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Measurement of Ambient Concentrations of Chlorinated Dioxins and Furans, and Polycyclic Hydrocarbons

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

MEASUREMENT OF AMBIENT CONCENTRATIONS OF CHLORINATED DIOXINS AND FURANS, AND POLYCYCLIC HYDROCARBONS

Final Report
Contract No. A932-093

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CONTENTS

CONTENTS
(Cont'd)

CONTENTS
(Cont'd)

CONTENTS
(Cont'd)

APPENDICES

LIST OF TABLES

LIST OF TABLES
(Cont'd)

LIST OF FIGURES

1.0 ABSTRACT

A comprehensive program of field sampling and laboratory analyses has been conducted at three (3) locations in California to assess ambient concentrations of a variety of semivolatile organic pollutants of regulatory significance to the California Air Resources Board (CARB).

Field sampling campaigns were conducted in Fresno, California during the calendar period December 17, 1990 through January 4, 1991; in Richmond, California during the calendar period January 24 to 25, 1991; and at two (2) separate stations vicinal to "Rice Straw" fields during active "burning" periods. The latter field program was conducted during the October 17 to November 8, 1990 calendar period.

State-of-the-art sampling and analyses procedures were employed to determine atmospheric burdens of a variety of toxicologically significant organics including: Polynuclear Aromatic Hydrocarbons (PAHs), Polychlorinated Dibenzodioxins and Dibenzofurans (PCDDs/PCDFs), nitro-PAHs and oxygenated-PAHs, and mutagenic activity.

It is anticipated that this work product will assist the ARB in their continued examination of the distribution and occurrences of PAHs, nitro-PAHs, oxygenated-PAHs, and PCDDs/PCDFs within the State of California. Further, these data will serve to augment the existing data base on population exposure to PCDDs/PCDFs and PAHs. PCDDs/PCDFs have been designated as Toxic Air Contaminants (TAC) by ARB in accordance with AB 1807 while PAHs are currently under consideration for listing as Toxic Air Contaminants.

The monitoring program made use of three (3) CARB sites and one (1) BAAQMD site as directed by the CARB. These included the Pleasant Grove (CARB) and Colusa County Fairgrounds sites (CARB) situated vicinal to the "Rice Straw" burning region, the Fresno CARB site and a site in Richmond, California owned and operated by the Bay Area Air Quality Management District (BAAQMD).

Actual sampling periods were selected by the CARB during each of the aforementioned calendar periods at each of the four (4) sites. Twelve-hour composite diurnal and nocturnal samples were collected during each session for PAH, nitro-PAH/oxygenated-PAH, and mutagen assay analyses. Twenty-four (24) hour composite samples were collected concurrent with a diurnal/nocturnal pair for PCDDs/PCDFs.

The highest concentrations of PAHs, nitro-PAHs/oxygenated-PAHs, PCDDs/PCDFs, as well as mutagen density were observed during the Fresno field program while the lowest concentrations were noted during the "Rice Straw" field program. Atmospheric burdens of PAHs and mutagenic activity during the "Rice Straw" field program are indicative of a rural setting not impacted by open burning of agricultural waste.

PAHs levels measured during the Fresno field program are indicative of wood combustion emissions. Elevated retene (a chemical signature for the combustion of coniferous woods) concentrations in concert with enhanced nocturnal PAH concentrations suggest strong influences from residential wood burning. The PCDDs/PCDFs concentrations measured during the Fresno program represent some of the highest levels reported to date in the open literature. The PCDDs/PCDFs congener class and isomer specific profiles are indicative of combustion source emissions.

The predominant PAHs measured during each of the three (3) field campaigns include naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and biphenyl. Photochemical reactions involving these parent compounds and OH radicals during diurnal periods result in elevated concentrations of 1-nitronaphthalene, 2-nitronaphthalene and 3-nitrobiphenyl. Mutagenic assay analyses of diurnal samples conducted during the Fresno field program suggest the presence of direct acting mutagenicity. Conversely, mutagenic assay data for nocturnal samples suggest a suppression of this direct-acting mutagenicity with +S9 activation.

Nearly equivalent concentrations of the four (4) oxygenated-PAHs were observed in the Fresno samples. The highest concentrations were observed for 9-fluorenone, while the lowest concentrations were observed for pyrene, 3-4 dicarboxylic acid anhydride.

2.0 SUMMARY AND CONCLUSIONS

2.1 Program Summary

A comprehensive program of field sampling and laboratory analyses has been conducted at three (3) locations in California to assess ambient concentrations of a variety of semivolatile organic pollutants of regulatory significance to the California Air Resources Board (CARB).

Field sampling campaigns were conducted in Fresno, California during the calendar period December 17, 1990 through January 4, 1991; in Richmond, California during the calendar period January 24 to 25, 1991; and at two (2) separate stations vicinal to "Rice Straw" fields during active "burning" periods. The latter field program was conducted during the October 17 to November 8, 1990 calendar period.

State-of-the-art sampling and analyses procedures were employed to determine atmospheric burdens of a variety of toxicologically significant organics including: Polynuclear Aromatic Hydrocarbons (PAHs), Polychlorinated Dibenzodioxins and Dibenzofurans (PCDDs/PCDFs), nitro-PAHs and oxygenated-PAHs, and mutagenic activity. PAHs were measured by ENSR's Wilmington, MA laboratory employing gas chromatography/mass spectrometry in the selected ion monitoring (SIM) mode, PCDDs/PCDFs were measured by Triangle Labs employing high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), nitro-PAHs/oxygenated-PAHs were measured by Battelle Labs, Columbus, Ohio, employing negative chemical ionization/gas chromatography/mass spectrometry (NCI/GC/MS), and mutagenic activity was measured by the University of California at Riverside employing the Ames mutagen assay procedure (TA98; +S9,-S9).

It is anticipated that this work product will assist the ARB in their continued examination of the distribution and occurrences of PAHs, nitro-PAHs, oxygenated-PAHs, and PCDDs/PCDFs within the State of California. Further, these data will serve to augment the existing data base on population exposure to PCDDs/PCDFs and PAHs. PCDDs/PCDFs have been designated as Toxic Air Contaminants (TAC) by ARB in accordance with AB 1807 while PAHs are currently under consideration for listing as Toxic Air Contaminants.

The monitoring program made use of three (3) CARB sites and one (1) BAAQMD site as directed by the CARB. These included the Pleasant Grove (CARB) and Colusa County Fairgrounds sites (CARB) situated vicinal to the "Rice Straw" Burning Region, the Fresno CARB site and a site in

Richmond, California owned and operated by the Bay Area Air Quality Management District (BAAQMD).

Actual sampling periods were selected by the CARB during each of the aforementioned calendar periods at each of the four (4) sites. Twelve-hour composite diurnal and nocturnal samples were collected during each session for PAH, nitro-PAH/oxygenated-PAH, and mutagen assay analyses. Twenty-four (24) hour composite samples were collected concurrent with a diurnal/nocturnal pair for PCDDs/PCDFs.

Specific observations and conclusions that can be derived from the results and discussion contained herein are as follows:

2.2 Conclusions and Observations

2.2.1 "Rice Straw" Program

1. Ambient PAH concentrations measured during the "Rice Straw" field program were considerably lower than data reported previously by Atkinson and Arey at Yuba City in the vicinity of open agricultural burning [2].

2. The relatively low PAH concentrations measured at the Pleasant Grove and Colusa Fairgrounds sites more closely approximate ambient concentrations indicative of rural settings worldwide.

3. Ambient PAH concentrations, when examined on a nocturnal versus diurnal basis, do not suggest any measurable differences between the two types of sampling periods.

4. Mutagen assay analyses indicate relatively low activity and mutagen density. The highest samples only approached 8-10 revertants/m^3, indicative again of rural settings not influenced by air emissions associated with open agricultural burning.

5. Examination of mutagen density data on a session specific basis, noting both nocturnal and diurnal concentrations, does not indicate any apparent trends. These findings corroborate the strong similarities noted in comparison of nocturnal and diurnal PAH data.

6. According to ARB, modifications to typical rice burning procedures may account for the unexpectedly low PAH levels noted during this study. In the 1980s, agricultural burning occurred during a "backing" wind instead of a "heading" wind as typically preferred prior to

this time. (ARB believes the adoption of this approach may result in improved combustion during open burning and subsequently result in a reduction in PIC (products of incomplete combustion) formation).

2.2.2 Fresno Field Program

PCDDs/PCDFs

1. The ambient PCDDs/PCDFs profile reported for the Fresno campaign suggests primarily combustion source emissions. Within the PCDDs congener classes (Cl_4-Cl_8) we find increasing ambient concentrations with corresponding increases in chlorine substitution ($Cl_4<Cl_5<Cl_6<Cl_7<Cl_8$). The PCDFs profile within the Cl_4-Cl_8 congener classes, conversely, indicates diminishing concentrations with corresponding increase in chlorine substitution ($Cl_4>Cl_5>Cl_6>Cl_7>Cl_8$).

2. The Fresno PCDDs/PCDFs concentrations represent some of the highest atmospheric burdens of PCDDs/PCDFs reported to date in the open literature. The highest concentrations are reported for the HxCDD, HpCDD and OCDD congener classes. The HxCDD values range from 1.7 to 7.7 pg/m^3, the HpCDD values range from 5.2 to 21 pg/m^3, and the OCDD values range from 9.2 to 32 pg/m^3.

3. The majority of the atmospheric burdens of PCDDs/PCDFs are represented by non 2,3,7,8-substituted species; (not of toxicological significance as defined by the California Department of Health Services).

4. 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 toxicological significance in all of the samples examined. Concentrations ranged from 2.24 pg/m^3 to a maximum value of 9.57 pg/m^3. These findings are coincident with the influence of combustion source emissions.

5. 1,2,3,7,8,9-HxCDD was observed to be the most predominant of the three 2,3,7,8-HxCDD isomers. This isomer is followed in significance by 1,2,3,6,7,8-HxCDD and 1,2,3,4,7,8-HxCDD.

6. All of the samples examined contained the majority of the 2,3,7,8-PCDF isomers. Of the nine (9) PCDF isomers 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8-HxCDF (0.129 pg/m^3 to 0.357 pg/m^3) and 2,3,4,6,7,8-HxCDF (<0.09 pg/m^3 to 0.20 pg/m^3) were the predominant species in the profile.

PAHs

7. Measured concentrations for the PAH target parameters are considerably higher than ambient levels gathered during previous California monitoring programs [1,2] as well as concentrations typically encountered in urban settings worldwide.

8. The PAH concentrations measured at the Fresno site more closely approximate values observed at the Concord, California and Mammoth Lakes, California sites as reported by Atkinson and Arey [2]. The latter site was in fact characterized as impacted by wood-stove emissions during the field sampling program.

9. The highest ambient concentrations are observed in all samples for naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and biphenyl.

10. Elevated concentrations of retene (1-methyl-7-isopropyl phenanthrene) were evident in all of the Fresno samples analyzed. Retene concentrations ranged from 4.2 to 72 ng/m^3 with an average concentration of 18.7 ng/m^3.

11. Higher concentrations of retene were observed in nocturnal sampling periods than in diurnal sampling periods. Average retene concentrations of 32.4 ng/m^3 and 10.5 ng/m^3 were measured for nocturnal and diurnal periods, respectively.

12. Conversely, retene concentrations at the "Rice Straw" and Richmond monitoring sites were considerably lower than those observed at the Fresno station. Values reported at the Colusa and Pleasant Grove sites ranged from 0.17 to 2.0 ng/m^3 while values at the Richmond site ranged from 0.87 to 2.9 ng/m^3.

13. The elevated retene concentrations observed in the Fresno sample set in concert with the higher nocturnal values provides strong evidence that the Fresno monitoring station was impacted by wood combustion emissions during the December 1990-January 1991 period in which this study was conducted.

14. In all instances the nocturnal average concentrations are noticeably higher than the corresponding diurnal average values. These findings are corroborated by our previous observations related to elevated nighttime values of retene. At the Fresno site, more widespread wood combustion likely to occur during evening or nighttime hours (e.g., residential heating) contributes significantly to air quality during this period. As evidenced by elevated levels of retene, the attendant elevated PAH concentrations are most likely associated with wood combustion, as well.

Mutagenicity Testing

15. The results of mutagenicity analysis for the Fresno field program indicate relatively high mutagen density in contrast to both the "Rice Straw" and Richmond sampling campaigns. The highest values are reported for the January 2-3 sampling period coincident with elevated PAH and PCDDs/PCDFs concentrations.

16. In an examination of the Fresno mutagenic activity data there is no apparent trend in comparison of noctumal and diurnal values.

17. Mutagenic activity data for the diurnal samples are comparable in comparison of values with activation (+S9) to those without activation (-S9). These data suggest the presence of direct-acting mutagenicity.

18. Mutagenic assay data for the Fresno noctumal samples indicate much greater activity for samples in the absence of S9 activation (-S9) than was observed with the addition of S9 (+S9). These data suggest a suppression of direct acting mutagenicity with +S9.

Nitro-PAH/Oxygenated-PAH

19. The highest ambient concentrations of the nitro-PAH and oxygenated-PAH target parameters were measured in the Fresno composite samples. The predominant nitro-PAH measured in the nocturnal sample was 9-nitrophenanthrene (0.43 ng/m^3) while 2-nitronaphthalene (0.55 ng/m^3) predominated in the diurnal Fresno sample.

20. With the exception of 9-nitrophenanthrene, higher concentrations of the nitro-PAH were observed in the diurnal composite sample than were observed in the composite noctumal sample.

21. Elevated concentrations of 1-nitronaphthalene, 2-nitronaphthalene and 3-nitrobiphenyl in the Fresno diumal sample (in contrast to the nocturnal composite) provide evidence for atmospheric photochemical reactions involving the respective parent PAH and OH radicals. Arey et al. report this to be a predominant reaction mechanism during daylight hours.

22. Nearly equivalent concentrations of the four (4) oxygenated-PAHs were observed in both the nocturnal and diumal composite samples. The highest concentrations were observed for 9-fluorenone (7.19 ng/m^3, 6.32 ng/m^3) while the lowest concentrations were observed for pyrene, 3-4 dicarboxylic acid anhydride (0.42 ng/m^3, 0.56 ng/m^3).

2.2.3 Richmond Field Program

PAHs

1. The PAH levels observed during the Richmond field program are in excess of those measured during the "Rice Straw" field program, yet markedly lower than values observed during the Fresno field program. The Richmond PAH levels are comparable to PAH levels in urban "settings" in the United States and worldwide.

2. The highest PAH concentrations were observed in all samples for naphthalene, 1-methylnaphthalene, 2-methylnapthalene and biphenyl. In a similar manner to the Fresno field program, the rank order of concentration for these four (4) isomers at Richmond were observed as follows: Naphthalene (avg = 290 ng/m^3), Biphenyl (avg = 238 ng/m^3), 2-methylnaphthalene (avg = 148 ng/m^3), 1-methylnaphthalene (avg = 60 ng/m^3).

3. Comparison of nocturnal and diurnal concentration data for the Richmond sample set do not suggest any measurable differences in the two types of sampling periods. In fact, considering the precision of the combined sampling and analysis scheme (±20%), the nocturnal vs. diurnal average concentrations for all of the PAHs examined are nearly identical.

Mutagenicity

4. The results of mutagenicity assay analyses for the Richmond field program indicate relatively low mutagenic activity in contrast to the previous Fresno program data. The reported values which are noticeably higher than the "Rice Straw" activity data are considerably lower than activity data reported by Atkinson and Arey for five (5) of the seven (7) stations in the aforementioned California study [2]. The mutagenic activity data reported herein are lower than the average values (revertants/m^3) reported for the same Richmond site during the July 1984-June 1988 period by BAAQMD [1].

5. Since both of the Richmond samples examined represent diurnal composites, little can be said concerning nocturnal vs. diurnal mutagenic activity.

Nitro-PAH/Oxygenated-PAH

6. The predominant nitro-PAHs measured in the Richmond diurnal composite sample were 9-nitrophenanthrene (0.178 ng/m^3) and 1-nitronaphthalene. The predominant nitro-PAH species

measured in the nocturnal composite sample were 1-nitronaphthalene (0.099 ng/m^3) and 2-nitronaphthalene (0.082 ng/m^3).

7. Equivalent concentrations of 9-fluorenone were observed in both the nocturnal (3.22 μg/m^3) and diurnal (3.63 μg/m^3) composite samples. Diurnal concentrations for the remaining three (3) oxygenated-PAH were higher than the corresponding nocturnal values. The concentration rank order for both the nocturnal and diurnal composite samples was as follows: 9-fluorenone > naphthalene - 1,8-dicarboxylic acid anhydride > benzo(a)anthracene - 7,12-dione > pyrene - 3,4-dicarboxylic acid anhydride.

3.0 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. The Rice Straw monitoring sites were not noticeably impacted by "Rice Straw" burning activities. Site selection needs to be reexamined in an effort to identify more representative monitoring stations should future monitoring be conducted.

2. Further examination of the conditions that precipitated adverse air quality conditions in place during the Fresno field program is recommended. An examination of the influence of localized meteorology and wood burning practices on each of the sampling days is warranted.

3. Further monitoring is warranted in the Fresno Metropolitan area to assess representativeness of data gathered during this program (e.g., annual exposure).

4. Further investigation is needed to identify sources of elevated PCDDs/PCDFs found in Fresno ambient samples. If atmospheric burdens are directly attributable to wood smoke emissions, the sources of precursor organic chlorine and/or inorganic chloride in the wood/fuel needs to be examined.

5. The significance of the oxygenated-PAHs in the ambient samples and in particular the elevated concentrations observed in the Fresno samples needs to be examined. In particular, the contribution of these species to the enhanced mutagenic activity of the Fresno samples needs to be evaluated.

6. The mutagenic assay data available from the Fresno monitoring campaign, while limited, suggest a suppression of direct acting mutagenicity with the addition of S9 (+S9). This trend is worthy of further examination perhaps as a component within continued monitoring efforts at the Fresno station.

4.0 INTRODUCTION

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). PAHs are presently under review for potential designation as Toxic Air Contaminants (TACs). Recently completed ARB-sponsored research efforts by ENSR (Ambient Monitoring for Selected PCDDs/PCDFs in the South Coast Air Basin) and the University of California at Riverside (Survey of Ambient Concentrations of Selected PAHs at Various Locations in California) established a baseline database for PCDDs/PCDFs and PAHs in the aforementioned regions.

ENSR Consulting and Engineering has been retained by the California Air Resources Board (ARB) to augment this existing database by conducting additional ambient monitoring for selected PCDDs/PCDFs and PAHs at various locations in the State of California. As part of this statewide monitoring program, ARB requested that ENSR conduct regionalized ambient monitoring for PCDDs/PCDFs (Table 4-1), PAHs (Table 4-2) and substituted PAHs (Table 4-3) at the following locations:

- Sutter and Colusa counties (rice straw burning);
- Richmond (oil refining and production);
- Fresno (residential wood smoke in wintertime).

Field sampling activities occurred during the period October 1990 through February 1991 at the sites/regions identified above. Sampling sites housed an array of PS-1 air samplers, sited in accordance with criteria for EPA TSP collection. Each PS-1 sampler incorporated a particulate filter and sorbent cartridge for collection of particulate-associated and vapor phase compounds, respectively.

A sample prioritization and validation scheme identified particular samples for initial laboratory analysis by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) for PCDDs/PCDFs and Gas Chromatography/Mass Spectrometry, Selected Ion Monitoring (GC/MS SIM) for PAHs. Selected samples already analyzed for PAHs were subjected further to mutagenicity testing. Of these, several were identified for analyses of nitro-PAH and oxygenated-PAH employing NCI GC/MS. Several team members provided analytical support for the program, as follows:

TABLE 4-1

PCDDs/PCDFs
Target Parameter Listing, Detection Limit Goals and Reported Concentration Ranges

Target Parameter	Detection Limit Goals[d]		Reported Range (pg/m^3)	
			Fresno	
	pg/sample	pg/m^3 @ 345 m^3 [a] Total Volume	Min	Max[b]
PCDD Congeners				
2,3,7,8 TCDD	10	0.029	0.012	0.027
1,2,3,7,8 PeCDD	20	0.058	0.084	0.201
1,2,3,6,7,8 HxCDD	20	0.058	0.087	0.384
1,2,3,7,8,9 HxCDD	20	0.058	0.133	0.581
1,2,3,4,7,8 HxCDD	20	0.058	0.219	1.68
1,2,3,4,6,7,8 HpCDD	20	0.058	2.24	9.57
OCDD	40	0.120	9.24	34.3
Total TCDD	40	0.120	0.220	0.612
Total PeCDD	40	0.120	0.370	1.68
Total HxCDD	40	0.120	1.67	7.84
Total HpCDD	40	0.120	5.20	22.0
PCDF Congeners				
2,3,7,8 TCDF	20	0.058	0.041	0.134
1,2,3,7,8 PeCDF	20	0.058	0.047	0.089
2,3,4,7,8 PeCDF	20	0.058	(0.071)	0.151
1,2,3,6,7,8 HxCDF	20	0.058	0.129	0.357

TABLE 4-1 (Cont'd)

PCDD/PCDFs
Target Parameter Listing, Detection Limit Goals and Reported Concentration Ranges

Target Parameter	Detection Limit Goals[d]		Reported Range (pg/m^3) Fresno	
	pg/sample	pg/m^3 @ 345 m^3 [a] Total Volume	Min	Max[b]
1,2,3,7,8,9 HxCDF	20	0.058	0.047	0.090
1,2,3,4,7,8 HxCDF	20	0.058	(0.089)	0.204
2,3,4,6,7,8 HxCDF	20	0.058	(0.027)	(0.051)[c]
1,2,3,4,6,7,8 HpCDF	20	0.058	(0.034)	0.473
1,2,3,4,7,8,9 HpCDF	20	0.058	(0.052)	0.069
OCDF	40	0.120	0.212	0.664
Total TCDF	40	0.120	0.798	2.31
Total PeCDF	40	0.120	1.92	0.73
Total HxCDF	40	0.120	0.532	1.41
Total HpCDF	40	0.120	0.049	1.01

[a] Anticipated air volume based on 24 hour sample collection period at a flow rate of 240 lpm.
[b] Values indicate maximum measured value and exclude non-detected values.
[c] No measured values for this parameter.
[d] Detection limit goals were established at the outset of the program and provided in ENSR Document 1200-008-155, "Measurement of Ambient PCDDs/PCDFs and PAHs in the Vicinity of Rice Straw Burning", October 1990.
( ) indicates detection limit value

TABLE 4-2

PAHs
Target Parameter Listing, Detection Limit Goals and Reported Concentration Ranges

Target Parameter	Detection Limit Goals[b]		Reported Range (ng/m^3)					
			Rice Straw		Richmond		Fresno	
	ng/sample	ng/m^3 @ 175 m^3 [a] total volume	Min	Max	Min	Max	Min	Max
Naphthalene	11	0.062	5.0	217	192	427	148	1357
2-Methyl naphthalene	11	0.062	2.6	529	114	214	113	882
1-Methyl naphthalene	11	0.062	1.3	64	46.3	89.3	52	391
Biphenyl	11	0.062	5.3	943	134	331	166	1114
Acenaphthylene	11	0.062	0.07	12	6.9	20.5	5.9	160
Acenaphthene	11	0.062	0.17	5.2	2.9	4.2	2.1	15
Fluorene	11	0.062	0.35	6.3	6.9	11.3	5.4	45
Phenanthrene	11	0.062	0.26	17	11.3	20.7	12	110
Anthracene	26	0.15	0.02	3.7	1.4	2.7	1.1	23
Fluoranthene	26	0.15	0.70	5.7	3.4	5.3	5.9	32
Pyrene	11	0.062	0.16	4.7	3.3	5.4	5.1	31
Retene	175	1.0	0.17	1.6	0.87	2.9	4.2	72
Benzo(a)anthracene	11	0.062	(0.03)	0.57	0.31	0.95	0.39	13
Chyrsene/Triphenylene	14	0.080	0.11	0.86	0.50	1.1	0.76	17
Benzo(b,j,k)fluoranthenes	18	0.10	(0.23)	4.2	0.74	2.0	1.4	25
Benzo(e)pyrene	11	0.062	(0.02)	1.6	0.36	0.83	0.46	9.3
Benzo(a)pyrene	13	0.074	(0.03)	1.8	0.23	0.95	0.31	12
Indeno(1,2,3, cd) pyrene	15	0.086	0.03	0.77	0.43	1.0	0.44	6.6

TABLE 4-2 (Cont'd)

PAHs
Target Parameter Listing, Detection Limit Goals and Reported Concentration Ranges

Target Parameter	Detection Limit Goals[b]		Reported Range (ng/m^3)					
			Rice Straw		Richmond		Fresno	
	ng/sample	ng/m^3 @ 175 m^3 [a] total volume	Min	Max	Min	Max	Min	Max
Dibenzo(a,c/a,h)anthracene	70	0.40	(0.05)	0.91	(0.20)	(0.24)	0.10	1.7
Benzo(g,h,i)perylene	14	0.080	0.04	1.3	0.82	1.4	0.47	7.2
Coronene	175	1.0	(0.06)	2.0	0.60	1.1	0.49	13

[a] Anticipated air volume based on 12 hour sample collection period at a flow rate of 240 lpm.

[b] Detection limit goals were established at the outset of the program and provided in ENSR Document 1200-008-155, "Measurement of Ambient PCDDs/PCDFs and PAHs in the Vicinity of Rice Straw Burning", October 1990.

( ) indicates detection limit value

TABLE 4-3

Substituted PAHs
Target Parameter Listing, Detection Limit Goals and Reported Concentration Ranges

	Detection Limit Goals[c]		Reported Range (ng/m^3)	
Target Parameter	ng/sample	ng/m^3 @ 175 m^3 [a] total volume	Min[b]	Max[b]
1-Nitronaphthalene	10	0.057	0.026	0.392
2-Nitronaphthalene	10	0.057	0.023	0.549
3-Nitrobiphenyl	10	0.057	(0.010)	0.257
9-Nitroanthracene	10	0.057	(0.010)	0.045
9-Nitrophenanthrene	10	0.057	0.020	0.432
8-Nitrofluoranthene	10	0.057	(0.010)	(0.014)
2-Nitrofluoranthene	10	0.057	(0.010)	0.146
1-Nitropyrene	10	0.057	(0.011)	0.044
2-Nitropyrene	10	0.057	(0.010)	(0.014)
6-Nitrochrysene	10	0.057	(0.010)	0.022
1,6-Dinitropyrene	10	0.057	(0.010)	(0.014)
9-Fluorenone	10	0.057	0.75	7.2
Naphthalene-1,8-dicarboxylic acid anhydride	10	0.057	0.18	4.79

TABLE 4-3 (Cont'd)

Substituted PAHs
Target Parameter Listing, Detection Limit Goals and Reported Concentration Ranges

	Detection Limit Goals[c]		Reported Range (ng/m^3)	
Target Parameter	ng/sample	ng/m^3 @ 175 m^3 [a] total volume	Min[b]	Max[b]
Benz[a]anthracene-7,12-dione	10	0.057	0.030	1.02
Pyrne-3,4-dicarboxylic acid anhydride	10	0.057	0.105	0.556

[a] Anticipated air volume based on 12 hour sample collection period at a flow rate of 240 lpm.

[b] All minimum values were observed in Rice Straw network samples; all maximum values were observed in Fresno samples.

[c] Detection limit goals were established at the outset of the program and provided in ENSR Document 1200-008-155, "Measurement of Ambient PCDDs/PCDFs and PAHs in the Vicinity of Rice Straw Burning", October 1990.

( ) indicates detection limit value

- HRGC/HRMS (PCDDs/PCDFs) - Triangle Laboratories, RTP, NC;
- GC/MS SIM (PAHs) - ENSR Consulting and Engineering, Wilmington, MA;
- Substituted PAHs - Battelle Laboratories, Columbus, OH; and
- Ames Testing - UCal Riverside, Riverside, CA.

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

- Section 1 - Abstract
- Section 2 - Summary and Conclusions
- Section 3 - Recommendations for Further Study
- Section 4 - Introduction
- Section 5 - Site Selection
- Section 6 - Sample Collection Procedures
- Section 7 - Field Sampling Program
- Section 8 - Evaluation criteria for the selection of field samples for analysis
- Section 9 - Analytical Procedures
- Section 10 - Quality Assurance/Quality Control
- Section 11 - Results
- Section 12 - Discussion of Results
- Section 13 - References
- Section 14 - Glossary of Terms

5.0 SITE SELECTION

5.1 Overview

ARB selected monitoring sites in the cities of Richmond and Fresno for air measurements activities under this program. Additional monitoring locations were selected in Colusa and Sutter counties to assess the environmental impact of rice straw burning in that region. Existing ARB air monitoring sites were utilized when possible to eliminate unnecessary site selection activity. These sites also provided reasonable security and sufficient electrical power for equipment operation. Richmond and Fresno sites were selected to ensure the accurate assessment of existing ambient PCDDs/PCDFs and PAHs levels in the area surrounding a particular site without bias from local source contributions. ARB's selection of sites vicinal to rice straw burning allowed an estimation of environmental impact from these agricultural burning activities. ARB maintained responsibility for the site selection process and confirmed that the network configuration described herein fulfilled program objectives.

5.2 Sampler Siting Criteria

Actual sampler placement at these sites incorporated the 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 and PAHs. Also, strong evidence exists demonstrating the tendency of PCDDs/PCDFs and PAHs to occur as constituents of suspended particulate matter. Therefore, all mechanisms which may interfere with the collection of TSP may also interfere with the collection of PCDDs/PCDFs and PAHs. 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).

To ensure 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 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 presence of 110 VAC, 20 AMPs at each sampling site. ARB assumed responsibility for site access, permission for use, electrical power and security.

TABLE 5-1

Sampler Siting Criteria

Siting Characteristic	Spacing Requirements
Height of sampler inlet above ground	1-15 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

5.3 Site Locations

Table 5-2 lists the exact addresses of each monitoring site utilized for the program. As noted in Table 5-2, ARB selected one site each at Richmond and Fresno; two monitoring sites were located in areas of expected impact from rice straw burning. Figures 5-1 and 5-2 contain U.S.G.S. maps showing the Pleasant Grove and Colusa County Fairgrounds site locations, respectively, utilized for the Rice Straw campaign. Figure 5-3 provides a U.S.G.S. map identifying the Richmond monitoring location and Figure 5-4 shows the location of the Fresno sampling station.

5.4 Site Descriptions

5.4.1 Rice Straw Program

The Rice Straw Pleasant Grove site was located on property owned and used by Tennco, a heavy equipment manufacturer. The general area surrounding the site consisted of open fields on flat terrain. Samplers were located approximately 1 meter above the ground level. The Rice Straw, Colusa site was located at the Colusa County fairgrounds, with air samplers situated approximately 3 meters above ground level. Both Rice Straw network sites utilized existing ARB monitoring locations.

5.4.2 Fresno Site

The Fresno monitoring station was collocated with an existing ARB monitoring site. The ARB monitoring site is situated in a primarily residential region of Fresno in the middle of the city. The immediate vicinity of the station is characterized by single family homes and some light commercial activities. The monitoring equipment was situated atop a building approximately 12½ feet above ground level. Collocated ARB monitoring instrumentation was in place at the site for the collection of carbon monoxide, (CO), PM_{10} and coefficient of Haze data.

5.4.3 Richmond Site

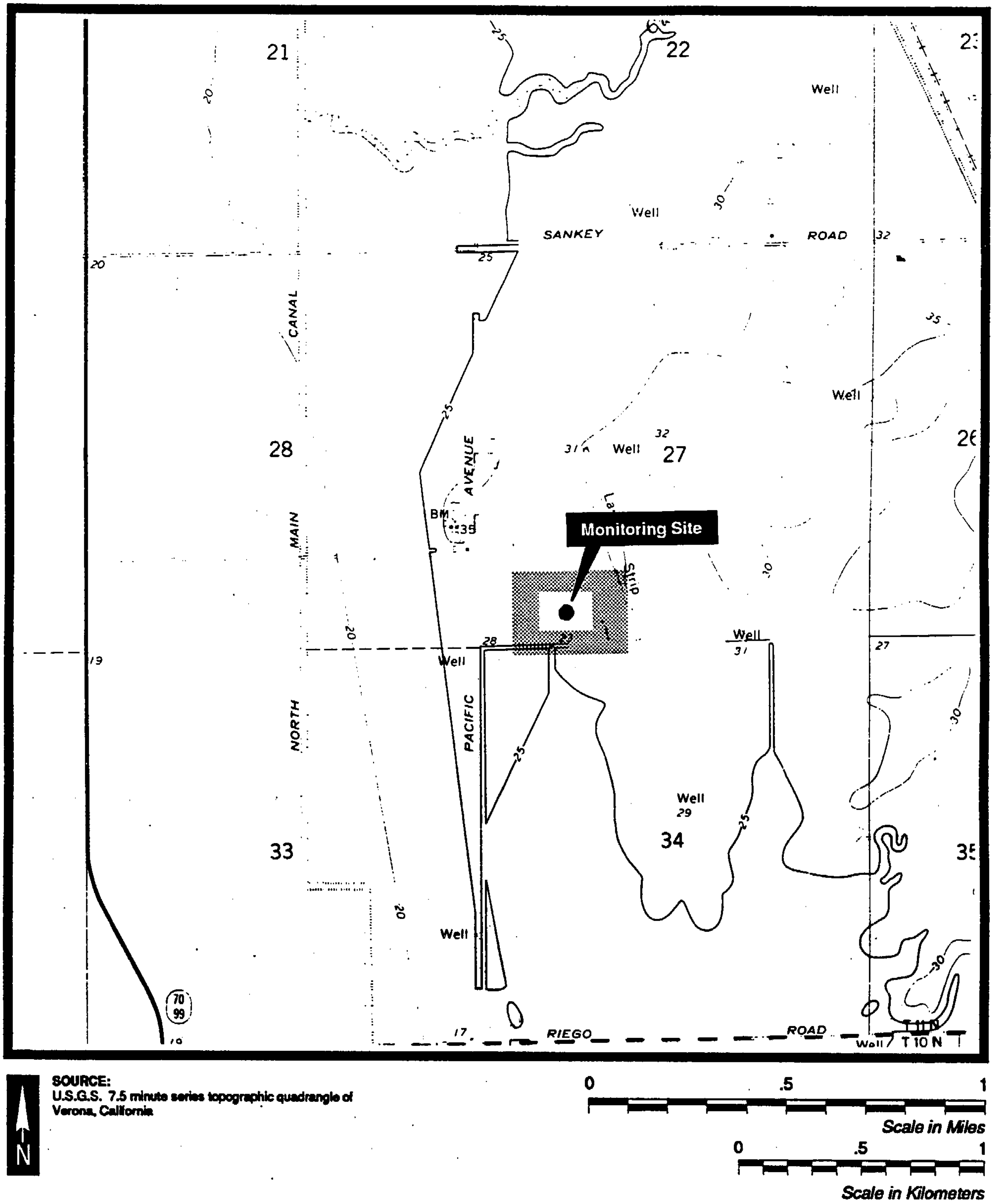
The Richmond monitoring station was collocated with an existing Bay Area Air Quality Management District (BAAQMD) site in metropolitan Richmond. The site is situated in a mixed use region comprised of residential areas to the east and south and light commercial (3/4 mile) to the west. A large oil refinery is situated approximately 1 mile to the west of the site. The industrial neighbor in closest proximity to the site is a roofing/asphalt batching plant situated approximately 3/10 of a mile to the north. The Richmond location was selected by BAAQMD so as to represent "outdoor community air and not to address specific industrial stationary source

TABLE 5-2

Monitoring Site Locations

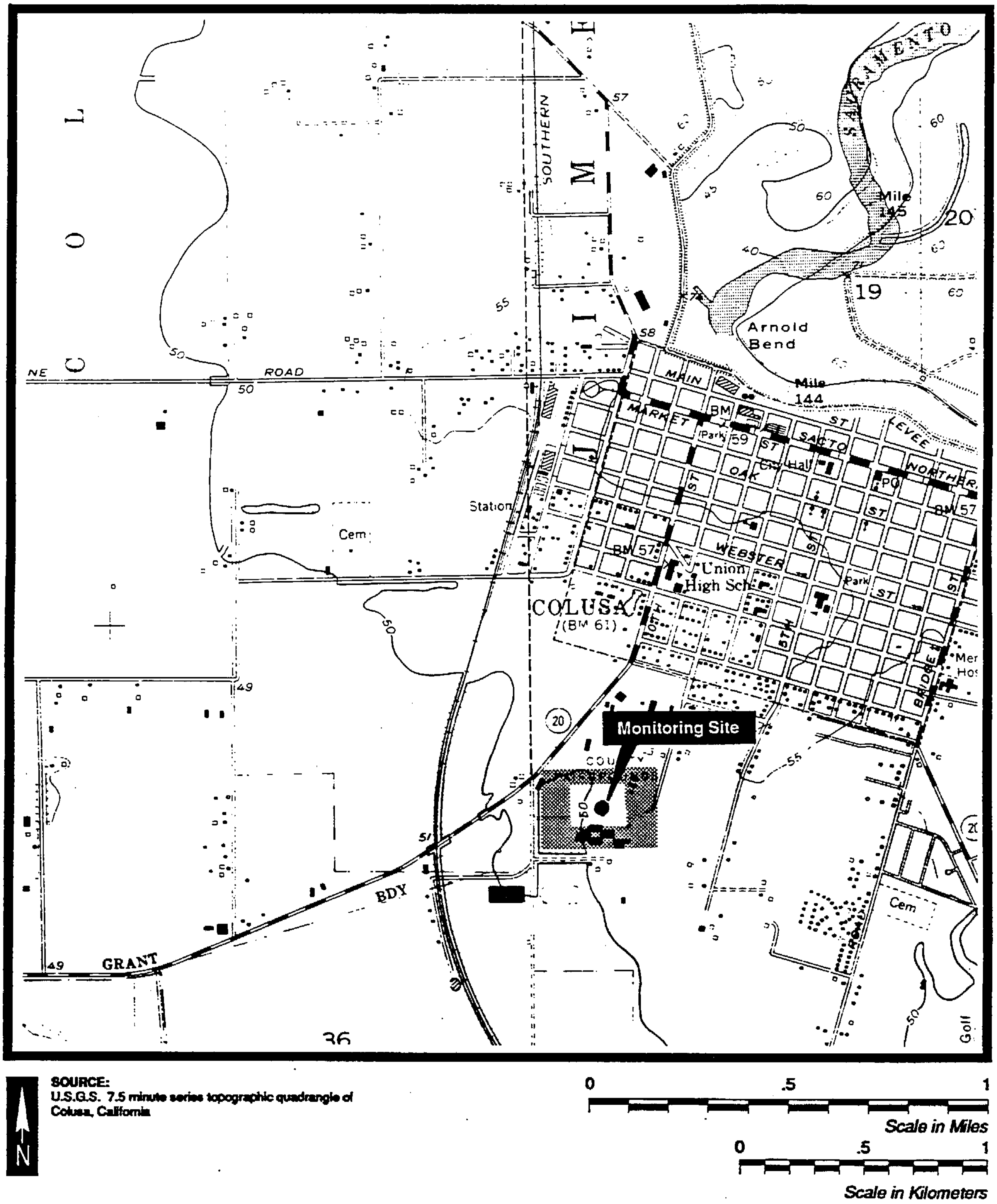
Network	Site Location	Site Affiliation
Richmond	1144 13th St., Richmond, CA	BAAQMD*
Fresno	3425 N. First St., 205-B, Fresno, CA	ARB
Rice Straw	Tennco property, 7310 Pacific Ave., Pleasant Grove, CA	None
Rice Straw	Colusa County Fairgrounds, Hwy. 20 Colusa, CA	ARB

*BAAQMD - Bay Area Air Quality Management District



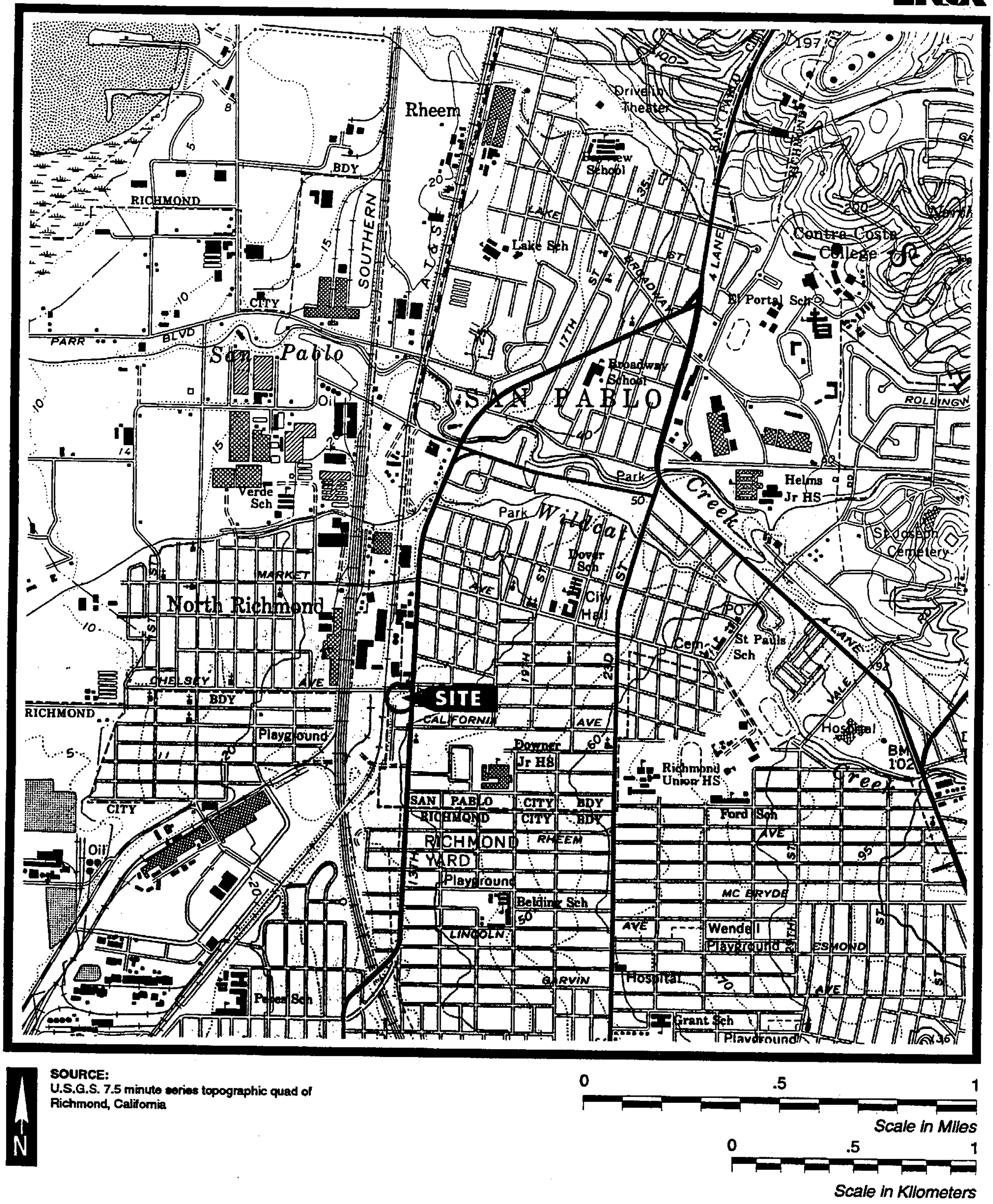
SOURCE:
U.S.G.S. 7.5 minute series topographic quadrangle of Verona, California

FIGURE 5-1
Rice Straw Network
Pleasant Grove Monitoring Site



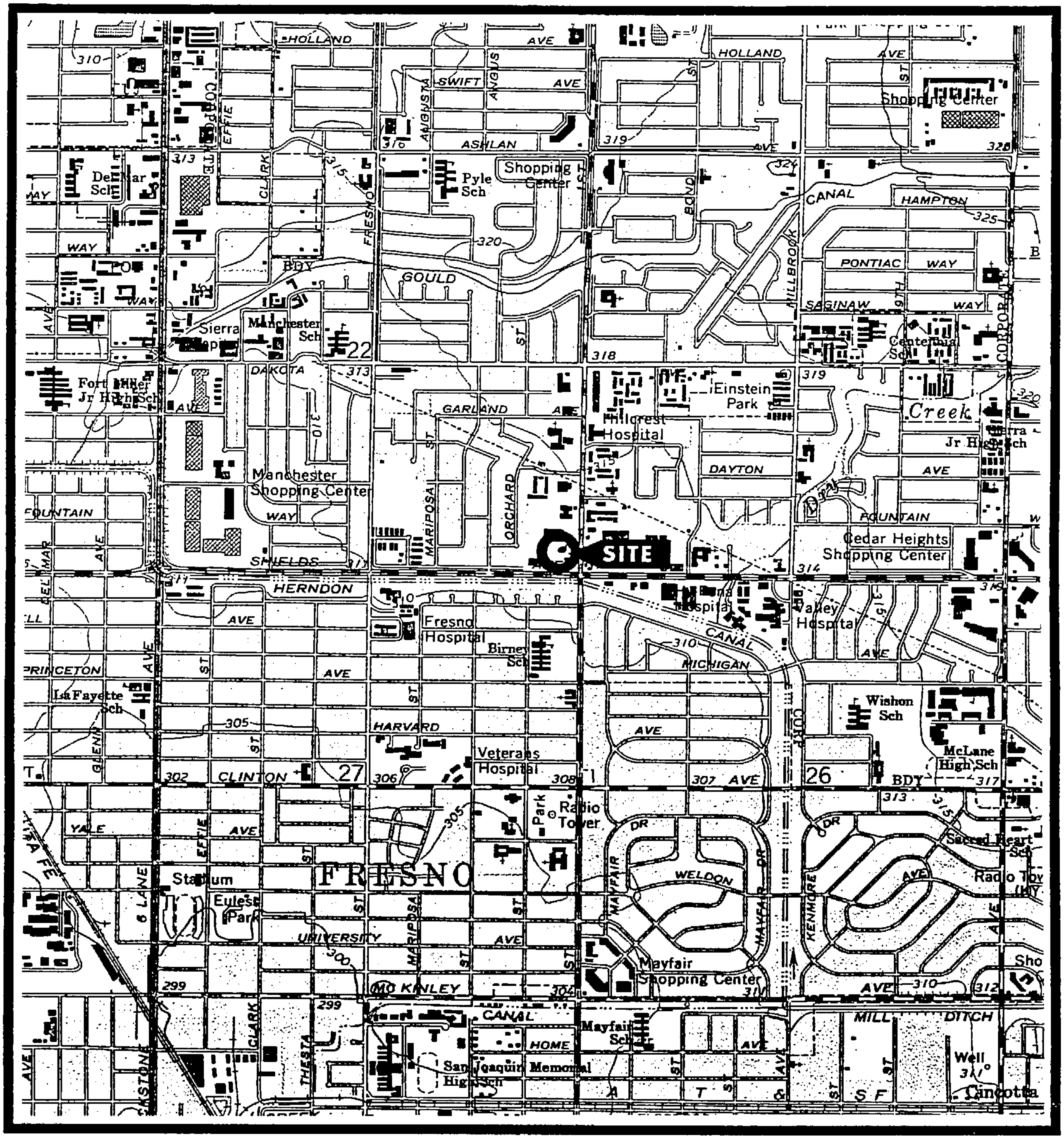
SOURCE:
U.S.G.S. 7.5 minute series topographic quadrangle of Colusa, California

FIGURE 5-2
Rice Straw Network
Colusa County Fairground Monitoring Site



SOURCE:
U.S.G.S. 7.5 minute series topographic quad of
Richmond, California

FIGURE 5-3
Richmond Monitoring Site



N

SOURCE:
U.S.G.S. 7.5 minute series topographic quad of Fresno, California

0 .5 1
Scale in Miles

0 .5 1
Scale in Kilometers

FIGURE 5-4
Fresno Monitoring Location

emissions. Mobile sources are believed to be the principal contributors to air quality at the Richmond site"[1].

6.0 SAMPLE COLLECTION PROCEDURES

6.1 Overview

General Metal Works Model PS-1 samplers were utilized to collect ambient air samples at each network. The sample collection system and operation procedures are described in the sections to follow, and are consistent with the approach contained in EPA Method T09.

6.2 Sample Collection System

General Metal Works Polyurethane Foam (PUF) PS-1 samplers were used to collect the selected polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDDs/PCDFs) congeners and PAHs listed in Tables 4-1 through 4-3. 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 guage, voltage variator, and elapsed timer. The sampling module contains two chambers as illustrated in Figure 6-2. The upper chamber supports the particulate filter media and the second chamber accommodates the sorbent trap.

Polyurethane foam (density = 0.022 - 0.025 g/cm^3) sheets were purchased from Olympic Foam Products and cut into 75 mm plugs using a cylindrical steel die mounted on a drill press. Samplers outfitted for collection of PCDDs/PCDFs utilized the 75 mm foam plugs, as illustrated in Figure 6-3. Samplers outfitted for collection of PAHs utilized a PUF/XAD "sandwich", as illustrated in Figure 6-4, consisting of 10 grams of XAD resin placed between two PUF sections of length 50 mm (lower) and 25 mm (upper). A 10.14-cm-diameter Gelman glass fiber filter will be used for collection of particulate. The entire sample module including PUF plug, XAD (for PAHs), filter, and glass cartridge was prepared as described in Section 5.

Following pretreatment procedures, sample cartridges were assembled by carefully placing PUF sections into the glass sampling cartridge with forceps to avoid touching the cleaned PUF with bare hands. Cotton gloves were worn at all times when handling cleaned PUF or filters, and care was taken to handle plugs only on methylene chloride cleaned aluminum foil and with methylene chloride cleaned forceps. Following pretreatment, the sampling cartridge was wrapped in

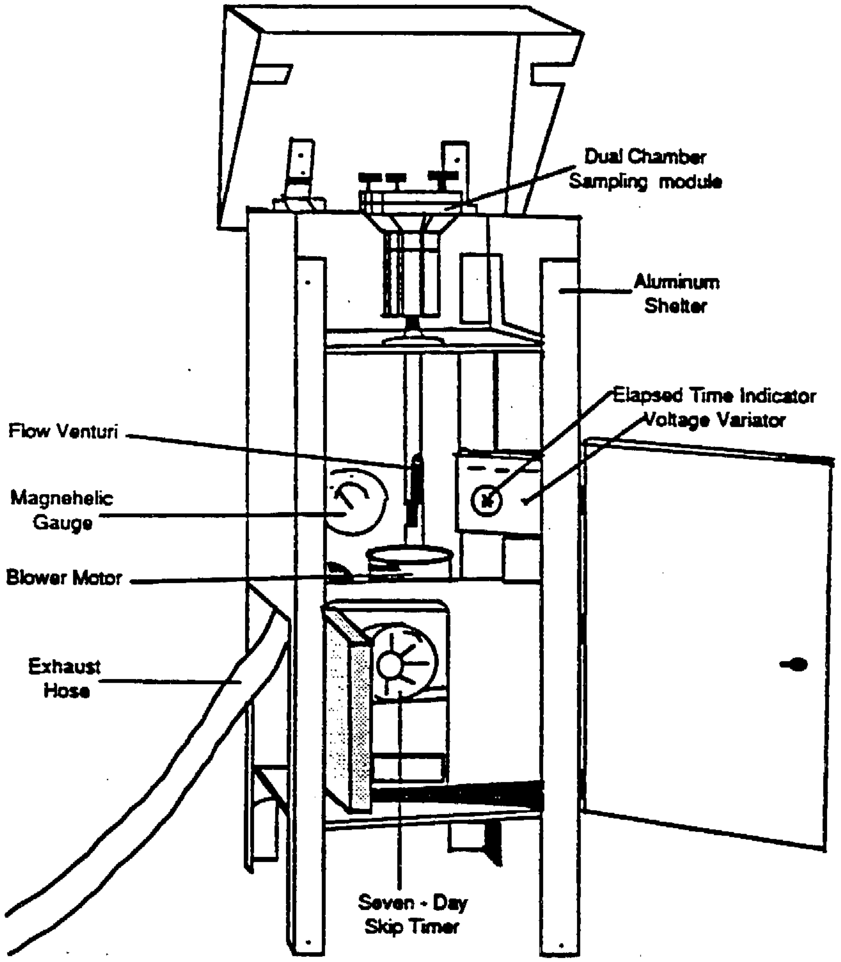


FIGURE 6-1

Schematic of PS-1 Sampler

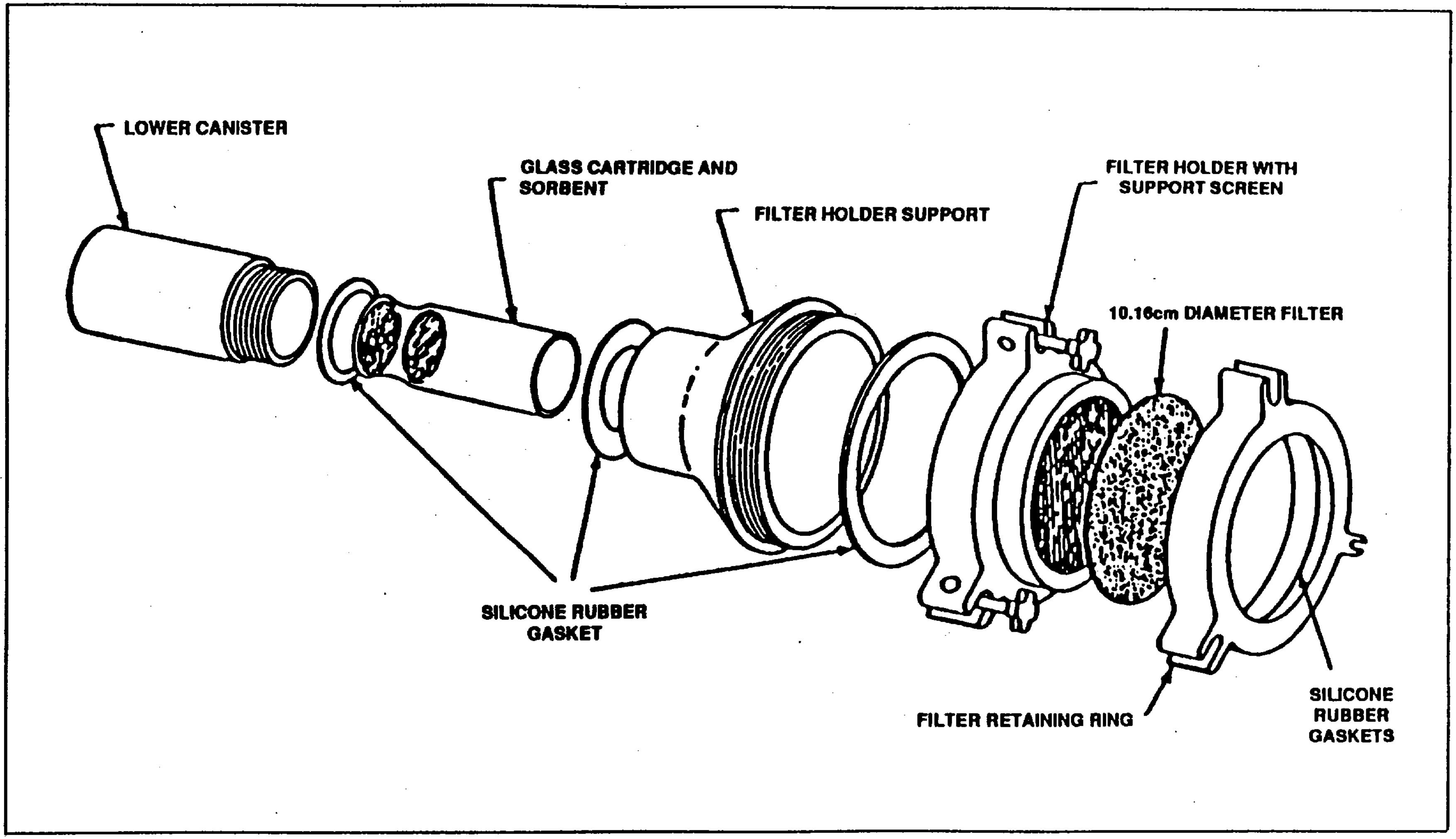


FIGURE 6-2

Schematic of Sampling Head

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

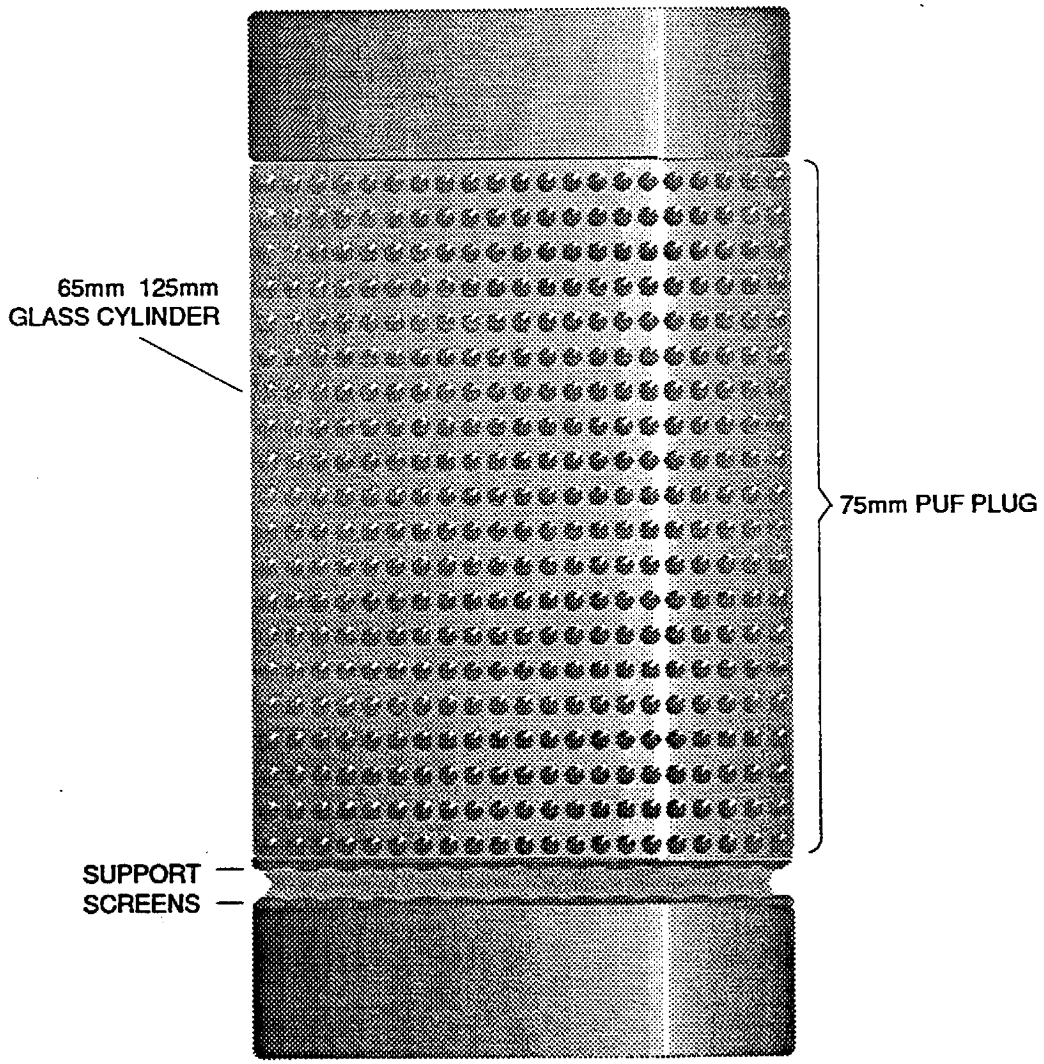


FIGURE 6-3
PUF Sampling Cartridge for Collection of PCDDs/PCDFs

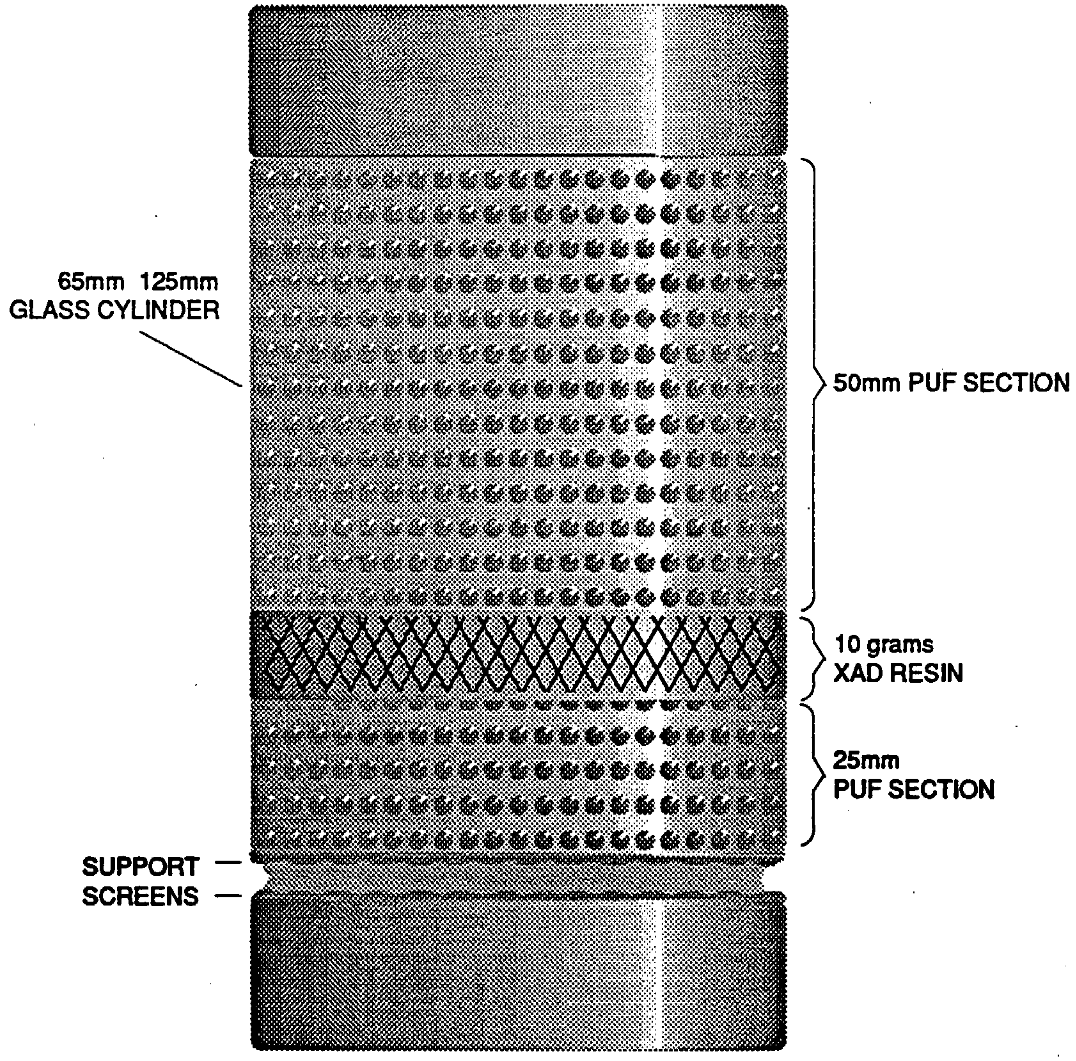


FIGURE 6-4
PUF/XAD "SANDWICH" for Collection of PAHs

methylene chloride-rinsed aluminum foil and placed in a sealed polyethylene bag until ready for use. Each glass PUF cartridge was labeled with a unique QC laboratory identification number. A sufficient number of cleaned samples were maintained in the laboratory as method blanks.

6.3 Sampler Calibration

ENSR field staff fully calibrated each PS-1 sampler prior to and following each sampling session. In addition, samplers underwent complete calibration following any sampler maintenance activity such as brush or motor replacement. The calibration procedure entailed attachment of a certified, calibrated orifice to the inlet of the sampler head. A water manometer secured to the calibrated orifice measured pressure differential at various flowrate settings. Manometer readings were recorded at five magnehelic settings during each calibration (20, 40, 50, 60 and 80) to establish the relation of pressure drop to magnehelic setting. A certified calibration curve generated from the orifice in the laboratory provided direct correlation of pressure drop to sampler flowrate. This allowed determination of sampler flowrate from the direct reading of the magnehelic gauge installed integral to each sampler. Certified orifice calibrations were conducted by BGI, Inc. of Waltham, MA prior to field use.

6.4 Sample Collection Flows and Volumes

Nominal flowrate and anticipated sample volumes for each system were as follows:

Target Parameter	Session Duration	Nominal Flowrate (lpm)	Nominal (m^3)	Approximate Hours of Operation
PCDDs/PCDFs	24 hrs	240	345	7 am to 7 am
PAHs (diurnal)	12 hrs	240	175	7 am to 7 pm
PAHs (nocturnal)	12 hrs	240	175	7 pm to 7 am

Sample collection flowrates were determined using the average of the initial and final magnehelic readings corrected to standard temperature and pressure. Actual air volumes associated with field samples are reported in Section 7 (see Tables 7-2 through 7-5).

6.5 Field Surrogate Spikes

Isotopically labeled surrogates, applied to each sorbent cartridge in advance of field sampling, provided a measure of accuracy for the combined sampling and analysis regime. Field surrogate recovery data also served to monitor the tendency for analyte breakthrough within each program sample.

Table 6-1 lists the five field surrogates applied to each dioxin/furan trap and the single surrogate applied to each PAH trap. Field surrogates were applied at the laboratory to the inlet end of each trap following sorbent cleanup and before shipment to the field.

6.6 Sample Shipping and Handling Procedures

All sample filters and cartridges were prepared and packaged at the laboratory prior to shipment for field use. The analytical laboratory wrapped each pretreated PUF cartridge in methylene chloride rinsed aluminum foil and placed sample ID tape onto each foil wrapped cartridge. This ID tape listed the date of preparation, spiking regime and laboratory project number. Each foil wrapped cartridge was then sealed in a polyethylene ziploc bag, wrapped in bubble wrap to prevent breakage during shipping and packed snugly into shipping containers. During sample set-up and recovery, field staff handled sampling cartridges and filters using clean, cotton gloves. PUF cartridge shipping materials (foil, ziploc bag, bubble wrap) were stored on-site during sampling. After completion of sampling, cartridges were repackaged as originally shipped and stored in coolers containing frozen ice packs. Sample shipment coolers were then shipped overnight to the laboratory sample bank.

6.7 Sample Chain-of-Custody and Documentation

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

- They provided a mechanism for assignment of responsibility for sample integrity.
- They provided 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.

TABLE 6-1

Field Surrogate Standards

Standard	Amount Spiked
1. PCDDs/PCDFs	
$^{37}Cl_4$-2,3,7,8-TCDD	100 pg
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100 pg
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	200 pg
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	200 pg
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	500 pg
2. PAHs	
fluorene-d_{10}	500 ng

7.0 FIELD SAMPLING PROGRAM

7.1 Network Design

Each site was installed with six PS-1 samplers, as listed in Table 7-1. Samplers outfitted for collection of PCDDs/PCDFs operated for a 24-hour period (approximately 7 am to 7 am). Samplers outfitted for collection of PAHs, operated for two 12-hour periods per day (diurnal sampling - 7 am to 7 pm; nocturnal sampling - 7 pm to 7 am). All sorbent cartridges were spiked in the laboratory prior to sampling with the applicable isotopically labeled compounds listed in Table 6-1. In addition, one field blank per day for each sorbent system (PCDDs/PCDFs and PAHs) was collected. Collocated samples were also collected during the program.

7.2 Rice Straw Campaign

Tables 7-2 and 7-3 list all samples collected at the Pleasant Grove and Colusa monitoring sites from October 8 through November 10, 1990. Sampling days were identified by CARB after consideration of a number of criteria including status of "rice straw" burning in fields vicinal to the monitoring sites as well as regional meteorology that would place monitoring stations in the downwind path of burning fields. (See Table 8-1 for a complete listing of criteria taken into consideration by CARB in the selection process.)

7.3 Fresno Campaign

Table 7-4 lists all samples collected at the Fresno monitoring site from December 17, 1990 through January 3, 1991. Sample sets were collected daily on each of five (5) days during this calendar period.

7.4 Richmond Campaign

Table 7-5 lists all samples collected at the Richmond Monitoring site from January 24 through January 27, 1991. Sample sets were collected daily on each of four (4) consecutive days during this calendar period.

TABLE 7-1

Summary of Network Design

Sampler No.	Target Parameter	Description
1	PCDDs/PCDFs	primary, field surrogate spiked
2	PCDDs/PCDFs	collocated, field surrogate spiked
3	PAHs	diurnal, field surrogate spiked
4	PAHs	diurnal, unspiked
5	PAHs	nocturnal, field surrogate spiked
6	PAHs	nocturnal, unspiked

TABLE 7-2
SAMPLE COLLECTION SUMMARY
PLEASANT GROVE SITE

	Polynuclear Aromatic Hydrocarbons				PCDD/Fs
	Diurnal		Nocturnal		
Sampling Date (1990)	Diurnal Spiked	Diurnal Unspiked	Nocturnal Spiked	Nocturnal Unspiked	24-hour Spiked
Oct 19	PG-1	PG-2	PG-3	PG-4	PG-5
Oct 22	PG-6	PG-7	PG-8	PG-9	PG-10
Oct 23 [a]	PG-11	PG-12		PG-13	PG-14
Oct 24	PG-15	PG-16		PG-17	PG-18
Oct 25	PG-19	PG-20		PG-21	PG-22
Oct 26 [c]	PG-23	PG-24		[b]	PG-25
Oct 29 [d]		PG-26		PG-27	PG-28
Oct 30 [d]		PG-29		PG-30	PG-31
Oct 31		PG-32		PG-33	PG-34
Nov 1		PG-35	PG-36	PG-37	PG-38 [f]
Nov 5		PG-39		PG-40	PG-41 [f]
Nov 7 [e]		PG-42 [f]		PG-43 [f]	PG-44
Nov 8 [e]		PG-42 [f]		PG-43 [f]	PG-47

[a] - samples PG-11 and PG-12 ran approximately 24 hours
[b] - sampler failure
[c] - samplers on Oct 26 set to run through weekend
[d] - field composite collected on Oct 29 and 30 for PAHs and PCDDs/PCDFs
[e] - field composite collected on Nov 7 an 8 for PAH only
[f] - collocated

Diurnal and nocturnal PAH samples were run for 12 hours except where noted. PCDDs/PCDFs samples were run for 24 hours except where noted.

TABLE 7-3
SAMPLE COLLECTION SUMMARY
COLUSA SITE

	Polynuclear Aromatic Hydrocarbons				PCDD/Fs
	Diurnal		Nocturnal		
Sampling Date (1990)	Diurnal Spiked	Diurnal Unspiked	Nocturnal Spiked	Nocturnal Unspiked	24-hour Spiked
Oct 16	CF-1	CF-2	CF-3	CF-4	CF-5
Oct 17	CF-6	CF-7	[a]	[a]	CF-8
Oct 18	CF-9	CF-10	CF-11	[b]	CF-12
Oct 19	CF-13	CF-14	CF-15	[b]	CF-16
Oct 22	CF-17	CF-18	CF-19	CF-20	CF-21
Oct 23	[c]	CF-22	CF-23	[c]	CF-24
Oct 24	CF-25		CF-26		CF-27
Oct 25 [d]	CF-28	CF-29	[a]	[a]	CF-30
Oct 26 [e]	CF-31	CF-32	CF-33	CF-34	CF-35
Oct 29 [f]		CF-36		CF-37	CF-38
Oct 30		CF-36		CF-37	CF-38
Oct 31 [g]		CF-39		CF-40	CF-41
Nov 1	CF-42	CF-43		CF-44	CF-45
Nov 5		CF-46		CF-47	CF-48 [i]
Nov 7		CF-49		CF-50 [i]	[a]
Nov 8		CF-51 [i]		CF-52 [i]	CF-53
Nov 10		[a]		CF-54 [i]	[a]

[a] - power failure at site
[b] - sampler timer failed to operate properly
[c] - sampler failure
[e] - samples CF-31, CF-32 and CF-35 set to run through weekend
[d] - sample CF-30 ran 9 hours due to power failure
[f] - CF-36 and CF-37 ran 24 hours, CF-38 ran 48 hours.
[g] - CF-39 ran 20 hours
[h] - field composite collected on Nov 7 an 8 for PAH only

Diurnal and nocturnal PAH samples were run for 12 hours except where noted.
PCDDs/PCDFs samples were run for 24 hours except where noted.

TABLE 7-4
SAMPLE COLLECTION SUMMARY
FRESNO SITE

Sampling Date	Sample ID	Target Compounds	Sampling Period	Spiking Status	flowrate (lpm)	sample volume (m^3)	Valid Sample
12-17-90	565	PCDD/Fs	24 hr	spiked	283.2	365.9	Yes
	117	PCDD/Fs	24 hr	spiked	284.9	367.0	Yes
	331	PCDD/Fs	Blank	spiked	---	---	Yes
	720	PAHs	diurnal	unspiked	268.7	151.6	Yes
	713	PAHs	diurnal	unspiked	251.3	120.6	Yes
	718	PAHs	nocturnal	unspiked	250.2	181.2	Yes
	690	PAHs	nocturnal	unspiked	266.8	181.7	Yes
	716	PAHs	Blank	unspiked	---	---	Yes
	719	PAHs	Blank	unspiked	---	---	Yes
12-18-90	399	PCDD/Fs	24 hr	spiked	308.8	265.9	Yes
	372	PCDD/Fs	24 hr	spiked	298.9	402.3	Yes
	388	PCDD/Fs	Blank	spiked	---	---	Yes
	603	PAHs	diurnal	unspiked	275.1	183.2	Yes
	699	PAHs	diurnal	unspiked	275.1	163.1	Yes
	693	PAHs	Blank	unspiked	---	---	Yes
1-2-91	377	PCDD/Fs	24 hr	spiked	307.1	414.3	Yes
	96	PCDD/Fs	24 hr	spiked	307.2	418.4	Yes
	109	PCDD/Fs	Blank	spiked	---	---	Yes
	350	PAHs	diurnal	spiked	277.2	184.4	Yes
	724	PAHs	diurnal	unspiked	267.4	170.1	Yes
	347	PAHs	nocturnal	unspiked	251.9	174.3	Yes
	327	PAHs	nocturnal	spiked	258.9	186.7	Yes
	630	PAHs	Blank	unspiked	---	---	Yes
	330	PAHs	Blank	spiked	---	---	Yes
1-3-91	160	PCDD/Fs	24 hr	spiked	290.8	187.8	Yes
	55	PCDD/Fs	24 hr	spiked	288.5	423.2	Yes
	207	PCDD/Fs	Blank	spiked	---	---	Yes
	321	PAHs	diurnal	spiked	279.3	179.0	Yes
	678	PAHs	diurnal	unspiked	271.3	183.9	Yes
	301	PAHs	nocturnal	unspiked	245.2	1.5	No [a]
	7-27-32	PAHs	nocturnal	spiked	262.9	196.6	Yes
	673	PAHs	Blank	unspiked	---	---	Yes
	302	PAHs	Blank	spiked	---	---	Yes

TABLE 7-4 (Continued)
SAMPLE COLLECTION SUMMARY
FRESNO SITE

Sampling Date	Sample ID	Target Compounds	Sampling Period	Spiking Status	flowrate (scm)	sample volume (m^3)	Valid Sample
1-4-91	42	PCDD/Fs	24 hr	spiked	287.0	411.8	Yes
	104	PCDD/Fs	24 hr	spiked	298.9	422.9	Yes
	40	PCDD/Fs	Blank	spiked	---	---	Yes
	333	PAHs	diurnal	spiked	295.4	196.7	Yes
	313	PAHs	diurnal	unspiked	275.1	172.8	Yes
	18	PAHs	nocturnal	spiked	258.3	184.2	Yes
	314	PAHs	nocturnal	unspiked	289.1	214.5	Yes
	355	PAHs	Blank	spiked	---	---	Yes
	341	PAHs	Blank	unspiked	---	---	Yes

[a] – sample invalidated due to power failure

TABLE 7-5
SAMPLE COLLECTION SUMMARY
RICHMOND SITE

Sampling Date	Sample ID	Target Compounds	Sampling Period	Spiking Status	flowrate (lpm)	sample volume (m^3)	Valid Sample
1-24-91	480	PCDD/Fs	24 hr	spiked	301.8	419.4	Yes
	561	PCDD/Fs	24 hr	spiked	286.2	393.8	Yes
	370	PCDD/Fs	Blank	spiked	---	---	Yes
	508	PAHs	diurnal	spiked	281.4	183.2	Yes
	337	PAHs	diurnal	unspiked	289.1	181.0	Yes
	357	PAHs	nocturnal	unspiked	233.0	168.0	Yes
	501	PAHs	Blank	spiked	---	---	Yes
	506	PAHs	Blank	unspiked	---	---	Yes
1-25-91	342	PCDD/Fs	24 hr	spiked	305.3	433.9	Yes
	386	PCDD/Fs	24 hr	spiked	289.7	403.6	Yes
	396	PCDD/Fs	Blank	spiked	---	---	Yes
	315	PAHs	diurnal	spiked	299.3	201.7	Yes
	412	PAHs	nocturnal	unspiked	238.3	175.9	Yes
	417	PAHs	diurnal	unspiked	285.5	194.4	Yes
	430	PAHs	Blank	spiked	---	---	Yes
	433	PAHs	Blank	unspiked	---	---	Yes
1-26-91	66	PCDD/Fs	24 hr	spiked	302.2	429.2	Yes
	325	PCDD/Fs	24 hr	spiked	293.3	387.4	Yes
	402	PCDD/Fs	Blank	spiked	---	---	Yes
	426	PAHs	diurnal	spiked	301.2	203.6	Yes
	494	PAHs	nocturnal	unspiked	256.8	184.9	Yes
	404	PAHs	nocturnal	spiked	294.5	225.6	Yes
	479	PAHs	Blank	unspiked	---	---	Yes
	418	PAHs	Blank	spiked	---	---	Yes
1-27-91	615	PCDD/Fs	24 hr	spiked	302.2	424.3	Yes
	614	PCDD/Fs	24 hr	spiked	296.8	404.5	Yes
	552	PCDD/Fs	Blank	spiked	---	---	Yes
	611	PAHs	diurnal	spiked	295.4	202.9	Yes
	478	PAHs	nocturnal	spiked	281.2	216.8	Yes
	437	PAHs	nocturnal	unspiked	255.1	177.3	Yes
	609	PAHs	Blank	spiked	---	---	Yes
	338	PAHs	Blank	unspiked	---	---	Yes

7.5 Meteorological Summary

Table 7-6 provides a summary of key meteorological parameters reported by the National Weather Service (NWS) on each day of sampling. NWS stations vicinal to each respective monitoring network were used, as follows:

Rice Straw Network: Sacramento, CA
Fresno Network: Fresno, CA
Richmond Network: San Francisco, CA

Complete daily summaries of local climatological data for each of these NWS stations are provided in Appendix D. All of these data were provided to ENSR Consulting and Engineering courtesy of the California Air Resources Board.

TABLE 7-6

Meteorological Data Summary - Sampling Session Specific

Date	NWS Station	Monitoring Network	Temp. Range (°F)	Wind Direction		Average Wind Speed (mph)	Average Barometric Station Pressure ("$H_2$0)
				Deg.	Vector		
1990 Oct. 16	Sacramento, CA	Rice straw	54-83	320	NW	9.2	29.87
17	Sacramento, CA	Rice straw	45-84	230	SW	4.1	29.91
18	Sacramento, CA	Rice straw	54-71	240	WSW	10.4	29.94
19	Sacramento, CA	Rice straw	52-73	320	NW	11.8	29.96
22	Sacramento, CA	Rice straw	49-81	320	NW	3.4	29.96
23	Sacramento, CA	Rice straw	48-83	340	NNW	3.4	29.98
24	Sacramento, CA	Rice straw	48-86	10	N	0.8	30.00
25	Sacramento, CA	Rice straw	49-84	180	S	3.3	30.00
26	Sacramento, CA	Rice straw	48-84	330	NNW	3.6	29.99
29	Sacramento, CA	Rice straw	52-74	180	S	7.2	29.98
30	Sacramento, CA	Rice straw	48-73	180	S	8.5	29.98
31	Sacramento, CA	Rice straw	49-70	190	S	7.5	29.96
Nov. 1	Sacramento, CA	Rice straw	40-67	330	NNW	11.8	30.03

TABLE 7-6 (Cont'd)

Meteorological Data Summary - Sampling Session Specific

Date	NWS Station	Monitoring Network	Temp. Range (°F)	Wind Direction		Average Wind Speed (mph)	Average Barometric Station Pressure ("$H_2$0)
				Deg.	Vector		
1990 Nov. 5	Sacramento, CA	Rice straw	42-72	330	NNW	9.8	29.99
7	Sacramento, CA	Rice straw	41-69	330	NNW	5.5	30.15
8	Sacramento, CA	Rice straw	41-74	330	NNW	1.3	30.22
10	Sacramento, CA	Rice straw	38-76	350	N	3.1	30.12
Dec. 17	Fresno, CA	Fresno	33-50	110	ESE	3.7	29.95
18	Fresno, CA	Fresno	30-55	110	ESE	1.4	29.78
1991 Jan. 2	Fresno, CA	Fresno	28-54	300	WNW	1.8	29.87
3	Fresno, CA	Fresno	40-50	140	SE	2.1	29.69
4	Fresno, CA	Fresno	44-49	70	ENE	3.2	29.78
24	San Francisco, CA	Richmond	41-58	240	WSW	6.9	30.13
25	San Francisco, CA	Richmond	39-55	210	SSW	5.9	30.07
26	San Francisco, CA	Richmond	41-56	270	W	8.0	30.13
27	San Francisco, CA	Richmond	42-54	250	WSW	8.9	30.04

8.0 VALIDATION AND SELECTION OF SAMPLES FOR ANALYSIS

A formal validation protocol was implemented for samples collected during this program. 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 by ARB for analysis. Final selection of validated samples for analysis required concurrence of ENSR and ARB staff. Sample validation criteria are detailed further below.

8.1 Field Sample Validation Criteria

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 and PAHs. The proper collection of partitioned particulate and vapor phases is particularly critical should samples be 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 to sample invalidation. No samples collected during this program were invalidated based on the requirements for physical integrity of sampling materials.

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.

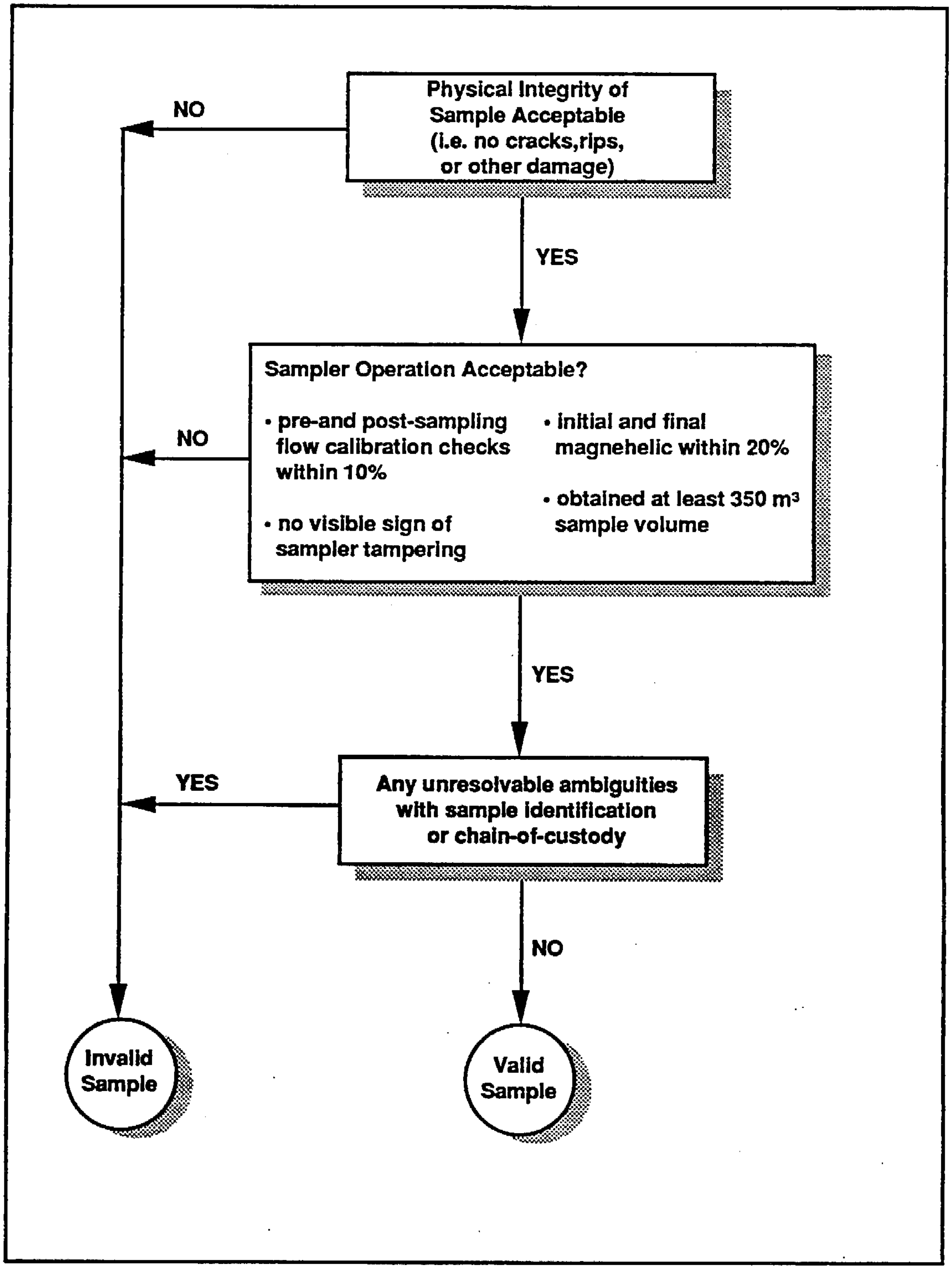


Figure 8-1
Sample Validation Protocol

Flow Rate Consistency

Accurate sample volume determination requires that a consistent flow rate be maintained throughout the sampling period. Flow rate consistency is confirmed by comparison of the initial and final magnehelic gauge 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.

Sampling Duration

Abbreviated sampling sessions due to sampler malfunction or power interruption may preclude collection of the desired sample volume. Such samples may be considered invalid and eliminated from consideration for analysis.

Sample Identification

No unresolvable ambiguities with sample identification or chain-of-custody resulted in sample invalidation.

Meteorology

Following validation of samples, session-specific meteorology is considered for final selection of samples for analysis. Optimum meteorological conditions for ambient monitoring include the absence of widespread precipitation during a sampling session. As such, all monitoring sessions conducted for this program were planned to coincide with periods of predicted clear weather, as predicted by ARB. Air sampling during periods of sustained, widespread precipitation may produce results which, in ENSR's judgement, do not represent actual ambient concentrations of the target parameters.

8.2 Selection of Field Samples for Analyses

8.2.1 Rice Straw Program

Sampling days were again selected on the basis of Rice Straw burning activity as provided by the Colusa County Department of Agriculture and Air Pollution Control District. This information was provided directly to the CARB. This information in concert with regional meteorological data was assessed by the CARB prior to authorization to commence sampling on any given day. The actual direction to commence sampling at any given time was provided to ENSR directly by representatives of the CARB.

All field samples were examined by ENSR employing the aforementioned sample validation criteria. An itemized listing of all samples collected noting all valid field samples was then forwarded to Ralph Propper at the CARB for consideration. The selection process employed by CARB for the identification of sampling days to undergo subsequent analyses included a number of components, as listed in Table 8-1.

The "Rice Straw" field sampling program began on October 16, 1990. Sampling sessions were conducted employing a two station network during the calendar period October 16 - November 11, 1990. On days in which samples were collected, twelve-hour composite samples were taken on both a diurnal and nocturnal basis for PAHs. In the majority of instances, these samples were collected in duplicate. Twenty-four (24) hour composite samples were collected each sampling day at each of the two sites for PCDDs/PCDFs.

Based upon the sample selection process outlined in Table 8-1, sampling days were identified for further examination. These were identified in a November 7, 1990 telephone conversation with Ralph Propper, the CARB Program Manager. The sampling dates selected for each of the two monitoring sites were provided as follows:

Pleasant Grove: October 23, 24, 25, 26 and 29
Colusa Fairgrounds: October 17, 18, 22, 23, 24, 25, 26, 29 and 30 (if available)

A complete inventory of samples available from these days was contained in a November 21, 1990 letter from Bruce Maisel (ENSR) to Ralph Propper (CARB). This listing, provided earlier in Section 7, provided the basis for samples authorized for PAH analysis and mutagenicity testing.

Additional sampling days were identified in a November 30, 1990 telephone conversation. These included the following days at each at the two (2) monitoring sites:

Pleasant Grove: November 5, November 7 and 8
Colusa Fairgrounds: October 31, November 5, 7 and 8

Particulate samples selected for mutagenicity testing are listed in Table 11-9 and Appendix C of this report.

No field samples were selected for PCDDs/PCDFs analyses. Two (2) composite samples were selected to undergo nitro-PAH and oxygenated-PAH analyses at Battelle Labs. Each of these

TABLE 8-1

Selection Criteria Employed by CARB for Identification of "Rice Straw" Sampling Days to Undergo Laboratory Analyses

- Visual observations provided by ENSR field personnel as to the color and loading of particulate filters. These observations were extracted from the field notes of the ENSR field personnel.
- Coefficient of Haze data collected by CARB at each of the two sites.
- Number (#) of acres of "Rice Straw" burned valley-wide on a calendar day basis.
- Number (#) of acres of "Rice Straw" burned in the vicinity of the two ambient monitoring stations, again on a daily basis.
- Collocated particulate data collected concurrently with some of the ambient sessions. (These data were collected by CARB personnel at a site other than the Colusa and Pleasant Grove sites).

composite samples represented a combination of nocturnal and diurnal samples from a number of sampling days.

8.2.2 Fresno Field Program

The Fresno Field sampling program commenced during December 1990 and continued into early January 1991. Sampling sessions were conducted on December 17 and 18, 1990 and January 2, 3, and 4, 1991. Twelve-hour composite samples were collected on both a diurnal and nocturnal basis for PAHs and mutagenicity testing. Accordingly, these samples were collected in duplicate. Twenty-four (24) hour composite samples were collected each of these days for PCDDs/PCDFs. A summary report of data pertinent to the Fresno Field Program, including an inventory of validated samples available for analysis, was provided to CARB on January 21, 1991. From the available sample inventory (see Section 7), a total of twenty-one samples were selected for extraction. Thirteen (13) of these samples underwent analyses for PAHs and the remaining eight (8) ambient samples were selected for PCDDs/PCDD analyses.

A total of five (5) sampling days were represented by these samples. The five (5) sampling days were selected by CARB based upon site specific meteorological conditions and relayed to ENSR in a February 22, 1991 telephone conversation. These days included December 17 and 18, 1990 and January 2, 3 and 4, 1991.

Based upon the PAH analysis, approximately 10 field samples were selected from the Fresno inventory for mutagen screening analyses. These consisted of individual sample extracts (nocturnal and diurnal) to be tested both with and without S9 activation. Based upon the results of these analyses in concert with the PAH data, two (2) composite samples were selected to undergo nitro-PAH and oxygenated-PAH analyses at Battelle Labs. These consisted of both a nocturnal composite sample and a diurnal composite sample.

8.2.3 Richmond Field Program

The Richmond field sampling program was conducted on each of four consecutive days during the calendar period January 24-27, 1991.

Twelve-hour composite samples for PAHs were collected each day on both a diurnal and nocturnal basis. Twenty-four (24) hour integrated samples were collected each day for PCDDs/PCDFs. All of the PCDDs/PCDFs samples were collected in duplicate. A Summary Report of data pertinent to the Richmond Field Program was contained in a February 27, 1991 letter from Gary Hunt (ENSR) to Ralph Propper, the CARB Program Manager.

From this available inventory, ambient air samples collected on January 24 and 25, 1991 were selected for extraction and subsequent PAH analyses.

Based upon the PAH results, a total of two (2) samples were ultimately subjected to mutagenicity testing. These consisted of individual sample extracts to be tested both with and without S9 activation. Based upon the results of these analyses in concert with the PAH data, two (2) composite samples were selected to undergo nitro-PAH and oxygenated-PAH analyses at Battelle Labs. These consisted of a nocturnal composite sample and a diurnal composite sample.

9.0 ANALYTICAL PROCEDURES

9.1 Overview and Team Organization

Laboratory analyses were provided for a variety of target parameters including PAHs, PCDDs/PCDFs, mutagenic activity, as well as selected nitro-PAH and oxygenated-PAH. The analytical services portion of the program was accommodated by a team comprised of ENSR, Battelle Labs, Triangle Labs and the University of California at Riverside, Battelle Labs and Triangle Labs served as subcontractors to ENSR while the University of California provided support under subcontract directly to the California Air Resources Board. Hence, UCal Riverside participated under the direction of the CARB. Refer to Table 9-1 for a listing of specific program assignments to each member of the analytical team, as well as identification of the Principal Investigator and Point of Contract for each respective organization.

9.2 Sorbent Preparation/Pretreatment and Surrogate Application

9.2.1 PCDDs/PCDFs

Ambient air samples were collected on polyurethane foam (PUF) sorbent traps which had been cleaned and spiked at Triangle Laboratories. The PUF cleanup was conducted in accordance with the method previously designed and validated by Triangle Laboratories under ENSR direction for air monitoring programs requiring optimal sensitivities. Foam plugs, cut by ENSR to exact specifications, were Soxhlet extracted through two solvent cycles, first for 16 hours with acetone and then for 16 hours with toluene. The PUF plugs were then air dried until all solvent had evaporated. The accompanying filters for the samplers were precleaned at Triangle Laboratories by Soxhlet extraction with toluene.

After the PUF plugs were air-dry, they were placed in glass cartridges with precautions taken to prevent accidental contamination. These were then spiked with a mix of isotopically labelled PCDDs and PCDFs to serve as field surrogates, as listed in Table 9-2. The surrogates were selected to represent the volatility range of target analytes, with particular emphasis on the more volatile species. Use of these surrogates allowed for detection of target analyte breakthrough, if it occurred at the high ambient air volumes collected. Recoveries were monitored by ENSR as a measure of combined sampling and analysis method performance.

TABLE 9-1

Sample Analysis Responsibilities - Assignment of Analyte(s) on a Laboratory-Specific or Team Member Basis

Team Member/Laboratory	Principal Investigator	Analyte/Responsibilities
Battelle Labs	Ms. Jane Chuang	Nitro-PAH and oxygenated - PAH analyses via NCI/GC/MS CH_2Cl_2 extracts
Triangle Labs	Hani Karam	• PCDDs/PCDFs (Cl_4-Cl_8 congener class sums and 2,3,7,8-substituted isomers) • Pretreatment and surrogate spiking of PUF and PUF/XAD-2 sorbent traps
ENSR	Ms. Marilyn Hoyt	• Extraction and concentration of particulate filter/sorbent samples for PAH analyses • PAH analyses via GC/MS/SIM
University of California at Riverside	Dr. Janet Arey	Mutagenicity testing of CH_2Cl_2 extracts

TABLE 9-2

Spiking and Fortification Solutions
Ambient Air Samples

Purpose	Compound	Quantity Applied (pg)
Field Applied Surrogates	$^{37}Cl_4$-2,3,7,8-TCDD	100
	$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	200
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	200
	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	500
Laboratory Extraction Recovery Standards	$^{13}C_{12}$-1,2,3,4-TCDD	200
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	200
Internal Standards for Quantification	$^{13}C_{12}$-2,3,7,8-TCDD	200
	$^{13}C_{12}$-1,2,3,7,8-PeCDD	200
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	200
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	200
	$^{13}C_{12}$-OCDD	500
	$^{13}C_{12}$-2,3,7,8-TCDF	200
	$^{13}C_{12}$-1,2,3,7,8-PeCDF	200
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	200
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	200
Alternate Standards	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	200
	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	200

9.2.2 PAHs

Ambient PAHs were collected using a PUF/XAD "sandwich" arrangement. The laboratory prepared PUF plugs as described in Section 9.2.1. XAD resin underwent sequential solvent extractions at the laboratory to remove impurities prior to field use. The XAD was initially washed with water and then soxhlet extracted for 16 hours with methanol. Two additional 16 hour soxhlet extractions with methylene chloride were performed. Approximately one-half of the PAH/XAD cartridges were spiked with isotopically labeled fluorene (D_{10}-fluorene) to serve as a field surrogate. The remaining PAH/XAD cartridges were utilized unspiked so as not to influence the mutagenicity assay. Recoveries of the PAH field surrogate were monitored by ENSR as a measure of method performance.

9.3 PCDDs/PCDFs (Triangle Labs)

Ambient air samples submitted to Triangle Laboratories were stored under controlled conditions pending analysis authorization. Sample cartridges were refrigerated in the dark at 4°C until program decisions regarding field sample validity and analysis priorities were finalized. Only those samples determined to require final HRGC/HRMS analysis were authorized for extraction; remaining samples of those collected were archived at Triangle as intact PUF samples.

As indicated previously, only field samples collected as part of the Fresno Campaign were selected for PCDDs/PCDF analyses.

Ambient air samples selected for analysis were fortified with the nine isotopically labelled internal standards identified in Table 9-2.

The ambient air sample, including the foam plug in the glass cartridge and the accompanying filter, were then placed directly in the Soxhlet extraction thimble, with care taken to prevent external contamination or sample loss. The sample was then extracted for sixteen hours with toluene.

At the end of the extraction process, the alternate standard mix was added to the toluene extract, which was then split into two portions. One portion was archived, with the other proceeding to cleanup and analysis.

Sample cleanup procedures for ambient air samples involved successive washes with concentrated sulfuric acid and sodium hydroxide followed by column cleanup on alumina and carbon columns.

All sample extracts were brought to a measured volume by the addition of the recovery standard mix prior to instrumental analysis.

Recovery standards and respective amounts added to the sample extracts prior to analyses are listed in Table 9-2. These recovery standards were used solely to quantify the absolute amount of the nine internal standards present in the final cleaned extract. The recoveries of the internal standards through the extraction and cleanup were monitored to assess laboratory performance, but their recovery does not affect native dioxin and furan quantitative values.

Sample extracts were analyzed on instrumentation as listed in Table 9-3. The VG 70S was the primary instrument for the initial analysis, with most confirmatory analyses performed on the VG 70S250. Instruments were tuned with PFK as directed in Method 8290 prior to sample analyses. All analyses were performed with the instrument operating in the selected ion monitoring mode, where two ions for each congener class are monitored for that period of time during which the class elutes. This operational mode provides selective detection and optimal sensitivity for target analytes.

Prior to instrument calibration, a mix of PCDDs and PCDFs containing the first and last-eluting isomers of each congener class was analyzed to verify the retention time windows for each congener class. Calibration was accomplished by analyses of five standard solutions. Relative response factors (RRFs) for each analyte were determined from their integrated ion areas in each standard, and the average RRF calculated. Calibration requirements for sample analyses included limits for the Percent Relative Standard Deviation for the relative response factors determined for each analyte over the calibration sequence and limits for the demonstrated ratios between the two ions monitored for each congener class. In addition, all peaks must demonstrate a signal/noise ratio greater than 2.5 in all solutions.

The instrument calibration and the retention time window settings were verified for each twelve hours of sample analyses by analyses of the midpoint calibration standard and the retention time window mix. Sample analyses were performed only after instrument performance had met all method criteria.

Instrumental quality assurance measures for all sample analyses included additional mass monitoring beyond that required to detect target analytes and isotopically labelled standards. Perfluorokerosene, the compound used to tune the instrument, was bled into the source at low levels on a continuous basis and one mass monitored for this compound at all times. This mass, called the "lock mass ion" demonstrates whether instrument mass calibration is constant or variable. Variability in the instrument response to the lock mass ion is generally a result of non-PCDD/PCDF organic compounds present in the sample extract and which affect the accuracy of

TABLE 9-3

Instrumentation for PCDD/PCDF Analysis

	System 1	System 2
Mass Spectrometer:	VG 70T	VG 70S
Data System:	VG 11/250	VG 11/250
Gas Chromatograph:	HP5790	HP5790
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 ballistacally then 3° C/min up to 300°

TABLE 9-3 (Cont'd)

Instrumentation for PCDD/PCDF Analysis

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°

the detection and/or quantitation of target PCDD and PCDF. Deflections in the signal for the lock mass occur when large amounts of organics enter the source and affect the ability of the instrument to correctly resolve the ion mass or alter sensitivity. These quantitative interferences cannot be detected in any other way. In addition, Triangle Laboratories monitored all sample analyses for polychlorinated ethers which, if present, can bias data for polychlorinated furans.

The initial analysis performed is the full-screen analysis for tetra- through octa-chlorinated dibenzodioxins and dibenzofurans. The DB-5 fused silica capillary gas chromatographic column used for this full-screen PCDD/PCDF analysis, however, does not fully resolve 2,3,7,8-TCDF from other TCDF isomers. If there are indications from the full-screen analysis that this isomer may be present in the sample, a second confirmation analysis must be performed using a DB-225 alternate column. During this analysis only tetrachlorinated species are measured.

Triangle Laboratories data reduction for samples involved several stages of computer and operator calculations and review. The initial report is computer-generated; for each congener class, the system searches and integrates peaks noted during the retention time window for each ion monitored. The computer checks for ion ratio and retention time matches of these peaks to that ratio required by the method and the times determined for the 2,3,7,8-substituted standards. Peaks which match both are quantified against the internal standards and reported as the 2,3,7,8-substituted isomers. These peaks and those additional peaks which match the ion ratio criterion but not the retention time criterion are summed and reported as Totals for the congener class. Peaks which are noted that meet the retention time but not the ion ratio for a 2,3,7,8-substituted PCDD of PCDF or which fail both criteria for identification are reported as Estimated Maximum Possible Concentration (EMPC). The full report generated by the software system includes:

- copies of all extracted ion chromatograms for all target analytes, internal standards and surrogates
- copies of extracted ion chromatographs for polychlorinated ethers which are potential interferents to certain polychlorinated furans
- integration tables for all analyte and standard peaks detected
- copies of extracted ion chromatogram for the PFK lock mass ion used to monitor quantitative interferences
- results for internal standard and surrogate recoveries
- results for target analytes and total congeners positively identified
- Estimated Maximum Possible Concentration results for total congeners and target analytes, where applicable

Separate reports are generated for each full-screen and confirmation analysis conducted for each sample.

9.3.1 Data Review

Triangle Laboratories mass spectroscopists review the data reports from the instrument and check integrations and identifications. Detection limits are determined from measurement of the signal to noise ratio in the ion channel used for 2,3,7,8-TCDD. Peaks are checked for integration accuracy, with particular attention paid to those which fail ion ratio criteria or are chromatographically poorly resolved. Lock mass ion chromatograms are reviewed and determinations of the potential impact of noted interferences are made. Data qualified flags are assigned to the reported values. Triangle Laboratories has thirteen different data qualifiers; these are defined in detail in Section 3.3.1 of their Data User Manual. Those commonly seen on effluent gas or ambient air samples include:

- B - Analyte was detected in the Method Blank.
- Q - Quantitative interferences may have biased data.
- RO - The ion ratio abundance for the internal standard failed to meet method criterion.
- V - Triangle Laboratories considers analyte data to be valid even though the recovery of an internal standard was below its control limit.
- PR - The peak was poorly resolved chromatographically.

ENSR data review of packages as supplied by Triangle Laboratories verified that analyses have been performed in full accordance with method requirements and have met specific program requirements.

9.4 Nitro-PAH/Oxygenated-PAH (Battelle Labs)

Sample extracts were combined and concentrated to 1 mL by Kuderna-Danish (K-D) evaporation. The concentrated sample extract was applied to a pre-packed (1 g) silica gel column. Two elution solvents were applied to the column in the following sequence: 4 mL of dichloromethane (DCM), and 4 mL of methanol. The DCM fraction was concentrated to 1 mL by K-D evaporation for GC/MS analysis. The methanol fraction was saved in the dark at -20°C. A laboratory method blank was prepared by the same procedure. Another method blank was spiked with a known amount (100 ng each) of each target analyte and fractionated by a silica gel column using the same procedure described before. The spiked and non-spiked method blank samples were also analyzed by GC/MS. The internal standard, 1-nitropyrene-d_9 was added to each sample extract prior to GC/MS analysis.

Negative chemical ionization (NCI), GC/MS was used to determine target analytes. A Finnigan TSQ GC/MS/MS operated in GC/MS mode was used. Methane was used as the carrier gas and reagent gas. The GC column was a DB-5 fused silica capillary column (30 m x 0.25 mm; 0.25

µm film thickness, Supelco). Data acquisition and processing were controlled by a Finnigan INCOS Model 2300 data system. The MS was operated in the selected ion monitoring (SIM) mode. Peaks monitored were the molecular ion peaks (M), M-1, and M+1 ion peaks. Identification of the target compounds was based on their GC retention times relative to the internal standard (1-nitropyrene-d_9). Quantification of target compounds were based on comparisons of the respective integrated ion current responses of the target ion to the internal standard, with average response factors of each target compound generated from analyses of standard solutions. Because only trace amounts of 2-nitrofluoranthene and 8-nitrofluoranthene are available, the standard solutions of these compounds were analyzed to determine their retention times relative to the internal standard. Quantification of these compounds was based on the average response factor of 1-nitropyrene. In addition, the pure standard of pyrene-3,4-dicarboxylic acid anhydride was not available. Quantification of this compound was based on the assumption that its response factor is one-half of the more volatile naphthalene-1, 8-dicarboxylic acid anhydride.

9.5 Mutagenicity Testing

For a description of the mutagenicity testing procedures employed by the University of California at Riverside, please refer to Appendix B of this document.

9.6 Polynuclear Aromatic Hydrocarbons (PAHs)

Analyses of PAH target parameters was performed at ENSR's laboratory in Wilmington, MA. The actual samples identified for analyses were selected from those listed previously in Section 7 employing the prioritization scheme discussed in Section 8.

Ambient air samples selected for analyses, consisting of both a particulate filter and corresponding sorbent trap were soxhlet extracted using methylene chloride. Extracts were subsequently concentrated employing Kuderna-Danish evaporation.

Instrumental analysis was conducted employing a gas chromatograph/mass spectrometer operating in the selected ion monitoring (SIM) mode. A listing of the PAH target parameters for which instrument calibration was established is shown in Table 9-4. A listing of the PAH target parameters, and associated internal standards as well as absolute retention times (RT in minutes) and retention time indices relative to the appropriate isotopically labeled internal standard (RRT=1.00) are also contained in Table 9-4.

TABLE 9-4

Polynuclear Aromatic Hydrocarbons - CARB Target Parameters (Gas Chromatograph Retention Times and Relative Retention Time Indices)

Compound Number		Compound Name	Retention Time	
			Min.	(Rel)
1)	*	D8-NAPHTHALENE	9.70	(1.00)
2)		NAPHTHALENE	9.75	(1.005)
3)		2-METHYLNAPHTHALENE	11.45	(1.180)
4)		1-METHYLNAPHTHALENE	11.69	(1.206)
5)	*	D10-ACENAPHTHENE	14.00	(1.00)
6)	**	2-FLUOROBIPHENYL	12.45	(.889)
7)		BIPHENYL	12.65	(.903)
8)		ACENAPHTHYLENE	13.63	(.973)
9)		ACENAPHTHENE	14.09	(1.006)
10)	***	FLUORENE-D10	15.30	(1.092)
11)		FLUORENE	15.37	(1.097)
12)	*	D10-PHENANTHRENE	17.66	(1.000)
13)		PHENANTHRENE	17.72	(1.003)
14)		ANTHRACENE	17.84	(1.010)
15)		FLUORANTHENE	20.74	(1.174)
16)		PYRENE	21.27	(1.204)
17)	*	D12-CHRYSENE	24.35	(1.000)
18)	**	TERPHENYL,D14	21.84	(.897)
19)		RETENE	22.19	(.911)
20)		BENZ(A)ANTHRACENE	24.32	(.999)
21)		CHRYSENE/TRIPHENYLENE	24.41	(1.002)
22)	*	D12-PERYLENE	27.69	(1.000)
23)		BENZO(B,J&K)FLUORANTHENES	26.95	(.973)

TABLE 9-4 (Cont'd)

Polynuclear Aromatic Hydrocarbons - CARB Target Parameters (Gas Chromatograph Retention Times and Relative Retention Time Indices)

Compound Number	Compound Name	Retention Time	
		Min.	(Rel)
24)	BENZ(E)PYRENE	27.47	(.992)
25)	BENZ(A)PYRENE	27.58	(.996)
26)	INDENO(123,CD)PYRENE	29.96	(1.082)
27)	DIBENZ(A,C/A,H)ANTHRACENE	30.00	(1.083)
28)	BENZO(GHI)PERYLENE	30.54	(1.103)
29)	CORONENE	35.12	(1.268)

*Internal Standard
**Lab Surrogate
***Field Surrogate

10.0 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; and
- 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 Triangle Labs, along with XAD sorbent material, 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 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.

10.4 Field Surrogate/Laboratory Surrogate Data

Prior to sample collection, PUF sorbent cartridges used for PCDDs/PCDFs collection were spiked with five field surrogate compounds, $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C_{12}$-2,3,4,7,8-PeCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF. 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 surrogate recovery (observed vs. applied) in program samples. The mean recoveries calculated for the TCDD, PeCDF, HxCDF, HxCDD and HpCDF field surrogates are 97%, 102%, 100%, 83% and 79%, respectively, as shown in Table 10-1. The mean recovery for the PAH field surrogate, fluorene D_{10}, was 71%, as listed in Table 10-2. All average field surrogate recoveries fall within the acceptable recovery window of 60% to 140% established at the outset of the program.

PAH analyses also incorporated the use of two laboratory surrogates (2-fluorobiphenyl and d_{14}-terphenyl) which were added to PAH samples prior to extraction. Recoveries of these PAH laboratory surrogates, which are quantitated against the PAH internal standards, provide a qualitative assessment of native PAH behavior through the extraction and analysis procedure. PAH laboratory surrogate recoveries are provided in Table 10-2.

An additional purpose served by the isotopically labeled field surrogates was to monitor the stability of analytes within actual field samples, and subsequent sample extracts throughout the lengthy time period that elapsed between field sampling, sample extraction and laboratory analyses.

TABLE 10-1
FIELD SURROGATE AND INTERNAL STANDARD RECOVERY DATA FOR PCDDs/PCDFs

	Field Surrogates Recoveries (%)					Internal Standard Recoveries (%)									Alternate Stnd Recoveries (%)	
Sample ID	TCDD (100 pg)	PeCDF (100 pg)	HxCDF (200 pg)	HxCDD (200 pg)	HpCDF (500 pg)	TCDF (200 pg)	TCDD (200 pg)	PeCDF (200 pg)	PeCDD (200 pg)	HxCDF (200 pg)	HxCDD (200 pg)	HpCDF (200 pg)	HpCDD (200 pg)	OCDD (400 pg)	HxCDF [b] (200 pg)	HxCDF [c] (200 pg)
388	92.4	90.3	88.7	79.0	79.3	61.9	67.5	52.1	92.0	77.4	99.2	52.6	53.7	33.0	57.4	97.2
372	96.6	113	111	74.2	79.1	66.7	68.9	47.5	64.6	59.3	78.9	54.4	47.2	33.2	57.2	80.1
331	101	99.7	99.3	79.2	91.7	50.5	49.0	50.1	67.4	66.8	90.7	46.2	46.9	27.5	55.8	76.8
117	88.3	100	104	85.7	78.8	75.2	84.1	61.4	79.8	71.4	79.0	55.6	54.5	43.9	63.3	82.3
565	110	107	102	81.4	75.0	75.1	75.6	60.8	81.5	67.2	74.2	45.9	40.7	27.5	59.7	60.9
Method Blank	100	106	95.4	75.5	85.2	48.8	51.9	51.8	102	63.4	84.0	55.3	56.9	46.5	59.1	61.1
96	86.2	100	102	72.7	83.6	95.4	90.7	71.3	126	[a]	[a]	[a]	[a]	[a]	[a]	[a]
109	104	112	85.8	113	60.0	44.3	59.7	53.6	72.3	89.1	75.2	43.0	39.5	16.8	55.3	73.9
377	94.8	92.4	113	116	78.2	63.0	75.7	69.7	76.2	40.1	39.2	27.0	27.5	16.6	38.7	43.5
Method Blank	95.7	97.5	101	52.9	77.5	44.6	48.6	39.4	50.7	33.1	60.7	22.8	22.9	16.8	26.4	42.1
AVERAGE	96.9	102	100	83.0	78.8	62.6	67.2	55.8	81.3	56.8	68.1	40.3	39.0	26.2	47.3	61.8
STD DEV	6.8	7.2	8.2	17.8	7.8	15.5	14.0	9.5	20.1	24.5	27.5	17.3	16.8	13.3	19.1	26.3

Spiking levels indicated in parentheses.

[a] - Qualitative interference with recovery standard precluded accurate determination of standard recovery.

[b]- $^{13}C_{12}$-1,2,3,7,8,9-HXCDF

[c]- $^{13}C_{12}$-2,3,4,6,7,8-HXCDF

TABLE 10-2

Field Surrogate and Laboratory Standard Recovery Data for PAHs

	PERCENT RECOVERY		
Sample ID	Flourene, D10 (field surrogate)	2-Fluorobiphenyl (lab surrogate)	Terphenyl, D14 (lab surrogate)
F1PP 718	75	78	256
F1PA 720	NS	72	132
F2PA 603	NS	48	101
F3PAS 350	70	60	105
F3PPS 327	84	56	179
F4PAS 321	84	84	131
F5PAS 333	91	78	94
F5PPS 18	68	47	73
M Blank	NS	65	86
F Blank 12-17-90	NS	44	87
F Blank 12-18-90	NS	53	98
F Blank 1-2-91	NS	49	80
F Blank 1-3-91	NS	61	87
F Blank 1-4-91	80	57	83
508 R1PAS	NS	51	68
357 R1PPU	NS	50	70
501 R1PBS (FB)	50	38	63
315 R2PAS	79	52	65
412 R2PPU	93	48	62
430 R2PBS (FB)	36	24	56
M Blank	NS	42	71
CF2D-S-515	88	69	135
CF3D-S-481	77	57	100
CF3N-S-499	69	NS	NS
493-PAHS	65	49	101
524-PAHS	71	48	105
514-PAHS	51	46	63
475-PAHS	58	NS	NS
516-PAHS	23	23	30
484-PAHS	57	NS	NS
519-PAHS	131	105	100
82780	120	74	110
509-PAH	61	NS	NS
COL-28	NS	NS	NS
591-PAHU	NS	NS	NS
85-PAHU	50	NS	NS
596-PAHU	NS	87	220
110-PAHU	NS	59	130
181-PAHU	NS	56	180

TABLE 10-2 (CONT'D)

Field Surrogate and Laboratory Standard Recovery Data for PAHs

Sample ID	PERCENT RECOVERY Flourene, D10 (field surrogate)	2-Fluorobiphenyl (lab surrogate)	Terphenyl, D14 (lab surrogate)
77-PAHU	NS	60	110
598-PAHU	NS	79	160
CF4-PAH-520 FB	46	36	69
FB3-PAH/513 FB	80	46	140
FB1-PAH-496 FB	NS	86	119
ENSR XAD	50	32	49
Supelco XAD	NS	79	92
Trip Blank	NS	27	81
AVERAGE	70.6	56.9	104
STD DEV	22.9	18.2	45.2

NS = not spiked

10.5 Laboratory Internal Standard Data

The nine isotopically labeled PCDDs/PCDFs internal standards listed in Table 10-3 were utilized to quantitate the target PCDDs/PCDFs selected for study. The PCDDs/PCDFs internal standards were spiked into each PUF cartridge at the laboratory just prior to soxhlet extraction, and were quantitated against isotopically labeled recovery standards. This approach allows for measurement of the quantitative recovery of the target PCDDs/PCDFs throughout the extraction and analysis procedure.

Table 10-1 provides a summary of PCDDs/PCDFs internal standard recoveries for each sample analysis. Data are provided for each of nine (9) isotopically labeled internal standards used in actual analyte quantitation as well as two (2) alternate standards (see Table 9-2). A statistical analysis of the percent recoveries obtained for the PCDDs/PCDFs internal standards allows for a determination of average recovery and standard deviation for each standard, as provided in Table 10-1. Recovery values found to lie outside established control limits (60% to 140%) still provide acceptable results because the signal-to-noise ratio exceeded 10:1 in these cases.

The five isotopically labeled PAHs internal standards listed in Table 10-3 were utilized to quantitate the target PAHs parameters. Unlike the PCDDs/PCDFs analytical approach (Method 8290) which incorporates internal standard spiking prior to sample extraction, the PAHs analysis method requires that PAHs internal standards be spiked into each sample extract prior to analysis. Potential losses of target analytes during extraction are qualitatively assessed through review of the PAHs laboratory surrogates, which are added to the sample prior to extraction.

10.6 Method Blanks

Quality control procedures included the analyses of several blank PUF and PUF/XAD 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. Method blanks showed no indication of laboratory contamination.

10.7 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

TABLE 10-3

Laboratory Internal Standards

Internal Standard	Quantitated Analytes
$^{13}C_{12}$-2,3,7,8-TCDD	TCDDs
$^{13}C_{12}$-1,2,3,7,8-PeCDD	PeCDDs
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	HxCDDs
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	HpCDDs
$^{13}C_{12}$-OCDD	OCDD/OCDF
$^{13}C_{12}$-2,3,7,8-TCDF	TCDFs
$^{13}C_{12}$-1,2,3,7,8-PeCDF	PeCDFs
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	HxCDFs
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	HpCDFs
d_8-naphthalene	PAHs
d_{10}-acenaphthene	PAHs
d_{10}-phenanthrene	PAHs
d_{12}-chrysene	PAHs
d_{12}-perylene	PAHs

recovery periods (approximately ten minutes total). In addition, field blanks were placed into and removed from the sampler head to mimic the procedures employed from program samples.

All field blank values for PAHs are reported in both units of ng (total) and ng/m^3 (see Tables 11-2, 11-4). These ng/m^3 concentrations are provided for relative comparison purposes assuming a nominal air volume of 180 m^3. Actual blank correction is in fact performed on an absolute ng basis and not on a concentration basis.

Field blank data were employed in the correction and reporting of all PAHs and PCDD/PCDF data. Values reported for nitro-PAHs, however, do not represent field blank-corrected values. This direction was the result of a consensus reached by the Project Team (see Section 11.4).

Analytical results reported for program samples are corrected using the corresponding field blanks as described in Section 11. Field blank results for the program reflected levels typical for ambient studies of this nature and generally parted minimal impact to analytical results reported in Section 11.0. The Fresno PCDDs/PCDFs field blank collected during the December 18/19 sampling session did show relatively higher contaminant levels of some 2,3,7,8-substituted PCDDs compared to the other PCDDs/PCDFs field blanks; the 2,3,7,8-substituted PCDFs for this blank were all non-detected.

10.8 Collocated Samplers

Collocated PCDDs/PCDFs sampler pairs were operated 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 establish the precision of the combined sample collection and analysis regime for PCDDs/PCDFs on a congener-specific basis. Two collocated PCDDs/PCDFs sample pairs collected at the Fresno site were selected for analysis.

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 result 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:

$$\frac{abs(X_1 - X_2)}{(X_1 + X_2)/2} X\,100$$

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 two collocated pairs are presented in Table 10-4. The average percent difference obtained for all measured pairs is 20.6%. This precision value falls well within the precision goal of 50% established at the outset of program.

10.9 Battelle Columbus - Analysis of Nitro-PAH and Oxygenated-PAH

Quality control data reported herein were provided to ENSR by Battelle Laboratories and were excerpted from the Final Report document contained in Appendix C.

Recovery data for the applicable target parameters are reported in Table 10-5. These data reflect actual recoveries of analytes spiked into the method blank which accompanied the six (6) composite field sample extracts through the entire analytical scheme at Battelle Labs. As shown in Table 10-5, recovery data for each of the analytes were in excess of 90%, signifying minimal loss of target analytes during the fractionation procedure and subsequent NCI/GC/MS instrumental analyses. Analysis of the companion laboratory method blank indicated that none of the target analytes were detected.

10.10 PAH Data Comparability (ENSR And Battelle Columbus)

Two (2) of the PAH target parameters fluoranthene and benzo(a)pyrene were common to the analyte lists examined by both ENSR and Battelle Columbus Labs. A summary of these data from the two (2) Fresno samples is provided in Table 10-6 for relative comparison purposes. Upon direct examination of these data we find better agreement in the benzo(a)pyrene values than can be found in the fluoranthene values.

Specific reasons for the lack of comparability in some of these values include the following:

(a) The ENSR data represent analyses of neat single samples while the Battelle data represent analyses of multiple sample composites. The ENSR data shown in Table 10-6 in fact represent average values for two separate sample analyses, while the Battelle data represent values for individual composite samples.

(b) Use of different analytical methods (see Section 9).

TABLE 10-4
PRECISION ASSESSMENT FOR PCDDs/PCDFs MEASUREMENTS APPROACH
(percent difference between measured values)

	FRESNO - 12/17 to 12/18/90			FRESNO - 1/2 to 1/3/91		
	(pg/m^3)			(pg/m^3)		
Parameter	ID 565	ID 117	% D	ID 96	ID 377	% D
2,3,7,8-TCDD						
1,2,3,7,8-PeCDD				0.192	0.201	4.6
1,2,3,4,7,8-HxCDD	0.292	0.357	19.9	0.287	0.384	28.9
1,2,3,6,7,8-HxCDD	0.456	0.458	0.3	0.581	0.500	15.0
1,2,3,7,8,9-HxCDD	0.820	0.935	13.1	1.68	1.05	46.1
1,2,3,4,6,7,8-HpCDD	9.57	9.21	3.8	7.93	7.63	4.0
OCDD	34.3	30.0	13.3	16.8	17.9	6.4
2,3,7,8-TCDF	0.134	0.090	39.6	0.0478	0.0521	8.7
1,2,3,7,8-PeCDF	0.084	0.089	5.4			
2,3,4,7,8-PeCDF				0.113	0.101	11.2
1,2,3,4,7,8-HxCDF	0.317	0.357	11.8	0.325	0.352	8.1
1,2,3,6,7,8-HxCDF	0.089	0.090	1.8			
2,3,4,6,7,8-HxCDF	0.121	0.171	34.1	0.204	0.167	20.0
1,2,3,7,8,9-HxCDF						
1,2,3,4,6,7,8-HpCDF						
1,2,3,4,7,8,9-HpCDF						
OCDF	0.664	0.466	35.1	0.212	0.521	84.6
TOTAL/OTHER TCDD	0.612	0.591	3.5	0.313	0.372	17.1
TOTAL/OTHER PeCDD	0.768	1.56	68.3	1.26	1.68	28.4
TOTAL/OTHER HxCDD	5.71	6.10	6.6	7.55	7.84	3.8
TOTAL/OTHER HpCDD	22.0	20.6	6.5	18.3	17.5	4.4
TOTAL/OTHER TCDF	2.31	2.23	3.3	1.39	1.69	19.4
TOTAL/OTHER PeCDF	1.92	1.68	13.3	1.36	1.35	0.6
TOTAL/OTHER HxCDF	1.13	1.24	9.4	1.41	1.40	1.2
TOTAL/OTHER HpCDF	0.049	0.447	160.3			

Percent difference calculated for parameters measured in both members of collocated pair.

% D = percent difference = ABS(M1-M2)/((M1+M2)/2)*100, where;
(M1 and M2 are collocated measurements, ABS = absolute value).

AVERAGE PERCENT DIFFERENCE (between measured pairs) = 20.6%

TABLE 10-5

Recovery Data of Spiked Target Compounds in the Method Blank (Battelle Labs)

Compound	Percent Recovery (%)
Fluoranthene	92
Benzo(a)pyrene	100
1-Nitronaphthalene	100
2-Nitronaphthalene	99
3-Nitrobiphenyl	97
9-Nitrophenanthrene	96
9-Nitroanthracene	98
2-Nitrofluoranthene	100
1-Nitropyrene	96
6-Nitrochrysene	100
1,6-Dinitropyrene	100
9-Fluorenone	92
Naphthalene-1,8-dicarboxylic acid anhydride	100
Benzo(a)anthracene-7,12-dione	97

TABLE 10-6

PAH Data Comparison[a] - ENSR and Battelle (Battelle Values in Parentheses)

Sample Code	**82935/82984[a,b]**	**82986/82981[a,b]**
Concentration	**ng/m^3**	**ng/m^3**
Fluoranthene	25 (12.34)	15.5 (8.90)
Benzo(a)pyrene	8.95 (7.37)	2.90 (2.34)

[a] Battelle values reported in parentheses.

[b] ENSR data represent averages of values reported for two individual samples. Battelle data represent values reported from analyses of the same two samples as composite sample extracts.

(c) Blank correction influences; field biased blank data were available for the ENSR PAH analyses but unavailable for the Battelle PAH analyses (see Section 10.7).

(d) The elapsed time differences between initial analyses of neat samples by ENSR and composite sample extracts by Battelle.

It should be noted that the quality of the PAH data was further supported by an independent evaluation of the ENSR data conducted by ARB staff. This latter effort consisted of a comparison of ENSR values for benzo(a)pyrene, indeno(1,2,3-cd) pyrene and benzo(g,h,i)perylene to those from a comparable ARB monitoring network. Values for these three (3) parameters were found to agree reasonably well.