accomplished through a program which requires prioritization of foodstuffs, field sampling, and state-of-the-art chemical analysis of selected foods.

The chemical analysis of the selected foods will be conducted for specific PCDD and PCDF compounds (compounds with four to eight chlorines and substituted in the 2, 3, 7, and 8 structural positions). These data will be used by ARB to assess the relative impact of dietary concentrations of these compounds versus airborne concentrations of the compounds on body burden levels of PCDD and PCDF in the general California population.

This QAPP addresses the quality control procedures and criteria that will be implemented throughout the analysis program. The objective of the program is to achieve accurate measurements of the residue levels of the 2,3,7,8-substituted PCDD and PCDF congeners in specific foodstuffs. Special emphasis will be given for selection of foodstuffs (beef, pork, poultry, eggs, and milk) of California origin. Specific QA criteria that are addressed in this document are (1) consistency of calibration ( $\pm 20\%$  variability of response factors for TCDD and TCDF, and  $\pm 30\%$  for all other congeners); (2) absolute method recoveries for all internal quantitation standards versus internal recovery standards (50-115%); (3) precision through the analysis of a control tissue matrix and duplicate analysis of specific design samples. The data quality objective for precision based on duplicate analyses is  $\pm 40\%$  for PCDD and PCDF responses that are present at greater than 10 pg/g; and (4) accuracy through the analysis of spiked tissue samples (50-130%).

## SECTION 4.0

### PROGRAM ORGANIZATION AND MANAGEMENT

The technical team will be led by Dr. John Stanley, who will serve as program manager. For management purposes, the program will be assigned to the Chemical Sciences Department, Dr. John E. Going, Director. Together they will ensure that all necessary resources are available, ensure that the program quality assurance coordinator is fully informed and involved in the program, and critically review all progress reports and interim or final reports to ARB.

#### 4.1 Program Manager

The program team will be managed by Dr. John S. Stanley. Dr. Stanley has the responsibility and authority to execute the program activities that are in compliance with contractual agreements. He is MRI's principal contact with the ARB project officer. He is responsible for:

- coordinating all phases of this sampling and analysis program,
- reviewing and approving all reports before submission to the ARB,
- assuring technical quality and performance,
- monitoring progress and adherence to schedules,
- monitoring expenditures in comparison to budgets and funding,
- interacting with MRI's Accounting and Contract Departments to ascertain that program cost accounting and contract requirements are fulfilled,
- addressing problems and taking corrective action in a timely and effective manner,
- assuring that all procedures and results are documented appropriately,
- reporting any problems associated with data quality to the department quality assurance coordinator (DQAC), and
- reporting regularly to MRI management.

As program manager, Dr. Stanley has the authority to direct all technical support activities toward completing the assigned work.

### 4.3 Task Leaders

Each project will be managed by a task leader. The task leaders will coordinate the activities with the MRI program manager. Each task leader is responsible for:

- planning activities to complete specific tasks,
- preparation of reports and protocols,
- ensuring the technical quality of the project,
- monitoring progress and adherence to schedules,
- monitoring expenditures in comparison to budgets and funding,
- reporting regularly to the MRI program manager, and
- addressing problems and taking corrective action in a timely and effective manner.

Each task leader has the authority to direct technical activities toward completing the assigned work.

The task leaders will report regularly to the program manager on the technical and financial status of active tasks. These weekly briefings will include the potential for problems with schedule, staffing, technical progress, or other areas which may affect the project.

Ms. Karin Bauer is the task leader responsible for developing the survey design and completing the necessary statistical analysis. As part of her responsibilities, Ms. Bauer will:

- design and implement the survey for the collection of samples,
- develop and test the questionnaire to gather demographic data,
- statistically analyze the results from the chemical analyses, and
- provide input to the project leader for the monthly and final reports.

Ms. Kay Turman is responsible for identifying collection sites and collection of the necessary samples. Ms. Turman will:

- identify collection sites that meet the requirements of the survey design,
- identify the sample collection procedures,

- prepare detailed sample collection protocols,
- provide the necessary sampling and shipping materials, and
- ensure that the samples collected meet the requirements of the survey design.

Mr. Paul Cramer will oversee the work for the preparation of samples for analysis by HRGC/MS. He will:

- be responsible for staff training and documentation,
- ensure that all analytical protocols are followed and documented,
- take corrective action for any problems and communicate action in writing to the QAC and department management,
- be responsible for sample custody,
- be responsible for document control, and
- be responsible for data traceability.

Mr. Cramer will be assisted in the sample preparation activities by Mr. Randy Ayling, Mr. Mike McGrath, and Mr. Mark Ross. Mr. Ayling, Mr. McGrath, and Mr. Ross have considerable experience in the preparation of samples (specifically foodstuffs, biological tissues, environmental samples) for PCDDs and PCDFs.

Mr. Kelly Thornburg will oversee the HRGC/MS analysis of the sample extracts for PCDDs and PCDFs. He will:

- ensure that all equipment calibration and maintenance procedures are followed,
- ensure that all analysis protocols are followed and documented,
- take corrective action for any problems and communicate action in writing to the program manager, QAC, and department management, and
- be responsible for sample custody and data traceability.

Mr. Thornburg will be assisted in the HRGC/MS analysis of the samples by Mr. David Mills, and Mr. Rick Robson. Dr. Thomas Sack will provide additional mass spectrometric expertise when necessary to overcome technical problems.

#### 4.2 Department Quality Assurance Coordinator (DQAC)

In addition to the key technical staff, MRI supports the involvement of a quality assurance coordinator (DQAC) to assess the quality of data. A DQAC will be involved in this program. The DQAC reports to the Chemical Sciences Department Director, Dr. John E. Goings.

Mr. Thomas Dux is the DQAC. He will:

- assist in preparing the quality assurance plan (QAP),
- work with the individual task leaders to ensure that all aspects of the QAP are addressed,
- conduct system and data audits and review reports as directed by department and program management,
- conduct performance audits as directed by the program manager,
- examine data books, records, forms, and any other hard-copy information, and
- reports audit results to department management and to the program manager.

## SECTION 5.0

### PERSONNEL QUALIFICATIONS

Midwest Research Institute's program team is comprised of professionals with demonstrated experience in the areas of survey design, statistical analysis of multivariate data, recruitment of medical professionals for collection of biological samples, coordination of biological sample analysis activities, and analysis of biological samples for ultratrace (1 to 10 parts per trillion) levels of PCDDs and PCDFs. The key technical staff available for this program are identified in Figure 4-1. This team of experienced professionals will ensure that the qualified resources are available to provide the necessary timely and thorough completion of the proposed program. Brief synopses on the specific areas of expertise for each of the key individuals are presented below.

Dr. John S. Stanley, Program Manager, has expertise in trace organic analysis using high resolution capillary gas chromatography, gas chromatography/mass spectrometry analysis, and high resolution mass spectrometry/selected ion monitoring for PCDD, PCDF, and PCB analyses.

Since joining MRI in 1981, Dr. Stanley has been project leader and task leader on several major analytical and environmental programs. Recently, he has directed a program to assess levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in human adipose tissues under a cooperative agreement between the U.S. Environmental Protection Agency (EPA) and the Veterans Administration (VA). The EPA/VA cooperative program has involved developing detailed analytical protocols and a quality assurance program plan for determination of PCDDs and PCDFs at concentrations of 1 to 10 pg/g (parts per trillion).

Dr. Stanley has also directed a series of Special Analytical Services projects under EPA's Contract Laboratory Program to provide analysis of soils, sediments, and water for low parts-per-trillion to parts-per-quadrillion levels of PCDDs. Dr. Stanley has also evaluated an HRMS method for TCDD determination in soil and water at low parts-per-billion to parts-per-quadrillion levels, conducted a method validation study of EPA Method 613, and prepared a literature review and recommendations for PCDD and PCDF analysis in biological matrices for EPA and the VA.

Another major research area has involved evaluating analytical protocols for polyhalogenated dibenzo-*p*-dioxins and dibenzofurans and PCBs in commercial products, waste products, air and flue gas emissions, and wastewaters. Dr. Stanley also coordinated laboratory analysis for a comprehensive assessment of PAHs, PCDDs, and PCDFs from various combustion sources (coal-fired utility boilers, municipal waste incinerators, hazardous waste incinerators, and hospital incinerators).

Mr. Thomas P. Dux, Chemist, serves as the department quality assurance coordinator (DQAC) for various MRI programs involving analytical and environmental chemistry. He is responsible for auditing and validating laboratory analytical data to ensure high technical accuracy and QA compliance; performing QA and editorial reviews of analytical reports, sampling and analysis plans, and project QA plans; conducting system audits of laboratory operations both at MRI and subcontractor facilities; preparing QA performance audit samples; instructing staff in QA/QC theory and practice; and developing and implementing project-specific QA plans and procedures. Currently, Mr. Dux is QAC on two projects, an installation restoration project under USATHAMA QA regulations and an EPA project for the Office of Solid Wastes. These projects require high-volume, fast-turnaround sample analysis and reporting, primarily using GC/MS, ICP, and GFAA techniques. They also require certification of USATHAMA methods plus modification and implementation of SW-846 protocols. Other assignments concern hazardous waste incinerator trial burns, engineering performance testing, and various EPA projects for the Office of Toxic Substances.

Karin M. Bauer, Senior Statistician, provides statistical and computational expertise in support of MRI research programs in such diverse fields as analytical chemistry, air and water quality assessment, microbiology, bio-organics, and traffic engineering. Her responsibilities include design and analysis of experiments, survey design and data reduction, preparation of statistical reports, and the development and implementation of quality assurance plans. Ms. Bauer is experienced in the use of statistical package programs such as SAS, BMDP, and SPSS and in the development of computer programs in Basic and Fortran. In recent years, she has been instrumental in developing a capability in pattern recognition at MRI in conjunction with MRI chemists.

Project activities have also involved multivariate statistical analysis of airborne emissions of PCDDs and PCDFs from municipal waste incinerators. Statistical methods such as pattern recognition techniques were used to explore relationships between emissions of specific organic pollutants and key combustion indicators. In the context of the National Human Adipose Tissue Survey, for which MRI is conducting broad scan chemical analyses of adipose tissue specimens, Ms. Bauer was instrumental in identifying the need for automated data transfer from the mass spectrometer onto the EPA mainframe. A majority of the work is being performed using in-house microcomputers with available software packages and customized supplemental software. In addition, various chemometric techniques will be identified and incorporated into the laboratory's QA program so that higher quality data may be produced.

Ms. Kay Turman, Chemist, has been a lead person in the collection of biological samples for MRI programs. Ms. Turman's responsibilities include coordination of the sample collection process, development of the necessary tracking documentation, archival of the collected samples, and interaction with the analytical laboratories.

Section No: 5.0  
Revision No: 0  
Date: 2/12/88  
Page: 3 of 3

Dr. Thomas M. Sack, Senior Mass Spectrometrists, has considerable experience with high resolution mass spectrometry (HRMS) and its use in chemical analysis. He is responsible for the operation and maintenance of a Kratos MS50TC high performance mass spectrometer as well as methods development for new applications. Dr. Sack is skilled in the application of many mass spectrometric techniques including GC/MS, HRMS, and alternate ionization techniques such as chemical ionization and desorptive ionization. His knowledge extends to the use of Finnigan/Incos and Kratos data systems for sophisticated data reduction and manipulation.

Since joining MRI in 1985, Dr. Sack has directed the implementation of pyrolysis GC/MS instrumentation and has been a key figure in its use for a wide range of experiments. Dr. Sack has coauthored a method for the determination of 2,3,7,8-TCDD by HRGC/HRMS and has acted as the mass spectrometry task leader for several projects involving the trace analysis of chlorinated dibenzodioxins and dibenzofurans. He is currently involved in the use of HRGC/HRMS to determine total tetrachlorodibenzodioxins, HRGC/LRMS to simultaneously determine tetra-octa chlorodioxins and furans in various matrices, pyrolysis GC/MS to study the thermal degradation of transformer utility materials, and FAB-MS to analyze polar and nonvolatile materials.

## SECTION 6.0

### FACILITIES, EQUIPMENT, CONSUMABLES, AND SERVICES

#### 6.1 Facilities and Equipment

##### 6.1.1 Evaluation

This project will require the use of general trace organic laboratory facilities and the mass spectrometry facility. These facilities were described in detail in the MRI proposal.

Sample preparation activities (dishwashing, compositing, extraction, and sample cleanup) will be completed in a laboratory (MRI, Lab 332-W) that has been designated for ultratrace analysis work only. This laboratory is equipped with five Class A hoods, one walk-in hood, and a canopied wash area.

##### 6.1.2 Inspection and Maintenance

MRI's maintenance program consists of both scheduled (or preventive maintenance) and nonscheduled maintenance procedures. Records of maintenance performed on the instruments are maintained in the respective instrument logbooks. In addition, any instrument repair not performed by the laboratory personnel is handled by the Instrument Services Department, which also adheres to a record-keeping program.

The scheduled maintenance program involves the service performance of certain instruments at regular intervals. The type of services included in this program is presented in Table 6-1.

The nonscheduled maintenance program involves the necessary servicing of equipment on an "as needed" basis. This can include items in the scheduled maintenance program but most often involves the type of service listed in Table 6-2.

##### 6.1.3 Calibration Procedures and Reference Materials

###### 6.1.3.1 GC/MS/Data System Calibration and Evaluation

Standard operating procedures (SOPs) for GC/MS data system (DS) calibration and evaluation have been prepared for each of the GC/MS/DS instruments that will be used for analysis for PCDDs and PCDFs in human adipose tissue. These SOPs will be available from MRI upon request.

Table 6-1. Scheduled Maintenance

| Equipment         | Service                    | Frequency      |
|-------------------|----------------------------|----------------|
| Kratos MS-50TC    | Check/change forepump oil  | 1 yr/as needed |
|                   | Check/change turbopump oil | 1 yr/as needed |
| Finnigan-MAT 311A | Change forepump oil        | 1 yr/as needed |
|                   | Check/change turbopump oil | 1 yr/as needed |

Table 6-2. Nonscheduled Maintenance

| Instrument                | Service                                     | Frequency of repair |
|---------------------------|---|---------------------|
| All mass spectrometers    | Ion source cleaning                         | As needed           |
|                           | Vacuum chamber bake-out                     | As needed           |
|                           | Electronic component repair                 | As needed           |
|                           | Replace or repair jet separator             | As needed           |
| All gas chromatographs    | Electronic component repair                 | As needed           |
|                           | Pneumatics repair/replacement               | As needed           |
| All computer data systems | Alignment of disk drives                    | As needed           |
|                           | Repair/replacement of electronic components | As needed           |

### 6.1.3.2 Calibration

MRI will use PCDD and PCDF calibration standards that have been previously used on existing adipose tissue programs. The calibration of the instruments will be conducted as described in "Routine Calibration," Section 8.2.6 of the attached protocol. If successful calibration is not achieved, MRI will conduct the following calibration procedure.

- 6.1.3.2.1 Calibration for quantitative measurements will be conducted with standards at a minimum of six concentration levels in the linear range of the instrument.
- 6.1.3.2.2 Standards will be run in triplicate at the beginning of the project and compared to an analysis of the blank samples. The results of the multipoint calibration curve will be used to establish the initial relative response factor (RRF) control charts for each analyte.
- 6.1.3.2.3 Following the multilevel calibration, analysis of samples will be initiated.
- 6.1.3.2.4 Single-point calibrations will be performed at the beginning and end of each working day to assure the instruments' stability. The RRF values from these single-point calibration curves will be appended to the RRF control charts for each target analyte.
- 6.1.3.2.5 The relative response factors (RRF) from the single-point calibration will be checked with the average RRFs from the multilevel calibration. The RRFs must agree within  $\pm 20\%$  for the 2,3,7,8-TCDD and 2,3,7,8-TCDF and  $\pm 30\%$  for the penta- through octachloro PCDDs and PCDFs. If the criterion is not met, the calibration standard must be reanalyzed or the calibration curve must be rerun. The HRGC/MS analyst is responsible for documenting the RRF values on a daily basis. The RRFs will be summarized and reported with the data from each sample batch.

### 6.1.3.3 Calibration Standards

Calibration standards have been obtained from all available sources including the EPA reference materials

repository. Noncertified compounds or solutions have been characterized for purity and interferences. Most of the PCDD and PCDF standards and internal standards have been acquired from Cambridge Isotope Laboratories (Woburn, Massachusetts). MRI recently participated in an interlaboratory comparison of the PCDD and PCDF standards. The results demonstrated that MRI's standards are in good agreement with other laboratories participating in that study. Additional detail is provided in Section 7.0 of this QAPP. Stock calibration standards will be prepared prior to sample analysis. Calibration over a defined concentration range will require serial dilution of the highest concentration standard to the required final concentration.

## 6.2 Consumables

All reagents including adsorbents, solvents, and other expendable reagents will be screened as blanks to check for impurities that might lead to false positive identification in actual tissue samples. Solvents will be purchased as distilled-in-glass pesticide quality.

Where possible, standards will be obtained from the EPA reference materials repository. Supporting documentation for the stated purity of all standard compounds will be requested as necessary and will be compared with in-house evaluations.

## SECTION 7.0

### DATA GENERATION

#### 7.1 Experimental Design

The experimental design for this program and the sources of samples are identified in Section 4.0 of the technical portion of the work plan and Appendix A of this report.

#### 7.2 Sample Tracking

The composited food samples will be analyzed as three or four batches of samples. Each sample batch will also include a laboratory method blank, a control QC sample, and a spiked sample. Up to 10% of the design samples will be analyzed in duplicate to provide within-batch precision estimates.

All design samples will be organized into batches following compositing of the individual food product. The analyst will assign laboratory codes (MRI Lab No.) to each sample.

The laboratory code is explained in the following example:

8922A02 - 01 - 11

MRI Project No./ARB Task No. - Batch No. - Sample Sequence No. Please note that Task 02 is equivalent to the ARB Task II as specified in the MRI proposal.

#### 7.3 Laboratory Analytical Procedures

Appendix B to the Phase I interim report provides the detailed analytical method for analysis of human adipose tissue for PCDDs and PCDFs. This protocol will be used for analyses of the composite food samples. Any deviation will be appropriately documented and reported in the final data report to ARB. Modifications in the procedure for extraction of milk and egg samples are anticipated at this time. This protocol describes procedures for glassware preparation, sample handling, extraction cleanup, isolation of PCDDs and PCDFs, instrument analysis, and reporting.

#### 7.4 Internal Quality Control Checks

The method accuracy and precision will be assessed by analyzing specific QC samples with each batch of samples. Other quality control checks will be routinely included to document instrument performance. These QC activities are described below.

##### 7.4.1 Method Blank

A method blank or procedural blank will be prepared with each sample batch. The method blank will be treated exactly as a sample although no sample matrix will be present. Method blanks will serve as indicators as to presence of artifacts from the sample preparation scheme. A positive identification of a target analyte in a method blank will require further evaluation of glassware, solvents, chromatographic reagents, etc., to isolate the material responsible for artifact contribution.

##### 7.4.2 Replicate Samples

As stated previously, at least 10% of the design samples will be included for replicate sample analysis to demonstrate the precision of the analytical method. Inclusion of replicates will be accomplished by selecting a composite sample of sufficient mass and splitting to provide two approximately equal aliquots. Each aliquot will be carried through the entire analytical procedure (extraction, cleanup, and instrumental analysis).

##### 7.4.3 Spiked Samples

A spiked sample will be included with each sample batch to demonstrate method accuracy. Samples spiked with target PCDDs and PCDFs will be prepared at two concentration levels to document method performance over the working range. The spiked samples will be prepared from the same composite sample that will also be analyzed in duplicate.

##### 7.4.4 Internal Standards

Stable isotope labeled PCDDs and PCDFs will be used for quantitation of the target analytes and to assess method performance on a per-sample basis.

###### 7.4.4.1 Quantitation Standards

Stable isotope labeled PCDDs and PCDFs will be added to each sample prior to sample preparation for use as internal quantitation standards. Since these compounds are taken through all method procedures, the data will

reflect method recovery. As noted in Table 7-1, carbon-13 labeled internal quantitation standards may be available for each PCDD and PCDF homolog and for specified congeners. Pairing of the specific congeners and carbon-13 analogs provides accurate measurements of the PCDD and PCDF levels.

#### 7.4.4.2 Recovery Standards

Additional stable isotope labeled PCDDs and PCDFs,  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and  $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD, will be added to the final extracts prior to HRGC/MS analysis to provide an accurate measurement of the method recovery for each of the internal quantitation standards.

#### 7.4.5 Calibration Standards

Calibration standards will be analyzed at the beginning and end of each day's run to document response factor variability and instrument sensitivity. This will be accomplished using a low level calibration standard ranging in concentration from 2.5 pg/ $\mu\text{L}$  each of 2,3,7,8-TCDD and 2,3,7,8-TCDF up to 12.5 pg/ $\mu\text{L}$  each of OCDD and OCDF (standard CS-7, Table 2, Appendix B) as the first standard of each day. The standard analyzed at the end of the analysis day will be selected from the remaining five calibration standards.

#### 7.4.6 Control Charts

Control charts will be used to demonstrate the consistency of individual target analyte RRF values over time.

#### 7.4.7 Reagent Blanks

Reagent blanks will be analyzed to identify sources of background if PCDDs and PCDFs are detected in method blanks.

### 7.5 Performance and Systems Audits

#### 7.5.1 Performance Audits

An audit may be conducted by the DQAC prior to analysis, if the procedure or instrument has changed, if analytical problems are suspected, and when requested. The audit will consist of:

Table 7-1. Calibration/Internal Standards

| Calibration standard | Internal standards                        |   |
|----------------------|---|---|
|                      | Quantitation                              | Recovery                                |
| <u>PCDD</u>          |   |   |
| 2,3,7,8-TCDD         | $^{13}\text{C}_{12}$ -2,3,7,8-TCDD        | $^{13}\text{C}_{12}$ -1,2,3,4-TCDD      |
| 1,2,3,7,8-PeCDD      | $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD     |   |
| 1,2,3,6,7,8-HxCDD    | $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD   | $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD |
| 1,2,3,7,8,9-HxCDD    |   |   |
| 1,2,3,4,7,8-HxCDD    |   |   |
| 1,2,3,4,6,7,8-HpCDD  | $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD |   |
| OCDD                 | $^{13}\text{C}_{12}$ -OCDD                |   |
| <u>PCDF</u>          |   |   |
| 2,3,7,8-TCDF         | $^{13}\text{C}_{12}$ -2,3,7,8-TCDF        |   |
| 1,2,3,7,8-PeCDF      | $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF     |   |
| 2,3,4,7,8-PeCDF      |   |   |
| 1,2,3,4,7,8-HxCDF    | $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF   |   |
| 1,2,3,4,8,9-HxCDF    |   |   |
| 1,2,3,6,7,8-HxCDF    |   |   |
| 1,2,3,7,8,9-HxCDF    |   |   |
| 1,2,3,4,6,7,8-HpCDF  | $^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF |   |
| 1,2,3,4,7,8,9-HpCDF  |   |   |
| OCDF                 |   |   |

- Issuing at least one performance audit sample with the first sample batch to the HRGC/MS analyst. The HRGC/MS analyst will analyze the sample as received and will report the concentration of the sample to the DQAC. If the results are within 70 to 130% of the concentration submitted, the analysis of samples will proceed. If the results do not meet this criterion, the calibration curve must be reestablished and the analysis of a second performance audit sample must be successfully completed.
- Preparing and submitting a report of the audit results to the program manager, applicable section heads, and the department director.

#### 7.5.2 Systems Audits

An audit will be conducted a minimum of one time by the DQAC. The audit will, where appropriate, include:

- Reviewing actual practices versus the protocol and reporting deviations from protocol.
- Inspecting calibration and maintenance records.
- Inspecting QC practices.
- Preparing and submitting a report to the program manager, applicable section heads, and the department director.
- Reviewing the reports to determine if QA objectives were met.
- Tracing selected analytical data to verify the calculations and the analytical results.
- Conducting additional audits as directed by the program manager or department director.

## SECTION 8.0

### DATA REDUCTION AND ANALYSIS

#### 8.1 Collection

Data collection will utilize both manual and computerized acquisition systems. All activities will be legibly recorded using permanent ink in the project notebook or on worksheets. Each person who records data will sign and date each sheet. Strip charts, magnetic tapes, etc., will be labeled with a format identifier, project number, date, the ID(s) of the instrument, and the name of the person responsible for the data recording equipment. Custody of the original data media will be the responsibility of assigned project staff until archived.

#### 8.2 Data Reduction

Standard data reduction procedures with built-in checks will be used. For example, if an integrator or computer is used to calculate concentrations, the standards used to generate the curve must be back-calculated using the curve to ensure satisfactory curve-fitting over the anticipated range. In addition, all sample manipulations (e.g., weighing, dilution, concentrations, etc.) must be clearly documented. One example of data reduction for HRGC/MS includes:

- Searching for the target compounds of interest using a computer automated search routine.
- Visually inspecting the quantitation report from the search to ensure that the internal standard was found by the search routine.
- Determining the relative response factor (RRF) for each of the native PCDD and PCDF analytes to the designated internal quantitation standard by using:

$$RRF = \frac{A_{STD} \cdot C_{IS}}{A_{IS} \cdot C_{STD}}$$

where  $A_{STD}$  = the sum of the areas of the integrated ion abundances for the analyte in question. For example, for TCDD,  $A_{STD}$  would be the sum of the integrated ion abundances for  $m/z$  320 and 322;

$A_{IS}$  = the sum of the areas of the integrated ion abundances for the labeled PCDD/F used as the internal quantitation standard for the above analyte. For example, for  $^{13}C_{12}$ -2,3,7,8-TCDD,  $A_{IS}$  would be the sum of the integrated ion abundances for  $m/z$  332 and 334;

$C_{STD}$  = concentration of the analyte in  $pg/\mu L$ ; and

$C_{IS}$  = concentration of the internal quantitation standard in  $pg/\mu L$ .

- Determining the relative response factor for the internal quantitation standard ( $RRF_{IS}$ ) for the data obtained during the analysis of the concentration calibration standard by using:

$$RRF_{IS} = \frac{A_{IS} \times C_{RS}}{A_{RS} \times C_{IS}}$$

where  $A_{IS}$  and  $C_{IS}$  are defined as given above;

$C_{RS}$  = concentrations of the internal recovery standard in  $pg/\mu L$ ;  
and

$A_{RS}$  = the sum of the areas of the integrated ion abundances for the labeled PCDD ( $^{13}C_{12}$ -1,2,3,4-TCDD or  $^{13}C_{12}$ -1,2,3,7,8,9-HxCDD). For example, for  $^{13}C_{12}$ -1,2,3,4-TCDD,  $A_{RS}$  would be the sum of the integrated ion abundance for  $m/z$  332 and 334.

Refer to Table 11, Appendix B, for pairing of the internal quantitation standards with the appropriate internal recovery standard.

- Confirming that responses for characteristic ions of PCDDs and PCDFs meet the qualitative criteria based on ion ratios and relative retention time (RRT) for specific 2,3,7,8-substituted congeners.
- Calculating the amounts of the target compounds found in the extract using:

$$C_{sample} = \frac{A_{sample} \cdot Q_{IS} \cdot 100}{A_{IS} \cdot RRF \cdot W_{AT} \cdot LC}$$

where  $C_{sample}$  = the lipid-adjusted concentration of PCDD or PCDF congener in  $pg/g$ ;

$A_{\text{sample}}$  = sum of the integrated ion abundances determined for the PCDD/PCDF in question;

$A_{\text{IS}}$  = sum of the integrated ion abundances determined for the labeled PCDD/F used as the internal quantitation standard for the above analyte;

$Q_{\text{IS}}$  = the amount (total pg) of the labeled internal quantitation standard added to the sample prior to extraction;

RRF = relative response factor of the above analyte relative to its labeled internal quantitation standard determined from the initial triplicate calibration;

$W_{\text{AT}}$  = weight (g) of original sample; and

LC = percent extractable lipid.

Refer to Table 11, Appendix B, for pairing of target analytes with the appropriate internal quantitation standard.

### 8.3 Data Validation

The data validation process will include:

- Validating all equations and computer programs and documenting the validation.
- Confirming that raw areas for internal recovery standards and calibration standards are near the expected value.
- Validating and checking electronic data transfer.
- Verification of all manual data transfers, and 5% of electronic data transfers.
- Checking calculations.
- Reporting of all associated blank, standard, and QC data along with results for analyses of each batch of samples.
- Maintaining records of reviewing, proofing, and validation.
- Reviewing and approving all data by the project staff.
- Reporting protocol deviations and assumptions with the results.

#### 8.4 Storage

Raw data will be documented in laboratory notebooks, on printer paper, as strip chart recordings, or may be stored on magnetic tape or disk. All data will be archived according to the existing MRI SOP (QA-7, Records Management Procedures).

SECTION 9.0

DATA QUALITY ASSESSMENT

9.1 Precision

The data from the analysis of the food samples will provide measures of method precision. These data will result from analysis of replicate samples. Method precision can also be assessed for each PCDD or PCDF homolog for a specific sample batch from the absolute recoveries of the internal quantitation standards in each sample. These data can also be assessed to provide additional precision estimates for the entire analysis program.

The measurement for precision of the replicates (greater than 2) will be the standard deviation (S.D.) and/or the relative standard deviation (RSD):

$$S.D. = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n - 1}} \qquad RSD = \frac{100\% \times S.D.}{\bar{X}}$$

where n = number of replicate determinations;

X<sub>i</sub> = an individual data point; and

$$\bar{X} = \text{mean} = \frac{\sum_{i=1}^n X_i}{n}$$

9.2 Accuracy

9.2.1 Performance Audit Samples

The accuracy for the performance audit samples (if requested by the program manager) will be assessed as percent recovery (R) as demonstrated below.

$$R = \frac{\text{Amount Found}}{\text{Amount Prepared}} \times 100$$

9.2.2 Spiked Samples

Accuracy of the HRGC/MS-SIM method for each PCDD and PCDF congener will be determined by analyzing the spiked and unspiked samples with each batch of samples. The measurement of accuracy for each spiked congener will be percent recovery (R).

$$R = \frac{\text{Spiked Sample Value} - \text{Unspiked Sample Value}}{\text{Amount Spiked}} \times 100$$

9.3 Quality Assurance Objectives

The quality assurance objectives are summarized in Table 9-1.

Table 9-1. QC Procedures and Criteria Analysis of Human Adipose Tissue Samples for PCDDs and PCDFs

| Analysis event                                   | Frequency  | QC criteria  | Corrective actions  | Responsibility            |
|--|--|--|---|---------------------------|
| <u>Instrument mass calibration</u>               | Daily; real-time interpretation  | Must demonstrate accurate mass calibration using per-fluorokerosene (PFK). First activity of analysis day.   | Recalibration. If criteria not achieved, do not proceed with analysis.  | MS analyst                |
| • PCDD/PCDF analysis (low resolution MS)         | First event of analysis day  | Using PFK, tune to a minimum resolution of 3,000 (10% valley) and optimal response and peak shape m/z 381. Adjust magnetic field to pass m/z 300 at accelerating voltage. Introduce PFK through direct inlet and acquire accelerating voltage scans from 8000 to 4000 V using Inco's Data System. Lockmass (m/z 381) identified in PFK spectrum used to update. Mass calibration ranges from 301 to 593 amu. | Refer to tuning and mass calibration procedure (Section 8.1.1 in Appendix B). If criteria cannot be achieved, instrument may require maintenance.   | MS analyst                |
| • 2,3,7,8-TCDD confirmation (high resolution MS) | First and last events of analysis day  | Using PFK, tune to minimum resolution of 10,000 (10% valley) and optimal response for m/z 254.986.   | Refer to tuning and mass calibration procedure (Section 8.2.1 in Appendix B). If criteria cannot be achieved, instrument may require maintenance.   | MS analyst                |
| <u>Column performance check</u>                  | Daily; real-time interpretation  | Must demonstrate isomer specificity for 2,3,7,8-TCDD before proceeding with analysis of calibration standard<br>• 60-m DB-5 column, 30-60% resolution (Section 8.1.3, Appendix B)<br>• 50-m CP Sil 88/60-m SP-2330, $\leq$ 25% resolution (Section 8.2.3, Appendix B)  | Adjust column length and reanalyze performance mixture. If necessary, install a new HRGC column and evaluate performance.   | MS analyst                |
| <u>Calibration standards</u>                     |  |  |   |                           |
| • Initial calibration                            | Precedes initial sample analysis   | Triplicate analysis of six concentration calibration standards. % RSD of RRF for triplicate analyses $\pm$ 30% for PCDD/PCDF, $\pm$ 20% for TCDD/TCDF; % RSD of RRF for mean RRF for all standards $\pm$ 30% for PCDD/PCDF, $\pm$ 20% for TCDD/TCDF (Sections 8.1.4, 8.1.5, 8.2.4, and 8.2.5 (Appendix B)).  | Prepare fresh concentration calibration standard.   | MS analyst<br>task leader |
| • Routine calibration                            | Precedes sample analysis on daily basis. Also must demonstrate calibration injection as last analysis day. | Measured RRF values for solution CS-7 (Appendix B, Table 2) must be within $\pm$ 30% for PCDD/PCDF and $\pm$ 20% for TCDD/TCDF.  | Reanalyze solution CS-7 or repeat the initial calibration sequence. (Sections 8.1.6, 8.1.7, 8.2.6, and 8.2.7, Appendix B). If calibration criteria are not met at the end of the day, all samples are subject to reanalysis by HRGC/MS. | MS analyst<br>task leader |

Section No: 9.0  
 Revision No: 0  
 Date: 2/12/88  
 Page: 3 of 4

Table 9-1 (cont inued)

| Analysis event                            | Frequency   | QC criteria   | Corrective actions  | Responsibility                   |
|---|---|---|---|----------------------------------|
| <u>Tridecane blank</u>                    | Precedes sample analysis following calibration standards; real-time daily | Blank run should not demonstrate positive responses (> 2.5 times S/H) for the (Section 13.1.1, Appendix B).   | Clean injection syringe, repeat blank analysis.   | MS analyst                       |
| <u>Samples/QC samples</u>                 |   |   |   |                                  |
| • Analysis                                | As submitted in sample batch; real-time                                   | See Sections 13.1 and 13.2, Appendix B. Document response of internal recovery standard(s) and compare to daily calibration standard. Internal recovery standard responses must be within 50% of response noted for calibration. Standard used to verify RRF values. Samples submitted as blinds to MS analyst. | If internal recovery standard noted to be < 50% of calibration standard, reanalyze and/or check mass calibration. | MS analyst                       |
| • Data interpretation                     | Following analysis of sample batch  | See Sections 9.0 and 14.0, Appendix B.  |   |                                  |
| - Performance evaluation samples          | Real-time   | Check solutions provided by QAC for measurement of accuracy, 70-130%. Do not proceed with sample analysis until notified of acceptable performance by the QAC.  | Reanalyze solution and/or calibration standard(s).  | MS analyst<br>QAC<br>Task leader |
| - External (blind)/ Internal (QC samples) |   | Accuracy should be within 50-130% of spike level. Recovery of internal quantitation standards should be within 50-115%.   | Reanalyze solution and/or calibration standards.  | MS analyst<br>QAC<br>Task leader |
| - Tissue samples                          |   | Recovery of internal quantitation standards should be within 50-115%.   | Reanalyze solution and/or calibration standards.  | MS analyst<br>QAC<br>Task leader |

## SECTION 10.0

### CORRECTIVE ACTION

The program manager or appropriate task leader has primary responsibility for taking corrective action; if he is unavailable, the DQAC will be contacted for instructions. Any problems resulting in loss of data or data integrity will be reported to the program manager and DQAC. Some of the types of problems and corrective actions to be taken are listed below.

#### 10.1 System Audits and Performance Audits

If problems are detected during any audit:

- The DQAC will immediately notify the program manager or appropriate task leader of the problem(s) and any action(s) he has taken. Notification can be verbal, followed by an audit memo.
- The program manager or task leader and the DQAC will then collectively decide on the appropriate action. The program manager or task leader will implement the corrective action, then prepare and send a memo of the corrective action taken to the DQAC. If necessary, the department director will be involved in the discussion of needs for corrective action.
- The ARB project officer will be notified of any unresolved problems by the program manager prior to submission of any data package.

#### 10.2 Data Outside Control Limits

At any time the data fall outside previously designated limits, the following corrective action is applied:

- Where appropriate, samples should be reanalyzed to bring data into control limits. This may constitute reparation of the samples in the laboratory and then redetermination with the appropriate instrument, if sufficient sample is available, or simply redetermination of the sample extracts previously prepared.
- If data are marginal or other reasons prevent reanalysis, the MRI task leader or program manager will consult with the DQAC for other appropriate action. If data outside the control limits are to be reported, the reason for the action must be documented and the report carefully annotated.

- If data are consistently out of the control limits, corrective action should be taken by the appropriate staff and documented in the notebook. The DQAC will be notified of the corrective action by the program manager or appropriate task leader.

### 10.3 Loss of Data

The MRI program manager will investigate the problem, then perform one or more of the following actions:

- If the problem is correctable, the problem/action-taken is documented in the project records. If necessary, the program manager then prepares and sends a problem/action-taken memo to the DQAC. Corrective action may include reanalysis of samples.
- If the problem is not correctable, the MRI program manager will assess the impact of the data loss, notify the DQAC and the department director, and discuss it with the ARB project officer.

## SECTION 11.0

### DOCUMENTATION AND REPORTING

#### 11.0 Documentation

All manual documentation will be performed as follows: all information will be entered in a bound laboratory book or established forms. All information will be recorded using permanent ink.

Where signatures are required, the following information will be entered in project records: printed name, signature, and written initials. The traceable initials may be used in place of the signature.

Manual and computerized documentation will include the following:

- Project identifiers (project number, task number, etc.)
- Staff identifiers (signature, printed name, or traceable initials)
- Equipment identifiers (type/model/serial number/etc.)
- Computer program identifiers (name of program/revision date/author).
- Subject identifiers (type/number/code/etc.)
- Date (month/day/year)

Manual corrections of original data/information will be performed as follows: draw a line through the erroneous information, leaving the original information legible. Add the correct information, sign (traceable initials are permitted), and date the correction. Explain the correction; use codes if explained in project records. Some code examples are: EE (entry error--transposition error, wrong page used, etc.); CE (calculation error--used wrong numbers, wrong program, etc.); TE (transposition error). Do not superimpose numbers; use error handling instead.

Corrections in computerized records must be traceable (i.e., initials/date/reason). The original value must be retained in the records.

Manual additions to original data/information must be signed (or initialed) and dated.

### 11.2 Record Keeping

The following records will be maintained as a minimum requirement:

- Equipment/instrument calibration/maintenance records.
- All information related to the project: technical plans, QA plans, additional protocols, raw data, source of data, methods of computation, validation data, final data, deviations from protocol, reports, communications, etc.

### 11.3 Reporting

Sample analysis data will be reported to the ARB project officer on a batch basis. The sample batch data will include all QC results (recovery data, accuracy of spiked sample analyses, method precision, etc.). All data (standards and samples) will be archived such that verification of calculations can be accomplished for each analysis event. The analytical method describes the calculations required to achieve RRF values and final lipid-adjusted concentrations. The MRI program manager will be provided examples of raw data and calculations on request. The final report to ARB will contain a summary of all design sample analyses and cumulative QA/QC data.

\*00000975\*



**ASSET**