Ambient Concentrations of PCDDs/PCDFs in the South Coast Air Basin

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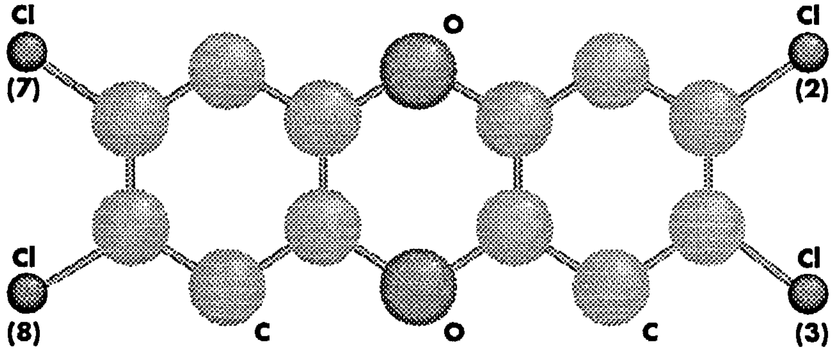

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IN MEMORIAM

This report is dedicated to the memory of Mr. Joseph Pantalone of the California Air Resources Board who served as the Program Manager of this research effort from the time of project inception in January 1987 until his untimely passing in 1988.

ACKNOWLEDGEMENT(S)

ENSR would like to extend a formal acknowledgement to the staff of the Research Division of the California Air Resources Board for their invaluable contributions and participation in this research effort. In particular, we would like to extend a note of thanks to the present Program Manager, Mr. Ralph Propper, and Mr. Joseph Pantalone, the former Program Manager to whom this report is dedicated. We would also like to formally express our appreciation to various members of the ARB Research Division staff who participated actively in the development and conduct of the field program, including Pat Randall, Tom Parker, Gary Yee, Gary Murcheson, Jack Paskind, John Batchelder, and Kitty Howard.

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for the review and validation of PCDDs/PCDFs analytical measurements provided by the subcontractor laboratory, ENSECO-CAL.

This report, entitled Ambient Concentrations of PCDDs/PCDFs in the South Coast Air Basin, was submitted in fullfillment of CARB Contract No. A6-100-32 by ENSR Consulting and Engineering (formerly ERT) under the sponsorship of the California Air Resources Board.

1. ABSTRACT

A comprehensive program of combined field sampling and laboratory analyses for selected isomers of PCDDs/PCDFs in the ambient atmosphere of the South Coast Air Basin has been completed. The program was conducted by ENSR Corporation, Acton, MA with the support of ENSECO-Cal Labs who conducted the analytical portion of the program. State-of-the-art sampling and analyses techniques (HRGC/HRMS) were employed to conduct a preliminary assessment of atmospheric burdens of PCDDs/PCDFs. The parameters of interest included fifteen PCDDs/PCDFs isomers of primary toxicological significance (2,3,7,8-substituted).

The monitoring network, comprised of eight stations, included a number of sites situated in primarily residental areas (San Bernardino, El Toro, and Reseda), as well as several sites in the vicinity of suspected sources of PCDDs/PCDFs (Cal Trans, Commerce, North Long Beach, West Long Beach).

Samples were collected via a regional network operated during each of four calendar quarters or seasons. A total of nine sampling sessions were completed during the calendar period of December 1987 to March 1989. Typically, 5 to 7 stations were in contemporaneous operation during a particular session. Sampling times were typically 24 hours in duration.

The highest concentrations of PCDDs/PCDFs congener class sums (Cl_4-Cl_8) and 2,3,7,8-substituted species were noted during a period predominated by off-shore air flows in December 1987, suggesting a regional air mass and transport phenomena. Concentrations of the PCDDs/PCDFs were diminished markedly in subsequent sessions where air flow patterns were primarily off-shore or of coastal origin. PCDDs/PCDFs congener profiles (Cl_4-Cl_8) and 2,3,7,8-substituted isomeric patterns strongly suggest combustion source influences in the majority of the sessions and samples examined. Ambient PCDDs/PCDFs concentrations expressed as toxic equivalent sums were the highest during the December 1987 session and lower thereafter.

The El Toro site, located south of Los Angeles, consistently showed the lowest measured PCDDs/PCDFs concentrations, as well as the lowest TEF weighted sum.

1,2,3,4,6,7,8-HpCDD was the most predominant 2,3,7,8-substituted species and most prevalent PCDD after OCDD. 2,3,7,8-TCDD was absent from almost all of the samples examined. Detection limits typically ranged from 10-20 fg/m^3.

2. SUMMARY AND CONCLUSIONS

2.1 Program Summary

A comprehensive program of field sampling and analyses for PCDDs/PCDFs isomers at selected sites in the South Coast Air Basin has been conducted. State-of-the-art sampling and analyses procedures were employed to determine atmospheric burdens of toxicologically significant PCDDs/PCDFs that presently persist in the South Coast Air Basin. This program represents a preliminary or initial baseline assessment of atmospheric burdens of PCDDs/PCDFs that presently exist at selected locations in the region. As a result of efforts conducted during Phase I of the program [23], high resolution gas chromatography in concert with high resolution or magnetic sector mass spectrometry (HRGC/HRMS) was selected as the preferred analytical method for the determination of trace concentrations of PCDDs/PCDFs in the atmosphere. This technique was recommended by ENSR in lieu of the low resolution or quadrupole mass spectrometry approach contained in the initial scope of work. This modification to the initial approach was primarily developed in response to the low or trace levels of PCDDs/PCDFs often present in the ambient atmosphere (10-20 fg/m^3). The selection of HRGC/HRMS as the method of choice was based upon the following:
1) comprehensive review of the open literature, 2) direct contact with other researchers actively involved in atmospheric measurement of PCDDs/PCDFs, 3) ENSR's (formerly ERT) direct experience in the conduct of numerous other programs (e.g., CT DEP) involving atmospheric measurements of trace concentrations of PCDDs/PCDFs.

The site selection process and network design was a collaborative effort involving ENSR and ARB. The resulting configuration included a number of sites in primarily residential areas such as San Bernardino, El Toro, and Reseda as well as a number of sites in regions believed to be influenced by one or more types of PCDDs/PCDFs source emissions categories. The latter included the selection of the Cal Trans site to assess the potential influences of automotive emissions, the Commerce site to assess the potential influences of an operational municipal solid waste incinerator and the West Long Beach and North Long Beach sites selected by the ARB on the basis of their proximity to a number of petroleum refineries.

Samples were collected via a regional network operated during each of four seasons or calendar quarters. It was believed that this approach more closely approximates an annualized average at each of the selected sites. Site specific meteorological data was collected at four of the sites employing an on site meteorological station deployed and maintained by personnel of the South Coast Air Quality Management District (SCAQMD). Air flow analysis data for six of nine sampling sessions were provided by the California Air Resources Board.

A total of nine (9) sampling sessions were conducted during the calendar period of December 1987 to March 1989. Samples from seven (7) of these sessions were selected for PCDDs/PCDFs analyses with the concurrence of the ARB. The first two (2) sampling sessions conducted in December of 1987 were approximately 36 hours in duration while the remaining seven (7) sessions were approximately 24 hours in duration. Four of the nine (9) sessions were operated midnite to midnite coincident with the EPA NASN six-day sampling schedule for TSP measurements. The results of the ambient monitoring program are contained in Section 11 and Appendices C, D and E of this report. The corresponding discussion of these data are contained in Section 12. Specific observations and conclusions derived from the results and discussion contained herein follows.

2.2 Conclusions and Observations

1. The highest ambient concentrations of PCDDs/PCDFs were noted during the December 1987 Winter sampling session (Session 1). This includes the highest concentrations of the 2,3,7,8-substituted target parameters of primary toxicological significance as well as the PCDDs/PCDFs congener class sums (Cl_4-Cl_8).
2. The highest average atmospheric burden of PCDDs/PCDFs expressed in units of pg/m^3 of toxic equivalents was noted during the December 1987 winter sampling session (0.669 pg/m^3). The average TEF contribution resulting from measured values was also the greatest during this session (0.598 pg/m^3 of 0.669 pg/m^3 total).
3. Meteorological conditions during the December 1987 sampling session indicate primarily off-shore air flows. This in conjunction with the influences of land borne combustion source influences may have given rise to the elevated concentrations of PCDDs/PCDFs observed across the regional network during this session.
4. PCDDs/PCDFs congener profiles in evidence during Session 1 as well as several other sessions strongly suggest that combustion sources are the major contributing factor to atmospheric burdens of PCDDs/PCDFs throughout much of the South Coast Air Basin.
5. PCDDs/PCDFs congener profiles and their relative intensities were nearly equivalent at a number of the sites in the network operating contemporaneously during the December 1987 session with the exception of the El Toro site. This suggests a regional air mass phenomena with combustion sources as the major contributing factor to ambient PCDDs/PCDFs burdens.

6. The combined sampling and analyses program described herein represents a sound preliminary assessment of the atmospheric burdens of PCDDs/PCDFs and in particular isomers of toxicologial significance that presently exist in the South Coast Air Basin. Accordingly, it suitably satisfies the primary objective of this research effort which was to determine baseline ambient concentration of PCDDs/PCDFs in the South Coast Air Basin particularly in areas of high population density. Continued sampling and analyses efforts may be warranted at these and other locations to establish the "true" representativeness of the existing data base. Particular attention must be focused on monitoring at all sites during a variety of atmospheric and meteorological conditions so as to provide truly annualized values for each location.
7. The majority of the atmospheric burdens of PCDDs/PCDF in the South Coast Air Basin are represented by non 2,3,7,8-substituted species; (not of toxicological significance as defined by the California Department of Health Services).
8. During periods of continued offshore air flow (e.g. air flow from inland areas) and/or stable meteolorological conditions, the atmospheric concentrations of 2,3,7,8-substituted PCDDs/PCDFs can be quite significant, approaching concentrations typically observed in wintertime in urban areas in the northeast or midwest U.S.
9. Congener profiles during a number of the sampling sessions are similar to those associated with either stationary or vehicular combustion sources. For example, ambient concentrations for each of the Cl_4-Cl_8 PCDFs congener classes were observed to increase with increasing chlorine substitution ($Cl_4 < Cl_5 < Cl_6 < Cl_7$).

10. Average PCDDs/PCDFs concentrations for all sessions with the exception of the December 1987 campaign (Session 1) represent values typically found in other U.S. urban and suburban locations.
11. 1,2,3,4,6,7,8-HpCDD is the most predominant PCDD (not including OCDD) and the most predominant 2,3,7,8 - substituted species of toxicolgical significance in all of the samples examined. Concentrations ranged from 0.11 pg/m^3 to a maximum value of 8.4 pg/m^3. The ubiquitous nature of this isomer is coincident with the influence of combustion source emissions.
12. 2,3,7,8-substituted HxCDDs persisted only in six samples, the majority of which were collected during the Winter 1987 session. The 1,2,3,7,8,9-HxCDD and the 1,2,3,6,7,8-HxCDD predominate over the 1,2,3,4,7,8-HxCDD. Other investigators typically report the 1,2,3,7,8,9-HxCDD to be the predominant HxCDD isomer of toxicological significance in the atmosphere.
13. 1,2,3,7,8-PeCDD was noted in only two samples analyzed, both of which were collected during the Winter 1987 session (0.12 pg/m^3 at Commerce and 0.19 pg/m^3 at Reseda).
14. TCDDs and in particular 2,3,7,8-TCDD are virtually non-existent in the South Coast Air Basin. 2,3,7,8-TCDD was confirmed in only two samples, both of which were collected during the Spring 1989 session (8.6 fg/m^3 at W. Long Beach and 34 fg/m^3 at the Cal Trans site). Detection limits for the majority of the samples ranged from 10-20 fg/m^3. The lower and upper detection limit boundaries were 4 fg/m^3 and 51 fg/m^3, respectively.
15. Vapor/particle partitioning data operationally defined by the sampling system were collected on two samples. These data suggest that the majority of the HxCDD, HpCDD and OCDD as well as the HxCDF, HpCDF and

OCDF are primarily particulate associated under ambient temperatures characteristic of Southern California. Conversely, TCDFs and PeCDFs are primarily partitioned in the vapor phase. No firm conclusions can be drawn about the vapor/particle partitioning of TCDD and PeCDD which were undetected in the two samples examined. We can hypothesize, however, that the TCDD, and in particular the 2,3,7,8-TCDD, will also be primarly vapor partitioned in the atmosphere owing to the observations and theoretical considerations of Hites and his co-workers [40, 41]. The predominant vapor partitioning of 2,3,7,8-TCDD occurrence may promote photochemical degradation of this isomer and account in part for its virtual absence in the atmosphere in Southern California.

16. The 2,3,7,8-PCDFs profile is predominated by 1,2,3,4,6,7,8-HpCDF (0.038 pg/m^3 to 1.58 pg/m^3) and 2,3,7,8-TCDF (0.011 pg/m^3 to 0.48 pg/m^3). 1,2,3,4,7,8,9-HpCDF is virtually non-existent in the samples examined. HpCDF was consistently present in higher concentrations than TCDF (10:1 ratio).
17. The highest concentrations of 2,3,7,8-PCDFs as well as the most diverse profile (Cl_4-Cl_8) were measured across the entire network during the December 1987 session. The profiles noted during this session are indicative of combustion sources in conjunction with the influences of regional air transport.
18. Both 2,3,7,8-substituted PeCDFs, when measured, were present in nearly equivalent concentrations.
19. 2,3,7,8-substituted HxCDF isomers were measured only during the December 1987 session. The predominant isomer was the 1,2,3,6,7,8-HxCDF (0.25 pg/m^3 at El Toro to 0.80 pg/m^3 at Reseda). 1,2,3,7,8,9-HxCDF

was not observed in any of these same samples. The remaining two 2,3,7,8-substituted HxCDF isomers were present in nearly equivalent concentrations.

20. The 2,3,7,8-substituted HxCDF profile noted during this program differs from that noted typically in the literature. In the majority of studies cited herein the three 2,3,7,8-substituted HxCDF isomers (1,2,3,7,8,9-HxCDF not present) contribute equally to the total HxCDF concentration. In the present study, the 1,2,3,6,7,8-HxCDF always appears at 2-3 times the levels noted for the remaining two. This may provide an exploratory path to addres the mix of source contributions in the South Coast region in future studies.

21. While PCDDs/PCDFs and their congener profiles serve as a good indicator of combustion source influences they are not as valuable in identifying specific emission categories or in source apportionment. Parameters more unique to a particular source category (vehicular or stationary) and/or more stable atmospheric surrogates are suggested for this purpose (metals, combustion gases etc.). An alternative for PCDDs/PCDFs would be to adopt a more sophisticated analytical technique employing high resolution gas chromatography/high resolution mass spectrometry in concert with a full array, of individual PCDDs/PCDFs isomers. The chromatographic resolution of the 38 possible TCDF positional isomers employing a full complement of calibration standards for instance would provide a more powerful tool for source discrimination (see Rappe Reference 14).

22. Confident measurement of TEF sums of less than 0.10-0.20 pg/m^3 is generally not achievable owing to limitations in sensitivity of the sample collection and analyses procedures.

23. TEF weighted sums for the majority of the samples examined were most strongly influenced by the contribution of the 2,3,7,8-TCDF isomer. This is attributable to 1) its ubiquitous nature, 2) its predominance in combustion source emissions, and 3) TEF weighting factor of 1.0.

24. The lowest ambient concentrations of PCDDs/PCDFs expressed as TEF weighted sums were observed at the El Toro site. The average contribution of the detected portion was 0.059 pg/m^3 for the seven samples examined.

25. Ambient concentrations of PCDDs/PCDFs and measured TEF weighted sums were markedly lower for sessions 3,4 and 5 in comparison to the December 1987 winter session (Session 1). On-shore air flow patterns which persisted during much of sessions 3, 4 and 5 may be a major contributing factor to the apparently diluted ambient concentrations.

26. Vehicular emissions are a likely source of elevated PCDDs/PCDFs levels noted at the Cal Trans site during sessions 5 and 7. The congener profile mimics a traditional combustion source profile. Confirmation of a vehicular contribution cannot be made, however, since conclusive evidence cannot be provided by examination of the congener profile currently available from these samples (see item 21 in this section).

27. From the entire population of eight sites, the highest site average for detected toxic equivalents was 0.552 pg/m^3 for the Commerce site (n=1). Of the seven remaining sites the highest site average for detected toxic equivalents was the San Bernardino site (n=5).

3. RECOMMENDATIONS

Recommendations are offered here on the basis of our experience in the conduct of the recently completed program. These include recommendations for future research as well as suggested improvements or modifications for incorporation into a continuation of this or another similar monitoring effort.

1. While it is our belief that the recently completed program represents a sound preliminary assessment of the atmospheric burdens of PCDDs/PCDFs in the South Coast Air Basin, further measurements are warranted. Some determination of the representativeness of the present data base needs to be made particularly as it applies to meteorology. If it can be determined that the meteorological conditions that most directly influence atmospheric concentrations of combustion by-products (e.g., PCDDs/PCDFs), as well as their transport and fate on an annualized basis were not truly representative during the present program then additional measurements are warranted.

2. Based upon the outcome of Item 1 a more extensive sampling and analyses program may be warranted to establish truly representative atmospheric concentrations of PCDDs/PCDFs and ultimately existing population exposures. More frequent sampling sessions may be necessary and under a wider variety or cross-section of meteorological conditions (e.g., stability classes).

3. Further examination of the sources of PCDDs/PCDFs and their relative contributions to atmospheric burdens in the South Coast Air Basin is needed. This may consist of an examination of emission inventory data for potential sources of PCDDs/PCDFs, as well as some dispersion modeling to estimate ambient concentrations. A mechanism to compare these estimated values to the measured ambient values on a semi-quantitative basis is needed.

4. Collocated parameters and/or surrogates for specific combustion source categories should be taken into consideration in the design of future ambient PCDDs/PCDFs measurement programs. Due to the predominant particle association of the majority of PCDDs/PCDFs congeners suggested collocated parameters might include TSP or PM_{10} measurements. Other combustion source surrogates include NO_x, CO, etc. Metals speciation via x-ray diffraction can also

provide a useful tool in "fingerprinting" specific types of combustion source particulates. Collocated parameters measured concurrently with PCDDs/PCDFs may also provide a means to derive a quantitative relationship between the two parameters (eg. TSP and PCDDs/PCDFs) and eventually a relaxation in the frequency and expense of the PCDDs/PCDFs measurements.

5. Further sampling programs should contain sites in the vicinity of other known or potential sources of PCDDs/PCDFs. These might include hospital waste incinerators, wire reclamation incinerators, and hazardous waste incinerators [23].

6. Selection of sites in future monitoring efforts, in particular those vicinal to stationary combustion sources, should make formal use of dispersion modeling. Historical review of ambient measurements that serve as surrogate parameters for combustion sources should also be explored. This data, if available (NO_x, PAH, etc.), might be valuable in the selection of candidate monitoring sites for PCDDs/PCDFs measurements.

7. Additional samples should be collected during periods in which off-shore air flows predominate. These conditions are indicative of air transport from inland areas towards the Pacific coast.

8. Further ascertain what contributions automobile emissions may have on atmospheric concentrations of PCDDs/PCDFs in the South Coast region. Alternatives to this end include more extensive field monitoring in locations where automobile emissions predominate (e.g., tunnel study), as well as in the vicinity of high-volume traffic. The ARB may want to consider the use of more sophisticated PCDDs/PCDFs isomer discrimination techniques as a means to identify a nearly unique vehicular source profile. An alternative again may be the selection of an appropriate surrogate parameter more indicative of various types of vehicular emissions (eg. diesel, automotive etc).

9. Incorporate background ambient monitoring site(s) into future measurement programs. A remote monitor or marine island location may be suitable. Perhaps collect some multimedia samples (e.g., soils, sediments, vegetation) that may serve as recipients of atmospheric particulate deposition. This will provide a better "picture" of transport to such a remote area.

10. If PCDDs/PCDFs levels found throughout much of the recent program are truly representative of ambient concentrations in the South Coast Air Basin on an annualized basis, then the ARB should explore paths to enhance the sensitivity of the measurement technique (<10 fg/m^3). This would result in a larger population of measured values in particular for the 2,3,7,8-substituted PCDDs/PCDFs. This, in turn, would lead to a greater number of detected TEF values and TEF sums. It is our recommendation that this be accomplished by use of one or more of the following: (1) collect larger sample volumes over the prescribed 24-hour sampling period (modify existing PS-1 samplers); (2) extend sampling period to 48-72 hours; and (3) enhance analytical sensitivity to 1-5 pg/sample.

4. INTRODUCTION

4.1 Project Background/Overview

The California Air Resources Board (ARB) has designated certain chlorinated dibenzofurans and dibenzodioxins to be toxic air contaminants subject to review and possible regulation in accordance with AB 1807 (Section 39650, et seq. of the California Health and Safety Code; Assembly bill 1807, Tanner, 1983). In response, the ARB has identified a requisite for the collection of background data to determine existing population exposures, as well as establish a "baseline" database of PCDD/PCDF concentrations in ambient air in the South Coast Air Basin. It is anticipated that such a database will be suitable for the assessment of what impacts, if any, the addition of selected combustion sources to the South Coast Air Basin will have on existing concentrations of PCDDs/PCDFs.

As a result, ENSR Consulting and Engineering (formerly ERT) was retained by ARB to conduct a "Study of Ambient Concentrations of Chlorinated Dibenzodioxins and Dibenzofurans in Urban Areas of the South Coast Air Basin." The purpose of this project was to determine baseline qualitative and quantitative data on the concentrations of certain chlorinated dioxins and furans in ambient air. The specific components of interest include those isomers (Cl_4-Cl_7) of polychlorinated dibenzodioxins and polychlorinated dibenzofurans that are chlorine substituted at the 2, 3, 7, 8 positions. This listing includes the 15 congeners shown in Table 4-1.

4.2 Program Purpose and Objectives

The primary purpose of the program was to determine existing or baseline ambient concentration of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (particularly 2, 3, 7, 8 substituted species) in the South Coast Air Basin.

TABLE 4-1

LISTING OF PCDD/PCDF ISOMERS SELECTED FOR SAMPLING AND ANALYSIS IN THE SOUTH COAST AIR BASIN

PCDD Isomers	PCDF Isomers
2,3,7,8 TCDD	2,3,7,8 TCDF
1,2,3,7,8 PeCDD	1,2,3,7,8 PeCDF
1,2,3,6,7,8 HxCDD	2,3,4,7,8 PeCDF
1,2,3,7,8,9 HxCDD	1,2,3,6,7,8 HxCDF
1,2,3,4,7,8 HxCDD	1,2,3,7,8,9 HxCDF
1,2,3,4,6,7,8 HpCDD	1,2,3,4,7,8 HxCDF
OCDD[a]	2,3,4,6,7,8 HxCDF
Total TCDDs	1,2,3,4,6,7,8 HpCDF
Total PeCDDs	1,2,3,4,7,8,9 HpCDF
Total HxCDDs	OCDF[a]
Total HpCDDs	Total TCDFs
	Total PeCDFs
	Total HxCDFs
	Total HpCDFs

[a] OCDD and OCDF added to target parameter list following completion of Session 2.

Samples were collected primarily in regions of high population density that contained potential sources of PCDDs/PCDFs. It was anticipated that this exercise would allow for an assessment of the incremental risks from PCDDs/PCDFs exposure associated with the addition of sources to the region.

Specific program objectives included the following:

- Determine, through a program of field sampling and laboratory analysis, the ambient concentrations of chlorinated dioxins and furans in the South Coast Air Basin, with particular attention to the following: 1) areas of high population density, 2) areas where selected types of incinerators and combustion sources are located which presently burn chlorine containing wastes and may give rise to PCDDs/PCDFs, and 3) areas in which such incinerators are proposed for the future.
- It is anticipated that the data obtained through this study will be used by ARB and others for both health assessment purposes and to compare current concentrations with future measurements.

4.3 Report Organization

The document to follow constitutes the Final Report for this program and contains the results of all Phase II activities. In accordance with Final Report format requirements put forth by ARB for research contracts and those of the National Technical Information Services (NTIS) as contained in "Guidelines to Format Standards for Scientific and Technical Reports", the report has been organized as follows:

- Section 1 - Abstract
- Section 2 - Summary and Conclusions
- Section 3 - Recommendations for Further Study

- Section 5 - Monitoring program design and sampling strategy. This includes a description of the site selection process as well as a site summary listing, including descriptions and exact locations of the sites actually used.
- Section 6 - Field Sampling Program. Contains a description of the sample collection procedures employed as well as field notes pertinent to each of the ambient monitoring sessions.
- Section 7 - Meteorological Monitoring. Provides meteorological data summaries for each of the sampling sessions employing data provided by the South Coast Air Quality Management District (SCAQMD).
- Section 8 - Evaluation criteria for the selection of field samples for analyses.
- Section 9 - Analytical Procedures. Including a detailed description of the High Resolution/Gas Chromatography/High Resolution Mass Spectrometry Procedures (HRGC/HRMS) employed.
- Section 10 - Quality Assurance/Quality Control
- Section 11 - Results. Contains ambient PCDDs/PCDFs data (pg/m^3) provided on a site specific basis. Site specific presentations of data as well as toxic equivalency sums using ARB weighting factors are also provided.
- Section 12 - Discussion of Results. Site specific and seasonal specific trends are examined. Site by site comparisons within a given sampling session are also examined. Available particle/vapor distribution data are discussed, as well as comparisons of program data to ambient concentrations available from the open literature and other ENSR PCDDs/PCDFs measurement programs.
- Section 13 - References
- Section 14 - Supplementary Bibliography
- Section 15 - Glossary of Terms

5. MONITORING PROGRAM DESIGN/SAMPLING STRATEGY

5.1 Overview

The monitoring program implemented for measuring background ambient levels of PCDDs/PCDFs in the South Coast Air Basin was developed through consideration of site selection procedures, sampler placement criteria, collection system characteristics, and sampling duration and frequency requirements. The site selection process, in particular, plays a critical role in the development of a viable air monitoring program. Sites were selected to ensure the accurate assessment of existing ambient dioxin/furan levels in the area surrounding a particular site.

After a site has been properly chosen using primary selection criteria (Section 5.2), consideration must be given to sampler placement at the site (secondary selection criteria, Section 5.3). Each sampler must be exposed to unrestricted airflow and therefore must be situated away from potential airflow obstructions such as buildings or trees. Site locations and sampler placement are described in Section 5.4.

5.2 Site Selection Process - Primary Considerations

The Phase I Summary Report issued by ENSR (formerly ERT) in July 1987 identified several criteria for selecting ambient monitoring sites commensurate with program objectives. These criteria focused on:

- area sources;
- combustion sources;
- population exposure; and
- background (urban, rural, marine).

Specifically, sites were selected in regions which satisfied one or more of the following criteria:

- Sites within geographical areas or regions which contained a concentration of combustion sources and area sources identified as potential emission sources of PCDDs/PCDFs.
- Sites within geographical areas or regions with high population density which also contained a concentration of potential PCDDs/PCDFs emission sources.
- Sites within geographical areas or regions of high population density which did not contain known PCDDs/PCDFs emission sources but in which a known number of these sources are proposed for location in the near future.
- Background (Urban) - Sites within geographical areas or regions with high population density which did not contain potential PCDDs/PCDFs emission sources.
- Background (Rural) - Sites within geographical areas or regions with low population density and no known or potential sources of PCDDs/PCDFs emissions.
- Background (Marine) - Sites situated offshore west of the mainland of the South Coast Air Basin with little or no population and no clearly identifiable potential PCDDs/PCDFs emissions sources. It was anticipated that such a site or sites would provide an indication of "true" ambient baseline and perhaps an indication of global concentrations of PCDDs/PCDFs that can be expected in a near "pristine" environment.

Further details on each of these primary siting criteria are provided in the discussion to follow.

Area Sources

Potential PCDDs/PCDFs area sources include hazardous waste sites, landfills (particularly those known to contain PCDDs/PCDFs-containing wastes or chlorinated precursors), wood treating facilities, agricultural burning, pesticide formulating operations and automobile emissions. South Coast locations of several area source categories are contained in the Phase I Summary Report [23].

Combustion Sources

Major potential combustion sources of PCDDs/PCDFs include hazardous waste incinerators, refuse-to-energy plants, sewage sludge incinerators, hospital incinerators, and wire reclamation operations. Locations of proposed and existing resource recovery facilities, hazardous waste incinerators, waste-to-energy projects, sludge incinerators, and biomass-to-energy facilities in the South Coast Air Basin and the locations of known hospital incinerators and wire reclamation incinerators are contained in the Phase I Summary Report [23].

Population Density

One of the main objectives of this sampling and analysis program was to assess the exposure of segments of the general population of the South Coast Air Basin to concentrations of PCDDs/PCDFs in the atmosphere. As such, site selection made use of population density data. South Coast population density data contained in the Phase I Summary Report was instrumental in the evaluation and selection of "candidate" monitoring sites.

Background Sites

It is ENSR's belief that background or "baseline" data is an integral component of any ambient monitoring program as it provides a basis to assess what impact, if any, potential PCDDs/PCDFs emission sources presently have on air quality in the affected region(s). Additionally, such data provides a statistical basis for future data comparisons in assessing the incremental impacts attributable to the addition of new sources to a particular region at a future date.

In accordance with the site selection criteria offered earlier, background sites should represent, to the extent possible, each of three source classifications; namely rural, urban, and marine. Actual monitors can be placed within each region out of areas impacted by existing point sources or fugitive emission area sources.

5.3 Site Selection Process - Secondary Requirements

5.3.1 Sampler Siting Requirements

After choosing preliminary monitoring sites based on the primary categories identified in the previous section, the actual PUF sampler siting was accomplished using criteria established for siting Total Suspended Particulate (TSP) samplers. The application of TSP sampler siting criteria to the siting of PUF samplers is practical because of the similar atmospheric behavior expected for both suspended particulates and ambient dioxins/furans. Also, strong evidence exists demonstrating the tendency of selected PCDDs/PCDFs to occur as constituents of suspended particulate matter particularly during colder times of the year. Therefore, mechanisms which may interfere with the collection of TSP may also interfere with the collection of PCDDs/PCDFs.

Table 5-1 summarizes the criteria for TSP monitor siting as described in EPA-450/4-80-012, Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD).

5.3.2 Practical Considerations

To insure representative results, each site must be reasonably secure from possible tampering. This is accomplished by placing PUF samplers away from crowded areas and inside a fenced or contained area. In addition, each site

TABLE 5-1
SITING CRITERIA

Siting Characteristic	Spacing Requirements
Height of sampler inlet above ground	2-15 meters
Distance of sampler from trees	>20 meters
Distance from sampler to obstacle	At least twice the height obstacle protrudes above sampler
Unrestricted airflow	270° arc of unrestricted space around sampler
Roof placement	>2 meters from any wall, parapet, penthouse, etc., and no nearby flues that may significantly impact sampling

must be accessible for a reasonable length of time each day to allow the field team to efficiently conduct the monitoring program. Electrical power requirements of the PUF samplers necessitate the availability of 110 VAC, 20 AMPs, at each sampling site.

5.3.3 Separation from Local Interferences

Locations which may have been affected by the use of herbicides, pesticides, and selected chlorinated compounds (e.g. chlorinated phenols and benzenes) should be avoided because these kinds of compounds may bias the measurements of existing background PCDD/PCDF levels. Herbicides and pesticides may be composed of chlorinated compounds which contain dioxins/furans or their chemical percursors. Common areas of herbicide/pesticide application include lawns, parks and power line right-of-ways. Precautions also must be taken to insure that sampling stations are not situated atop or in the immediate vicinity of pressure treated wood products which may be impregnated with chlorinated phenolics.

5.4 Candidate Monitoring Sites

As part of the Phase I portion of this program, eleven "candidate" monitoring sites, listed in Table 5-2 were initially selected based on the primary and secondary selection criteria detailed in the proceeding subsections of this document. These criteria included combustion and area source locations, population density data, and practical considerations including power and security availability and availability of local meteorological data. Final monitoring sites actually used in the program were selected by ARB staff and are described in Section 5.5.

TABLE 5-2

"CANDIDATE" MONITORING SITE LOCATIONS - SOUTH COAST AIR BASIN

SITE	ADDRESS	SCAQS PARTICIPANT	PRIMARY CRITERIA COMBUSTION SOURCE	AREA SOURCE	POPULATION EXPOSURE	URBAN BACKGROUND	RURAL BACKGROUND	MARINE BACKGROUND	SECONDARY CRITERIA POWER AVAILABLE	SECURITY AVAILABLE	METEORLOGICAL DATA AVAILABLE	COMMENTS
ANAHEIM	1010 S. HARBOR BLVD.	YES		X	X				X	X	X	
BURBANK	288 WEST PALM AVE.	YES			X	X			X	X	X	
BURBANK	272 E. OLIVE AVE.	NO			X	X			X	X	X	SPECIAL SCAQMD AIR TOXICS PROGRAM
AZUZA	803 N. LOREN AVE.	YES	X	X					X	X	X	
HAWTHORNE	5234 W. 120TH ST.	YES	X	X					X	X	X	
EL MONTE	9528 TELSTAR AVE.	NO		X	X				X	X	X	TEMPORARY STATION OPERATED BY CARB
LOS ANGELES	1630 N. MAIN ST.	YES	X	X	X				X	X	X	
LOS ANGELES	430 E. 7TH ST.	NO	X	X	X				X	X	X	SPECIAL SCAQMD AIR TOXICS PROGRAM
LONG BEACH	LONG BEACH CITY COLLEGE	YES	X	X	X				X	X	X	
POMONA	POMONA COLLEGE	YES	X	X					X	X	X	
IRVINE	15029 SAND CANYON	NO					X		X	X	X	SPECIAL SCAQMD AIR TOXICS PROGRAM
RIVERSIDE	5888 MISSION ST., RUBIDOUX	YES		X					X	X	X	
SAN NICHOLAS IS.		YES						X	X	X	X	

5.5 Actual Monitoring Sites

5.5.1 Site Identification

Based on the groundwork for primary site selection, as described in Section 5.1, the following five sites were initially selected for the Phase II monitoring program.

- Reseda - Site located in a primarily residential area so as to provide a measure of urban population exposure.
- El Toro - Selected to serve in same manner as Reseda site.
- San Bernardino - Selected to serve in same manner as Reseda and El Toro sites.
- Commerce - The Commerce Resource Recovery Facility is located here. A site located in the vicinity of the facility was selected to assess existing population exposure potentially related to emissions from the Commerce facility.
- North Long Beach - The Long Beach area was targeted by ARB as a region potentially impacted from oil industry activity.

During the course of the program, additional sites were incorporated into the monitoring network. These included:

- Cal Trans - Located at the interchange of Interstate 5 and California State Highway 2. This site was selected to assess potential impacts from mobile sources (e.g., automobiles).

- Carson - ARB staff recommended use of this Long Beach area site because of its proximity to the nearby Shell and Exxon Oil Refineries.

- West Long Beach - ARB staff also recommended use of this Long Beach area site because of its proximity to the nearby ARCO Oil Refinery.

A final site, located at Cedars-Sinai Medical Center, was proposed to assess ambient background PCDDs/PCDFs levels in the vicinity of a hospital waste incinerator. Site acquisition problems prevented use of this proposed monitoring location during the program. ENSR recommends that future ambient monitoring programs be designed to assess impacts of hospital waste incinerators on ambient PCDDs/PCDFs levels by selection of monitoring locations nearby an operational hospital waste incinerator (such as Cedars-Sinai).

5.5.2 Site Descriptions

W. Long Beach - Site located on property owned by the Westside Church of the Nazarene and leased by The Learning Institute, a combination elementary school and day care center. No potential localized PCDDs/PCDFs interferences were noted at this site. The sampler was placed on the roof of the school building (~4 meters above the street level) toward the front near Santa Fe Avenue. The building is located in a mostly residential area. Santa Fe Avenue is a main thoroughfare, four lanes in width, with average daily traffic estimated at 2,500 to 3,000 vehicles.

Carson - Site located at the Gas Appliance Company, which is involved in the manufacture of commercial gas cooking equipment. The building is located in a light industrial area. The sampler was located at the back of the building on the roof (~7 meters above street level). Across the street to the east of the building there is a facility that grinds wood chips into a mulch mixture. This facility generates some airborne sawdust during the regular work day, although there is a sprinkling system in use to keep the dust at a minimum. The only other potential interference noted was the occasional painting of some of the fixtures at the Gas Appliance Company. Any painting would be halted during the week of the sampling sessions.

<u>Reseda</u> - Site located at existing SCAQMD site in Reseda. The sampler was situated on the roof of the building (~4 meters above street level) toward the front near Gault Road. The building is located in a mostly residential area, several blocks east of Reseda Blvd. No potential localized PCDDs/PCDFs interferences were noted at this site.

<u>San Bernardino</u> - Site located at existing SCAQMD site in San Bernardino. The sampler was located at ground level (sampler intake ~ 1 meter above ground level). The area immediately surrounding the site was lightly residential with open field areas nearby.

<u>El Toro</u> - Site located at an existing SCAQMD site. The sampler was situated at ground level (sampler intake approximately 1 meter above ground level). The site abutted a fire station and was situated approximately 30 feet from the street. The area surrounding the site was primarily residential.

<u>Cal Trans</u> - Site located at the intersection of Interstate 5 and California State Highway 2 at a Cal Trans operations center. The sampler was located atop a one-story building in the center of the property. The area immediately surrounding the site contained on and off ramps for the I-5/Route 2 interchange.

Commerce - The Commerce monitoring site was located in a large, maintained, grassy lot south of the Commerce National Bank near the intersection of Washington Boulevard and Fidelia Streets. Washington Boulevard is directly southwest of the monitoring site. The Santa Ana Freeway is located approximately 800 feet to the northeast. There are buildings and trees 10 to 25 feet tall located within 100 feet to the west and north. Larger trees and one-story buildings are located within 150 to 250 feet to the west. Washington Boulevard and the Santa Ana Freeway were noted to be heavily traveled thoroughfares.

North Long Beach - Site located at existing SCAQMD site in Long Beach. The sampler was situated on the roof of the building (~ 4 meters above street level) toward the front near Long Beach Blvd. The building is located in a business district bordering on a residential area. The site is located approximately 1 mile north of Interstate 405.

5.5.3 Site Locations

Figure 5-1 shows the eight site locations utilized in the program and selected based on the criteria discussed in Sections 5.2 and 5.3. Table 5-3 lists the addresses and other pertinent information pertaining to each site.

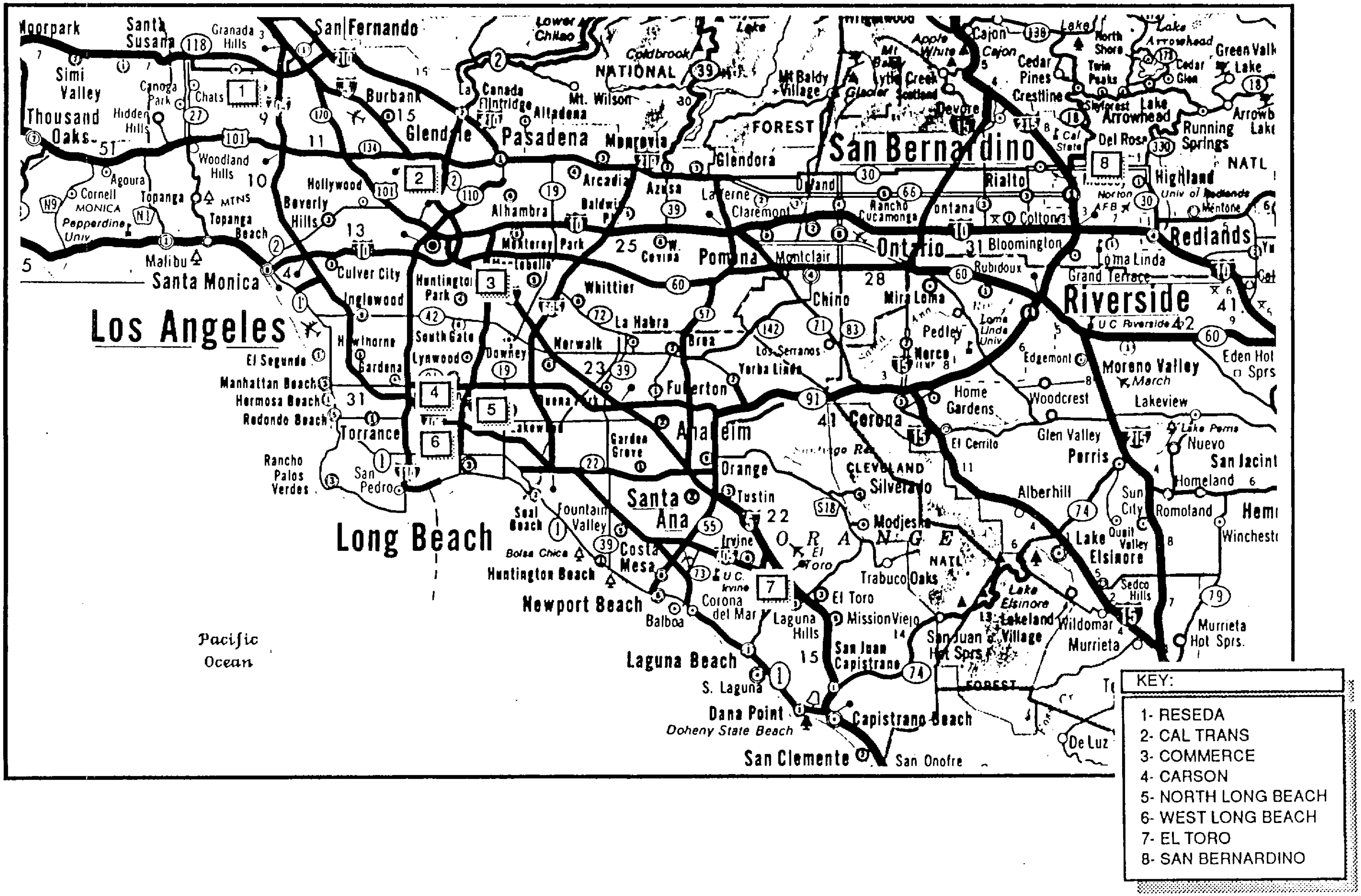

KEY:
1- RESEDA
2- CAL TRANS
3- COMMERCE
4- CARSON
5- NORTH LONG BEACH
6- WEST LONG BEACH
7- EL TORO
8- SAN BERNARDINO
Los Angeles
Long Beach
San Bernardino
Riverside
Santa Ana
Anaheim
Pasadena
Glendale
Burbank
San Fernando
Santa Monica
Torrance
Pomona
Ontario
Redlands
Corona
Newport Beach
Laguna Beach
San Clemente
Lake Elsinore
Pacific Ocean

Figure 5-1

TABLE 5-3
MONITORING SITE SUMMARY

Site	Address
Reseda	18330 Gault Road, Reseda
El Toro	23022 El Toro Road, El Toro
San Bernardino	24302 E. 4th Street, San Bernardino
Cal Trans	Intersection of I-5 and Rte. 2, Los Angeles
N. Long Beach	3648 Long Beach Boulevard, Long Beach
W. Long Beach	Corner of Santa Fe Avenue and 29th Street, Long Beach
Carson	20915 Brant Avenue, Long Beach
Commerce	Intersection of Washington Boulevard and Fidelia Street, Commerce

6. FIELD SAMPLING PROGRAM

6.1 Sample Collection Procedures

6.1.1 Sample Collection System

General Metal Works Polyurethane Foam (PUF) PS-1 samplers were used to collect selected polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDDs/PCDFs) isomers which include all fifteen 2,3,7,8-congeners listed in Table 4-1. The PS-1 is basically a modified high-volume air sampler which employs both a glass fiber filter and a sorbent trap to collect semi-volatile organic compounds associated with particulate matter as well as those in the vapor state. The General Metal Works PS-1 sampler shown in Figure 6-1, is equipped with a by-pass blower motor arranged with an independent cooling fan. This feature permits the motor to operate at low sampling flow rates for periods of long duration without motor failure from overheating. Air flow rates are variable up to 280 liters per minute. The units are also equipped with a 7-day timer, magnehelic flow gauge, voltage variator, and elapsed timer.

The sampling module contains two chambers. The upper chamber supports the particulate filter media and the second chamber contains a glass cartridge containing a section of polyurethane foam (PUF). The sample module arrangement is illustrated in Figure 6-2. The polyurethane foam (density = 0.022 - 0.025 g/cm^3) was purchased from Olympic Foam Products. A steel die was used to cut the foam sheets into 75 mm plugs. A 10.16-cm-diameter Gelman glass fiber filter was used in conjunction with the glass cartridge/PUF plug for sample collection. The entire sample module including PUF plug, filter, and glass cartridge, was pretreated as described in Section 9 of this document.

Figure 6-1

Schematic of PS-1 Sampler

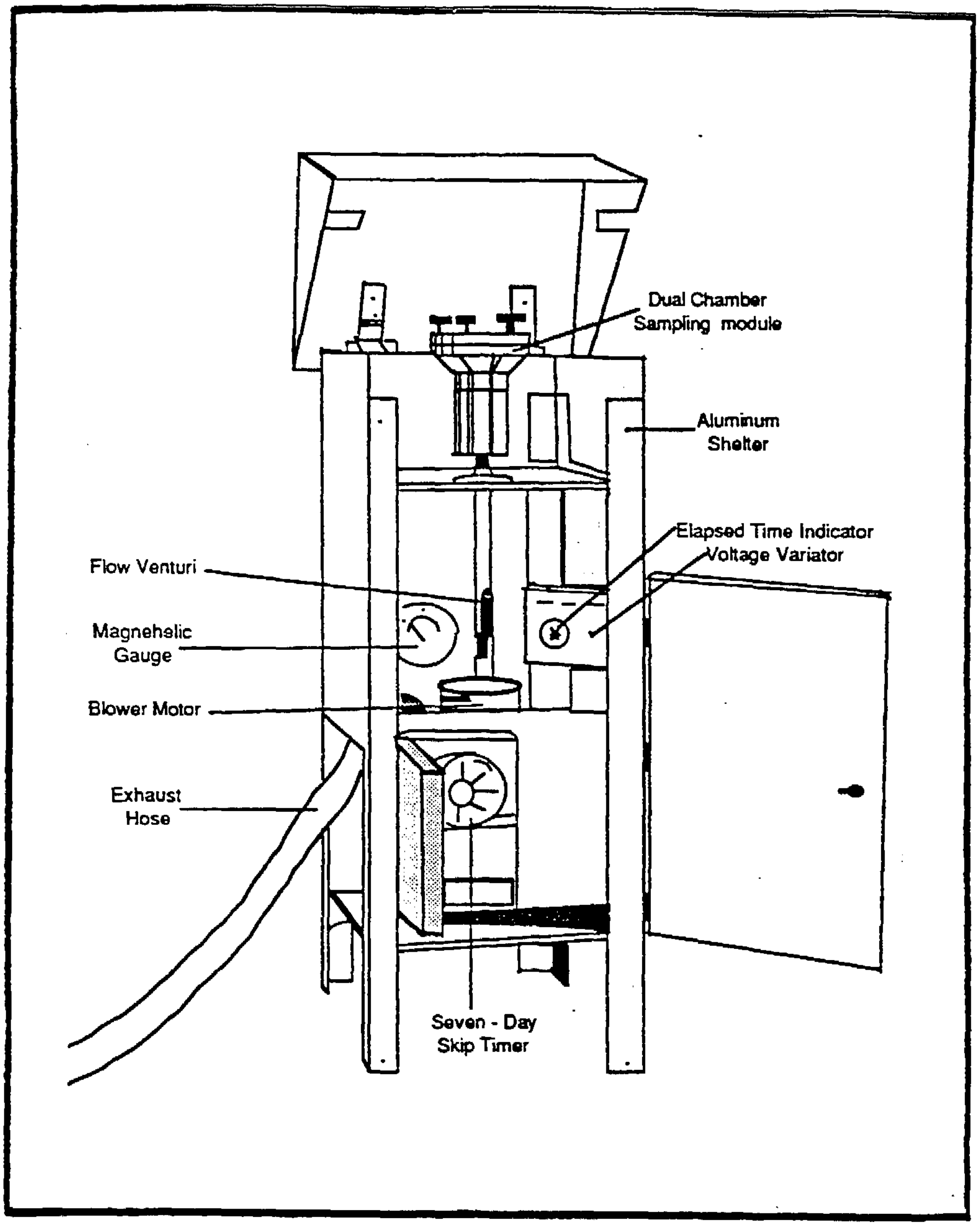
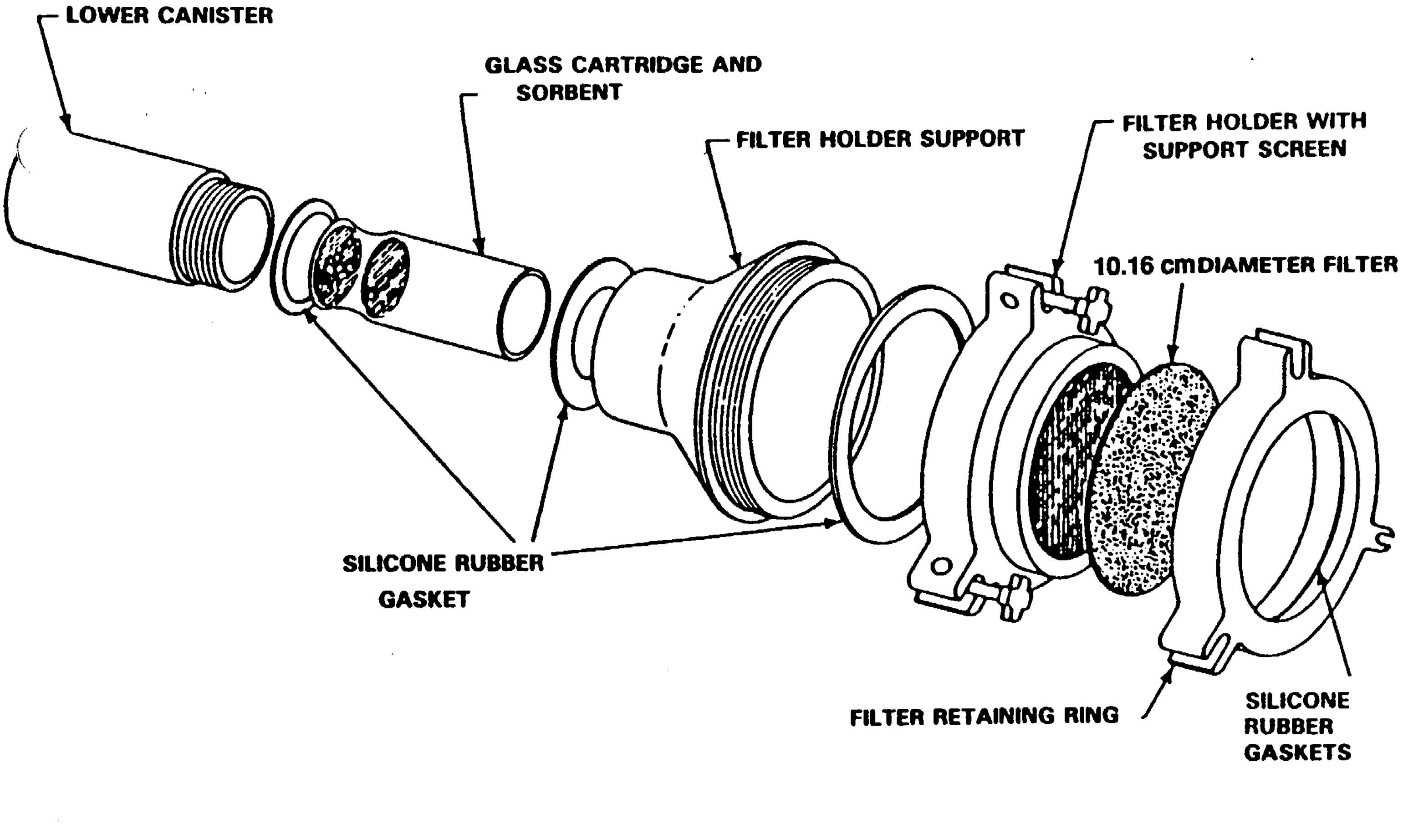


Figure 6-2

Schematic of Sampling Head

(Adapted from "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air," Method T09, EPA-600/4-84-041, April 1984)



Following the pretreatment procedures, the sample cartridges were assembled by carefully placing the PUF plug into the glass sampling cartridge with forceps. Cotton gloves were worn at all times when handling cleaned PUF and associated filter media. Care was also taken to handle PUF plugs only on methylene-chloride-cleaned aluminum foil and with methylene-chloride-cleaned forceps. The sampling cartridge was wrapped in methylene-chloride-rinsed aluminum foil and stored in sealed polyethylene bags until ready for use. ENSR SOP 2622-020, "Collection of Semi-Volatile Organics in Air Using Solid Sorbents", contained in the Phase I Summary Report, further details the procedures used for sample collection.

Each cartridge was labeled with a unique laboratory identification number. Ten percent of the sample cartridges combined with a glass fiber filter were submitted for a quality control check, consisting of a sample preparation and analysis scheme identical to that prescribed for actual air samples. The acceptance criteria were established to be consistent with the detection limits anticipated for each compound. In a similar manner, solvents and reagents prescribed in the analytical procedures were also evaluated using established criteria. This was accomplished by preparing and analyzing a reagent blank along with the QC sample. The reagent blanks consisted of only the glassware, solvents and spikes used for the QC samples, and were used to detect contamination from these sources. Any measured interferences due to inefficient sample sorbent cleanup would necessitate the recleaning of all components of the sample sorbent media and cartridge as described above. A sufficient number of cleaned samples were maintained in the laboratory for laboratory method blanks and spikes.

6.1.2 Field Blanks

One field blank was collected during each sample session to assess field-specific contamination. Field blanks were placed open to the ambient atmosphere for the duration of the sample set-up and recovery periods. Field blanks were also placed into and removed from a sampler head to mimic conditions encountered by actual program samples. Analytical results obtained from each field blank were used to blank correct data obtained from actual program samples.

6.1.3 Sampler Calibration

The PS-1 samplers were calibrated prior to and at the conclusion of each sampling session, as specified in ERT SOP 2620-300 contained in ERT Document No. P-E509-400-01, "Ambient Concentrations of PCDDs/PCDFs in the South Coast Air Basin", June 1987.

ENSR conducts both pre-and post-operational sampler calibration checks using the calibration orifice without placement of the PUF sorbent cartridge in the sampler head. It has been our experience that this approach represents a performance equivalent to calibrations conducted in the normal use configuration with the sorbent cartridge in place. A second calibration approach would entail installation of the calibration orifice in conjunction with a PUF cartridge and filter. ENSR believes that the pressure drop caused by simultaneous use of these three items would actually be higher than that encountered in the normal use configuration. Therefore, use of the calibration orifice alone for calibrating the samplers produces a pressure drop which more closely resembles the drop encountered during actual sampling. The validity of this calibration procedure was confirmed by a flow audit of ENSR PUF samplers conducted by the Minnesota Pollution Control Agency (MPCA) during a recent program. The results of the audit showed ENSR flow measurements and MPCA flow measurements (obtained using a mass flowmeter) to agree within 8% for all samplers.

6.2 Sampling Parameters

6.2.1 Sample Collection Flows and Volumes

As discussed in the ENSR Phase I Summary Report it was anticipated that ambient PCDDs/PCDFs concentrations present in the South Coast Air Basin are likely to occur in the fg/m^3 range (e.g., 10-100 fg/m^3), particularly in the case of the individual 2,3,7,8-substituted congeners. This was anticipated as a result of the literature survey conducted as part of the Phase I work scope as well as ambient monitoring conducted by ENSR under contract to the State of Connecticut [8,10] and the subsequent to the issue of the Phase I Summary Report. As a consequence, optimal detection limits could only be achieved through the use of higher than normal air volumes in conjunction with high resolution mass spectrometry (HRMS). The former condition can be met by a combination of increased sampler flows and/or sampling intervals extended beyond the nominal 24 hour period suggested in ENSR's proposal document. Table 6-1 lists the anticipated detection limits for each target PCDD/PCDF congener at 350 m^3 and 540 m^3 sample volumes. The use of high resolution mass spectrometry as a means to enhance sensitivity is discussed in more detail in Section 9.

6.2.2 Surrogate Spikes

A critical component of the program specific quality control regime involved the use of isotopically labeled surrogates applied to the inlet end of each PUF sorbent cartridge prior to commencement of the sample collection sequence. Field surrogates listed in Table 9-1 were applied to each cartridge in the laboratory following clean-up and before

TABLE 6-1

PCDD/PCDF ISOMERS - LOWER DETECTION LIMITS GOALS

Volume[c]	ARB TEF[a]	Anticipated Lower Limits of Detection[d] Pg/Sample[d]	 Pg/m3 @ 350 m3 Total Volume[b]	 Pg/m3 @ 540 m3 Total
PCDD Isomer				
2,3,7,8 TCDD	1		0.03	0.02
1,2,3,7,8 PeCDD	1		0.06	0.04
1,2,3,6,7,8 HxCDD	0.03		0.06	0.04
1,2,3,7,8,9 HxCDD	0.03		0.06	0.04
1,2,3,4,7,8 HxCDD	0.03		0.06	0.04
1,2,3,4,6,7,8 HpCDD	0.03		0.06	0.04
OCDD	-		0.12	0.08
PCDF Isomer				
2,3,7,8 TCDF	1		0.06	0.04
1,2,3,7,8 PeCDF	1		0.06	0.04
2,3,4,7,8 PeCDF	1		0.06	0.04
1,2,3,6,7,8 HxCDF	0.03		0.06	0.04
1,2,3,7,8,9 HxCDF	0.03		0.06	0.04
1,2,3,4,7,8 HxCDF	0.03		0.06	0.04
2,3,4,6,7,8 HxCDF	0.03		0.06	0.04
1,2,3,4,6,7,8 HpCDF	0.03		0.06	0.04
1,2,3,4,7,8,9 HpCDF	0.03		0.06	0.04
OCDF	-		0.12	0.08

---

[a] TEF - Toxic Equivalency Factor.

[b] 24-hour sample

[c] 36-hour sample

[d] Based upon absolute lower limit of senitivity (Pg) for analytical procedure as provided to ENSR by Enseco-Cal and contained in the Phase I summary report

shipment to the field. Recovery of these surrogates in subsequent analyses served as a measure of analyte retention in the sorbent. A more detailed discussion regarding use of field surrogates appears in Sections 9 and 10.

6.2.3 Sample Shipping and Handling Procedures

All sample filters and cartridges were prepared and packaged for field use at the laboratory prior to shipment to the monitoring sites. Each cartridge was wrapped in solvent-rinsed aluminum foil, placed individually in a ziploc plastic bag, and shipped to the field in a styrofoam cooler. After completion of sampling, each cartridge was repackaged using the same foil and bag, and repacked into a cooler containing ice packs. The sample coolers were shipped within 24 hours to the laboratory sample bank.

6.2.4 Sample Chain-of-Custody and Documentation

Sample control, including chain-of-custody and documentation procedures, were essential to this program. Chain-of-custody procedures serve two purposes:

- They provide a mechanism for assignment of responsibility for sample integrity.
- They provide physical evidence of the history and integrity of each sample, from collection through analysis and data reporting.

Documentation procedures included mechanisms to assure the use of proper sample handling and proper labeling and tracking from sample media preparation in the laboratory through sample collection, and transportation to the laboratory sample bank. Detailed sample control and chain-of-custody procedures can be found in ERT Document No. P-E509-400-01, "Ambient Concentrations of PCDDs/PCDFs in the South Coast Air Basin", June 1987.

6.3 Sampling Schedule and Frequency

The field program commenced December 2, 1987, and continued through March 29, 1989. During this period, nine discrete sample sets were collected, representing four seasonal efforts (winter, spring, summer, fall), at the sites identified in Section 5. Table 6-2 lists the samples collected in each sampling session and at each monitoring site. As indicated in this table, ENSR collected 44 program samples, 17 collocated samples and ten field blanks during the course of the study for a total of 71 samples. Of the 71 samples collected, 38 were chosen for combined HRMS analysis (filter and sorbent cartridge analyzed together) and two for separate HRMS analysis (filter and sorbent cartridge analyzed separately). Samples were selected for analysis using the sample validation process described in Section 8. All samplers were operated concurrently during each sampling session. Table 6-3 lists all samples collected during the course of the program, and indicates which of these were selected for analysis.

6.4 Session Summary Notes

The following section summarizes each of the nine sampling sessions with regard to site selection, sampler operation and sample validation.

6.4.1 Session 1 - December 1 through December 3, 1987

The following sites were used during Session 1:

- Commerce
- El Toro
- Reseda
- San Bernardino
- North Long Beach

TABLE 6-2

SAMPLE COLLECTION FREQUENCY

	Session Number									Total
Site	1	2	3	4	5	6	6A	6B	7	(by site)[d]
Field Blank	x	x	x	x	x	x[a]	x	x	x	10
Reseda	x	x	x	x	x[c]	x[c]			x[c]	10
Cal Trans			x	x	x	x			x	5
San Bernardino	x	x	x	x	x	x			x	7
N. Long Beach	x[c]	x	x[c]	x[c]	x[c]	x	x[b]	x[b]	x[c]	20
W. Long Beach					x	x			x	3
Carson					x	x			x	3
El Toro	x[c]	x[c]	x[c]	x[c]	x	x			x	11
Commerce	x	x								2
Total (by session)[d]	8	7	8	8	10	10	5	5	10	71

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[a] two field blanks collected
[b] collocated site (four samplers)
[c] collocated site (two samplers)
[d] includes collocated samples
[x] sample collected

TABLE 6-3

SAMPLE COLLECTION AND ANALYSIS AUTHORIZATION SUMMARY

Session Information	Sample ID	Site	Analyzed	Sample Volume (scm)
Session 1	7/87-16	San Bernardino	X	562.0
Sampling Period:	8/26-89	El Toro	X	569.3
12/1-12/3/87	7/87-20	El Toro	X	587.5
Duration: ~ 36 hrs	8/26-75	N. Long Beach	X	569.6
	8/26-71	N. Long Beach		[a]
	7/87-29	Commerce	X	562.4
	7/87-2	Reseda	X	564.7
	7/87-23	Field Blank	X	---
Session 2	8/26-82	San Bernardino		574.8
Sampling Period:	7/27-38	El Toro		566.2
12/10-12/11/87	7/27-35	El Toro	X	582.0
Duration: ~ 36 hrs	7/87-25	N. Long Beach		[b]
	8/27-79	Commerce		[b]
	8/26-69	Reseda	X	582.1
	7/27-39	Field Blank	X	---
Session 3	8/87-39	San Bernardino	X	381.0
Sampling Period:	7/88-51	El Toro	X	380.8
7/26/88	8/87-48	El Toro	X	352.8
Duration: ~ 24 hrs	7/87-16	N. Long Beach		[d]
	8/87-52	N. Long Beach		[d]
	8/26-69	Cal Trans	X	394.7
	7/88-52	Reseda	X	385.8
	100	Field Blank	X	---
Session 4	7/87-11	San Bernardino	X	385.6
Sampling Period:	8/26-88	El Toro	X	387.7
7/28/88	8/26-78	El Toro		355.3
Duration: ~ 24 hrs	7/27-33	N. Long Beach	X	376.8
	7/87-18	N. Long Beach	X	376.1
	7/88-53	Cal Trans	X	392.8
	8/26-71	Reseda	X	393.1
	97	Field Blank	X	---
Session 5	7/87-18	San Bernardino	X	396.4
Sampling Period:	207	N. Long Beach		[a]
9/26-9/27/88	7/27-33	N. Long Beach	X	393.1
Duration: ~ 24 hrs	195	Carson	X	335.8
	7/87-22	W. Long Beach	X	361.4
	7/88-53	El Toro	X	370.7
	7/87-11	Reseda		367.2
	100	Reseda	X	392.4
	SN 32267	Cal Trans	X	368.2
	127	Field Blank	X	---

TABLE 6-3 (Continued)

Session Information	Sample ID	Site	Analyzed	Sample Volume (scm)
Session 6	SN 31914	Reseda		406.8
Sampling Period:	SN 32266	Reseda		364.0
9/29/88	7/88-51	San Bernardino		361.1
Duration: ~ 24 hrs	8/87-48	Carson		324.2
	SN 32120	N. Long Beach		391.2
	97	W. Long Beach		384.3
	8/26-69	El Toro		384.3
	8/26-711	Cal Trans		364.5
	7/88-52	Field Blank		---
	8/87-39	Field Blank		---
Session 6A	A1-126	N. Long Beach		396.0
Sampling Period:	A1-144	N. Long Beach		384.3
11/2/88	B1-132	N. Long Beach	X [c]	366.3
Duration: ~ 24 hrs	B1-136	N. Long Beach		322.9
	FB-1	Field Blank		---
Session 6B	A2-148	N. Long Beach		[d]
Sampling Period:	A2-146	N. Long Beach		[d]
11/4/88	B2-100	N. Long Beach		364.1
Duration: ~ 24 hrs	B2-131	N. Long Beach		352.8
	FB-2	Field Blank		---
Session 7	SP-129	N. Long Beach	X [c]	367.9
Sampling Period:	SP-133	N. Long Beach		[e]
3/29/89	SP-22	W. Long Beach	X	373.2
Duration: ~ 24 hrs	SP-67	Carson	X	371.3
	SP-85	Cal Trans	X	356.8
	SP-78	San Bernardino	X	376.4
	SP-87	El Toro		318.0
	SP-100	Reseda	X	336.5
	SP-195	Reseda	X	356.0
	SP-83-FB	Field Blank	X	---

---

[a] Sampler malfunction. Sample eliminated from future consideration for analysis.

[b] Heavy particulate loading caused significant flow restriction preventing accurate sample volume determination. Sample not selected for subsequent analysis.

[c] Filter and foam analyzed separately.

[d] Power interruption.

[e] Initial and final magnehelic readings differed by ~ 20%, thereby precluding accurate sample volume determination. These samples were not considered further in selection of samples for analyses.

scm - standard cubic meters

Collocated samplers were installed at the N. Long Beach and El Toro sites. All samplers were set to run at a flow rate of approximately 260 lpm for 36 hours, resulting in a total sample volume of approximately 560 m^3. Samplers were set to begin sampling between 2100 and 2400 on 12-1-87 for 36 hours. Samples were collected on 12-3-87. One of the sampler motors failed at the collocated N. Long Beach site. Field staff removed the motor for repair and invalidated the sample (ID 8-26-71) collected from the disabled sampler.

6.4.2 Session 2 - December 10 through December 11, 1987

Sites used during Session 2 were identical to those used for Session 1. Collocated samplers were installed at the El Toro site. All samplers were set to run at a flow rate of approximately 260 lpm for 36 hours, resulting in a total sample volume of approximately 560 m^3. Samplers were set to begin operation at 000 hours (midnight) December 10, 1987 for 36 hours. Samples were collected on December 11, 1987. All samplers performed properly during this session. At two sites (N. Long Beach and Commerce), however, heavy particulate loading greatly reduced the sampler flowrate during the course of the sampling session, thereby precluding accurate sample volume determination for these samples. The affected samples (IDs 7-87-25 and 8-27-79) were invalidated and eliminated from consideration for analysis. To control this excessive particulate loading problem in the future, subsequent monitoring sessions utilized 24 hour sampling periods. Further, this sample duration would permit operation concurrent with the 24 hour EPA NASN TSP schedule as directed by ARB.

6.4.3 Session 3 - July 26, 1988

The following sites were used during Session 3:

- El Toro
- Reseda
- San Bernardino
- Cal Trans
- North Long Beach

Collocated samplers were installed at the N. Long Beach and El Toro sites. All samplers were set to run at a flow rate of approximately 260 lpm for 24 hours, resulting in a total sample volume of approximately 380 m^3. Samplers were set to begin sampling at 000 hours (midnight) July 26, 1988 for 24 hours, concurrently with the EPA 6-day TSP sampling program. Samples were collected on July 28, 1988. The two samplers located at the N. Long Beach site operated for approximately 3 hours due to a power interruption resulting from a circuit overload. As a result, these two samples (IDs 7-87-16 and 8-87-52) were invalidated. Field staff also noted that an aerial insect spraying operation began at approximately 2100 July 25th, in the vicinity of the Reseda monitoring site.

6.4.4 Session 4 - July 28, 1988

Sites used during Session 4 were identical to those used for Session 3. Collocated samplers were installed at the N. Long Beach and El Toro sites, as in Session 3. All samplers were set to begin operation at 000 hours (midnight) July 28, 1988 and allowed to run for 24 hours. A flow rate of approximately 260 lpm was used, resulting in a total sample volume of approximately 380 m^3. All samplers operated properly for the duration of the sampling session.

6.4.5 Session 5 - September 26 through September 27, 1988

The following seven sites were used during Session 5:

- Reseda

- Cal Trans
- North Long Beach
- West Long Beach
- Carson
- El Toro
- San Bernardino

Collocated samplers were installed at the Reseda and N. Long Beach sites. Samplers located at San Bernardino, North Long Beach and Carson were set to begin operation at 2245, 1845 and 1715, respectively on September 26, 1988. All other samplers were set to begin operation at 2400. All samplers were set to run for 24 hours at a flow rate of approximately 260 lpm, resulting in a total sample volume of approximately 380 m^3. One of the N. Long Beach samplers failed during this session and, as such, the sample collected from this sampler (ID 207) was invalidated and eliminated from consideration for analysis.

6.4.6 Session 6 - September 29, 1988

Sites used during Session 6 were identical to those used for Session 5. Collocated samplers were installed at the Reseda site. Samplers were set to operate for 24 hours beginning at 000 hours (midnight) September 29, 1988 at a flow rate of approximately 260 lpm. This resulted in a total sample volume of approximately 380 m^3. Samples were collected September 30, 1988. All samplers operated properly during this session.

6.4.7 Sessions 6A and 6B - November 2 and 4, 1988

In an effort to acquire additional fall seasonal data at the N. Long Beach site, and provide valid samples to replace those collected during Session 6, two additional 24-hour sampling sessions were conducted at this site. Both sessions involved installation of two sets of collocated samplers (four samplers total), each set on a different electrical circuit. Samplers were set to begin operation at 000 hours (midnight) on November 2 and 4, 1988 for Sessions 6A and 6B, respectively. Samplers were allowed to run for 24 hours, resulting in sample volumes of approximately 350 m^3. A power failure during Session 6B invalidated one of the collocated pairs (IDs A2-148 and A2-146) collected during this session. Session 6A was conducted coincident with the EPA TSP 6-day monitoring cycle.

6.4.8 Session 7 - March 29, 1988

ENSR conducted sampling Session 7 on March 29, 1988 to obtain spring seasonal measurements for ambient PCDDs/PCDFs. The March 29 sampling date was selected to coincide with the EPA TSP 6-day monitoring cycle. PS-1 samplers were deployed to the following seven sites:

- North Long Beach
- West Long Beach
- Carson
- El Toro
- Reseda
- San Bernardino
- Cal Trans

Collocated samplers were placed at the Reseda and N. Long Beach sites. All samplers were set to run at a flow rate of approximately 255 lpm for 24 hours, resulting in a total sample volume of approximately 370 m^3. Samplers were set to operate from midnight to midnight (000 hours to 2400 hours) on March 29, 1988.

During inspection of the monitoring network on March 29, 1988, it was discovered that the N. Long Beach site had lost power for approximately 45 minutes at some time between sampler set-up and inspection. ENSR and ARB staff agreed to adjust the timers on the two N. Long Beach samplers to ensure proper shut-off at midnight, thereby maintaining contemporaneous sampling with EPA TSP collection. It was also discovered that the Carson site had lost power for approximately 2-1/2 hours between sampler set-up and the session start time. ENSR and ARB staff agreed on the importance of obtaining a 24-hour sample at this site and as such, allowed the sampler to continue operation past the intended midnight shut-off time until a full one-day sample had been collected. Samplers at all other sites were operating properly. Samples were collected on March 30, 1989.

Upon arrival at the El Toro site for sampler collection, it was noted that power had been disconnected to the sampler. Inspection of the sampler timer indicated that this power interruption had occurred at approximately 9 p.m. the evening before. As such, a 21-hour sample was collected at the El Toro site. It should also be noted that the final magnehelic check performed on sampler #32266 (containing sample ID SP-129) at N. Long Beach showed a reading approximately 20% below the initial magnehelic setting. As such, this sample was invalidated. All other samples collected during Session 7 were valid.

7. METEOROLOGICAL MONITORING

7.1 Overview

Meteorological monitoring plays a key role in the interpretation of monitoring programs conducted to quantify background concentrations of PCDDs/PCDFs in ambient air. PCDDs/PCDFs levels measured at the various network sites may be influenced by local meteorology, as described below:

- Winds originating predominantly from W through SW vectors (e.g. off the ocean) may serve to disperse the existing ambient PCDDs/PCDFs burden in the LA Basin.
- High wind speeds (i.e., relatively unstable air mass) may also create significant atmospheric mixing, thereby reducing measured levels of PCDDs/PCDFs in the ambient air.
- Specific wind vectors may place a particular site directly downwind of a PCDDs/PCDFs source.

These possibilities should be addressed when comparing measured PCDDs/PCDFs levels obtained from various sites during the same time period.

To acquire valid meteorological data at locations in the South Coast Air Basin which would be directly applicable to the PCDDs/PCDFs background ambient monitoring program, several ambient monitoring sites used in the network were selected based on the presence of existing meteorological monitoring equipment. The following ambient monitoring sites contained meteorological monitoring stations maintained by the South Coast Air Quality Management District (SCAQMD):

- Reseda
- North Long Beach

- El Toro
- San Bernardino

7.2 Meteorological Data

Meteorological data (wind speed, wind direction and temperature) collected at Reseda, North Long Beach, El Toro and San Bernardino sites were obtained from SCAQMD as hourly averages for each ambient monitoring session conducted during the program. Dates and times of the air sampling periods are as follows:

Session No.	TSP Coincident	Start Time		End Time	
1	No	2100	12-01-87	1200	12-03-87
2	Yes	000	12-10-87	1200	12-11-87
3	Yes	000	7-26-88	2400	7-26-88
4	No	000	7-28-88	2400	7-28-88
5	No	1715	9-26-88	2400	9-27-88
6	No	000	9-29-88	2400	9-29-88
6A	Yes	000	11-02-88	2400	11-02-00
6B	No	000	11-04-88	2400	11-04-88
7	Yes	000	3-29-89	0300	3-30-89

Windrose plots illustrating wind direction frequency and wind speed frequency for each meteorological monitoring site and sampling session are contained in Appendix B. A summary of wind direction frequencies is found in Table 7-1. Air flow charts (developed by the Air Resources Board, Meteorological Section) detailing surface and directional characteristics present over the South Coast Air Basin during each session are provided in Appendix A.

7.3 Meteorological Summaries

Air flow charts (contained in Appendix A) provide general information regarding air mass movements in the South Coast region. Knowledge of air flow trends which occurred during

TABLE 7-1

SUMMARY OF WIND DIRECTION FREQUENCY

	San Bernardino	Long Beach	Reseda	El Toro
1.	65% NNE/NE 15% Variable 20% Calm	60% NNE/NE/ENE 15% W 20% Variable 5% Calm	30% Variable 70% Calm	35% ENE 15% WNW 30% Variable 20% Calm
2.	65% NNE/NE 25% Variable 10% Calm	20% NNE 10% W 45% Variable 25% Calm	20% N 50% Variable (S thru W) 30% Calm	40% ENE/E 35% Variable (S thru W) 25% Calm
3.	65% SSW/SW 15% Variable 20% Calm	45% W/WNW 20% S/SSE 25% Variable 10% Calm	70% ENE/E/ESE 30% Calm	40% WNW/NW 30% Calm 30% Variable
4.	80% S/SSW 10% Variable 10% Calm	40% S/SSE 35% W/WNW 20% Variable 5% Calm	100% Variable (E thru S)	65% SSE/S/SSW 20% WNW 10% Variable 5% Calm
5.	50% SW/WSW 15% Variable 35% Calm	50% WSW/W/WNW 35% Variable 15% Calm	25% SE 15% WSW 25% Variable 35 % Calm	35% WNW 30% ENE/E 20% Variable 15% Calm
6.	35% NW/NNW 25% NNE/NE/ENE 15% Variable 25% Calm	15% W 25% SSW 55% Variable 5% Calm	80% Variable 20% Calm	35% WNW/NW 50% Calm 15% Variable
7.	40% SW/WSW 40% Variable 20% Calm	20% W 15% S 35% ESE/SE 30% Variable	60% NW through NNE 20% Variable 20% Calm	75% NNE/NE 10% Variable 15% Calm

each monitoring period assists in describing trends in South Coast Air Basin atmospheric burdens of PCDDs/PCDFs. For the purposes of this program, South Coast air flow patterns will be described as either on-shore or off-shore. On-shore air flow indicates general air mass movement from the Pacific Ocean toward the South Coast inland areas. Off-shore airflow indicates general air mass movement from South Coast inland area toward the Pacific Ocean. Though the identification of air flows as either on-shore or off-shore is a simplified summary of the often complex air flow patterns occurring in Southern California, this approach does serve to provide additional information useful in describing variation in atmospheric PCDDs/PCDFs burdens noted to occur between different sampling sessions.

Table 7-2 identifies air flow patterns as either off-shore or on-shore at six-hour intervals for each sampling session. In addition, session by session meteorological summaries follow.

Session 1

Air flow charts contained in Appendix A show air flow originating from the South Coast inland areas and moving generally SW toward the Pacific Ocean. This pattern appeared to be maintained throughout most of Session 1, as four of the five charts for this period reflect this land to sea air flow.

Session 2

Air flow charts contained in Appendix A show varying air flow patterns occurring during the Session 2 sampling period. The early portion of the session encountered air masses flowing generally from south coast inland areas toward the Pacific Ocean. This trend reversed midway through the monitoring period to produce generally onshore air flow for the remainder of the sampling session.

TABLE 7-2

SUMMARY OF AIR FLOW PATTERNS

	Sampling Day 1			Sampling Day 2(a)	
	0400	1000	1600	0400	1600
Session 1	Off-shore	Off-shore	On-shore	Off-shore	Off-shore
Session 2	Off-shore	Off-shore	On-shore	Off-shore	On-shore
Session 3	On-shore	On-shore	On-shore		
Session 4	On-shore	(b)	On-shore		
Session 5	Off-shore	On-shore	On-shore		
Session 6	Off-shore	On-shore	On-shore		

(a)Applies to 36 hour session only.

(b)Negligible air flow movement noted.

Off-shore - indicates general air flow from South Coast inland areas toward Pacific Ocean.

On-Shore - indicates general air flow from Pacific Ocean toward South Coast inland areas.

Session 3

Air flow charts contained in Appendix A show air flow originating from the Pacific Ocean and moving generally toward south coast inland areas. This pattern was maintained throughout the entire Session 3 monitoring period.

Session 4

Air flow charts contained in Appendix A show air flow originating from the Pacific Ocean and moving generally toward South Coast inland areas. This pattern was maintained for much of the Session 4 monitoring period.

Session 5

Air flow charts contained in Appendix A show air flow originating from the South Coast inland areas and moving generally SE toward the Pacific Ocean early in Session 5. This off-shore pattern reversed to an on-shore pattern during the middle part of the monitoring period as indicated by the 1000 PST 9-27-88 air flow chart, and appeared to continue throughout the remainder of the session.

Session 6

Air flow charts contained in Appendix A show air flow originating early in the session from the South Coast inland areas and moving generally off-shore toward the Pacific Ocean. This off-shore trend reversed to an on-shore pattern during the middle portion of the monitoring period as indicated by the 1000 PST 9-29-88 air flow chart, and appeared to continue throughout the remainder of the session.

8. VALIDATION AND SELECTION OF SAMPLES FOR ANALYSIS

A formal validation and selection procedure was implemented to select samples for analysis. This procedure, summarized in Figure 8-1, assesses sample integrity, sampler operation, and sample identification issues for each individual sample. Only those samples deemed valid through application of the sample validation protocol discussed in this section were considered for analysis.

Final considerations applied to selection of validated samples included contractual obligations (42 analyses required), need for collocated sampler data (for QA/QC precision assessment), the importance of field blank data (used to "blank correct" program samples as described in Sections 10 and 11), and the desire to obtain data from samples collected contemporaneously with the EPA TSP 6-day program. Samples were selected for analysis from the later sessions (5, 6, 6A, 6B, and 7) with concurrence of ARB staff.

Physical Integrity

Field staff members inspect each sample cartridge and filter immediately prior to and at the completion of each sampling session to ensure the physical integrity of the collected sample. Glass cartridges are inspected for cracks or chips which may prevent formation of an adequate seal while seated in the sampler head. Glass fiber filters are inspected for tears which, if present, could affect the collection of particulate-associated PCDDs/PCDFs. The proper collection of partitioned particulate and vapor phases is particularly critical in samples selected to undergo separate filter/foam analyses. Samples containing components which do not display appropriate physical characteristics as identified above are invalidated and eliminated from consideration for analysis. In addition, visible physical signs of sampler tampering may lead

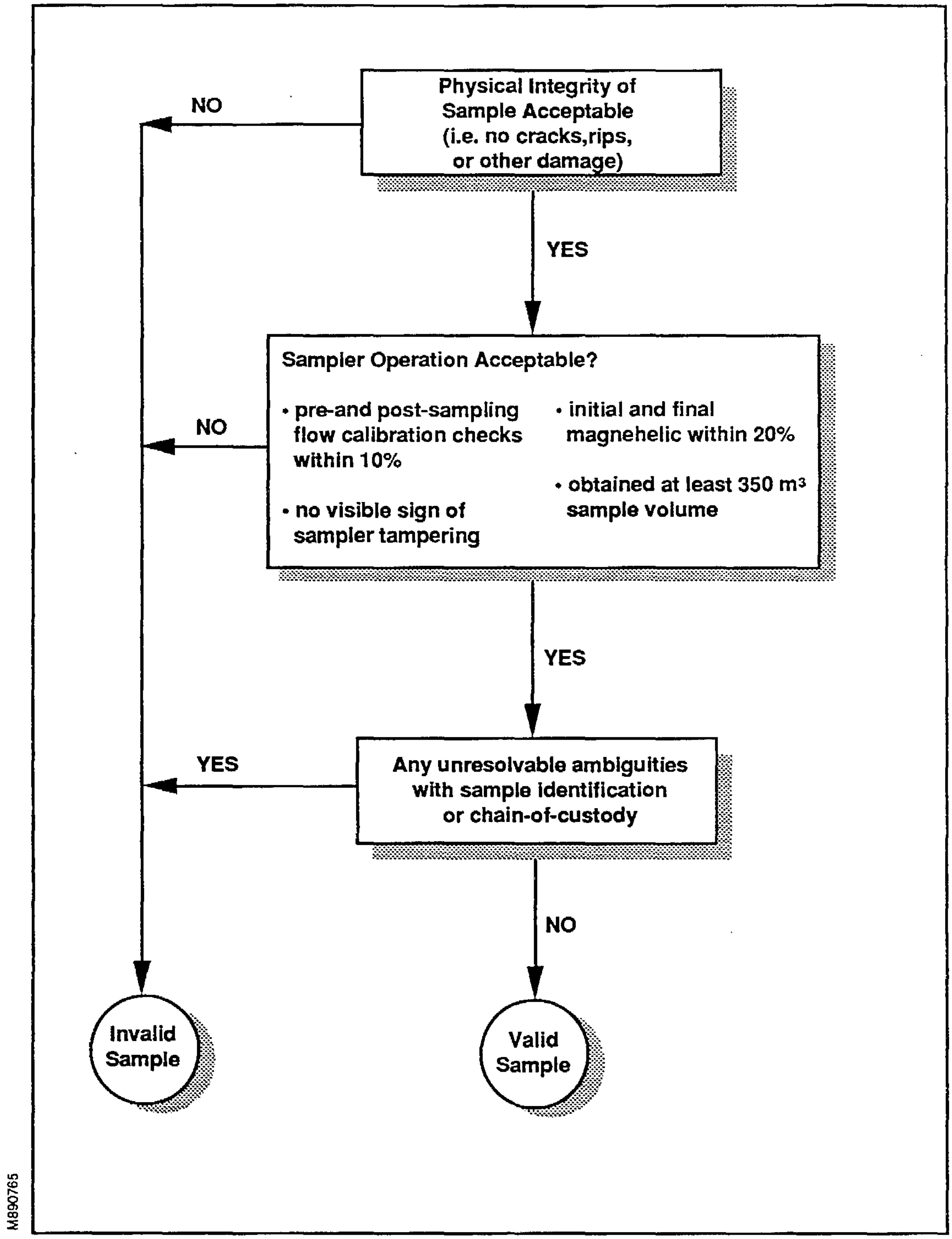

Figure 8-1
Sample Validation Protocol

to sample invalidation. No samples collected during this program were invalidated based on the requirements for physical integrity of sampling materials described herein.

Sampler Calibration Check

All samplers undergo a calibration check prior to and at the completion of each sampling session in order to confirm proper sampler operation. Pre- and post-calibration check points must fall within 10 percent of the existing full sampler calibration curve to be considered valid. Samplers not meeting the pre-calibration criteria are recalibrated prior to their use in the next sampling session.

Samples contained in samplers not meeting the post-calibration criteria are invalidated and eliminated from consideration for analysis. No samples collected during this program were invalidated due to post-calibration failure.

Flow Rate Consistency

Accurate sample volume determination requires that a consistent flow rate be maintained throughout the sampling period. Flowrate consistency is confirmed by comparison of the initial and final magnehelic guage readings which, if differing by more than 20 percent, indicates the occurrence of a significant variation in flow rate during the session.

Samples collected in samplers not meeting this criteria are considered invalid and eliminated from consideration for analysis. Sample IDs 7-87-25 and 8-27-79 collected during Session 2 and Sample ID SP-133 collected during Session 7 were invalidated based on this criteria.

Sampling Duration

Samplers are set at a particular flow rate based on the anticipated session duration to produce a sample volume of at least 350 m^3 to ensure attainment of program detection limit goals. Abbreviated sampling sessions due to sampler malfunction or power interruption may preclude collection of the desired 350 m^3 sample volume.

Such samples may be considered invalid and eliminated from consideration for analysis. Sample IDs 8-26-71 (Session 1), 207 (Session 5), A2-148 and A2-146 (Session 6B) were invalidated due to abbreviated sampler operation.

Meteorology

Another consideration applied in the selection of samples for analysis includes assessment of sample session meteorology. Optimum meteorological conditions for ambient background monitoring included the absence of widespread precipitation during a sampling session. All monitoring sessions conducted for this program were planned to coincide with periods of predicted clear weather because air sampling during periods of sustained, widespread precipitation may produce results, which in ENSR's judgement, do not represent actual ambient concentrations of dioxins and furans. No precipitation occurred during any of the sampling sessions and, as such, no samples were invalidated due to poor meteorological conditions.

Sample Identification

Any unresolvable ambiguities with sample identification or chain-of-custody result in sample invalidation. No such sample identification problems occurred during this program.

9. ANALYTICAL PROCEDURES

9.1 Overview

Sample analyses for polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) were performed by Enseco-CAL Laboratory (Sacramento, CA) under subcontract to ENSR. ENSR and Enseco-CAL have collaborated to develop and validate methods for ambient monitoring programs and as such, analyses performed for this program incorporated technical and method advances of proven benefit.

As discussed in the Phase I Summary Report, technological advances identified after the proposal stage of this program would allow us to enhance sensitivities for PCDDs/PCDFs in ambient air. Prior to the start-up of the California program, Enseco-CAL Laboratory had participated in an ENSR method validation study for ambient dioxin/furan monitoring programs under the sponsorship of the Connecticut Department of Environmental Protection. PUF sorbent samplers were evaluated for potential interferents to dioxin/furan analyses and cleanup methods were examined. Analysis methods which provided femtogram-per-cubic meter (fg/m^3) detection limits for PCDDs and PCDFs were also established. ENSR selected magnetic sector high resolution mass spectrometry (HRMS) at this time for PCDDs/PCDFs ambient monitoring programs. This provided state-of-the-art analytical selectivity and sensitivity towards the target analytes. Detection limit goals, defined to accommodate likely ambient concentrations of PCDDs and PCDFs in the South Coast Air Basin, were met through the combined sampler preparation and analytical method improvements achieved previously by ENSR and Enseco-CAL.

Air samples were analyzed for individual 2,3,7,8-chlorinated dibenzodioxins and dibenzofurans as listed in Table 4-1, and for total levels of each congener class (Cl_4 - Cl_8). While the analyses of PCDDs/PCDFs congener class sums (Cl_4 - Cl_8) were not expressly required in the program work scope, these measurements have been provided at no additional cost, as they were obtained as part of the required analyses for the 15 2,3,7,8-substituted PCDDs/PCDFs of primary toxicological significance to the ARB.

The discussion to follow contains a synopsis of the sorbent (PUF) preparation, sample preparation and cleanup procedures employed by Enseco-CAL throughout the course of this program. A synopsis of the analyses employing high resolution gas chromatography (HRGC) in concert with high resolution or magnetic sector mass spectrometry (HRMS) is also provided. Further details on each of these analytical protocols are contained in the Enseco-CAL Standard Operating Procedures (SOPs) provided initially to the ARB as Appendix F of the Phase I Summary Report.

9.2 Sorbent preparation and Surrogate Application

Enseco-CAL submitted each assembled sorbent trap, including glass cartridge, filter and polyurethane foam plug, for laboratory cleanup prior to field use following procedures established by ENSR and Enseco-CAL prior to the start of this program. Successive 16-hour soxhlet extractions with acetone and toluene were performed to remove residual organics from the foam cartridge. After cleaning, the units were air-dried until all solvent had evaporated.

Prior to sample collection in the field, each PUF cartridge was spiked at Enseco-CAL Laboratory with a surrogate cocktail containing three of the four isotopically labeled field surrogates as listed in Table 9-1. These were applied to the "head", or just below the inlet surface of every sorbent cartridge at a level of 500 picograms each. Each cartridge was subsequently air dried in a hood prior to disposition to the field. Recoveries of the surrogates were measured as part of each final analysis. The surrogates chosen included $^{37}Cl_4$-2,3,7,8-TCDD and $^{13}C_{12}$-2,3,7,8-TCDF, and hence represent the more volatile classes of PCDDs and PCDFs.

TABLE 9-1

SPIKING AND FORTIFICATION SOLUTIONS

ENSECO-CAL LABORATORY

Purpose	Compound	Quantity Applied (pg)	Concentration at time of analysis (pg/ul) 10 ul extract
Field Surrogates	$^{37}Cl_4$-2,3,7,8-TCDD	500	50
	$^{13}C_{12}$-2,3,7,8-TCDF	500	50
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	500	50
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	500	50
Internal Standards for Quantification	$^{13}C_{12}$-2,3,7,8-TCDD	1000	100
	$^{13}C_{12}$-1,2,3,7,8-PeCDD	2500	250
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	2500	250
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	2500	250
	$^{13}C_{12}$-OCDD	5000	500
Laboratory Extraction Recovery Standards	$^{13}C_{12}$-1,2,3,4-TCDD	2000	200
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	2000	200

Accordingly, their behavior on the PUF during the sample collection and subsequent analysis regime provides a "worst-case" representation of retention for the higher molecular weight PCDD/PCDF congeners, as well. Surrogate recoveries also constitute a measure of the precision and accuracy of the combined sample collection and analysis regime. Cumulative surrogate recovery data from the laboratory were monitored by ENSR during the course of the program. A summary of these results with associated statistical analyses is provided in Section 10.

9.3 Sample Extraction and Cleanup

At the conclusion of each sampling session, the PUF cartridges were returned to Enseco-CAL Laboratories. All submitted samples were protected from light and stored at 4°C awaiting ENSR authorization for extraction and analysis.

Sample preparation and analysis followed the guidelines of U.S. EPA Method 8280*. This method was originally published for the analyses of PCDDs and PCDFs by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). At the time of program initiation, Enseco-CAL had validated a Statement of Work for the extension of Method 8280 incorporating high resolution mass spectrometry (HRMS). A copy of the Enseco-CAL document "Total and/or 2,3,7,8-substituted Dioxin and Furan Analysis Statement of Work" was provided for review in the Phase I summary report.

Those samples authorized for analysis were spiked prior to extraction with a mix of isotopically labeled PCDDs to serve as internal standards for the analysis. Method 8280, both as initially published for LRMS and as amended to incorporate

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*Test Methods for Evaluating Solid Waste, U.S. EPA SW-846, Third Edition, November 1986.

HRMS, depends upon these internal standards for accurate quantification of target analytes. The five labeled polychlorodibenzodioxin internal standards listed in Table 9-1 were spiked onto the head of each polyurethane foam plug as the first step of sample preparation. All native dioxins and furans collected from the ambient air were quantified against these internal standards. The addition of internal standards at this point eliminated uncertainty in the measurements of dioxins and furans in actual samples due to possible losses during the extraction and cleanup steps.

After fortification with the internal standards, each PUF sample was placed directly into a Soxhlet extraction vessel. Extreme care was taken to prevent external contamination or sample loss during this transfer. The entire sample, including foam plug, filter and glass cartridge, was then extracted with toluene for 16 hours.

The resulting extracts from the foam samples likely contained a wide range of semivolatile organics collected from the ambient air. The sensitivity and selectivity of the mass spectral analysis for PCDDs and PCDFs are optimized when other organics are removed. Method 8280 suggests a variety of procedures appropriate for the cleanup of extracts from environmental media. Enseco-CAL routinely employed cleanup procedures to remove acidic and basic species followed by column chromatography to isolate the PCDDs and PCDFs from closely-related neutral organics.

Details of the cleanup procedures followed by Enseco-CAL Laboratory are found in the Phase I Summary Report [23]. The acid/base sample cleanup was accomplished with the mixed bed chromatographic column described as the IFB Column Clean-Up Option. This cleanup procedure was followed by carbon column chromatography as detailed in Option D2 and a final basic alumina mini-column chromatography procedure as entitled "Volume Reduction of Tetradecane" in their Statement of Work. The sample was concentrated to approximately 1 ml for column application in each step. Following the final procedure, the sample was taken to a volume of 10 µl for GC/MS analysis.

9.4 HRGC/HRMS Analyses

The measurement of picogram levels of PCDDs and PCDFs requires state-of-the-art instrumentation operating at maximum sensitivity and resolution. The instrumentation and operating conditions utilized at Enseco-CAL for this program are listed in Table 9-2. All instruments were properly tuned with perfluorokerosene (PFK) as directed in Method 8280.

Extracts were fortified with a mix of recovery standards, as identified in Table 9-1. Two isotopically labeled dioxins were used to quantify the recoveries of the labeled internal standards added prior to sample extraction. While the recovery standards do not directly impact the values calculated for native species, their addition allows a measure of overall extraction efficiencies and cleanup recoveries for each sample. Internal standard recovery data provide a measure of the precision and accuracy of the sample preparation and analysis portion of the program. Cumulative data from the laboratory were monitored by ENSR to ensure consistent performance over the program.

A gas chromatographic column performance solution was analyzed prior to analysis of each sample group to establish retention time windows for PCDD and PCDF congener classes. The performance solution contained the first and last eluting isomers for each congener class of PCDDs and PCDFs and allowed for precise determination of the time windows during which isomers for which standards were not available might be detected.

Prior to all sample analyses, the mass spectrometers were calibrated with a set of initial calibration solutions as shown in Table 9-3. The instruments were operated in the selected ion monitoring mode, with two masses monitored for each

TABLE 9-2

INSTRUMENTATION FOR PCDD/PCDF ANALYSIS

ENSECO-CAL LABORATORY

Systems:	Finnegan 8230 HRGC/HRMS Finnegan 8400 HRGC/HRMS VG 70-250S (2 Systems)
Operating Mode:	Selected ion monitoring
Resolution:	8000

Gas Chromatography Conditions

Primary Analysis

Column Type	DB-5
Length(m)	60
i.d. (mm)	0.25
Film Thickness (um)	0.25
Carrier Gas	Helium
Carrier Gas Flow (mL/min)	1-2
Injection Mode	splitless
Valve Time (s)	30
Initial Temperature (°C)	150
Program Temperature	150° C to 190° C ballistically then 3° C/min up to 300°

TABLE 9-2 (continued)

INSTRUMENTATION FOR PCDD/PCDF ANALYSIS

Gas Chromatography Conditions

2,3,7,8 - TCDF Confirmation Analysis

Column Type	DB 225
Length(m)	60
i.d. (mm)	0.25
Film Thickness (um)	0.25
Carrier Gas	Helium
Carrier Gas Flow (mL/min)	1-2
Injection Mode	splitless
Valve Time (s)	30
Initial Temperature (°C)	150
Program Temperature	150° C to 190° C ballistically then 3° C/min up to 300°

PeCDD and HxCDD Confirmation Analyses

Column Type	SP 2331
Length(m)	60
i.d. (mm)	0.25
Film Thickness (um)	0.25
Carrier Gas	Helium
Carrier Gas Flow (mL/min)	1-2
Injection Mode	splitless
Valve Time (s)	30
Initial Temperature (°C)	190
Program Temperature	190° C to 255° C at 10° C/min

TABLE 9-3

COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS FOR ENSECO-CAL LABORATORY

Compound	Concentrations (pg/uL)				
Sol. Number	1	2	3	4	5
2,3,7,8-TCDD	20	50	250	500	1000
2,3,7,8-TCDF	20	50	250	500	1000
1,2,3,7,8-PeCDD	20	50	250	500	1000
1,2,3,7,8-PeCDF	20	50	250	500	1000
2,3,4,7,8-PeCDF	20	50	250	500	1000
1,2,3,4,7,8-HxCDD	20	50	250	500	1000
1,2,3,6,7,8-HxCDD	20	50	250	500	1000
1,2,3,7,8,9-HxCDD	20	50	250	500	1000
1,2,3,4,7,8-HxCDF	20	50	250	500	1000
1,2,3,6,7,8-HxCDF	20	50	250	500	1000
1,2,3,7,8,9-HxCDF	20	50	250	500	1000
2,3,4,6,7,8-HxCDF	20	50	250	500	1000
1,2,3,4,6,7,8-HpCDD	20	50	250	500	1000
1,2,3,4,6,7,8-HpCDF	20	50	250	500	1000
1,2,3,4,7,8,9-HpCDF	20	50	250	500	1000
OCDD	20	50	250	500	1000
OCDF	20	50	250	500	1000
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	250	250	250	250	250
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1000	1000	1000	1000	1000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1000	1000	1000	1000	1000
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1000	1000	1000	1000	1000
$^{13}C_{12}$-OCDD	1000	1000	1000	1000	1000

TABLE 9-3 (continued)

COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS
FOR ENSECO - CAL LABORATORY

Compound	Concentrations (pg/uL)		
Sol. Number	1	2	3
<u>Surrogate</u> <u>Standards</u>			
$^{37}Cl_4$-2,3,7,8-TCDD	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	250	250	250
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1000	1000	1000
$^{13}C_{12}$-1,2,3,4,7,8-HpCDF	1000	1000	1000
<u>Recovery</u> <u>Standard</u>			
$^{13}C_{12}$-1,2,3,4-TCDD	250	250	250
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	250	250	250

congener class of dioxins and furans. Response factors for each analyte in each solution were measured relative to a labeled standard as specified below:

Analytes	Internal Standard
TCDDs and TCDFs	$^{13}C_{12}$-2,3,7,8-TCDD
PeCDDs and PeCDFs	$^{13}C_{12}$-1,2,3,7,8-PeCDD
HxCDDs and HxCDFs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
HpCDDs and HpCDFs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
OCDD and OCDF	$^{13}C_{12}$-OCDD

Average relative response factors were calculated for each analyte, and the percent relative standard deviation determined for each.

The integrated ion abundance ratio for the two monitored masses for each analyte was calculated to check the accuracy of the instrument tune. Special attention was also given to gas chromatographic retention time stability and mass spectrometer signal-to-noise (S/N) ratios for each monitored mass. Criteria for acceptable calibration were as follows:

1. The integrated ion abundance ratio for all analytes (M/M+2 or M+2/M+4) must be within 15% of the theoretical value. The acceptable integrated ion abundance ranges for chlorine-containing compounds are:

   M/M+2
      tetra 0.65-0.89
      penta 0.52-0.70
   M+2/M+4
      hexa 1.05-1.41
      hepta 0.87-1.17
      octa 0.75-1.10

2. The signal-to-noise ratio must be greater than 2.5 for all monitored ions in all six solutions.

3. The relative percent standard deviations for the mean response factors for each of the unlabeled standards and labeled reference compounds must be less than 20 percent.

Checks of instrument calibration were performed for every 12 hours of operation. Enseco-CAL used Solution 2 as listed in Table 9-3 for calibration checks. To be acceptable, the continuing calibration had to meet the following criteria:

1. The measured response factors for all unlabeled and labeled standards were within 20 percent of the mean value established during the initial calibration.
2. The integrated ion abundance ratios were within allowed limits as detailed above.

After all tuning and calibration criteria were met, program samples were analyzed. Specific 2,3,7,8-substituted isomers of PCDDs and PCDFs identified in samples met the following criteria:

1. The integrated ion abundance ratios were within 15 percent of the theoretical values as listed above.
2. The retention times for analytes with corresponding 13C-labeled standards were within 3 seconds of their respective standards.
3. The relative retention time (RRT) for specific 2,3,7,8-substituted isomers that did not have a corresponding 13C-labeled standard fell within 0.005 RRT units of the RRT established for that isomer in the continuing calibration analysis.
4. The signal-to-noise ratios for monitored ions were greater than 2.5.

Non-2,3,7,8-substituted compounds present in the samples were included in the totals calculated for each congener class if the following criteria were met:

1. The integrated ion abundance ratio met the same criterion applied to 2,3,7,8-substituted isomers.
2. The retention time fell within the windows established by the initial analysis of the column performance check solution.
3. The signal-to-noise ratio was greater than 2.5.

The 2,3,7,8-substituted PCDDs and PCDFs which met the above criteria for positive identification were quantified using response factors determined from the continuing calibration check standard. For the total homologous PCDD/PCDF concentrations (e.g., total HxCDDs), the average of the response factors determined for congeners present in the calibration mix was used in the calculation.

The initial HRGC/HRMS analysis resolved the majority of 2,3,7,8-substituted PCDD and PCDF isomers. Additional confirmatory analyses were performed on all program samples with positive results for 2,3,7,8-TCDF, as this isomer was known to coelute on the DB5 column with other tetrachlorinated furan isomers. During the course of the monitoring program, Enseco-CAL Laboratories determined that certain non-2,3,7,8 isomers of the penta and hexa congener classes might also pose coelution problems leading to data biased high for the target analytes. An additional confirmatory analysis on a third column was performed on all samples with positive results for these classes beginning with samples submitted from Session 3. Final reported data in all cases represents the combination of data from the original and confirmatory analyses. Surrogate and internal standard recovery data for each sample were reported from the initial analyses.

9.5 Data Review

Enseco-CAL Laboratories provided ENSR with Document Control packages containing all laboratory records received and generated during the sample handling. These packages included copies of Chain-of-Custody forms and all raw data and calculation sheets. Ion chromatograms for all monitored masses for each sample analysis, as well as the ion integration measurements were provided for ENSR review. Data for instrument calibrations, method blanks and laboratory spike analyses were also submitted.

ENSR reviewed all submitted data and verified measurements for reported dioxin and furan congeners. Enseco-CAL performed all peak area measurements under direct analyst control during the initial phases of the program. ENSR review of the data focused upon agreement between the raw data and final report; chromatograms were visually inspected to determine that no peaks had been overlooked, and calculations were checked for accuracy.

Review of data indicated that the majority of measurements were the result of accurate calibration, appropriate analyses and correct calculations. When calculation errors or peak omissions were detected by ENSR review, the laboratory was notified and corrected final report forms were submitted to ENSR. These cases could be categorized as isolated data reduction errors which affected individual samples, and which were corrected prior to final data reporting.

Surrogate and internal standard data were monitored by ENSR on an ongoing basis for the program and are presented in Section 10 of this report. Samples from Session 5 were inadvertently spiked prior to analysis with an internal standard solution containing two of the three field surrogates; as a result, recovery data could be calculated for only one surrogate for this set. Samples from Session 7 were spiked with a field surrogate mix containing 1,2,3,4,6,7,8-HpCDF instead of the HxCDF isomer used for previous sessions. ENSR does not have a historical database on recoveries of this hepta isomer as a field surrogate. Sample SP-83-FB, the field blank for Session 7, had a recovery of the HpCDD field surrogate which fell below three standard deviations of the mean recovery for all field surrogates. Internal standard recoveries for all samples fell within control limits statistically established from this and other ENSR PCDDs/PCDFs ambient monitoring programs.

10. QUALITY ASSURANCE/QUALITY CONTROL

10.1 Introduction

This study incorporated a formal Quality Assurance/Quality Control (QA/QC) program structured to provide quality control checking, corrective action and quality assessment activities. The objectives of the QA program included the accumulation of data demonstrating that:

- the sorbent was free of target compounds and interferants prior to sample collection;
- the volume of sampled ambient air and the time period over which it was collected have been accurately measured;
- the target compounds were efficiently retained on the sorbent throughout each sampling event;
- the sampled ambient air was the only source of target compounds represented in the final measurement results;
- the target compounds were efficiently extracted from the sorbent;
- the clean-up and concentration of extracts has been performed without significant loss of target compounds;
- the target compounds have been accurately identified and quantified.

This section describes the quality control procedures implemented to provide the above assurances, and presents quality assessment results.

10.2 Sorbent Pretreatment Procedures

PUF sorbent "plugs" were die-cut from 4'x4'x3" stock supplied to ENSR by Olympic Foam Products and shipped to the analytical laboratory for cleanup. The cleanup procedure involved successive soxhlet extractions of the entire filter/PUF/cartridge system for 16-24 hours in acetone followed by toluene. The components were then air dried until all solvent evaporated. Following complete drying of the pretreated sample cartridges, isotopically labeled surrogate compounds were applied to each sample cartridge, as detailed further in Section 10.5.

10.3 Flowrate Measurement

Samplers were calibrated prior to each sampling session (ERT SOP No. 2622-021) and checked following the completion of each session. As previously discussed in Section 8.3 of this report, initial and final flowrate calibrations must be within ±10% of each other for the sample to be considered valid.

The flowrate calibration standard was an orifice connected to the inlet of each sample cartridge, in place of the filter and sorbent trap. The orifice was NBS-traceably calibrated against a rootsmeter. All flowrate measurements were standardized to 760 mm Hg and 25°C.

Although no formal flowrate calibration audit was conducted as part of this ARB program, such an audit was performed by the Minnesota Pollution Control Agency (MPCA) on ENSR PS-1 samplers identical to those used for this program. The results of this audit showed the mean difference between ENSR's sampler flowrates and MPCA's audit flowrates to be 2.3%.

10.4 Field Systems Audit

ARB staff conducted two field audits to evaluate sample handling procedures, recordkeeping, sampler siting, sampler maintenance and other details of the field sampling operation. ARB staff visited the monitoring network during the week of September 26, 1988 for fall sessions five and six. Corrective actions suggested and implemented as a result of this audit included replacement of motors and brushes in all PS-1 samplers prior to each remaining monitoring campaign and acquisition of additional fall season collocated sampler data at the North Long Beach monitoring site (Sessions 6A and 6B, conducted in November 1988). Results of a similar ARB audit of the March 1989 spring sampling campaign required no major corrective action items.

10.5 Field Surrogate Data

Prior to sample collection, PUF sorbent cartridges were spiked with 500 pg of three of the following four surrogate compounds, $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C_{12}$-2,3,7,8-TCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF and $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD.

The surrogate compounds were spiked just below the inlet surface of the PUF plug at the laboratory following completion of the cleanup procedure described in Section 10.2 and prior to disposition to the ENSR field team.

Use of field surrogates allowed for an assessment of accuracy of the combined sampling and analysis regime by examining the average field-applied surrogate recovery (observed vs. applied) in program samples. The mean recoveries calculated for the TCDD, TCDF, HxCDF and HpCDD field surrogates are 79%, 82%, 79% and 57%, respectively, as shown in Table 10-1.

With the exception of the hepta surrogate, all average recoveries fall within the acceptable recovery window of 60% to 140% established at the outset of the program (see Phase I Summary Report). Formal conclusions regarding the low hepta field surrogate average recovery are difficult to formulate due to its use in only one sampling Session (8 samples).

10.6 Laboratory Internal Standard Data

Five isotopically labeled internal standards were spiked into each PUF cartridge just prior to soxhlet extraction. This

TABLE 10-1

FIELD SURROGATE AND INTERNAL STANDARD RECOVERY DATA

		FIELD SURROGATE RECOVERIES (%) [c]				INTERNAL STANDARD RECOVERIES (%) [c]				
Session Number	Sample ID	TCDD	TCDF	HxCDF	HpCDF	TCDD	PeCDD	HxCDD	HpCDD	OCDD
Session 1	7-82-2	96	96	87		70	66	82	64	
	7-87-29	96	100	82		68	65	86	67	
	8-26-75	92	92	78		71	77	99	75	
	7-87-16	75	86	80		76	66	58	44	
	7-87-23	77	89	80		90	80	80	76	
	8-26-89	78	79	76		95	74	66	52	
	7-87-20	86	82	76		94	83	76	67	
Session 2	7-27-35	78	65	46		90	76	79	62	
	8-26-69	84	70	64		98	92	82	74	
	7-27-39	82	70	62		96	86	88	80	
Session 3	7-88-52	106	112	112		84	78	80	114	74
	8-26-69	130	98	90		90	69	72	99	70
	8-87-48	136	120	116		90	78	78	104	72
	8-26-71	124	112	108		107	80	80	108	84
	100	100	94	82		90	76	79	104	70
	7-88-51	90	80	70		79	62	65	85	55
	8-87-39	74	72	56		67	50	52	66	42
Session 4	7-87-11	116	100	90		97	62	61	83	75
	7-88-53	120	104	94		93	74	72	99	76
	7-87-18	86	82	68		78	60	73	77	52
	97	48	48	36		46	29	30	39	25
	7-27-33	128	114	98		106	77	75	98	76
	8-26-88	128	94	98		98	82	80	108	75
Session 5	100	52	[b]	[b]		47	20	68	58	33
	195	36	[b]	[b]		63	70	84	72	45
	7-87-22	50	[b]	[b]		49	64	84	73	42
	7-27-33	29	[b]	[b]		56	68	86	70	39
	7-88-53	28	[b]	[b]		50	27	106	54	28
	7-87-18	33	[b]	[b]		55	46	103	62	44
	127	64	[b]	[b]		44	44	94	55	36
	SN 32267	28	[b]	[b]		40	40	96	54	38
Session 6A	B1-132	25	24	50		39	48	81	67	26
	B1-132F	[a]	[a]	[a]		26	39	48	48	22
Session 7	SP-78	60	49		28	20	48	30	55	28
	SP-67	68	59		67	28	60	59	75	39
	SP-22	96	87		47	37	104	76	100	48
	SP-129F	[a]	[a]		[a]	30	86	62	84	44
	SP-129	88	80		77	32	100	70	92	51
	SP-85	70	78		66	28	64	60	78	37
	SP-83	55	66		38	26	48	38	73	35
	SP-195	76	68		69	29	73	61	76	36
	SP-100	67	61		61	24	64	56	72	34
Average Recovery		79	82	79	57	64	66	73	75	48
Standard Deviation		30	21	20	16	27	19	17	19	18
Population (n)		40	32	24	8	42	42	42	42	32

[a] - No field surrogates applied to filter.
[b] - Laboratory unable to report TCDF and HxCDF recoveries. See Section 9 for further details.
[c] - Blank table entries indicate compound not spiked. Formal compound identities are given in Table 9-2.

procedure allows for quantitation of the various congener classes selected for sampling and analysis, and provides for measurement of the quantitative recovery of the target compounds throughout the extraction and analysis procedure. Table 10-2 lists the five internal standards applied to each sample, and the congener class quantitated by each. A statistical analysis of the percent recoveries obtained for these five compounds from each sample allows for determination of an average recovery and standard deviation for each standard, as displayed in Table 10-1. Any recovery value found to lie outside ± 2σ from the mean for each standard is considered an outlier, and data quantitated using that standard have been noted.

10.7 Method Blanks

Quality control procedures included the analyses of several blank PUF sample cartridges which were pretreated and processed through the sample preparation procedures. Analytical results obtained from these method blanks provide verification of sorbent clean-up, as well as a means of detecting contamination introduced in the laboratory. All of the method blanks analyzed by ENSECO-CAL Laboratories showed no indication of laboratory contamination.

10.8 Field Blanks

Field blank samples exposed to field conditions were analyzed to assess possible contamination throughout the sample collection and analysis process. Unlike method blanks, field blanks are sensitive to field-derived sample contamination, contributed by passive deposition and sample handling. Field blanks were open to the atmosphere for the duration of the sample set-up and recovery periods (approximately ten minutes total). In addition, field blanks were placed into and removed

TABLE 10-2

LABORATORY INTERNAL STANDARDS

Internal Standard	Quantitated Analytes
^{13}C-2,3,7,8-TCDD	TCDDs and TCDFs
^{13}C-1,2,3,7,8-PeCDD	PeCDDs and PeCDFs
^{13}C-1,2,3,6,7,8-HxCDD	HxCDDs and HxCDFs
^{13}C-1,2,3,4,6,7,8-HpCDD	HpCDDs and HpCDFs
^{13}C-OCDD	OCDD/OCDF

from the sampler head to mimic the procedures employed for program samples. Analytical results reported for program samples are corrected using the corresponding field blanks as described in Section 11. All TEF summaries were calculated using field blank-corrected data.

10.9 Collocated Samplers

10.9.1 Overview

Collocated sampler pairs were placed at one or two pre-selected sites during each sampling session. Samples from each collocated pair were collected, handled and analyzed in an identical manner. Moreover, each sampler pair operated concurrently and at nearly identical flow rates. Collocated sampler data obtained in this manner establishes the precision of the combined sample collection and analysis regime on a congener-specific basis.

10.9.2 Precision of Actual Measurements (Quantitative Assessment)

Each pair of collocated values for a particular 2,3,7,8-substituted isomer falls into one of three categories as follows:

- Detected or measured values are reported in both of the collocated samplers.
- The collocated pair data results in one detected value and one non-detected value.
- The collocated pair results consist of two non-detected values.

Comparisons involving two detected values provide the only quantitative estimate of precision. Precision for collocated data pairs was calculated as follows:

$$\frac{\text{abs } (X_1 - X_2)}{(X_1 + X_2)/2} \times 100$$

where X_1 and X_2 represent collocated measured data points (pg/m^3) and 'abs' indicates absolute value.

Precision data in the form of percent differences for the four collocated pairs are presented in Table 10-3. The average percent difference obtained for all measured pairs is 27%. Based upon these precision data, ENSR would like to offer the following observations:

2,3,7,8-TCDD/TCDF and 2,3,7,8-Substituted PeCDD/PeCDF Isomers - The potential contribution to the TEF sum is the greatest for these congeners (TEF of 1.0), and as such, assessing the precision of these measurements is of the greatest importance. The absence of the Cl_4 and Cl_5 2,3,7,8-substituted PCDDs isomers from the collocated pairs however, precludes assessing reliable measurement precision for these isomers.

The Cl_4 and Cl_5 2,3,7,8-substituted PCDFs on the other hand, appeared with greater frequency in the collocated samples. Based on the collocated sampler data contained in Table 10-3, the average precision obtained for these isomers, expressed as a percent difference, was 16% (n=4). This precision value falls well within the precision goal of 50% established at the outset of program (Phase I Summary Report), and shows improved precision for the congeners when compared to the average percent difference obtained for all measured data pairs of 27%.

Comparability of Numbers of Isomers Detected Within a Congener Class - This particular situation is applicable only to non-2,3,7,8-substituted PCDD/PCDF congener classes and not the individual 2,3,7,8-substituted target compounds. It has been

TABLE 10-3
COLLOCATED SAMPLER DATA (pg/m^3)
(percent difference between measured values)

	El Toro - Session 1			El Toro - Session 3			N L Bch - Session 4			Reseda - Session 7		
	pg/m3			pg/m3			pg/m3			pg/m3		
Parameter	8-26-89	7-87-20	% D	7-88-51	8-87-48	% D	7-27-33	7-87-18	% D	SP-195	SP-100	% D
2,3,7,8-TCDD												
TOTAL TCDD												
1,2,3,7,8-PeCDD												
TOTAL PeCDD										0.020		[a]
1,2,3,4,7,8-HxCDD												
1,2,3,6,7,8-HxCDD												
1,2,3,7,8,9-HxCDD												
TOTAL HxCDD	0.11	0.027	121							0.090	0.077	15.1
1,2,3,4,6,7,8-HpCDD	0.25	0.26	3.9				0.29	0.24	18.9	0.13	0.11	11.3
TOTAL HpCDD	0.46	0.46	0.0				0.53	0.24	75.3	0.27	0.24	11.5
OCDD	NR	NR		0.82	0.79	3.7	1.6	1.9	17.1	0.98	1.10	11.2
2,3,7,8-TCDF	0.021	0.027	25.5							0.037	0.029	22.5
TOTAL TCDF	0.32	0.27	16.9							0.20	0.24	18.9
1,2,3,7,8-PeCDF	0.077	0.068	12.7									
2,3,4,7,8-PeCDF	0.077	0.080	3.4									
TOTAL PeCDF	0.56	0.29	63.5							0.070	0.11	41.5
1,2,3,4,7,8-HxCDF	0.15	0.10	40.0									
1,2,3,6,7,8-HxCDF	0.25	0.15	50.0									
2,3,4,6,7,8-HxCDF												
1,2,3,7,8,9-HxCDF												
TOTAL HxCDF	0.36	0.40	10.5							0.19	0.14	27.5
1,2,3,4,6,7,8-HpCDF										0.059	0.048	21.5
1,2,3,4,7,8,9-HpCDF												
TOTAL HpCDF										0.11	0.048	76.7
OCDF	NR	NR								0.13	0.12	10.9

[a] - Single measured value in collocated data pair precludes calculation of percent difference in this case.
NR - Not reported by laboratory.
% D - Percent difference calculated using the formula provided in Section .

AVERAGE PERCENT DIFFERENCE (between measured pairs) = 27.1 %

our observation that the percent differences between measured values in collocated pairs for congener classes is most strongly influenced by the number of isomers reported in each of the two samples and not the reported sum of their concentrations. Due to the nature of the analytical measurements, concentrations reported for PCDD/PCDF congener classes are a direct function of the number of individual isomers identified. For example, there are 22 individual TCDD isomers. If an identical number of these isomers are not identified and quantitated for the TCDD congener class within each of the collocated samples, then the concentration sum reported for this congener class will not be directly comparable. For this reason, concentrations reported for individual 2,3,7,8-substituted PCDDs/PCDFs in collocated pair samples provide a more reliable measure of the precision of the combined sample collection and analysis regime.

The collocated sampler data contained in Table 10-3 show precision of 2,3,7,8-substituted congeners and congener class totals to be 18% and 36%, respectively.

10.9.3 Qualitative Precision Assessment

In addition to the quantitative precision assessment described in Section 10.9.2 for the combined sampling and analysis resume, a qualitative assessment may also be provided. As discussed, specific precision values (expressed as percent differences) may be ascribed to collocated sampler data pairs containing two measured values. A data pair containing two non-detected values provides useful information as well, as it offers a qualitative confirmation of acceptable precision. Of the 98 collocated data pairs (4 collocated samples times 24 or 25 data pairs per sample), 97 contained either two measured values or two non-detected values. This exceptional reproducibility between collocated sampler data pairs indicates that the likelihood of false positives (detecting a congener when it is not actually present) and false negatives (not detecting a congener when it is actually present) in other program samples is minimal.

10.9.4 Precision Assessment - Summary

The monitoring plan for this study identified a precision goal of ±50%. The quantitative precision assessment provided by all measured value comparisons (27%) agrees well with that objective. Table 10-4 further summarizes the quantitative and qualitative precision results obtained for the program.

TABLE 10-4
PRECISION ASSESSMENT SUMMARY

1. Quantitative Precision Summary (data pairs containing two measured values).

All Measured Value comparisons	27%
2,3,7,8-substituted congeners only	18%
Congener class totals only	36%
2,3,7,8-substituted TCDDs/TCDFs and PeCDDs/PeCDFs (important because of unity TEF)	16%

2. Qualitative Precision Summary (consideration of all data pairs).

Number of pairs containing either two detected values or two not-detected values	97 pairs
Number of pairs containing one detected value and one not-detected value	1 pair
Total number of collocated data pairs	98 pairs

11. RESULTS

11.1 Introduction

As discussed previously in Section 6.2, a total of 71 samples were collected during the course of the 16-month field program. These included 44 ambient air samples, 17 collocated samples, and 10 field blanks. From this sample population, a total of 38 samples (particle filter/sorbent cartridge combined) were selected for PCDDs/PCDFs analyses via HRGC/HRMS. Two additional samples were submitted for analyses of the particulate filter and sorbent trap, separately.

All samples were submitted to ENSECO-CAL Laboratories for analyses of the 2,3,7,8-substituted analytes and the Cl_4-Cl_8 PCDDs/PCDFs congener classes (see Table 4-1). Blank corrected analytical results (pg) for each parameter were used in concert with the corresponding sample volume (m^3) to derive ambient concentrations (see Table 6-3) in units of pg/m^3 for all analyzed samples. Data from the target 2,3,7,8-substituted PCDDs/PCDFs species as listed in Table 4-1 were used to derive a weighted toxic equivalent sum for each ambient sample by using the TEF model adopted by ARB. TEF data, provided on a site-specific basis, in concert with data available to ENSR by means of the open literature, provide the basis for the discussion of results in Section 12.

11.2 Site-Specific Presentation of Ambient PCDDs/PCDFs - 2,3,7,8-Substituted Congeners

Graphical representations of ambient concentrations measured for the 2,3,7,8-substituted PCDDs/PCDFs target parameters are provided on a site-specific basis in Appendix D. For easier reference, each congener was assigned a unique congener code, as listed in Table 11-1. Measured values only are shown in each of the respective plots. Non-detected values for the applicable parameters are not shown.

TABLE 11-1

SUMMARY LISTING OF 2,3,7,8 SUBSTITUTED PCDDs/PCDFs - GRAPH CODING SYSTEM (see Appendix D)

PCDDs			PCDFs		
Congener Class	Number	Isomer	Congener Class	Number	Isomer
Cl_4	1	2,3,7,8-TCDD	Cl_4	8	2,3,7,8-TCDF
Cl_5	2	1,2,3,7,8-PeCDD	Cl_5	9	1,2,3,7,8-PeCDF
Cl_6	3	1,2,3,4,7,8-HxCDD	Cl_5	10	2,3,4,7,8-PeCDF
Cl_6	4	1,2,3,6,7,8-HxCDD	Cl_6	11	1,2,3,4,7,8-HxCDF
Cl_6	5	1,2,3,7,8,9-HxCDD	Cl_6	12	1,2,3,6,7,8-HxCDF
Cl_7	6	1,2,3,4,6,7,8-HpCDD	Cl_6	13	2,3,4,6,7,8-HxCDF
Cl_8	7	OCDD	Cl_6	14	1,2,3,7,8,9-HxCDF
			Cl_7	15	1,2,3,4,6,7,8-HpCDF
			Cl_7	16	1,2,3,4,7,8,9-HpCDF
			Cl_8	17	OCDD

11.3 Site-Specific Presentation of Ambient PCDDs/PCDFs - Congener Class Totals (Cl_4-Cl_8)

Ambient concentrations of PCDDs/PCDFs expressed as congener class sums (Cl_4-Cl_8) are reported on a site-specific basis in the discussion to follow. These data, which were not expressly required under the scope of work for the present contract, are reported here for each of the eight sites. It is our anticipation that these PCDDs/PCDFs congener class totals data will be instrumental in comparison of PCDDs/PCDFs congener profiles on a site-specific and session-specific basis. Profile analyses represent the most useful means to compare program data to other PCDDs/PCDFs data available in the open literature. These data will be of the greatest use in examining congener profiles on a site-specific basis in an attempt to identify potential source(s) contributions incident upon each individual site. Results shown in each of the plots to follow represent measured values only. Non-detected values for applicable parameters are not represented.

11.3.1 Carson

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted for each of two samples collected at the Carson site as shown in Figure 11-1.

A single sample is provided representing the fall of 1988 and a second sample representing the spring of 1989. A scale of 0-2.0 pg/m^3 is used in the representation of the ambient concentration axis.

11.3.2 El Toro

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted for each of four samples collected at the El Toro

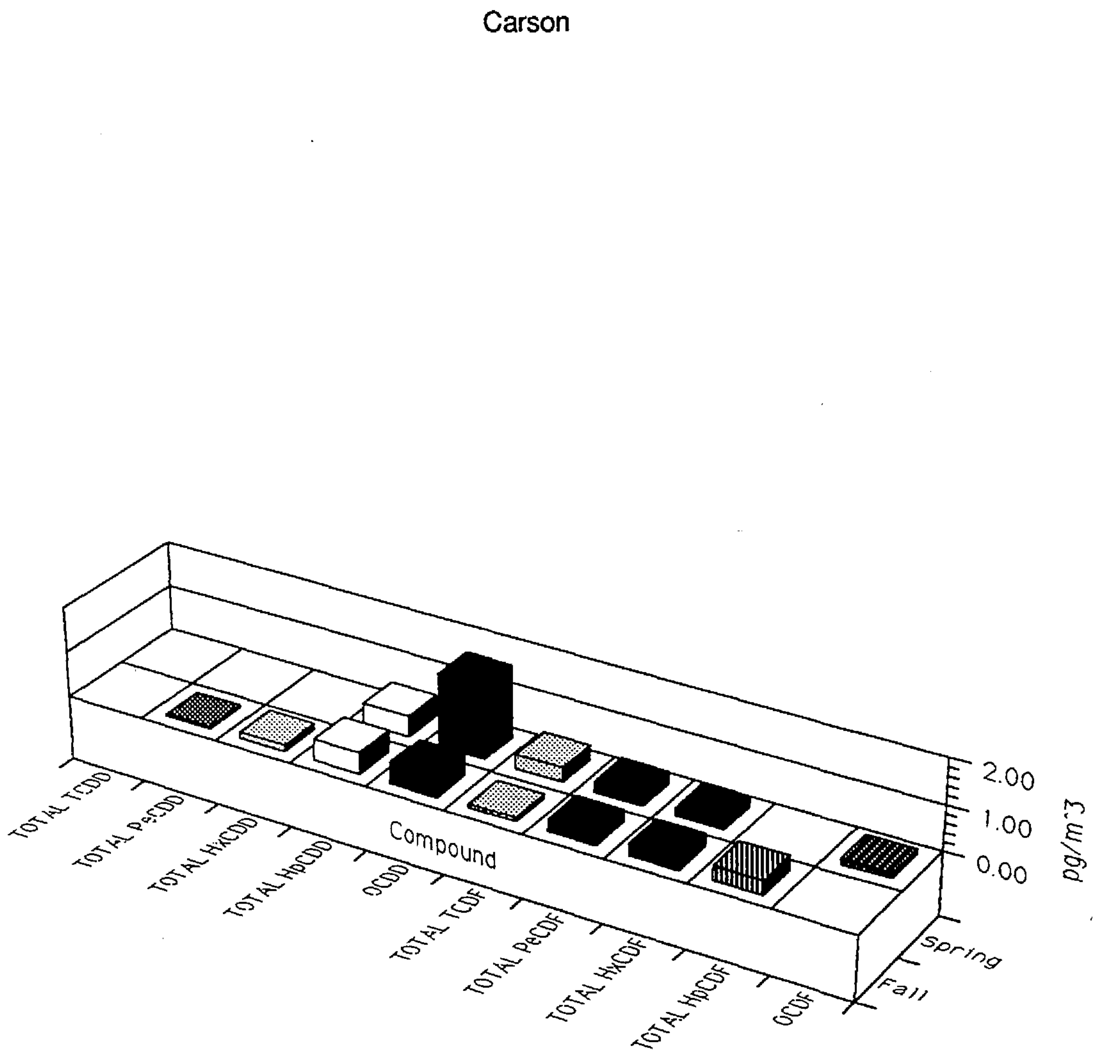


Figure 11-1
PCDDs/PCDFs Congener Class Sums - Carson Site

site as shown in Figure 11-2. A single sample is shown representing the winter of 1987, a second sample representing the fall of 1988 and a collocated sampler pair taken in the summer of 1988. A scale of 0-0.8 pg/m^3 is used in the representation of the ambient concentration axis.

11.3.3 North Long Beach

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted for each of six samples collected at the North Long Beach site. As shown in Figure 11-3, single samples were collected in each of the four seasons. Two collocated sampler pairs were also analyzed, one each in the summer and fall. A scale of 0-8.0 pg/m^3 is used in the representation of the ambient concentration axis.

11.3.4 West Long Beach

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted for each of two samples collected at the West Long Beach site. As shown in Figure 11-4, single samples were collected in each of two seasons, spring 1989 and fall 1988. A scale of 0-4.0 pg/m^3 is used in the representation of the ambient concentration axis.

11.3.5 San Bernardino

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted for five samples collected at the San Bernardino site. As shown in Figure 11-5 at least one sample was collected in each of the four seasons. A collocated sampler pair was analyzed in the summer of 1988 session only. A scale of 0-10 pg/m^3 is used in the representation of the ambient concentration axis.

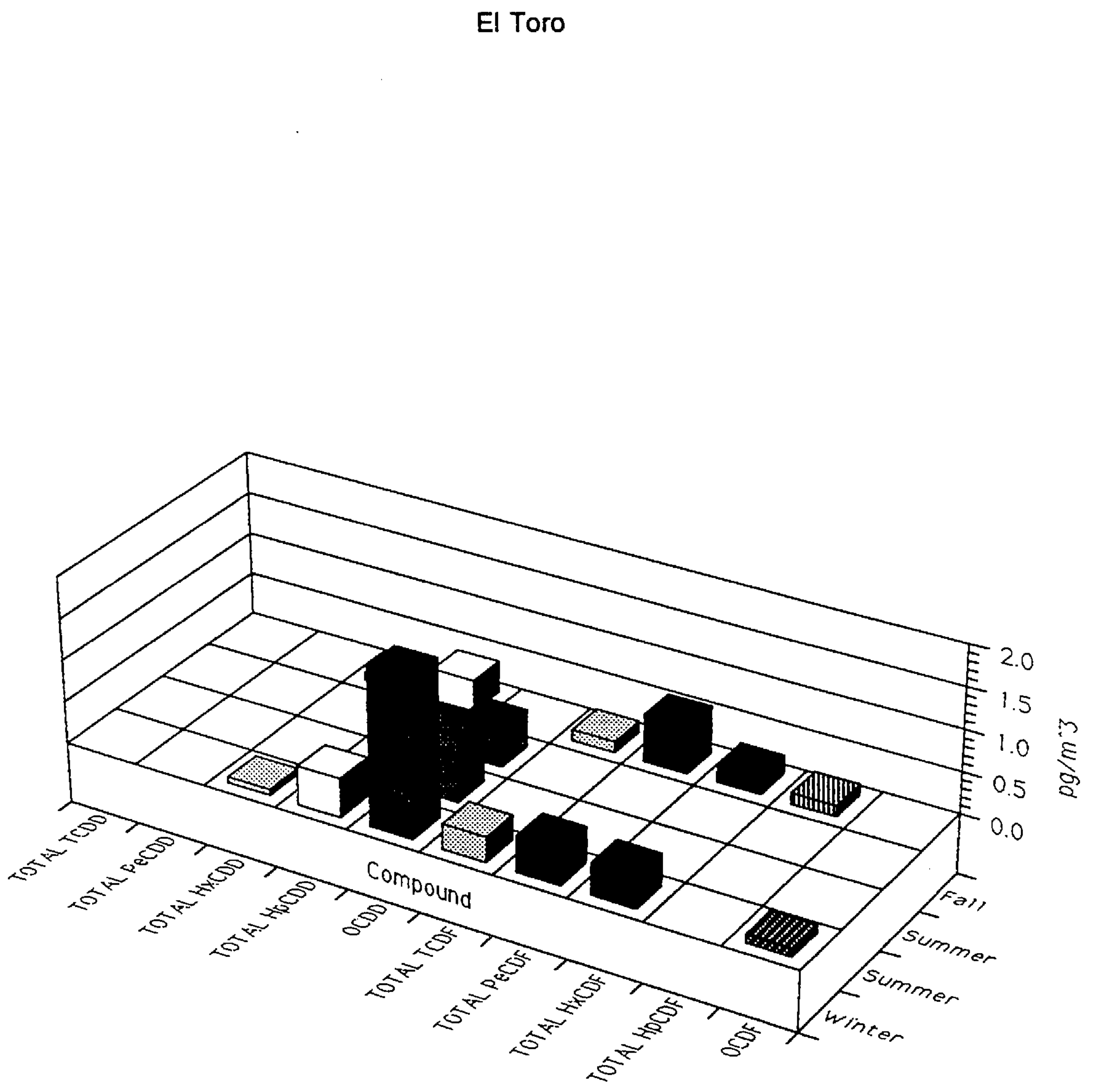


Figure 11-2
PCDDs/PCDFs Congener Class Sums - El Toro Site

▨ TOTAL TCDD
▨ TOTAL PeCDD
▨ TOTAL HxCDD
☐ TOTAL HpCDD
■ OCDD
▨ TOTAL TCDF
■ TOTAL PeCDF
■ TOTAL HxCDF
▥ TOTAL HpCDF
▨ OCDF

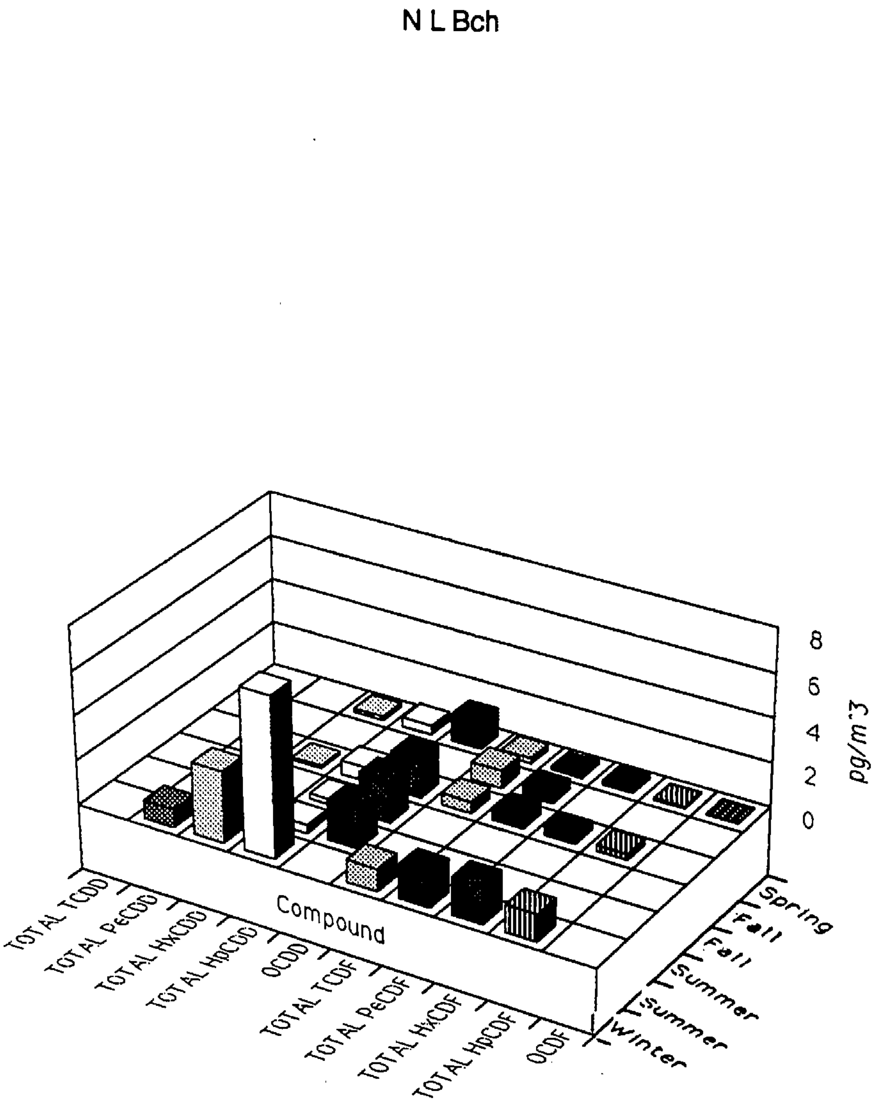


Figure 11-3
PCDDs/PCDFs Congener Class Sums - N. Long Beach Site

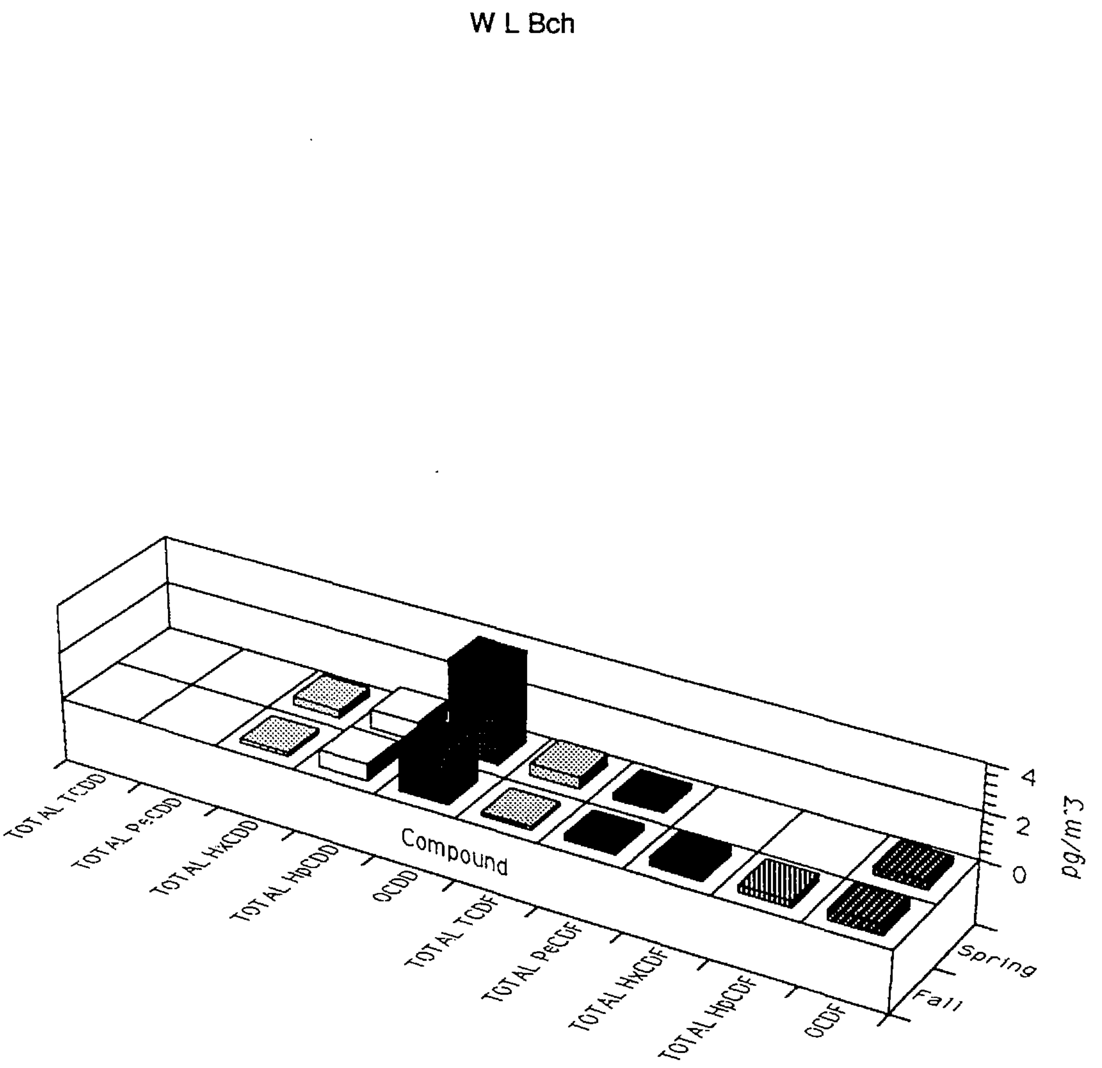


Figure 11-4
PCDDs/PCDFs Congener Class Sums - W. Long Beach Site

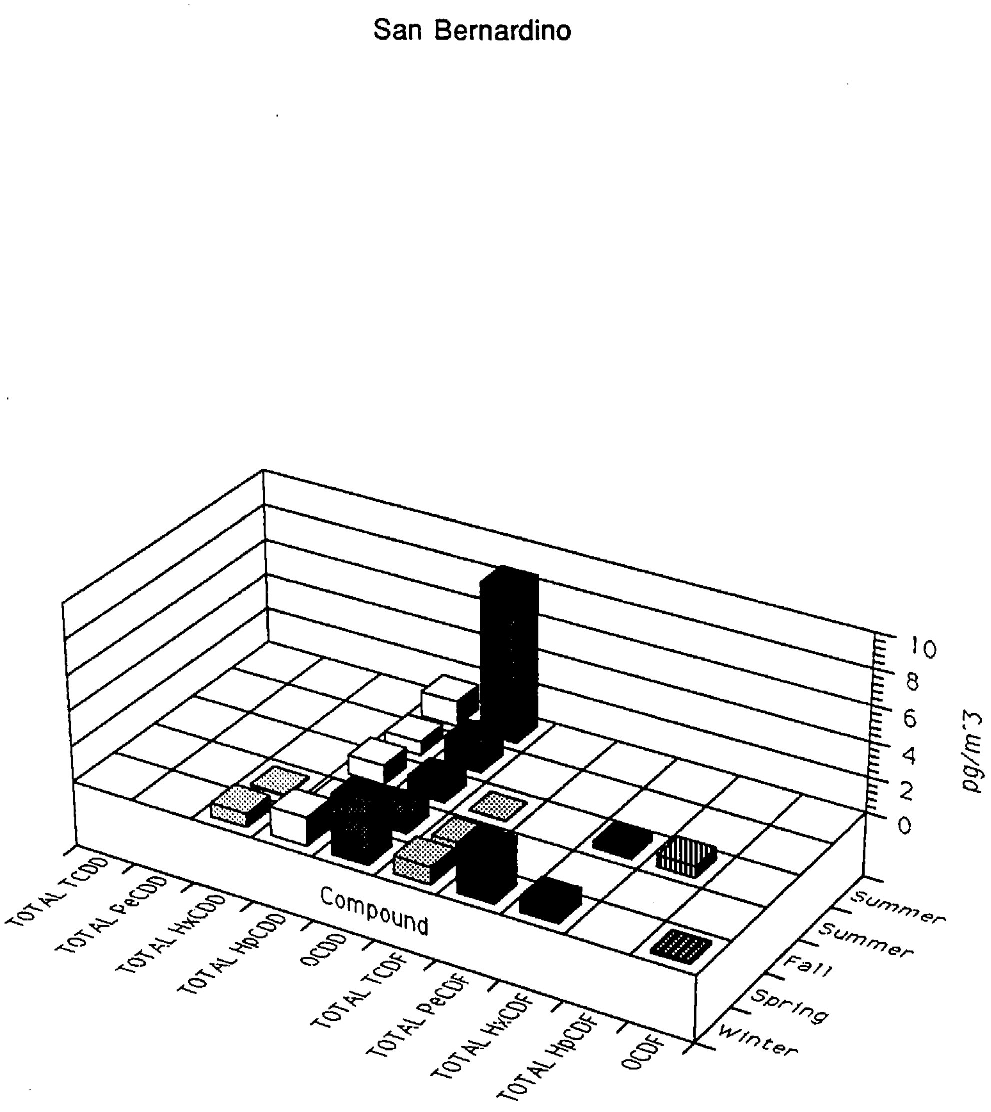


Figure 11-5
PCDDs/PCDFs Congener Class Sums - San Bernardino Site

- ▨ TOTAL TCDD
- ▨ TOTAL PeCDD
- ▨ TOTAL HxCDD
- ☐ TOTAL HpCDD
- ▨ OCDD
- ▨ TOTAL TCDF
- ■ TOTAL PeCDF
- ■ TOTAL HxCDF
- ▥ TOTAL HpCDF
- ▨ OCDF

11.3.6 Cal Trans

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted for four samples collected at the Cal Trans site. As shown in Figure 11-6 a total of four samples were submitted for analyses, two each in the summer 88' and fall 88'. A scale of 0-4.0 pg/m^3 is used in the representation of the ambient concentration axis.

11.3.7 Reseda Site

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted for six samples collected at the Reseda site. As shown in Figure 11-7, a total of six samples were submitted for analyses representing each of the four seasons. A scale of 0-20 pg/m^3 is used in the representation of the ambient concentration axis.

11.4 Site-Specific Presentation of Ambient Data - 2,3,7,8-Substituted PCDDs/PCDFs Expressed as Toxic Equivalent Totals (TEF/TEQ)

Ambient measurements data for each analyzed sample are summarized in Appendix C. These data in turn were applied to the ARB Toxic Equivalents Model to derive toxics equivalents data for each sample. Toxic equivalents are presented on an isomer specific basis (2,3,7,8-substituted), as well as a sum for each individual sample in Appendix C of this report. These TEF data are summarized for all samples in Table 11-2. These toxic equivalents data indicate the contribution of measured congeners as separate from the contribution of the non-detected species. The maximum TEF sum that is shown, however, represents the contribution of both the measured and non-detected toxic equivalents data for each sample. These sum data represent a maximum or "worst-case" TEF sum for each sample.

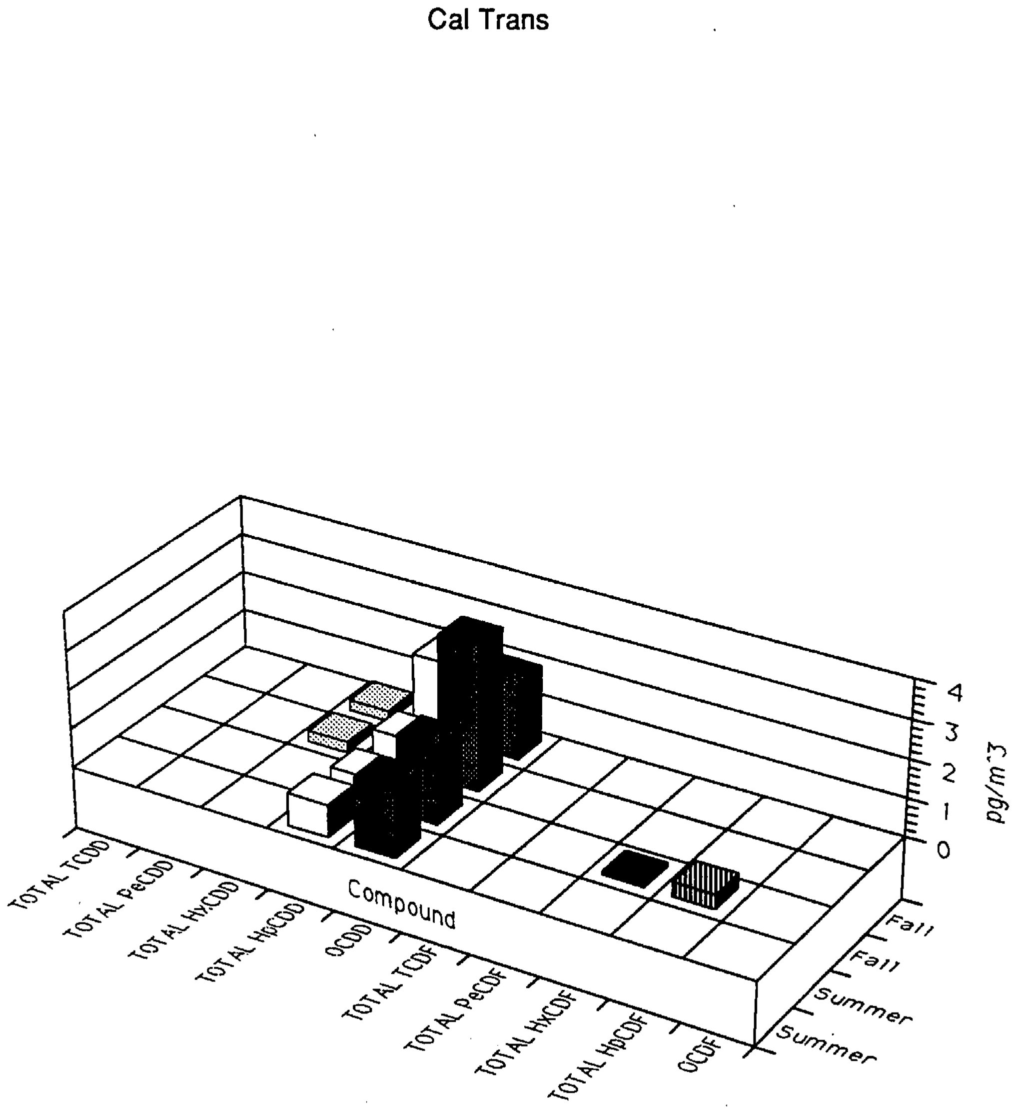


Figure 11-6
PCDDs/PCDFs Congener Class Sums - Cal Trans Site

▒ TOTAL TCDD
▩ TOTAL PeCDD
░ TOTAL HxCDD
□ TOTAL HpCDD
■ OCDD
▒ TOTAL TCDF
■ TOTAL PeCDF
■ TOTAL HxCDF
▥ TOTAL HpCDF
▨ OCDF

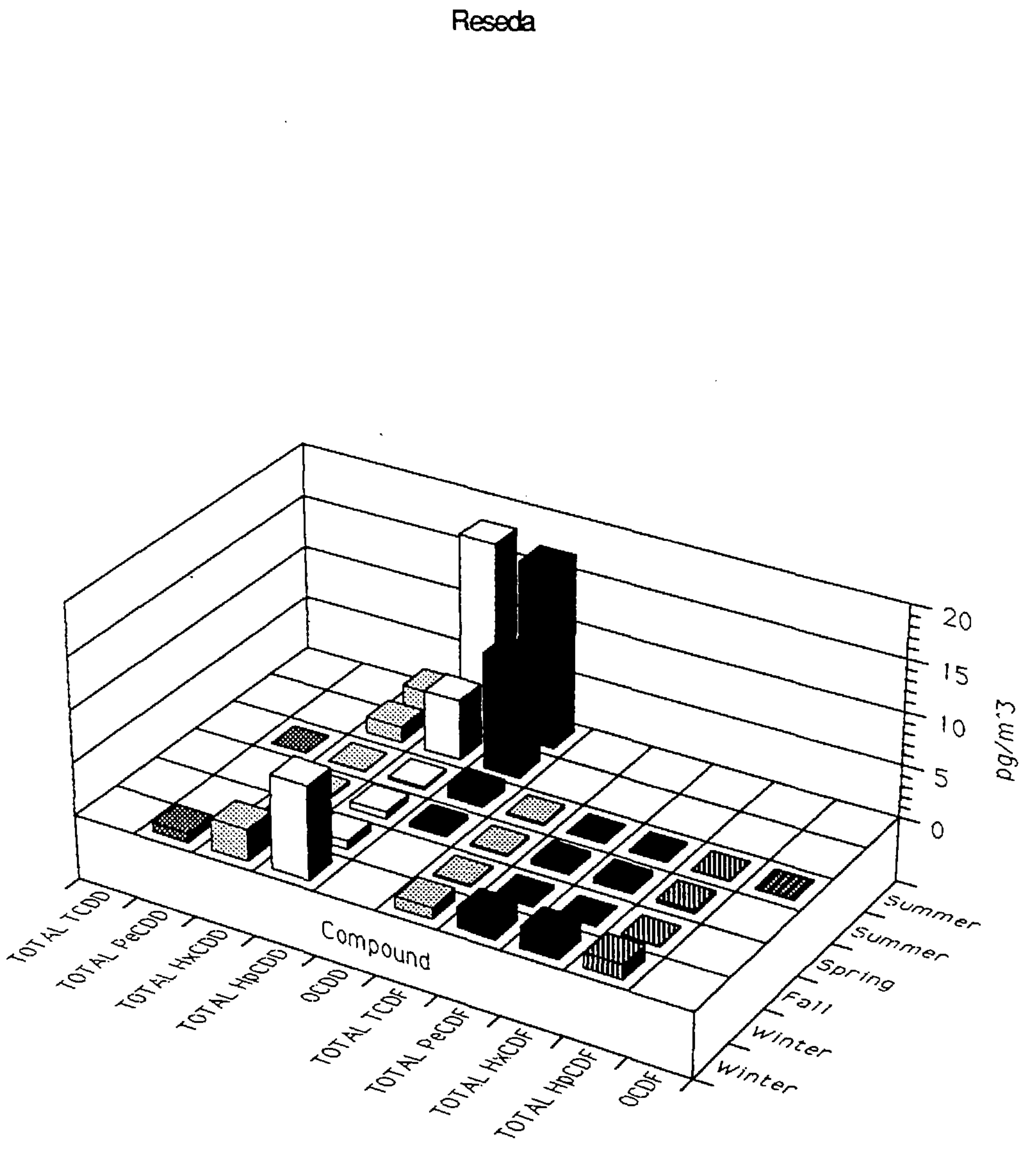


Figure 11-7

PCDDs/PCDFs Congener Class Sums - Reseda Site

TABLE 11-2

SOUTH COAST AMBIENT PCDDs/PCDFs MONITORING PROGRAM

Toxic Equivalents Data Summary

SAMPLE INFORMATION			TEF CATEGORY [a] (TEF values have units of pg/m3)		
Session Number	Site Description	Sample ID	Detected	ND	Maximum
1	Reseda	7/87-2	0.676	0.026	0.702
	Commerce	7/87-29	0.552	0.043	0.595
	N L Bch	8/26-75	0.491	0.127	0.618
	San Bern	7/87-16	2.083	0.145	2.228
	El Toro	8/26-89	0.196	0.066	0.262
	El Toro	7/87-20	0.191	0.089	0.280
2	Reseda	8/26-69	0.010	0.082	0.092
	El Toro	7/27-35	0.004	0.098	0.102
3	Reseda	7/88-52	0.104	0.279	0.383
	Cal Trans	8/26-69	0.014	0.246	0.260
	San Bern	8/87-39	0.015	0.309	0.324
	El Toro	7/88-51	0.000	0.202	0.202
	El Toro	8/87-48	0.000	0.274	0.274
4	Reseda	8/26-71	0.264	0.193	0.457
	Cal Trans	7/88-53	0.018	0.204	0.222
	San Bern	7/87-11	0.141	0.274	0.415
	El Toro	8/26-88	0.000	0.149	0.149
	N L Bch	7/27-33	0.009	0.188	0.197
	N L Bch	7/87-18	0.007	0.246	0.253
5	Reseda	100	0.059	0.130	0.189
	Carson	195	0.012	0.088	0.100
	W L Bch	7/87-22	0.028	0.087	0.115
	N L Bch	7/27-33	0.033	0.107	0.140
	El Toro	7/88-53	0.024	0.094	0.118
	San Bern	7/87-18	0.051	0.141	0.192
	Cal Trans	SN 32267	0.430	0.152	0.582
6B	N L Bch [b]	B1-132	0.026	0.130	0.156
7	San Bern	SP-78	0.033	1.005	1.038
	Carson	SP-67	0.031	0.103	0.134
	W L Bch	SP-22	0.525	0.115	0.640
	N L Bch [b]	SP-129	0.018	0.082	0.100
	Cal Trans	SP-85	0.132	0.038	0.170
	Reseda	SP-100	0.043	0.049	0.092
	Reseda	SP-195	0.033	0.044	0.077

[a] – Three TEF categories have been established as follows:
- * Detected –– TEF sum originating from measured values
- * Not Detected (ND) –– TEF sum originating from detection limits
- * Maximum –– Detected TEF + Not Detected TEF

[b] - Data represents combination of separate filter/foam analyses.

11.5 Session-Specific Presentation of Ambient Data - PCDDs/PCDFs Expressed as Congener Class Sums (Cl_4-Cl_8)

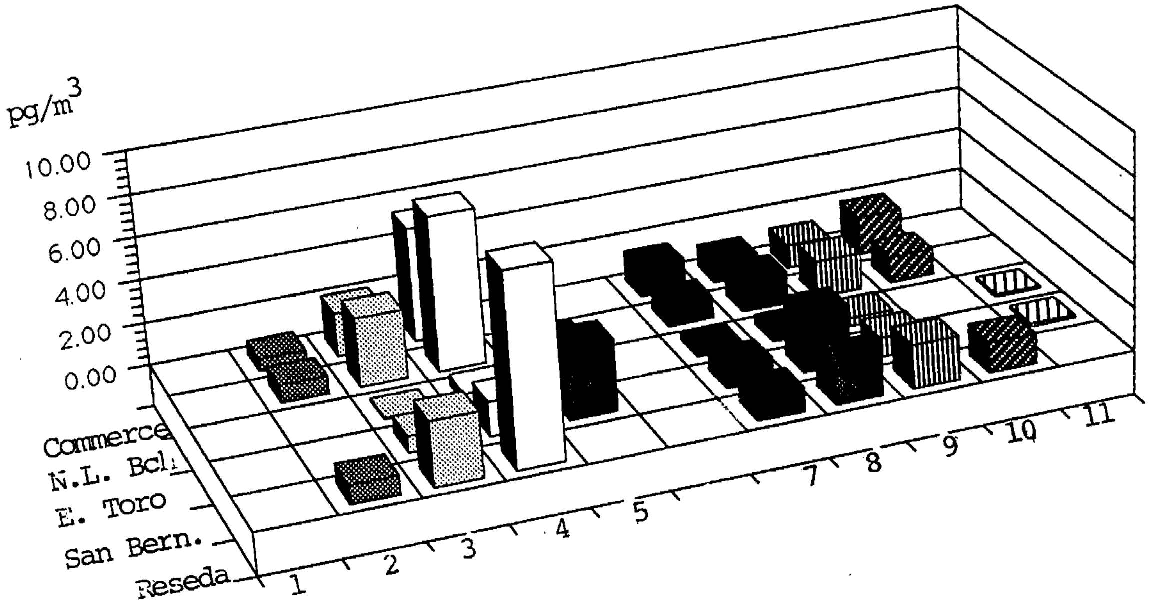
Ambient concentrations of PCDDs/PCDFs expressed as congener class sums (Cl_4-Cl_8) are reported on a session-specific basis in the section to follow. These data, which were not expressly required under the scope of work for the present contract, are reported here for each of seven sessions from which ambient samples were selected for analysis. It is our anticipation that data in this format will assist us in both a quantitative and qualitative comparison of data from session to session, as well as site-specific contribution within a given session. Measured values only are shown in each of the respective graphs. Non-detected values for the applicable parameters are not shown.

11.5.1 Session 1 (Winter 1987) - December 1-3, 1987

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted in Figure 11-8 for each of five samples collected during the calendar period December 1-3, 1987. Results provided for El Toro represent the average of two collocated samples at that site. A scale of 0-10 pg/m^3 was selected to represent the ambient concentration axis for Session 1 data.

11.5.2 Session 3 (Summer 1988) - July 26, 1988

Results for PCDDs/PCDFs (Cl_4-Cl_8) congener class sums are plotted in Figure 11-9 for each of five samples collected and analyzed from Session 3 (July 26, 1988). This session represents one of two summer sampling sessions. Again, results provided for El Toro represent the average of two collocated samples at that site. A scale at 0-12 pg/m^3 was selected to represent the ambient concentration axis.



Key for x-axis

1	TCDD	|	7	TCDF
2	PeCDD	|	8	PeCDF
3	HxCDD	|	9	HxCDF
4	HpCDD	|	10	HpCDF
5	OCDD	|	11	OCDF

Figure 11-8
PCDDs/PCDFs Congener Class Sums - Session 1

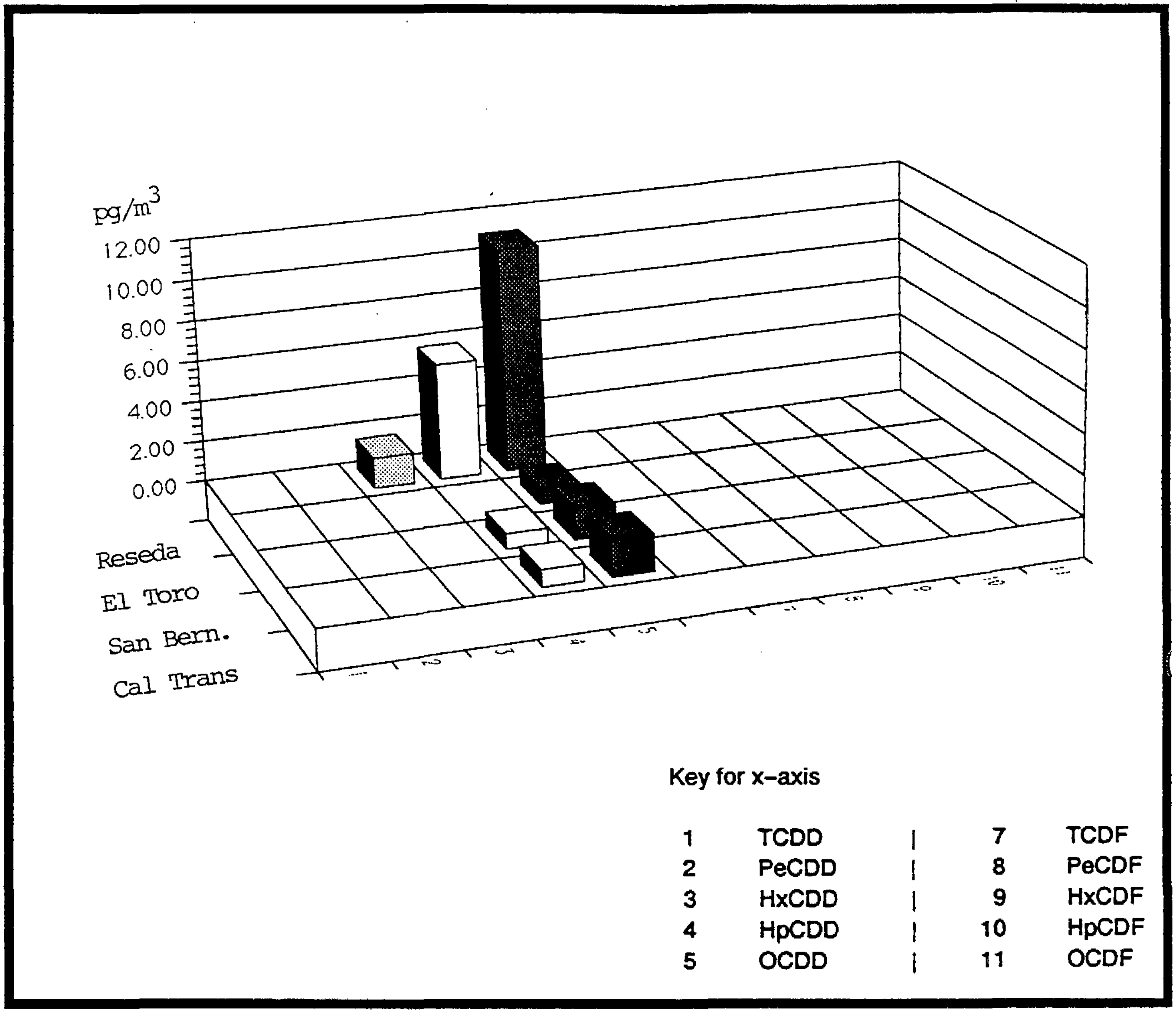


Figure 11-9
PCDDs/PCDFs Congener Class Sums - Session 3

11.5.3 Session 4 (Summer 1988) - July 28, 1988

Results for PCDDs/PCDFs (Cl_4-Cl_8) as congener class sums are plotted in Figure 11-10 for each of six samples analyzed from those collected during Session 3 (July 28, 1988). This session represents the second of the two summer sampling sessions. Results are provided separately for each of two collocated samples at the North Long Beach site. A scale of 0-20 pg/m^3 was selected to represent the ambient concentration axis.

11.5.4 Session 5 (Fall 1988) - September 27, 1988

Results for PCDDs/PCDFs (Cl_4-Cl_3) expressed as congener class sums are plotted in Figure 11-11 for each of seven samples analyzed from those collected during Session 5 (September 27, 1988). This session represents the first at four fall sampling sessions. A scale of 0-25 pg/m^3 was selected to represent the ambient concentration axis.

11.5.5 Session 6B (Fall 1988) - November 5, 1988

Only a single sample from session 6B was selected for analyses. This sample was selected for separate filter and foam analyses. Accordingly, no session-specific plot is provided here.

11.5.6 Session 7 (Spring 1988) - March 5, 1988

Results for PCDDs/PCDFs (Cl_4-CL_3) expressed as congener class sums are plotted in Figure 11-12 for each of seven samples analyzed from those collected during Session 7 (March 29, 1989). This session represents the spring sampling session for this program. Note that separate set of results are provided for each of two collocated samples from the Reseda

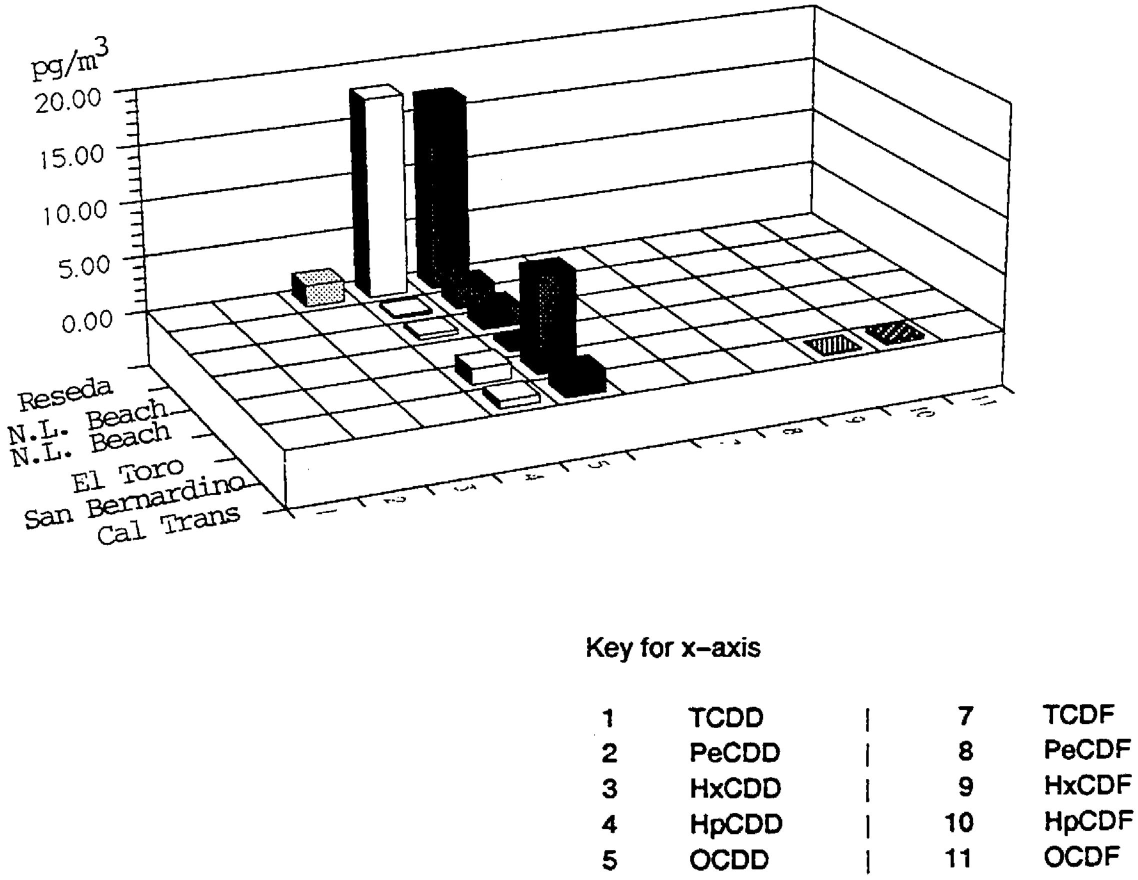


Figure 11-10
PCDDs/PCDFs Congener Class Sums - Session 4

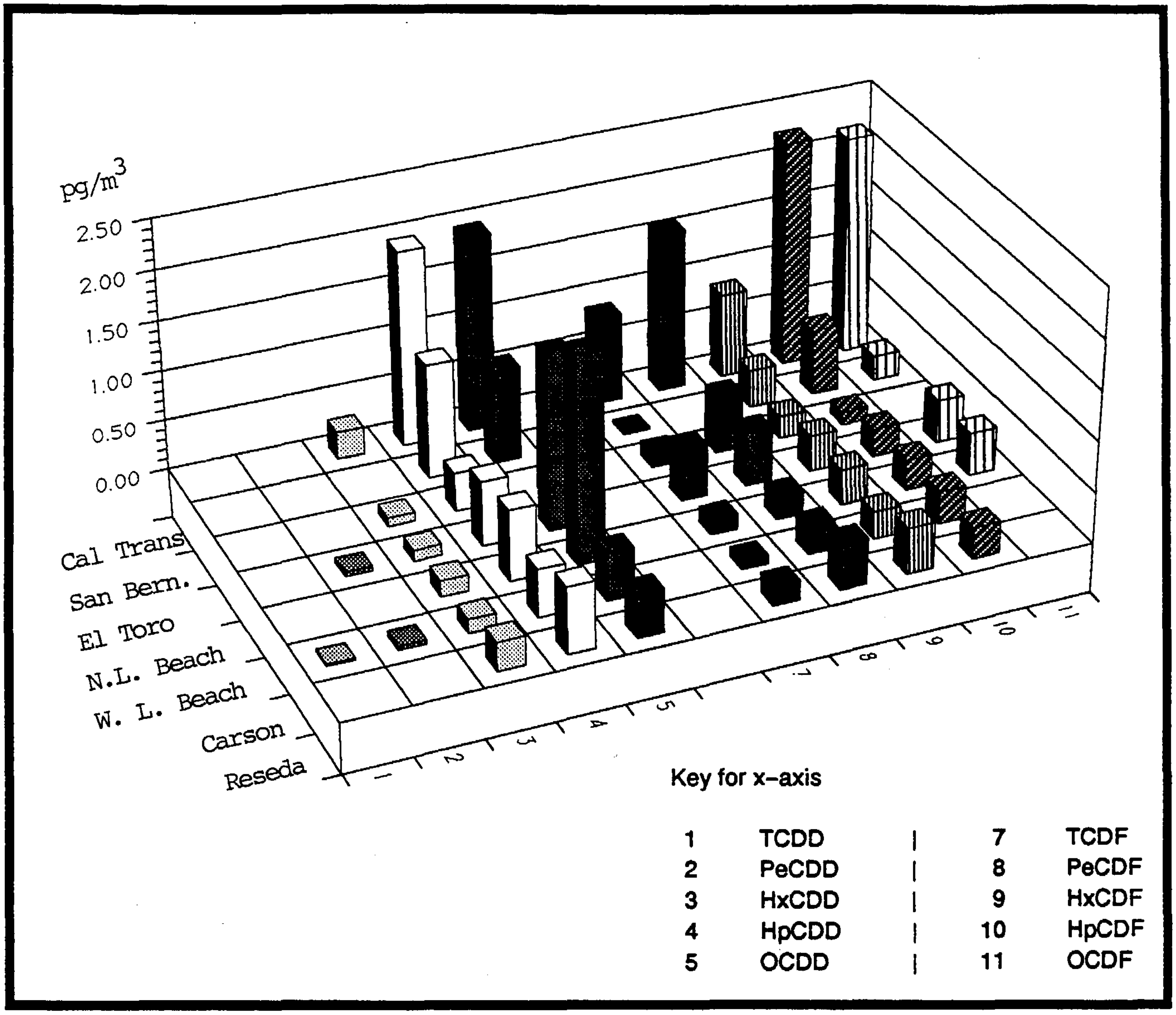


Figure 11-11
PCDDs/PCDFs Congener Class Sums - Session 5

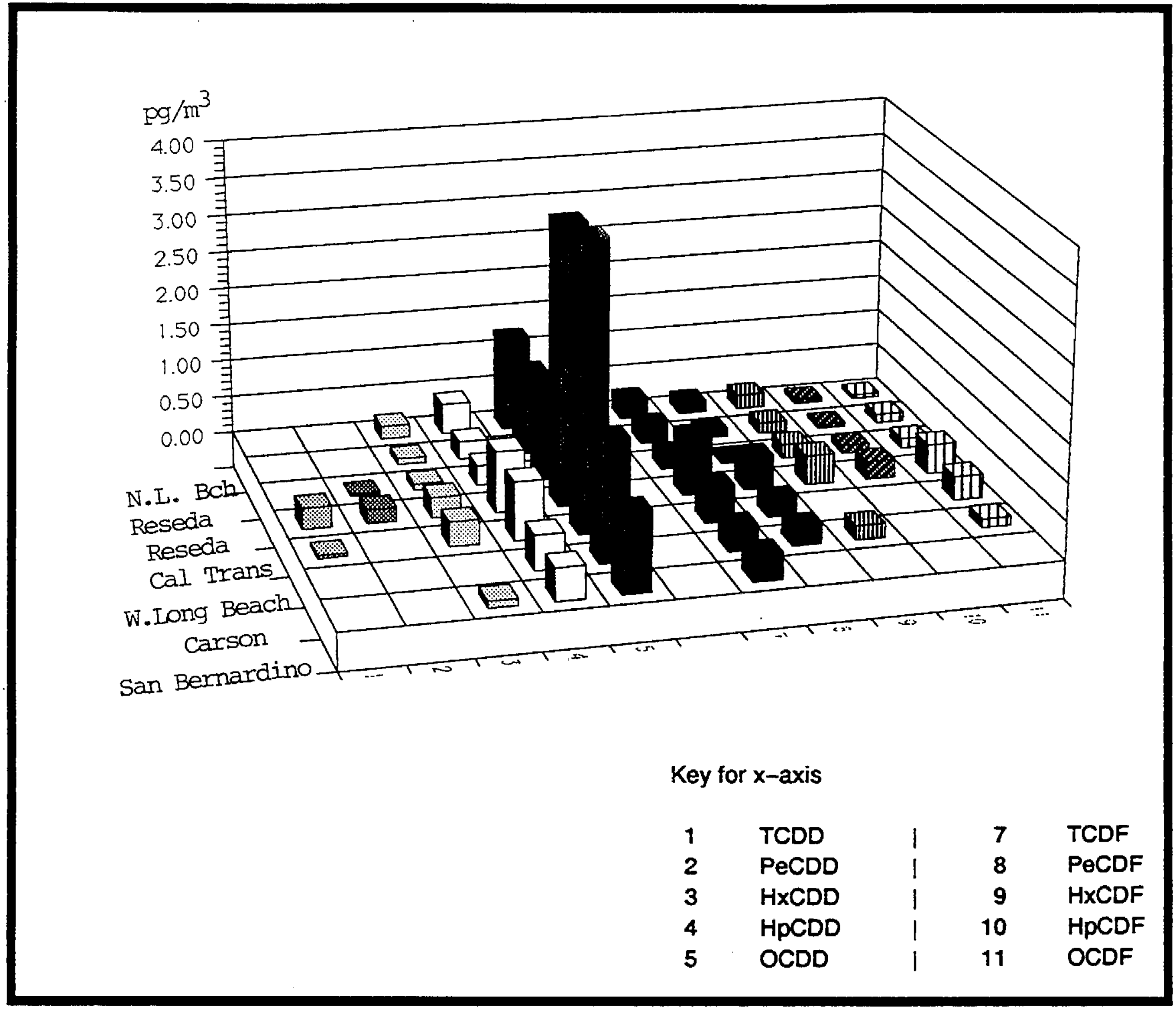


Figure 11-12
PCDDs/PCDFs Congener Class Sums - Session 7

site. A scale of 0-4 pg/m^3 was selected to represent the ambient concentration axis.

11.6 Particulate/Vapor Distribution Data

Two samples were selected for separate analyses of the particulate filter and PUF sorbent cartridge. As noted previously in Table 6-3, these included two samples from the North Long Beach site, one from Session 6A (B1-132) and one from Session 7 (SP-129). Results of these analyses are provided in Figures 11-13 and 11-14, respectively. Note that each plot identifies both the particulate-associated and corresponding vapor-associated concentration on a congener sum-specific basis.

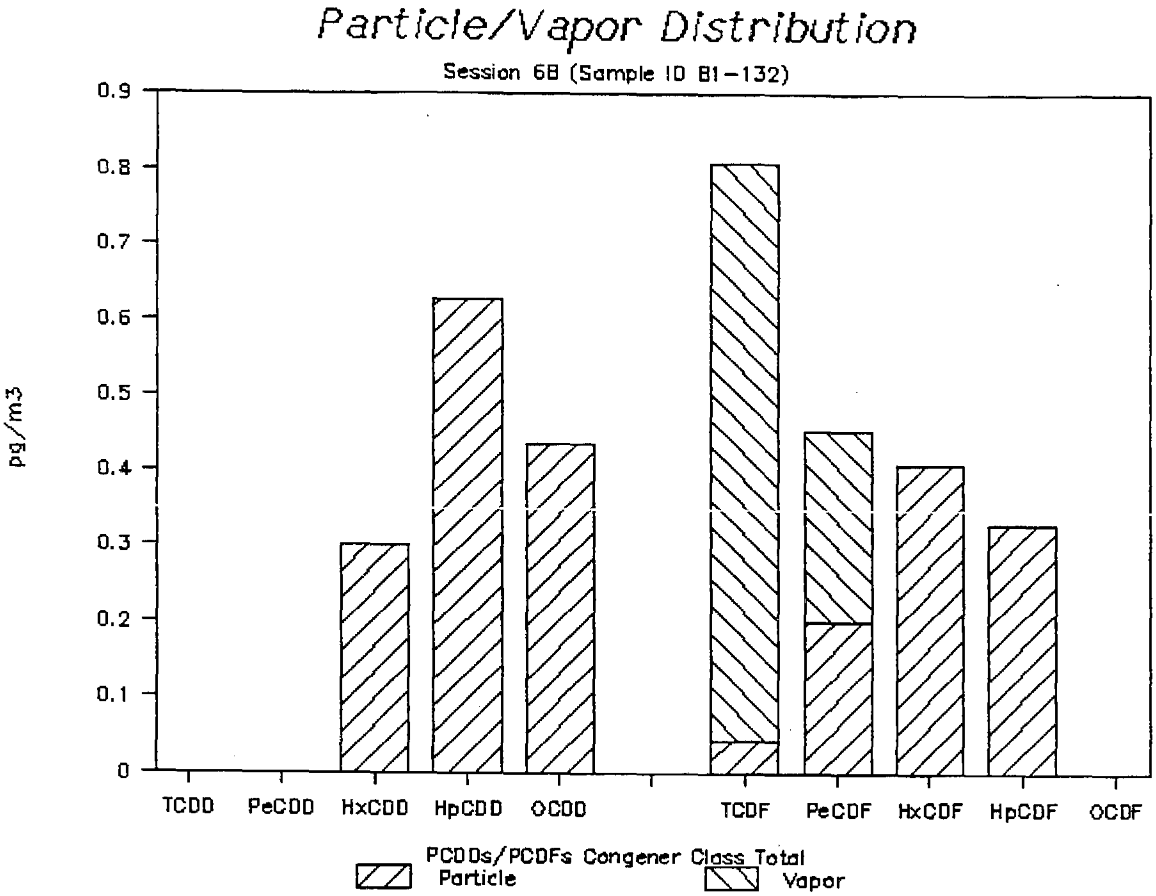


Figure 11-13
Particle/Vapor Distribution Data - Session 6B

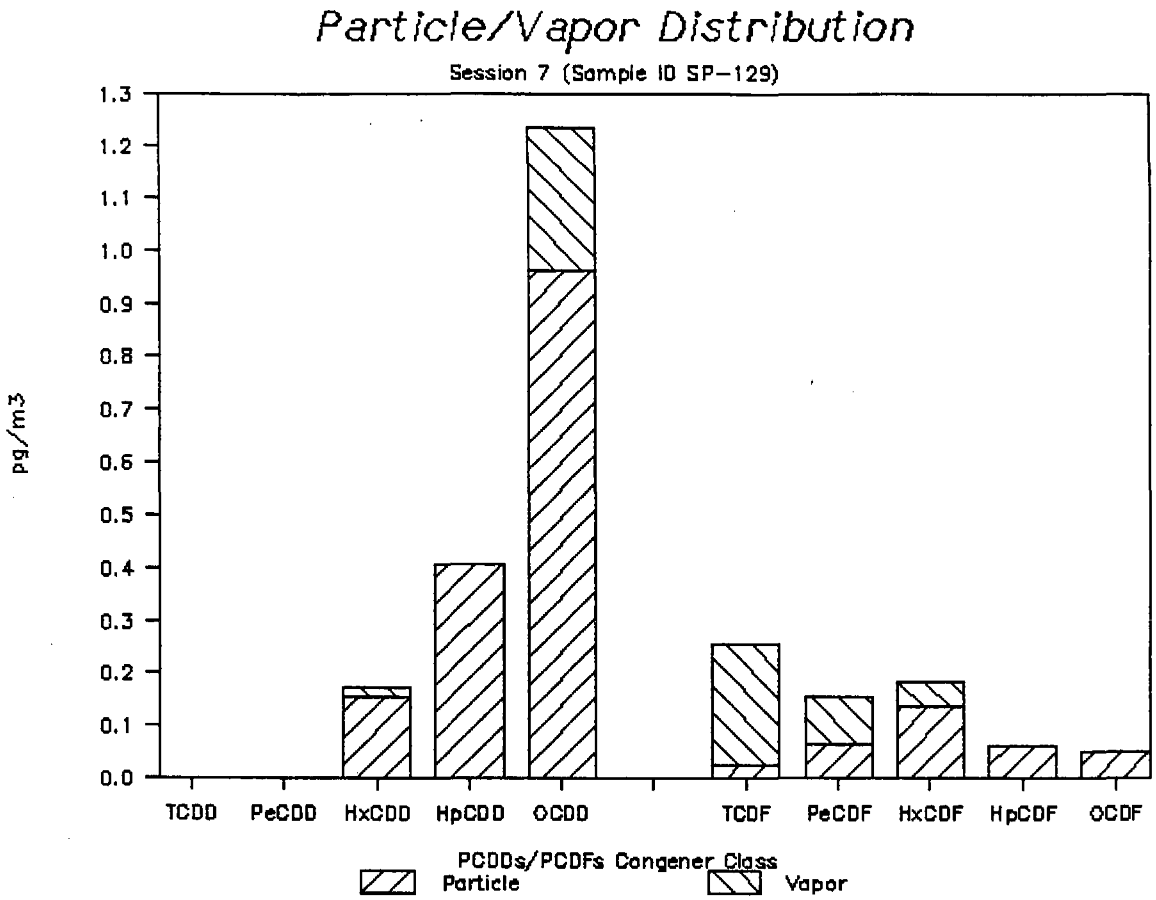


Figure 11-14
Particle/Vapor Distribution Data - Session 7

12. DISCUSSION OF RESULTS

12.1 Introduction

The primary purpose of this program was to establish existing or baseline ambient concentrations of PCDDs/PCDFs and in particular 2,3,7,8-substituted species in the South Coast Air Basin. To this end a program of field sampling and analyses was conducted in the South Coast Air Basin during the calendar period of December 1987 to March 1989.

The discussion to follow in addition to its focus on the aforementioned program objective will attempt to address the quantitative and qualitative significance of the PCDDs/PCDFS data on a site-specific and session-specific basis.

Our discussion will make use of the raw data tables summarized in Appendix C, as well as the graphical illustrations contained in the previous section entitled Results (Section 11). The site summary data in concert with the description of the site and its environs contained in Section 5 will be examined for site-specific trends. Particular attention will be focused on congener profiles and the influences that localized source categories may have on specific site profiles. The session specific data summaries in concert with the meteorological data contained in Section 7 and Appendix A will be examined to identify what influences local or regional meteorology may have on session-specific trends.

Site-specific meteorological data in the form of wind rose plots will also play a role in the interpretation of site-specific and/or session-specific data trends. Program data will also be compared/contrasted to ambient data available to ENSR through other ambient monitoring programs [4-10] supplemented to a great extent by information contained in the open literature [1-3,11-14,16-17,34,35,39-41].

Actual literature references incorporated into the discussion to follow are cited in Section 13. Additional related references are provided in the Supplementary Bibliography contained in Section 14.

12.2 Site-Specific Data - 2,3,7,8-Substituted PCDDs/PCDFs

As noted in the aforementioned program objectives the primary focus of the program was to establish atmospheric burdens of 2,3,7,8-substituted PCDDs/PCDFs that presently exist at selected locations within the South Coast Air Basin. To this end the discussion here will initially focus on the distribution and occurrences of each of the target parameters identified in Table 4-1. (The reader is referred to Section 11, Appendix C and D for the initial stages of our discussion).

12.2.1 Distribution and Occurrences of 2,3,7,8-Substituted PCCDs/PCDFs - General Discussion

PCDDs - Polychlorinated Dibenzodioxins

The majority of the samples selected for analyses contained one or more of the 2,3,7,8-substituted PCDDs listed in Table 4-1. The most predominant species was the OCDD isomer while the most predominant isomer of toxicological significance (TEF weighting factor of 0.03) was 1,2,3,4,6,7,8-HpCDD. This isomer persisted in all of the samples examined with the exception of many of the El Toro samples. Measured concentrations ranged from 0.11 pg/m^3 to a maximum of 8.4 pg/m^3 with the highest concentrations typically measured at the Reseda site. The predominance of the 1,2,3,4,6,7,8-HpCDD as the most persistent 2,3,7,8-substituted PCDD isomer second only to OCDD is consistent with the observations of others in the open literature [1,2,4,14,35]. Further, it has been our experience in numerous ambient monitoring programs that this is the predominant isomer of toxicological significance [5-10,15] present in ambient air. This particular trend is prevalent at sites known to be influenced by stationary or mobile combustion source emissions [14,2,4,17] Czuczwa reports this isomer to be persistent in urban particulate, as well as sediment cores in Siskiwit Lake. In both ambient particulate and sediment samples examined the 1,2,3,4,6,7,8-HpCDD constitutes approximately 55% of the HpCDD-total [35]. Hunt and Maisel report similar findings for a Northeast U.S. coastal metropolitan region in wintertime [4]. Our results corroborate their findings.

The 2,3,7,8-substituted HxCDD isomers persist only in six of the samples examined. The majority of which were collected during the December 1987 winter session (Session 1) and at the Reseda site. The 1,2,3,7,8,9-HxCDD and 1,2,3,6,7,8-HxCDD predominate over the 1,2,3,4,7,8-HxCDD isomer. The highest concentrations overall were noted from analyses of the December 1987 winter samples (1,2,3,7,8,9-HxCDD noted at 0.35 pg/m^3 for Reseda and North Long Beach and 0.27 pg/m^3 for Commerce; 1,2,3,6,7,8-HxCDD noted at 0.39 pg/m^3 for North Long Beach, 0.35 pg/m^3 for Reseda and 0.25 pg/m^3 for Commerce). Again, it has been noted in the open literature [12,13,14], as well as numerous other baseline ambient monitoring programs conducted nationwide [4-10,15] that the 1,2,3,7,8,9-HxCDD is the predominant HxCDD isomer of toxicological significance typically found in the atmosphere.

1,2,3,7,8-PeCDD was found in only two of the samples submitted for analyses, both of which were collected during the December 1987 Winter session (0.12 pg/m^3 at Commerce and 0.14 pg/m^3 at Reseda).

The isomer of primary toxicological significance, 2,3,7,8-TCDD, is virtually absent in the atmosphere of the South Coast Air Basin. Detection limits for the majority of samples ranged from 10-20 fg/m^3. The lower and upper boundaries for detection limits were 4 fg/m^3 and 51 fg/m^3, respectively.

The presence of 2,3,7,8-TCDD was confirmed in only two samples, both of which were collected during the Spring of 1989 (Session 7). A concentration of 8.6 fg/m^3 was reported for the West Long Beach site while a higher concentration of 34 fg/m^3 was reported for the Cal Trans site. The virtual absence of the 2,3,7,8-TCDD isomer in the ambient air of Southern California is again consistent with observations made by others throughout the Continental United States, and worldwide [1-17].

It should be noted that 2,3,7,8-TCDD which has been traditionally associated with a wide variety of combustion sources typically comprises a very small fraction of the total TCDD emitted and an even smaller portion of the total PCDDs (Cl_4-Cl_8) attributable to stationary and mobile combustion source emissions [18-23]. Rappe reported that the 2,3,7,8-TCDD comprises approximately 3% of the total TCDDs contained in the emissions of a Swedish fluidized bed incinerator [22]. This value is contrasted to a 0.3% contribution for the 2,3,7,8-TCDD in the emissions of a Canadian incinerator [22]. Further, Hites and his co-workers have postulated that the 2,3,7,8-TCDD in particular which is primarily associated with the vapor phase in the atmosphere is more subject to direct photochemical degradation [35,40,41]. This particular phenomena can be expected to be more significant in Southern California where available intensity of sunlight and photochemistry is a more dominant factor. Further, ambient temperatures on an annualized basis in Southern California will favor the 2,3,7,8-TCDD in the vapor phase over the particulate phase. Conversely, colder temperatures such as those characteristic of the Northeast U.S. in wintertime will favor particulate association of the 2,3,7,8-TCDD [4].

PCDFs - Polychlorinated Dibenzofurans

The majority of the samples examined contained at least one of the 2,3,7,8-substituted PCDFs identified as target parameters in Table 4-1. Of the nine PCDF target parameters listed the 2,3,7,8-TCDF and the 1,2,3,4,6,7,8-HpCDF appeared most often. Measured concentrations for the 1,2,3,4,6,7,8-HpCDF as noted in Section 11 and Appendix C ranged from a low value of 0.038 pg/m^3 at the North Long Beach site in the Spring of 1989 (Session 7) to a maximum value of 1.58 pg/m^3 at the Cal Trans site in the Fall of 1988 (Session 5). Measured values for the 2,3,7,8-TCDF ranged from a low value of 0.011 pg/m^3 at the North Long Beach site in the Spring of 1989 (Session 7) to a maximum value of 0.48 pg/m^3 at the West Long Beach site in the Spring of 1989 (Session 7).

The 1,2,3,4,7,8,9-HpCDF was not measured in all but one of the samples examined. The virtual predominance of the 1,2,3,4,6,7,8-HpCDF is corroborated by ambient measurements collected globally by a number of other investigators [2,4-10,14-15,17]. Rappe and Kjeller in fact, report the 1,2,3,4,6,7,8-HpCDF to be the most predominant of the four possible positional isomers of HpCDFs [14]. In numerous ambient measurements collected in Hamburg, FRG during the calendar period 1985-1986 the 1,2,3,4,6,7,8-HpCDF was observed to consistently represent 60-70% or more of the total concentration of Hepta CDFS. In this study the authors cited primarily combustion sources (mobile and stationary) as the major contributors to the atmospheric burden of PCDDs/PCDFs. Similar conclusions may be drawn from data presented here in this program. The 2,3,7,8-substituted PCDDs/PCDFs profiles observed in Hamburg, FRG and here in this study suggest primarily combustion source influences [14].

Target PCDFs parameters other than 2,3,7,8-TCDF and 1,2,3,4,6,7,8-HpCDF were generally only noted during the December 1987 sampling session (Session 1). The highest overall concentrations of 2,3,7,8-substituted PCDFs, as well as the most diverse congener profile were measured across the entire regional monitoring network during this same December 1987 sampling session. During this sampling exercise 1,2,3,7,8-PeCDF concentrations ranged from a low of 0.077 pg/m^3 at the El Toro site to a high of 1.9 pg/m^3 at the San Bernadino site. The 2,3,4,7,8-PeCDF concentrations ranged from a low of 0.077 pg/m^3 at the El Toro site to a high value of 0.13 pg/m^3 at the North Long Beach site. In most samples the reported concentrations for each of the two 2,3,7,8-PeCDF species were equivalent. The only exception was the San Bernadino site (Session 7) in which the concentrations differed by a factor of 20:1 (0.10 pg/m^3 for 2,3,4,7,8-PeCDF and 1.9 pg/m^3 for 1,2,3,7,8-PeCDF). The approximately equal distribution of the total 2,3,7,8-PeCDF concentrations between each of the two possible isomers, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF, is consistent with trends noted by other researchers [2,11,12,13,14].

Rappe and Kjeller report that the two PeCDF isomers of toxicological significance in this study comprised merely 15-20% of the total atmospheric PeCDFs burdens typically present in the ambient air of Hamburg, FRG during a 1985-86 measurement campaign [14].

The 2,3,7,8-substituted HxCDF isomers were only measured during the December 1987 Winter sampling session. Detection limits in the majority of samples from those sessions in which they were not observed ranged from 0.01 pg/m^3 to 0.10 pg/m^3.

The predominant HxCDF isomer during the December 1987 Winter session was the 1,2,3,6,7,8-HxCDF. Measured concentrations ranged from 0.25 pg/m^3 at the El Toro site to 0.80 pg/m^3 at the Reseda site. In the majority of the samples the 1,2,3,4,7,8-HxCDF and 2,3,4,6,7,8-HxCDF isomers were present in nearly equivalent concentrations The 1,2,3,7,8,9-HxCDF isomer was not observed in any of the Session 7 samples examined. Detection limits ranged from 0.023 pg/m^3 to 0.11 pg/m^3 in the six samples analyzed.

The trends observed during this study related to the 2,3,7,8-substituted HxCDFs profile are again consistent with trends reported in the open literature [2,11-14]. More specifically, the 1,2,3,7,8,9-HxCDF consistently represents the smallest contribution to the total HxCDF of the four 2,3,7,8-substituted HxCDF isomers. In the majority of the other studies cited here the three remaining 2,3,7,8-substituted HxCDFs contribute to the total HxCDF concentration equally. None of the three appear to predominate

[2,11-14]. This differs from our observation in the present study for instances when one or more of the isomers are measured. For example,, the 1,2,3,6,7,8-HxCDF always appears at the highest measured concentrations often by a factor of 2-3 times the remaining two isomers. Perhaps this can be attributable to the mix of emission sources that contributed to the regional PCDDs/PCDFs profile noted across the network during the December 1987 winter sampling campaign (Session 7). A plot of the 2,3,7,8-substituted PCDDS/PCDFs profile for the December 1987 sampling session (#7) is provided in Figure 12-1. Isomer-specific concentrations are plotted in units of pg/m^3 for each of the sites in contemporaneous operation during this period. Note the strong similarities in congener profiles and equivalent concentrations of isomers present at each of the five (5) locations. These data suggest a regional air mass or regional transport phenomena [4,12].

12.3 Toxic Equivalents Data - General Discussion

12.3.1 Introduction

At the direction of ARB, ENSR was instructed to express the ambient PCDDs/PCDFs data as Toxic Equivalents. This entails entering the blank-corrected ambient concentration data for each of the 2,3,7,8-substituted PCDDs/PCDFs (see Table 4-1) into the California Toxic Equivalency Factor Model (TEF) developed by the California Department of Health Services [24]. Simply, the measured ambient concentration or detection limit ("< value") for each of the 15 target parameters is multiplied by the corresponding weighting factor from the model for that parameter. The product is a weighted ambient concentration expressed as Toxic Equivalents in units of pg/m^3. Each of these results are then summed to obtain a Toxic Equivalents sum in pg/m^3 for each sample. The California DHS TEF model noting the corresponding weighting factor for each of the 2,3,7,8-substituted PCDDs/PCDFs is

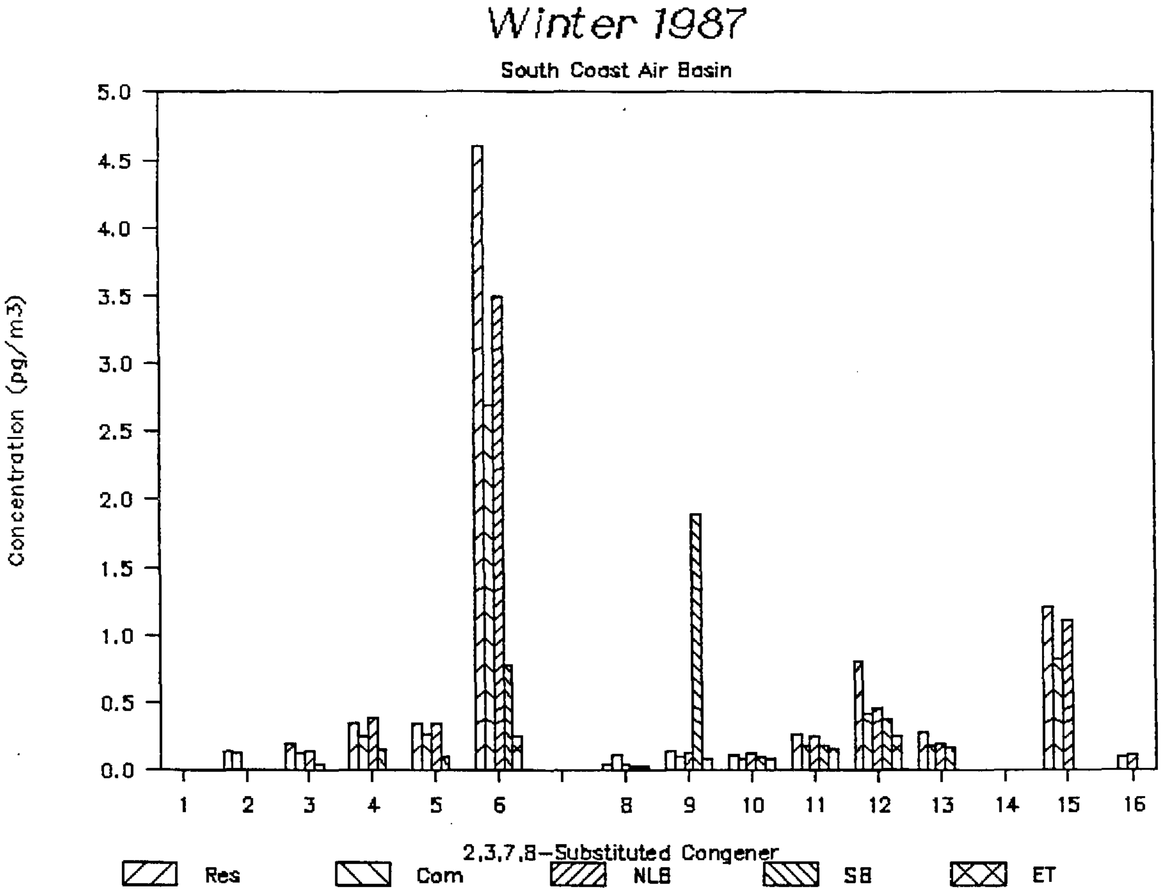


Figure 12-1
Ambient Concentrations of 2,3,7,8 Substituted PCDDs/PCDFs in the South Coast Air Basin - Site Specific Concentrations (pg/m^3) During the December 1987 Winter Sampling Campaign (Session No. 7, December 2-3, 1987)

(Note: Table 11-1 Identifies Each of the 2,3,7,8 Isomers Numerically Identified in Figure 12-1) presented in Table 12-1. Other TEF models adopted by a variety of regulatory agencies worldwide are also summarized for comparison purposes in Table 12-1. In the course of the discussion to follow, the reader is referred to Table 11-2 which contains the TEF weighted sums on both a session-specific and site-specific basis. The raw ambient data and corresponding toxic equivalents weighted concentration for each isomer on a sample-by-sample basis is provided in Appendix C of this report. Note that for clarification purposes the TEF sum for each sample is comprised of three components: 1) a detected TEF sum which represents the contribution made by measured concentrations of the target parameters only. 2) a non-detected TEF which represents the maximum contribution made by target parameters not measured in that particular sample. This product represents a maximum value resulting from multiplication of the detection limit times the corresponding TEF Factor. 3) a maximum or "worst-case" TEF which is the sum of the detected TEF plus the non-detected TEF. Each of the three types of TEF data will be incorporated into the discussion to follow.

12.3.2 Session Specific Trends

Sample-specific TEF weighted sums arranged by session are summarized in Table 11-2. Average TEF sum values for each site and each session are summarized in Table 12-2. As would be expected the maximum detected TEF weighted sums were observed during the December 1987 Winter sampling campaign (Session 1). As presented earlier the highest measured concentrations of 2,3,7,8-substituted PCDDs/PCDFs were also observed during this session.

Session 1 - December 2-3, 1987

The highest measured or detected contribution to a site-specific TEF weighted sum of 2.08 pg/m^3 was observed at the San Bernadino site. The most significant contribution to

TABLE 12-1. TOXIC EQUIVALENCY FACTOR (TEF) MODELS

Congener or Homologous Group	[25] US EPA	[26] Nordic	[27] Swiss	Olie [29] ommoner [30]	New York (USA) [31]	Calif. (USA) [24]	[32] Ontario	[33] Inter-national
2,3,7,8-TCDD	1	1	1	1	1	1	1	1
OTHER TCDD	0.01	0	0.01	1	0	0	0.01	0
1,2,3,7,8-PeCDD	0.5	0.5	0.1	0.1	1	1	0.1	0.5
OTHER PeCDD	0.005	0	0.1	0.1	0	0	0.1	0
1,2,3,4,7,8-HxCDD	0.04	0.1	0.1	0.1	0.03	0.03	0.1	0.1
1,2,3,6,7,8-HxCDD	0.04	0.1	0.1	0.1	0.03	0.03	0.1	0.1
1,2,3,7,8,9-HxCDD	0.04	0.1	0.1	0.1	0.03	0.03	0.1	0.1
OTHER HxCDD	0.0004	0	0.1	0.1	0	0	0.1	0
1,2,3,4,6,7,8-HpCDD	0.001	0.01	0.01	0.1	0	0.03	0.01	0.01
OTHER HpCDD	0.00001	0	0.01	0.1	0	0	0.01	0
OCDD	0	0.001	0	0	0	0	0.0001	0.001
2,3,7,8-TCDF	0.1	0.1	0.1	0.1	0.33	1	0.5	0.1
OTHER TCDF	0.001	0	0.1	0.1	0	0	0.5	0
1,2,3,7,8-PeCDF	0.1	0.01	0.1	0.1	0.33	1	0.5	0.5
2,3,4,7,8-PeCDF	0.1	0.5	0.1	0.1	0.33	1	0.5	0.05
OTHER PeCDF	0.001	0	0.1	0.1	0	0	0.5	0
1,2,3,4,7,8-HxCDF	0.01	0.1	0.1	0.1	0.01	0.03	0.1	0.1
1,2,3,6,7,8-HxCDF	0.01	0.1	0.1	0.1	0.01	0.03	0.1	0.1
2,3,4,6,7,8-HxCDF	0.01	0.1	0.1	0.1	0.01	0.03	0.1	0.1
1,2,3,7,8,9-HxCDF	0.01	0.1	0.1	0.1	0.01	0.03	0.1	0.1
OTHER HxCDF	0.0001		0.1	0.1	0	0	0.1	0
1,2,3,4,6,7,8-HpCDF	0.001	0.01	0.01	0.1	0	0.03	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.001	0.01	0.01	0.1	0	0.03	0.01	0.01
OTHER HpCDF	0.00001	0	0	0.1	0	0	0.01	0
OCDF	0	0.001	0	0	0	0	0.0001	0.001

TABLE 12-2

SOUTH COAST AMBIENT PCDDs/PCDFs MONITORING PROGRAM
Average Toxic Equivalents by Site and Session (pg/m3)

Average Toxic Equivalents by Site (pg/m3)

Site	n	Detected	ND	Maximum
Reseda	7	0.170	0.115	0.285
Commerce	1	0.552	0.043	0.595
N. Long Beach	6	0.097	0.147	0.244
San Bernardino	5	0.465	0.375	0.839
El Toro	7	0.059	0.139	0.198
Cal Trans	4	0.149	0.160	0.309
Carson	2	0.022	0.096	0.117
W. Long Beach	2	0.277	0.101	0.378

Average Toxic Equivalents by Session (pg/m3)

Session Number	n	Detected	ND	Maximum
1	6	0.598	0.071	0.669
2	2	0.007	0.090	0.097
3	5	0.027	0.262	0.289
4	6	0.073	0.209	0.282
5	7	0.091	0.114	0.205
6B	1	0.026	0.130	0.156
7	7	0.116	0.205	0.322

Three TEF categories have been established as follows:
- * Detected -- TEF sum originating from measured values
- * Not Detected (ND) -- TEF sum originating from detection limits
- * Maximum -- Detected TEF + Not Detected TEF

this value was the measured concentration of the 1,2,3,7,8-PeCDF (1.9 pg/m^3) which has a weighting factor of 1.0. Measured concentrations of analytes at all sites contributed significantly to the maximum TEF weighted sum whereas the contribution of the non-detected TEF portion often represented <10% of the total. Both the lowest measured or detected TEF and the lowest maximum TEF were observed at the El Toro site.

Ambient PCDDs/PCDFs data for the least impacted of the sites, El Toro, is plotted in Figure 12-2 as a Toxic Equivalents Sum using the TEF models shown in Table 12-1. Note the influence of the California DHS TEF model on the El Toro ambient air data in comparison to the other models noted.

A review of the wind rose data and corresponding meteorological summary contained in Section 7 in conjunction with the air flow charts in Appendix A indicates air transport during this session as originating primarily from Southern California inland areas. Air transport moved generally in a southeasterly direction towards the Pacific Coast. These meteorological influences could account for the apparent regionalized atmospheric concentrations of PCDDs/PCDFs in evidence during Session 1. More specifically, with the exception of the El Toro site positioned well to the southeast of Los Angeles ambient concentrations of PCDDs/PCDFs at the remaining sites were equivalent to one another. This suggests a regional air transport phenomena perhaps moving along a southeast vector with El Toro well downwind out of the maximum area of influence. Unfortunately, meteorological conditions that prevailed during Session 1 were not repeated during any of the remaining monitoring sessions that took place during this program. The influences of regional air masses and regional transport on atmospheric concentrations of PCDDs/PCDFs have been documented by other investigators [4,12]. Rappe and co-workers for instance report on the influences of long-range transport of atmospheric particulate on atmospheric PCDDs/PCDFs particularly during episodic or inversion type conditions.

AMBIENT PCDDs/PCDFs DATA EXPRESSED AS TOXIC EQUIVALENTS FOR SELECTED TEF MODELS

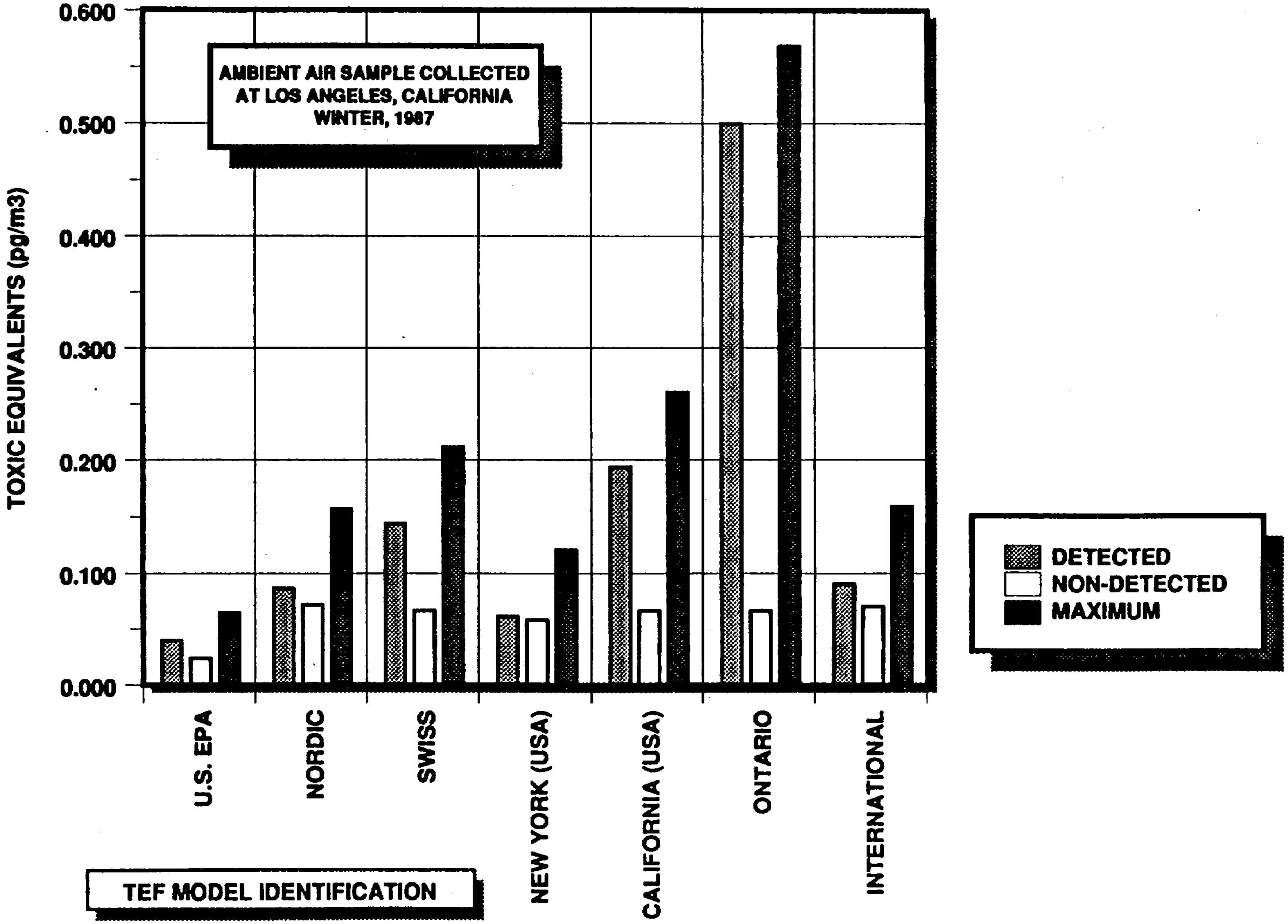


Figure 12-2

Ambient PCDDs/PCDFs Data for the El Toro Site (Session #7) Expressed as a Toxic Equivalent Sum Using a Series of Globally Recognized Models (Reference 34 Maisel and Hunt)

Under stable atmospheric conditions such as these the contribution of local sources to PCDDs/PCDFS burdens are of secondary importance [12]. Hunt and Maisel report further on particulate associated PCDDs/PCDFs and the role it may play in influencing atmospheric concentrations of PCDDs/PCDFs in a coastal metropolitan region in the Northeast U.S. in winter. In this study a regional air transport phenomena resulted in nearly identical PCDDs/PCDFs isomeric profiles and isomer concentrations being measured at a number of ambient stations operating contemporaneously across a large coastal region [4].

The regional profile presented earlier in Figure 12-1 for the 2,3,7,8-substituted species strongly suggests the influence of combustion source emissions on atmospheric burdens of PCDDs/PCDFs during the December 1987 sampling session (Session 1). This is further supported by the three-dimensional plot of the PCDDs/PCDFs congener class sums (Cl_4-Cl_8) for Session 1 as shown in Figure 11-8. The likely influences of combustion source emissions on profiles of the 2,3,7,8-substituted PCDDs/PCDFs have been demonstrated previously in this report. Trends in the 2,3,7,8-substituted PCDDs/PCDFs profiles in concert with the profile of PCDDs/PCDFs congener sums (Cl_4-Cl_8) shown in Figure 11-6 strongly suggest the influences that multiple combustion sources may have on regional air quality in the South Coast Air Basin.

In fact, the concentrations of the 2,3,7,8-substituted species, as well as the congener class sums are well above those reported typically for other U.S. and global locations [1-17]. The values reported here are more consistent with concentrations reported in northeastern and midwestern locations in wintertime [4,5,6], European locations during smog or stabilized atmospheric conditions [2,12], as well as in the immediate influence of a "problem" combustion point source known to represent a significant source of PCDDs/PCDFs [2]. In the latter example the "problem" source was a copper reclamation plant.

Session 2 - December 10-11, 1987

Only two ambient samples were examined during this second of two December 1987 wintertime sessions. Detected TEF and maximum TEF contributions were comparable for both sites, El Toro and Reseda. The major factor in the maximum TEF value was the contribution of the non-detected TEF portion. Average TEF contributions for the two sites are summarized in Table 12-2.

Session 3 - July 26, 1988

Detected TEF sums ranged from 0.0 to 0.105 for the five samples examined. The highest TEF sum attributable to a measured value of 0.01 pg/m^3 occurred at the Reseda site; the highest maximum TEF sum of 0.32 pg/m^3 occurred at the San Bernadino site owing to a 0.31 contribution from the non-detected portion. Both the lowest measured TEF and smallest maximum TEF sums occurred at the El Toro site.

Overall, the TEF sums represented by the detected portion observed at all sites during Session 3 were the smallest of all the sessions examined in which five or more stations were analyzed. This may be attributable in part to the predominance of on-shore air flow patterns during this sampling session. The meteorological data provided in Section 7 (Table 7-2) and Appendix A indicates general air flow from the Pacific coast towards Southern California inland regions during Session 3. As shown in Table 12-2 the average TEF sum for the detected contribution was 0.027. The average maximum TEF sum of 0.289 pg/m^3 was influenced by the non-detected portion.

As shown in Figure 11-9 the PCDDs/PCDFs congener sum profile (Cl_4-Cl_8) is predominated by the Cl_6-Cl_8 PCDDs. Owing to the lack of other measured parameters (PCDFs) little can be said about the significance of the Session 3 congener sum profile.

Session 4 - July 28, 1988

The maximum and minimum TEF sums attributable to measured values again occurred at the Reseda (0.26 pg/m^3) and El Toro (0.0 pg/m^3) sites, respectively. The maximum TEF sum (total of detected and non-detected) of 0.457 pg/m^3 also occurred at the Reseda site, while the corresponding minimum value of 0.15 pg/m^3 occurred at the El Toro location.

As noted in Table 12-2 the maximum TEF sum is influenced primarily by the non-detected contribution. While the absolute PCDDs/PCDFs concentrations are somewhat higher than Session 3 the congener profiles are nearly identical. This is typified by the predominance of the HxCDD, HpCDD, and OCCD congener classes. Again, little can be said about the significance of the congener profiles in the identification of source categories and their relative contributions during Session 4. As noted in Table 7-2 and Appendix A, air flow patterns during much of this session were on-shore. This general air flow from the Pacific coast towards South Coast inland areas is corroborated by the site-specific meteorological data summarized in Table 7-1. Winds emanated primarily from the south, south-southwest (S/SSW) at the San Bernardino site (80%) during much of Session 4. Winds at Reseda were highly variable originating from primarily the east to south quadrant. Wind patterns at each of these sites would suggest primarily land borne air transport during much of Session 4. Interestingly enough, the highest concentrations of 2,3,7,8-substituted PCDDs/PCDFs, as well as the highest detected TEF sums were observed at these two sites.

Session 5 - September 27, 1988

With the sole exception of the Cal Trans site (0.43 pg/m^3) detected TEF sums were comparable to those observed during Session 3 and were among the lowest values observed for a single session during the entire program. Detected TEF sums not including the Cal Trans site ranged from values of $0.012\ pg/m^3$ to $0.059\ pg/m^3$. The corresponding maximum TEF sums ranged from $0.099\ pg/m^3$ to $0.19\ pg/m^3$. While off-shore air flow patterns were in evidence early in Session 5, the majority of the sampling period was predominated by on-shore air flow patterns. The average detected TEF sums for Session 5 are shown in Table 12-2. Note the significant influence of the Cal Trans site (see Table 11-2) on this value.

A review of the PCDDs/PCDFs profiles indicates primarily combustion source patterns during Session 5. (Refer to the previous discussion on the 2,3,7,8-substituted species, as well as the session-specific plot of the PCDDs/PCDFs congener sums (Cl_4-Cl_8) as shown in Figure 11-11. Note in particular the predominance of the hexa, hepta, and octa PCDDs at each of the sites, as well as the prevalence of the Cl_4-Cl_8 PCDFs. This pattern was virtually absent from the previous two sessions. The apparent predominance of combustion source influences on the Cal Trans profile is evident in the 3-dimensional plot for Session 5 shown in Figure 11-11. The proximity of the Cal Trans station to the highway interchange strongly suggests a primarily automotive emissions influence on the PCDDs/PCDFs congener profile at this location. In fact, the area in the immediate vicinity of the sampler contained on- and off-ramps for the I-5/Route 2 highway interchange. Sufficient data is not available from these analyses or in the open literature to confidently state that the only influences at this site are vehicular emissions.

Air flow patterns during much of this session were primarily on-shore, perhaps contributing to the smaller concentrations of PCDDs/PCDFs observed. With the exception of the Cal Trans site which may have been directly influenced by automotive emissions, the PCDDs/PCDFs concentrations at the remaining six sites are typical of concentrations noted in other urban and suburban locations throughout the U.S. and worldwide [1-17].

Session 7 - March 29, 1989

The highest detected TEF contributions were observed for the West Long Beach and Cal Trans sites with values of 0.53 pg/m^3 and 0.13 pg/m^3, respectively. Detected TEF values for the remaining five samples ranged from 0.018 to 0.043 pg/m^3. The highest maximum TEF sum of 1.04 pg/m^3 was observed at the San Bernardino site. This anomalous value, however, is attributable to an elevated detection limit of <0.93 pg/m^3 for the 1,2,3,7,8-PeCDD isomer. Maximum possible TEF sum values of 0.64 pg/m^3 and 0.17 pg/m^3 were observed at the West Long Beach and the Cal Trans sites, respectively. Maximum possible TEF sums for the four remaining samples ranged from 0.077 to 0.13 pg/m^3.

The average detected TEF contribution for the seven site network was 0.116 pg/m^3 (see Table 12-2). This value was second only to the value observed during Session 1, December 1987, when the highest PCDDs/PCDFs concentrations were observed. Again, the profiles shown in Figure 11-12 and as discussed previously for Session 7, suggest primarily combustion source influences. Again, these patterns and the relative concentrations of PCDDs/PCDFs are most pronounced at the West Long Beach and Cal Trans' sites (Note the profiles and their intensities at these sites as shown in Figure 11-12). Air flow analysis data were not provided for this session and accordingly, the air flow pattern cannot be identified. However, the site-specific meteorological data available from the Reseda and El Toro SCAQMD stations (see Table 7-1) indicate wind vectors predominating from the northwest, north-northeast, and northeast during much of the sampling period. These data would suggest primarily land derived air mass influences on the network during Session 7.

12.4 Particle/Vapor Distribution Data

As noted previously in Section 11, two of the samples were selected with the concurrence of ARB technical personnel to undergo analyses of the particulate filter and sorbent trap separately. It was anticipated that such analyses would provide an operationally defined partitioning of PCDDs/PCDFs between the particulate and corresponding vapor phase and an approximate indication of the particle/vapor partitioning of PCDDs/PCDFs that occurs in southern California.

The results of these analyses are plotted in Figures 11-13 and 11-14. These plots represent the total ambient concentrations as well as the vapor and particulate associated contributions for each of the PCDDs/PCDFs congener classes. Note that due to the dynamic process of high volume sampling, these partitioning data cannot accurately represent the total distribution of the majority of the PCDDs/PCDFs between particulate and vapor phases. As a result the partitioning data shown here are operationally defined by the sampling system. As shown here, the majority of the HxCDD, HpCDD and OCDD congener class sums are particulate associated in the atmosphere at southern California. Similarly, the HxCDF, HpCDF and OCDF congener classes are predominantly particulate associated in each of the two samples examined.

These observations are consistent with those of Hites and his co-workers who report that at warm temperatures such as those indicative of southern California (16-20°C), the majority of the Cl_4-Cl_5 PCDFs are vapor associated while the majority of the Cl_6-Cl_8 PCDDs/PCDFs are particulate associated [37, 28, 40, 41]. He further states that vapor/particulate partitioning of PCDDs/PCDFs in the atmosphere is influenced almost exclusively by individual component vapor pressure and the ambient temperature. As a result, the PCDDs/PCDFs of primary toxicological significance (Cl_4-Cl_5) can be expected to be predominantly vapor associated in the ambient atmosphere of southern California. This trend is directly attributable to the ambient temperatures prevalent in the study region during much of the calendar year. Conversely, in colder temperatures such as those indicative of the northeast United States during the winter months.

All of the Cl_4-Cl_8 PCDDs/PCDFs can be expected to be primarily particulate associated [4,15]. The prevalence of the vapor associated Cl_4-Cl_5 PCDDs/PCDFs in the study region during much of the year may contribute significantly to their photochemical losses via degradation processes. Again Hites and his colleagues report that the vapor phase PCDDs/PCDFs are more subject to direct photochemical degredation than are their particulate associated counterparts [40,41].

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15. GLOSSARY OF TERMS

PCDDs -	polychlorinated dibenzodioxins
PCDFs -	polychlorinated dibenzofurans
ARB -	Air Resources Board
SCAQMD -	South Coast Air Quality Management District
Congener -	member of particular PCDDs/PCDFs class (e.g. TCDD)
Isomers -	compounds with same molecular weight but different chemical structure
TCDD -	tetrachlorodibenzodioxin
TCDF -	tetrachlorodibenzofuran
PeCDD -	pentachlorodibenzodioxin
PeCDF -	pentachlorodibenzofuran
HxCDD -	hexachlorodibenzodioxin
HxCDF -	hexachlorodibenzofuran
HpCDD -	heptachlorodibenzodioxin
HpCDF -	heptachlordibenzofuran
OCDD -	octachlorodibenzodioxin
OCDF -	octachlorodibenzofuran
HRGC -	high resolution gas chromatography
HRMS -	high resolution mass spectrometry
pg -	picograms (10^{-12} grams)
m^3	cubic meters
TEF -	toxic equivalency factor
TSP -	total suspended particulate
PSD -	prevention of significant deterioration
PUF -	polyurethane foam
PS-1 -	General Metals Works air sampler
Field blank -	sample used to assess field/laboratory contamination
Method blank -	sample used to assess laboratory contamination
SOP -	standard operating procedure
MPCA -	Minnesota Pollution Control Agency

Collocate -	Two or more samplers placed at the same site
EPA -	Environmental Protection Agency
NASN -	National Air Sampling Network
Magnehelic -	indicates sampler air flow
2,3,7,8-substituted	PCDDs/PCDFs - chlorines bonded in the 2,3,7 and 8 positions
PFK -	perfluorkerosene (MS tuning)
Method 8280 -	EPA analytical method for PCDDs/PCDFs
Sorbent -	Material used to collect target analytes (PUF)
fg -	femtograms (10^{-15} grams)
lpm -	liters per minute
NBS -	National Bureau of Standards
ENSR -	formerly ERT
QA/QC -	Quality Assurance/Quality Control