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

Executive Summary
Prepared for:
California Air Resources Board
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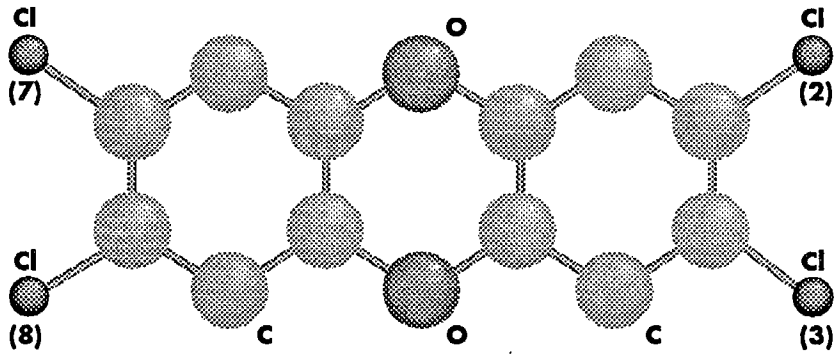

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ENSR

Formerly ERT

ENSR Project No.: 1200-005
ENSR Reference No.: 51-GTH-127

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November 1, 1989

Ms. Laura Kinney
Contract Administrator
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Subject: Submittal of Draft Final Report and Draft Executive Summary entitled "Ambient Concentrations of PCDDS/PCDFS in the South Coast Air Basin" (CARB Contract A6-100-32, ENSR Contract 1200-005)

Dear Ms. Kinney:

Enclosed please find 20 copies each of the Draft Final Report and Draft Executive Summary entitled Ambient Concentrations of PCDDS/PCDFS in the South Coast Air Basin. These documents constitute the reporting requirements for all Phase II activities as specified in the CARB agreement with ENSR Consulting and Engineering (CARB Contract A6-100-32). As such it contains the results of all ambient PCDDS/PCDFS measurements collected during the Phase II Field Program.

The enclosed document was prepared in accordance with format requirements for Final Reports associated with CARB Research Contracts. Further it is consistent with the requirements of the National Technical Information Services (NTIS) as put forth in Guidelines to Format Standards For Scientific and Technical Reports.

The enclosed document was prepared under the direction of the CARB Program Manager, Mr. Ralph Propper, who will process the report through the CARB review process as appropriate. It is ENSR's understanding that CARB will review and comment on the enclosed document within 60 days of receipt. ENSR will prepare final versions of each of these documents within 30 calendar days from receipt of CARB review comments.

Should you or any of the CARB Review Staff require any additional information or should you have any questions upon receipt of these documents, please do not hesitate to contact me directly (508-635-9500 x4404). Thank you in advance for your consideration and the opportunity to work with the Research Division of the California Air Resources Board (CARB).

Sincerely,

Gary T. Hunt

Gary T. Hunt
Program Manager and
Director Air Toxics Monitoring
and Chemistry
ENSR Consulting and Engineering

GTH/cw

Enclosures

cc: R. Propper, CARB
B. Maisel, ENSR
J. Spaulding, ENSR
M. Hoyt, ENSR

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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.

A special note of thanks is extended to the South Coast Air Quality Management District (SCAQMD) and in particular Mr. Bill Bope for the use of SCAQMD monitoring sites in the collection of field program samples and collocated meteorological data to assist us in the interpretation of program data.

ENSR would also like to acknowledge our subcontractor laboratory ENSECO-CAL labs of Sacramento, Calif who conducted the PCDDs/PCDFs analysis via High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS). In particular we'd like to extend a warm note of thanks to Dr. Michael Mille and Mr. William Luksemburg for their enthusiasm, and cooperation in this research effort.

Lastly, ENSR would like to acknowledge and extend a warm note of thanks to the key members of their technical staff in Acton, Massachusetts and Camarillo, California who were primarily responsible for the successful completion of this program. In particular we'd like to acknowledge Mr. Gary Hunt who served as the overall Program Manager and Principal Investigator, Mr. Bruce Maisel and Mr. Rick Rumba who directed the field operations, Ms. Ellen Soppe who assisted them in the field sampling effort and Ms. Marilyn Hoyt who served as the

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

This executive summary report and companion 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. SUMMARY AND CONCLUSIONS

1.1 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.

It is anticipated that this work product will assist the ARB in their continued examination of the distribution and occurrences of PCDDs/PCDFs in the South Coast Air Basin. Further, these data will provide a preliminary assessment of present population exposure to PCDDs/PCDFs which have been designated as Toxic Air Contaminants (TAC) by ARB in accordance with AB 1807.

As a result of efforts conducted during Phase I of the program, 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 detemination 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 (eg. CNDEP) 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 each of six sampling sessions (not Session 7) 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. Specific observations and conclusions that can be derived from the results and discussion contained in the companion report are as follows.

1.2 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 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 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. As such, it suitably satisifes the primary objectives of this research effort as put forth in the Phase I Summary Report. 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-HxDD. 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 (Session 7). (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 (90%) and PeCDFs (50%) are primarily partitioned in the vapor phase. No firm conclusions can be drawn about the V/P 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 contained in the open literature. 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 source in conjunction with the influences of regional air transport.

18. Both 2,3,7,8-substituted PeCDFS, when measured were present in 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 in the companion report 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 address 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 suite, 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.

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.
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).

2. 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 representated during the present program, then additional measurements are warranted.

2. A more extensive sampling and analyses program would then 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.

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. Collection of additional samples 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.

3. MONITORING NETWORK DESIGN - SITE SELECTION

The monitoring network consisted of eight sites situated in the South Coast Air Basin (SCAB). Primary site selection criteria focused on establishing monitoring stations in regions containing potential PCDDs/PCDFs combustion sources and area sources. Areas of high polution density were also targeted as viable monitoring locations in an effort to assess potential exposure of ambient PCDDs/PCDFs to the general SCAB population. As such, the monitoring network included a number of sites situated in primarily residential 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). Air monitor placement at each site was accomplished using EPA criteria established for siting total suspended particular (TSP) samplers, and by considering the requirement that samplers be separated from potential localized interferences. (e.g., roof top vents and stacks.)

4. FIELD PROGRAM

The ambient monitoring program commenced on December 2, 1987 and continued through March 29, 1989, during which time nine discrete sample sets were collected. Each sample session normally involved the operation of five to seven stations and included the collection of one or two collocated samples and one field blank. Implementation of this sampling regime resulted in the collection of 71 samples (filter plus sorbent cartridge), of which 40 were selected for HRMS analysis using a sample prioritization process. This prioritization process involved the implementation of a formal validation and selection procedure which assessed sample integrity, sampler operation and sample identification issues for each individual sample. Samples not meeting the criteria outlined in this procedure were deemed invalid and discounted from analysis. Session-specific meteorology also played a role in the sample prioritization process, as samples collected during periods of little or no precipitation were considered particularly suitable for analysis.

During each of the sampling sessions, critical meteorological parameters including wind speed, direction and ambient temperature were monitored on a continuous basis employing site-specific meteorological stations operated by the South Coast Air Quality Management District (SCAQMD) and located at the Reseda, San Bernardino, North Long Beach, and El Toro sites. This information was collected concurrently with the operation of each of the sampling sessions. Air flow charts for each sampling period were also provided to ENSR Corporation by the California Air Resources Board.

5. SAMPLE COLLECTION AND ANALYSIS PROCEDURE

General Metal Works Polyurethane Foam (PUF) PS-1 samplers were used to collect PCDDs/PCDFs including the fifteen isomers of primary toxicological significance. The samplers are essentially modified high volume air samplers employing a glass fiber filter and sorbent trap to collect particulate-associated and vapor-phase PCDDs/PCDFs, respectively. Air flow rates between 140 and 220 lpm were utilized, in conjunction with 24 to 36 hour sample sessions to produce sample volumes between 350 m^3 and 540 m^3. Calibration of all PS-1 samplers were confirmed prior to and at the conclusion of each sampling session.

All program samples selected to undergo analyses for the target parameter list were subjected to analyses employing high-resolution gas chromatography in concert with high-resolution or magnetic sector mass spectrometry (HRGC/HRMS). ENSR (formerly ERT) selected Enseco-Cal Laboratories of Sacramento, CA to conduct these analyses. 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,
- $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD.

Recoveries of the surrogates were measured as part of each individual sample analysis and were used to assess sample retention of the target "native" PCDD/PCDF congeners, as well as the precision and accuracy of the combined sample collection and analysis regime.

Samples were prepared for analysis following the protocol outlined in USEPA Method 8280. This method requires the addition of five isotopically labelled standards prior to sample extraction as follows:

- $^{13}C_{12}$-2,3,7,8-TCDD,
- $^{13}C_{12}$-1,2,3,7,8-PeCDD,
- $^{13}C_{12}$-1,2,3,6,7,8-HxCDD,
- $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD,
- $^{13}C_{12}$-OCDD.

All native dioxins and furans collected from the ambient air were quantified against these internal standards. After fortification with internal standards, the PUF samples were soxhlet extracted with toluene, subsequently dried, and then cleaned by column chromatography. These extracts were then appropriately stored awaiting authorization from ENSR (formerly ERT) for complete PCDD/PCDF analyses.

6. QUALITY ASSURANCE/QUALITY CONTROL

A formal quality assurance/quality control program was implemented and included the use of method blanks and field-biased blanks. Field blanks were used to correct analytical data by subtracting any congener quantity detected in the field blank from the amount detected for that same congener in actual samples. This procedure eliminated the contribution of field-derived PCDDs/PCDFs not resulting from collection of ambient air. Method blanks, used to assess laboratory contamination, showed no significant levels of target parameters.

An additional quality control measure employed in the program involved the use of isotopically labeled surrogates, applied to each sample prior to shipment to the field. Average recoveries for the isotopically labelled 2,3,7,8-TCDD, TCDF, HxCDF and HpCDF field surrogates utilized in the program were 79%, 82%, 79%, and 57%, respectively. Similarly, isotopically labeled laboratory internal standards were spiked into each sample just prior to GC/MS analysis. Average recoveries for the tetra, penta, hexa, hepta and octa 2,3,7,8-standards were 64%, 66%, 73%, 75%, and 48%, respectively. Surrogate and internal standard recoveries were monitored by ENSR (formerly ERT) on an ongoing basis for the program.

A final QA/QC measure employed included the placement of collocated sampler pairs at one or two pre-selected sites during each sampling session. Collocated sampler data offered a means to establish the precision of the combined sample collection and analysis regime. Four collocated pairs collected as part of the program were authorized for HRMS analyses. Precision data in the form of percent differences were calculated for all collocated congener pairs containing two detected values. The average percent difference for all such comparisons was 27%. These precision results met the precision goals established at the outset of the program.