

California Environmental Protection Agency



Air Resources Board

California Ambient Dioxin Air Monitoring Program (CADAMP)

Project Plan for Monitoring During 2005

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2005 CADAMP Monitoring Project Workplan Summary

The purpose of the 2005 CADAMP monitoring is to collect additional data on ambient concentrations of dioxins, furans, dioxin-like polychlorinated biphenyl (PCB) congeners, and polybrominated diphenyl ethers in California. Two sites from the original CADAMP monitoring network, Rubidoux and Livermore, will continue with ambient sampling and two additional sites, Fresno and the Westside Elementary School in Five Points, a rural community in the San Joaquin Valley Air Basin, will be added. Monitoring at Rubidoux, Livermore, and Fresno will be representative of urban areas. The rural Westside Elementary site will provide data representative of a non-industrial, low population, rural area for comparison with data from urban sites and will complement data obtained from USEPA's National Dioxin Air Monitoring Network (NDAMN).

The samplers at each site will be operated on a 28-day cycle as follows. A polyurethane foam filter (PUF) and a quartz fiber filter (QFF) will be installed and ambient air will be collected for five days. The QFF will then be removed and replaced with a clean QFF to prevent particulate overload and ambient air will be collected for another five days. The second QFF will then be harvested and additional sampling will be conducted. For each 28-day cycle, or sampling moment, there will be four QFFs and one PUF that collect ambient air for 20 out of 28 days. There will be a total of thirteen sampling moments for 2005 monitoring, beginning January 13, 2005, and ending January 10, 2006.

Staff from the South Coast Air Quality Management District and Bay Area Air Quality Management District will operate the dioxin samplers at Rubidoux and Livermore, respectively. ARB staff will operate samplers at Fresno and the Westside Elementary sites and will provide technical support for all sites with respect to calibrations, maintenance, and repairs. AXYS Analytical Services, Ltd., under contract to the ARB, will perform all dioxin sample analyses consistent with the CADAMP Quality Assurance Project Plan.

Details of all aspects of this program may be found on the web:
<http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm>.

2005 CADAMP Monitoring Project Workplan

I. Introduction

Until January 2005, the California Ambient Dioxin Air Monitoring Program (CADAMP) consisted of a monitoring network of ten sites in the Bay Area and South Coast. At the end of 2004, the decision was made to reduce the network in the Bay Area and South Coast to one site in each region and establish two additional sites in the San Joaquin Valley. The revised network of four sites would operate for approximately one year and would provide air data on dioxins and dioxin-like compounds in an area of the state that had not been part of the original CADAMP network.

The sites remaining in operation in the Bay Area and South Coast, Livermore and Rubidoux, respectively, were chosen for several reasons. First, to provide continuity of data collection in two regions of the state that had been the focus of intensive dioxin air monitoring since the end of 2001. Second, Livermore and Rubidoux, showed elevated average air concentrations, as compared with other CADAMP sites, of either dioxins or particulate matter based on earlier monitoring data. Finally, data collected in Livermore and Rubidoux, coincident with those data collected at the San Joaquin Valley sites, will provide data to compare heavily populated regions of northern and southern California with data collected from the central portion of the state.

Within the San Joaquin Valley two sites have been established. An urban site, located in downtown Fresno, is intended to provide data on urban ambient concentrations of dioxins, furans, dioxin-like PCBs, and PBDEs. A second, rural site is located at the Westside Elementary School in Five Points. Five Points is a rural community with a population of approximately 2000 located about 40 miles southwest of Fresno. The Westside Elementary School site is intended to provide comparison data with those collected from the urban Fresno site and will supplement data collected under the USEPA's National Dioxin Air Monitoring Network (NDAMN) at a limited number of rural sites in California (Figure 1).

Ambient air samples collected at each of the four 2005 modified CADAMP network sites will be analyzed for the same dioxin and dioxin-like analytes as earlier in the program: polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). Data reporting from the contract laboratory to the California Air Resources Board's (ARB) Monitoring and Laboratory Division (MLD) will remain the same as with the earlier CADAMP monitoring.

Please refer to <http://www.arb.ca.gov/aaqm/gmosopas/dioxins/dioxins.htm> for the following CADAMP documents and information that are also applicable to the modified CADAMP network monitoring for 2005:

- 1) California Ambient Dioxin Air Monitoring Program Quality Assurance Project Plan (QAPP);

- 2) Field Operation of the California Ambient Dioxin Air Monitoring (CADAMP) Sampling Network;
- 3) Standard Operating Procedures for Andersen Instruments Polyurethane Foam (PUF) Sampler--Special.

II. Background

Dioxins and furans are highly toxic chemicals that are formed as unwanted by-products during certain combustion and chemical manufacturing processes. The ARB and USEPA have identified dioxins as toxic air contaminants (TACs) and hazardous air pollutants (HAP), respectively. Numerous studies, including the USEPA's *Draft Dioxin Reassessment*, document dioxins as carcinogenic.

Dioxins are also known to cause other non-cancer health-related problems, including birth and developmental defects. Under the Children's Environmental Health Protection Act (SB25, Escutia, 1999), the California Office of Environmental Health Hazard Assessment (OEHHA) evaluated available health information on TACs and developed a list of five TACs that might cause children and infants to be especially susceptible to illness. Dioxins were chosen as one of the key TACs through SB25 legislation.

Dioxins and dioxin-like chemicals are emitted into the atmosphere from a variety of sources including cars and trucks, waste incineration, chemical manufacturing plants, and other combustion sources that burn fuel or chlorine-containing waste. Emissions have been greatly reduced over the years. However, from the 2002-2004 CADAMP data it is evident they continue at a reduced level.

Airborne emissions can be inhaled directly or deposited to contaminate vegetation, which are eaten by animals and humans. Deposition onto food sources is a principle avenue of human exposure. Reservoir sources, such as soil and sediment that contain deposits from prior years' emissions, and manufactured materials that contain dioxins that may later be released into the circulating environment, may also be a significant source.

Among dioxin-like compounds, two specific PBDE mixtures have become the focus of recent California legislation. Beginning January 1, 2008, State law prohibits the manufacture, processing, or distribution of products containing more than one-tenth of one percent penta- or octabrominated diphenyl ethers (AB302, Chan, 2003). PBDEs are commonly used as flame-retardants in many consumer products, including foam, textiles, and computer circuit boards. PBDEs are environmentally persistent and have also appeared in human tissue.

The passage of Assembly Bill 302 by the California legislature reflects the increasing concern the public has about the health impacts and environmental fate of dioxins and dioxin-like chemicals. To date, there is limited information on dioxin source emissions and ambient air concentrations in California. This lack of air data has made it difficult to adequately address the public's health concerns and provide data from studies on the transport and fate of these toxic air contaminants.

Apart from CADAMP, most dioxin monitoring to date has been done in food growing regions to gather information about the air to food pathway of human exposure. The population-oriented nature of the State's dioxin air monitoring program and its urban emphasis complements the rural focus of the USEPA's NDAMN. Together, data from the California program and NDAMN will enhance our understanding of exposure from multiple airborne pathways.

III. Monitoring Locations

Monitoring for dioxins will be conducted at the following sites beginning in January 2005. All dioxin monitoring is expected to end in June of 2006.

Livermore (San Francisco Bay Area Air Basin)

Livermore was chosen as one of the original dioxin monitoring sites because it is impacted by several categories of pollutant emissions due to its location near freeways and light industry, and because of the population density of the area. Sampling at Livermore began in 2002. For 2005, Livermore will serve as the single Bay Area monitoring site.

Riverside-Rubidoux (South Coast Air Basin)

Rubidoux, located in Riverside County, was chosen as one of the original dioxin air monitoring sites due to its proximity to mobile source emissions and because it consistently records one of the highest levels of particulate in the South Coast Air Basin. Sampling at Rubidoux began in 2002 and will serve as the South Coast Air Basin site for the 2005 monitoring.

Fresno (San Joaquin Valley Air Basin)

The Fresno air monitoring site, located at the Fresno 1st Street air monitoring station downtown, is close to Highway 41 and was chosen for 2005 dioxin monitoring because of its urban location near mobile source emissions. The Fresno 1st site will provide the opportunity to add ambient dioxin measurements collected in an urban area of the San Joaquin Valley to the existing data set.

Westside Elementary School – Five Points (San Joaquin Valley Air Basin)

The Westside Elementary School will be the second dioxin air monitoring site in the San Joaquin Valley Air Basin. This site will provide data for comparing rural and urban dioxin monitoring sites within and between air basins and will be operated concurrently with Livermore, Rubidoux, and Fresno from June 2005 through December 2005. Following the expected closure of the Livermore and Rubidoux sites in January of 2006, the Westside site will continue to be operated concurrently with the Fresno site from January through June of 2006.

Figure 1 below shows each of the four sites for the 2005 ambient dioxin air monitoring program. Table 1 gives specific information on site locations and contacts for sampling and media shipment (see Sections V – VIII for details on sample media used for dioxins and shipping/labeling information).

Figure 1
2005 CADAMP Air Monitoring Sites



Table 1
Site Contact Information

Site Name	Location	Media Shipping Address	Operator	Phone
Rubidoux	South Coast AQMD 21865 E. Copley Drive Diamond Bar, CA 91765-4182	(Same as Location Address)	Richard Parent	(909) 967-4511
Livermore	Bay Area AQMD 793 Rincon Avenue Livermore, CA 94550	Fed Ex World Center 7275 Johnson Drive Pleasanton, CA 94558	Gary Zoppo	(925) 455-1554
Fresno	CARB 3425 N. First Street, Suite 205B Fresno, CA 93726	(Same as Location Address)	Patrick Seames	(559) 228-1825
Five Points	Westside Elementary School 19191 W. Excelsior Five Points, CA 93624	CARB 3425 N. First Street, Suite 205B Fresno, CA 93726	George Jung	(559) 734-0659

IV. Personnel

Bay Area Air Quality Management District (BAAQMD) staff will conduct the sample media (Polyurethane Foam (PUF) and Quartz Fiber Filter (QFF)) installation, sample collection and packaging, and shipping for the Livermore monitoring site. Staff from the South Coast Air Quality Management District (SCAQMD) will conduct the same for the Riverside-Rubidoux site. District staff will also perform routine sampler maintenance as needed. ARB staff will conduct sampler operation and routine maintenance at the Fresno 1st Street and Westside Elementary sites (see Table 2).

Staff from the ARB's Operation Support Section will perform sampler calibrations and calibration orifice certifications for all sites. ARB staff will also maintain a supply of sampler replacement parts and sampling supplies for use by each site operator and will perform major sampler repairs if needed. Please refer to the "Field Operation of the California Ambient Dioxin Air Monitoring (CADAMP) Sampling Network" for specific roles and responsibilities for each group.

Table 2

Monitoring Program Contacts

<i>Name</i>	<i>Phone</i>	<i>E-mail</i>	<i>Responsibilities</i>
Kathy Gill – ARB/MLD	(916) 445-9483	kgill@arb.ca.gov	Monitoring program coordinator, QA/QC
Reggie Smith – ARB/MLD	(916) 327-1238	rsmith@arb.ca.gov	Manage ARB field staff and operations
Matt Quok – ARB/MLD	(916) 445-2555	mquok@arb.ca.gov	Sampler installation, calibration, and repair
Pam Riley – AXYS Analytical	(250) 655-5800	priley@axys.com	Media shipments and sample receipt; laboratory project management

V. Monitoring Methods

As with earlier CADAMP monitoring, 2005 monitoring will be performed using USEPA Method TO-9A. Dioxin samplers will be operated in the standard configuration as described in Method TO-9A, but the sampling period will be extended to cover an entire month (i.e., 480 hours total - 20 out of every 28 days). Per Method TO-9A, the dioxin sampler collects atmospheric particulate material on a QFF. The vapor phase constituents pass through the QFF and impinge on a pre-cleaned PUF plug inside a glass cartridge. The PUF is augmented with XAD-2 resin between two portions of PUF forming a PUF-XAD-PUF "sandwich." QFFs are replaced weekly to prevent overloading the filter with particulate. The PUF sandwich remains in place for the four weeks of the sampling moment. For 2005, there will be a total of 13 28-day sampling moments.

The contract laboratory, AXYS Analytical Services, Ltd., will provide each operator with pre-cleaned sampling media, PUF and QFFs, each month. They will also provide packing materials and shipping containers as well as all necessary paperwork for chain-of-custody and customs clearance. A media request form (Table 3) was created to communicate monthly requirements to the laboratory. The CADAMP monitoring coordinator will submit this form to the laboratory.

Table 3

Laboratory Media Request Form

Shipping Instructions for (Date) Sampling Moment						
Site	Samples	Collocated	Field Blank	Total per site	Comments	Shipping Address
Rubidoux (RUB)	1	0	0	1		Richard Parent 21865 E. Copley Drive, Diamond Bar, CA 91765-4182
Livermore (LIV)	1	0	1*	2	HOLD FOR PICKUP (925) 455-1554; Label cooler on outside with "Livermore"	Gary Zoppo Fed Ex World Center 7275 Johnson Drive, Pleasanton, CA 94558
Fresno (FRE)	1	1	0	1		Pat Seames 3425 N. First Street, Suite 205B, Fresno, CA 93726
Five Points (FP)	1	0	0	1		George Jung 3425 N. First Street, Suite 205B, Fresno, CA 93726
Total number of shipments:						
Total number of media sets:						
Shipments due at sites no later than:			Date			
Pre-spike all media for D/F, PCB, and PBDE analysis						
* Field Blank will rotate among sites						
Ship media on Monday for Tuesday delivery with installation on Tuesday or Wednesday						

The sampling schedule for 2005 is detailed in Table 4. The first sampling moment will start in January and will run for three weeks. All other moments will consist of four weeks. Typically, the PUF and first QFF are installed on Tuesday or Wednesday. The sampler timer is set to start the sampling pump at midnight on Wednesday and stop five (5) days later. The QFF is then removed and replaced and sampling resumes at midnight on Wednesday. At the end of the fourth week the fourth filter and the PUF are removed. The PUF and four filters are shipped to the laboratory for analysis and a new PUF and new filter are installed for the next sampling moment.

Detailed procedures for sampler operation, QFF and PUF retrieval, and shipment to the laboratory can be found in the field operation procedure and the sampler standard operation procedure on the CADAMP website:
<http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm>.

VI. Field Quality Assessment Samples

Field quality assessment samples will consist of collocated samples to assess overall system precision and field blank samples for contamination, if any. Collocated samples will be collected at the Fresno urban site (1st Street station) every other sampling period for a total of six (6) collocated samples in 2005. One field blank sample will be collected at one site each quarter and will be rotated among the four sites. The field blank schedule is included in Table 4.

VII. Sample Labeling

The PUF cartridges and the petri dishes containing the sample QFFs will be labeled using the following naming convention:

Site Abbreviation - Sampler Type - Start Date - Media - Sample Type

The stations will be abbreviated in the following manner:

Livermore:	LIV
Rubidoux:	RUB
Fresno	FRE
Five Points	FP

The sampler types are abbreviated as follows:

CADAMP (modified TO-9A) primary sampler:	TO
CADAMP collocated sampler:	CO

Start Date is the date the sampler begins running (*not the PUF/filter install date*) and is formatted mmddyy. For field blanks, the "start date" is also the date the associated sampler began running, not the date the PUF is collected. The field blank QFFs are labeled with the dates the associated sample QFFs are collected.

Table 4
CADAMP 2005 Sampling Schedule

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	Field Blank		
JANUARY ('05)													N																					Livermore
FEBRUARY		Q							R	N					Q								Q											
MARCH		Q							R	N					Q								Q								Q			
APRIL							R	N					Q						Q							Q								Fresno
MAY				R	N					Q					Q									Q								R		
JUNE		R	N					Q						Q								Q							R	N				
JULY						Q						Q							Q								R	N						
AUGUST			Q						Q						Q									R	N						Q			Five Points
SEPTEMBER							Q						Q							R	N					Q								
OCTOBER				Q							Q							R	N						Q									
NOVEMBER		Q							Q							R	N						Q							Q				
DECEMBER							Q							R	N							Q						Q						Rubidoux
JANUARY ('06)			Q							R																								

KEY:

- N Begin new sampling moment - timer start on Wednesday at midnight
- R QFF and PUF recovery and reload - samples to be shipped to lab within 24 hours
- Q QFF change on Tuesday or Wednesday
- Represents one full cycle from sampling start to retrieval of PUF.

Media Type is abbreviated as follows:

PUF cartridge: **P**
QFF filter: **F**

Sample Type is abbreviated in the following manner:

Sample: **S**
Field Blank: **B**

The following are examples for the naming conventions (e.g., for a sampling period starting on 01/13/04 (media installed on 01/12/04), PUF collected on 01/26/04):

<i>PUF Sample:</i>	<i>Filter Sample:</i>
FRE-TO-011304-P-S	FRE-TO-011304-F-S
(01/26/04 collection date)	FRE-TO-011904-F-S
	FRE-TO-012604-F-S

<i>PUF Blank:</i>	<i>Filter Blank:</i>
FRE-TO-011304-P-B	FRE-TO-011304-F-B
(01/26/04 collection date)	FRE-TO-011904-F-B
	FRE-TO-012604-F-B

VIII. Sample Shipment

Once all QFFs and PUF are retrieved on the final day of the sampling moment, they will be securely packaged with blue ice in a sturdy container supplied by the laboratory. Samples will be shipped under chain-of-custody by overnight courier to:

Pam Riley
AXYS Analytical Services, Ltd.
2045 Mills Road
Sidney, British Columbia
V8L3S8 Canada

Samples may be shipped for Saturday delivery only if the laboratory is notified in advance of shipping. For all shipments, an e-mail notification, including the tracking number, will be sent to Ms. Riley at AXYS and to the monitoring program coordinator, Ms. Kathy Gill, at ARB/MLD.

IX. Sample Analysis

All sample analysis will be conducted in accordance with methods used previously in CADAMP. The four QFFs and one PUF sandwich are combined and extracted as one sample. The single extract is used for analysis of dioxins, furans (USEPA Method

TO9-A), 14 dioxin-like PCBs (USEPA Method 1668A), and 44 PBDE congeners (draft USEPA Method 1614) by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

A low detection limit is necessary because many of the PCDD, PCDF, and PCB congeners of concern are normally detected in ambient air at very low concentrations. Achieving low detection limits is possible by using extended sampling periods to collect material sufficient to detect 2,3,7,8-TCDD at 0.2 femtograms per cubic meter (fg/m³). Since non-detect is seldom observed using the extended sampling approach, the low detection limit provides for a more accurate determination of toxicity equivalence (TEQ) (see the California Ambient Dioxin Air Monitoring Program Quality Assurance Project Plan (QAPP) for more information).

X. Quality Assurance

The overall quality assurance objective for this project is to produce well-documented data of known quality. The quality of data has traditionally been assessed by the use of data quality indicators. Generally accepted practice expresses data quality in terms of precision, accuracy, representativeness, completeness, and comparability. The detection limit is also specified as an important data quality descriptor. This information will be used to assess the usability of the monitoring data. Laboratory and method data quality indicators will be reviewed, evaluated, and reported along with project monitoring results.

The quality assurance program for CADAMP, and for the monitoring conducted in 2005, will include the following components as described in the referenced documents:

- Estimated data accuracy and precision,
- Estimated data completeness and representativeness,
- A statement of data comparability with the NDAMN program,
- Laboratory system and performance audits,
- Field system and performance audits,
- A statement of data usability based on the above data quality indicators.

XI. Reporting

Following quality assurance checks, dioxin data will be made available to all interested parties via the ARB's dioxin program web site:

<http://www.arb.ca.gov/toxics/dioxins/info.htm>

2005 CADAMP Reference Page

Purpose: To continue collecting data for dioxins/furans, PCB congeners, and PBDE at selected CADAMP sites and to add one rural and one additional urban site to supplement both CADAMP and NDAMN

Duration: One year starting January 13, 2005, and ending January 10, 2006 (South Coast and Bay Area sites). One year starting June 2, 2005, and ending June 1, 2006 (San Joaquin Valley sites).

Sampling Scheme: 28-day cycle for each sampling moment – install PUF and QFF on Wednesday for midnight run start, run for five days, change QFF (event 1), run for five days, change QFF (event 2), run for five days, change QFF (event 3), run for five days, collect PUF and final QFF (event 4 and end of moment), ship PUF and four QFFs to lab for analysis, install new PUF and new QFF for next moment. There will be 13 sampling moments for each site in 2005/2006.

Contacts:

<i>Name</i>	<i>Phone</i>	<i>E-mail</i>	<i>Responsibilities</i>
Kathy Gill – ARB/MLD	(916) 445-9483	kgill@arb.ca.gov	Monitoring program coordinator
Reggie Smith – ARB/MLD	(916) 327-1238	rsmith@arb.ca.gov	Sampler parts and supplies
Matt Quok – ARB/MLD	(916) 445-2555	mquok@arb.ca.gov	Sampler calibration and repair
Pam Riley – AXYS Analytical Services, Ltd. 2045 Mills Road Sidney, British Columbia V8L3S8 Canada	(250) 655-5800	priley@axys.com	Media shipments, sample receipt

Sites:

<i>Site Name</i>	<i>Location</i>	<i>Media Shipping Address</i>	<i>Operator</i>	<i>Phone</i>
Rubidoux (1 sampler)	South Coast AQMD 21865 East Copley Drive Diamond Bar, CA 91765-4182	Same	Richard Parent	(909) 967-4511
Livermore (1 sampler)	Bay Area AQMD 793 Rincon Avenue Livermore, CA 94550	Fed Ex World Center 7275 Johnson Drive Pleasanton, CA 94558	Gary Zoppo	(925) 455-1554
Fresno (2 samplers)	CARB 3425 N. First Street, Suite 205B Fresno, CA 93726	Same	Patrick Seames	(559) 228-1825
Five Points (1 sampler)	Westside Elementary School 19191 W. Excelsior Five Points, CA 93624	CARB 3425 N. First Street, Suite 205B Fresno, CA 93726	George Jung	(559) 734-0659

Website:

Additional information regarding CADAMP can be found at:
<http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm>